NIST-JANAF Thermochemical Tables. I. Ten Organic Molecules Related to Atmospheric Chemistry

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The structural, spectroscopic, and thermodynamic properties of 10 gas phase organic molecules related to atmospheric chemistry, including three peroxides and four carboxylic acids, are reviewed. The calculation of the thermochemical tables involved the critical evaluation of new spectroscopic data, enthalpy of formation determinations, and the use of recent internal rotation data. Since insufficient information to characterize all 10 molecules exists, estimation schemes were used to provide the missing experimental and theoretical data. © *2001 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved.*

Key words: critical evaluation; enthalpy of formation; group additivity method; heat capacity; internal rotation; molecular structure; normal coordinates; spectroscopic properties; thermodynamic properties; transferable force fields.

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1. Introduction

A large number of biogenic and industrial polutant species play a direct or indirect role in tropospheric smog chemistry. Modeling of the kinetics of tropospheric chemical reaction processes often requires thermodynamic data. In the following, evaluated thermodynamic data for a few smaller organic species including some peroxides relevant to smog chemistry and atmospheric chemistry in general are presented.

The ideal gas thermodynamic properties of the polyatomic molecules were calculated by standard statistical mechanical methods in which a rigid-rotor harmonic-oscillator model, modified where appropriate for internal rotations, was assumed for each compound. The statistical formulas for thermodynamic functions are discussed in several textbooks, review articles, and reference books.[1–6] Molecular and spectroscopic constants needed for the calculations were selected from the literature. In a few cases missing data were estimated by analogy to related compounds. For some molecules, the fundamental frequencies were estimated by normal coordinate calculations using force constants transferred from related molecules and the program NCA written by Novikov and Malyshev.[7]

To evaluate the internal rotational contributions to the thermodynamic functions, the internal rotational partition function was formed by the summation of internal rotational energy levels for each rotor. These energy levels were obtained by the diagonalization of the one dimensional Hamiltonian using a potential function of the form

$$V(\varphi) = \frac{1}{2} \sum_n V_n (1 - \cos n\varphi), \tag{1}$$

where φ is the internal rotational angle. The method of generating the internal rotation energy levels has been described by Lewis *et al.*[8,9] The constant required to generate the internal rotational energy levels for each rotor is the internal rotational constant (F) or reduced moment of inertia of the rotating group (I_r). Where available, the V_n terms and internal rotational constant were taken from spectroscopic data. If the F value was unavailable, it was calculated from the reduced moment of inertia with the relationship

$$F = h/8\pi^2 c I_r. \tag{2}$$

The value of I_r was calculated using molecular structural parameters with a computer program based on a method of calculating the reduced moments of inertia developed by Pitzer and Gwinn.[10,11]

A molecular model of an equilibrium mixture of *trans* and *cis* isomers was employed for calculating the thermodynamic functions of glyoxal.[4,12,13] This method uses the enthalpy difference between the two conformers to calculate the equilibrium mole fraction of each species. From these data and thermodynamic functions of two conformers, values of thermodynamic functions were calculated, allowing for the mixing of two conformers.

The sources of uncertainties in the calculated thermodynamic functions arise from uncertainties in the molecular constants used in the calculations as well as deviations from the rigid-rotor harmonic-oscillator model. In this work the uncertainties in the thermodynamic functions were estimated by the procedure developed by Gurvich *et al.*[6] This approach predicts the uncertainties in the thermodynamic functions $S°(T)$ and $C_p°(T)$ for simple molecules such as C_3N_2O reasonably well. For molecules with one or more internal rotations, the additional uncertainties due to deviations from the rigid-rotor harmonic-oscillator model are difficult to assess. The largest uncertainty probably arises from the anharmonicity of the asymmetric torsion. This will have little effect at room temperature but may be significant at the higher temperatures. The total estimated uncertainties in the thermodynamic functions $S°(T)$ and $C_p°(T)$ in the range between 298.15 and 2000 K are given in the discussions for each molecule.

Based on the selected values of the molecular constants, the ideal gas thermodynamic functions, heat capacity, $C_p°(T)$, entropy, $S°(T)$, enthalpy $[H°(T) - H°(298.15\,\mathrm{K})]$, and the Gibbs energy function $\{-[G°(T)-H°(298.15\,\mathrm{K})]/T\}$, have been calculated for selected temperatures up to 2000 K at the standard state pressure, $p°=0.1\,\mathrm{MPa}$. (In the tables that follow in a few cases excited electronic states have been factored into the calculations; the energy of an electronic state relative to the ground electronic state is given as ε_Γ; the degeneracy of electronic states are referred to in these tables as the ''quantum weight,'' g_Γ.) The enthalpy of formation values $[\Delta_f H°(298.15\,\mathrm{K})]$ were selected by analyzing experimental studies which may result in the enthalpies of formation determination. In the absence of experimental data, the $\Delta_f H°(298.15\,\mathrm{K})$ values were estimated by approximate methods accepted as standard for organic molecules and radicals.[14,15]

The calculated values of the enthalpy difference, $[H°(T) - H°(298.15\,\mathrm{K})]$, and entropy, $S°(T)$, of the ideal gas were combined with values of the enthalpies and entropies of the elements in their reference states to derive values of enthalpy of formation $(\Delta_f H°)$, Gibbs energy of formation $(\Delta_f G°)$, and the logarithm of the equilibrium constant of formation $(\log K_f°)$ of the substances as a function of temperature over the range of 0–2000 K.

Values used here of $[H°(T)\text{-}H°(298.15\,\mathrm{K})]$ and $S°(T)$ for the elements in their reference states $[H_2$(g), C(cr, graphite), O_2(g), N_2(g), F_2(g), Cl_2(g), and Br_2(cr,liq,$T<332.503\,\mathrm{K}$) and Br_2(g,$T>332.503\,\mathrm{K}$)] are those given in the JANAF Thermochemical Tables.[5]

References

[1] K. S. Pitzer, *Quantum Chemistry* (Prentice–Hall, Englewood Cliffs, NJ, 1953).

[2] J. G. Aston and J. J. Fritz, *Thermodynamics and Statistical Thermodynamics* (Wiley, New York, 1959).

[3] G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, *Thermodynamics*, 2nd ed. (McGraw–Hill, New York, 1961).

[4] S. G. Frankiss and J. H. S. Green, *Chemical Thermodynamics* (The Chemical Society, London, 1973), Vol. 1, Chap. 8, pp. 268–316.

[5] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed. [J. Phys. Chem. Ref. Data **14**, Suppl. 1 (1985)].

[6] L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1989), Vol. 1, Part 1.

[7] V. P. Novikov and A. I. Malyshev, Zh. Prikl. Spektrosk. **33**, 545 (1980).

[8] J. D. Lewis, T. B. Malloy, Jr., T. H. Chao, and J. Laane, J. Mol. Struct. **12**, 427 (1972).

[9] J. D. Lewis and J. Laane, J. Mol. Spectrosc. **65**, 147 (1977).

[10] K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. **10**, 428 (1942).

[11] K. S. Pitzer, J. Chem. Phys. **14**, 239 (1946).

[12] K. S. Pitzer, J. Chem. Phys. **5**, 473 (1937).

[13] J. G. Aston and G. Szasz, J. Chem. Phys. **14**, 67 (1946).

[14] N. Cohen and S. W. Benson, Chem. Rev. **93**, 2419 (1993).

[15] D. R. Stull, E. G. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Krieger, Malabar, FL, 1987).

2. Bromoacetic Acid, CH_2Br—COOH

Bromoacetic acid ($C_2H_3BrO_2$) Ideal gas $M_r = 138.9485$

$\Delta_f H°(0\ K) = -364.6 \pm 3.1\ kJ\ mol^{-1}$

$S°(298.15\ K) = 337.0 \pm 5.0\ J\ K^{-1}\ mol^{-1}$ $\Delta_f H°(298.15\ K) = -383.5 \pm 3.1\ kJ\ mol^{-1}$

Molecular constants

Point group: C_s

Symmetry number: $\sigma = 1$

Ground electronic state: $\tilde{X}\ {}^1A$

Energy: $\epsilon_X = 0\ cm^{-1}$

Quantum weight: $g_X = 1$

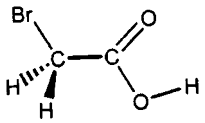
Vibrational frequencies, ν_i, and degeneracies g_i

Symmetry		ν_i, cm^{-1}	g_i
A'	ν_1	3566	1
	ν_2	3037	1
	ν_3	1808	1
	ν_4	1449	1
	ν_5	1325	1
	ν_6	1208	1
	ν_7	1047	1
	ν_8	908	1
	ν_9	747	1
	ν_{10}	589	1
	ν_{11}	384	1
	ν_{12}	180	1
A''	ν_{13}	3076	1
	ν_{14}	1243	1
	ν_{15}	806	1
	ν_{16}	611	1
	ν_{17}	489	1
	ν_{18}	...[a]	1

[a] Instead of torsional mode $\nu_{18} = 47\ cm^{-1}$, the contributions due to the internal rotation about C—C bond were calculated from the potential: $V(\varphi) = \frac{1}{2}V_3(1 - \cos 3\varphi)$, where φ is the torsional angle, $V_3 = 450\ cm^{-1}$.

CH_2Br top: Reduced moment of inertia, $I_r = 2.8300 \times 10^{-39}\ g\ cm^2$, Symmetry number, $\sigma_m = 1$.

Geometry



$r(C—C) = 1.51 \pm 0.01$ Å
$r(C{=}O) = 1.21 \pm 0.01$ Å
$r(C—O) = 1.36 \pm 0.01$ Å
$r(C—Br) = 1.95 \pm 0.02$ Å

$r(C—H) = 1.09 \pm 0.02$ Å
$r(O—H) = 0.97 \pm 0.02$ Å
$\angle C—C{=}O = 126 \pm 1°$
$\angle C—C—O = 111 \pm 1.5°$
$\angle C—C—Br = 112.5 \pm 1.5°$
$\angle C—C—H = 112 \pm 2°$
$\angle H—C—H = 109.5 \pm 1°$
$\angle C—O—H = 106 \pm 1°$
$\varphi(O{=}C—C—Br) = 0.0°$
$\varphi(O{=}C—O—H) = 0.0°$

Rotational constants in cm^{-1}:

$CH_2{}^{79}BrCOOH$	$A_0 = 0.348\,921$	$B_0 = 0.050\,528$	$C_0 = 0.044\,536$
$CH_2{}^{81}BrCOOH$	$A_0 = 0.348\,916$	$B_0 = 0.050\,066$	$C_0 = 0.044\,176$

Product of moments of inertia: $I_A I_B I_C = 28\,178 \times 10^{-117}\ g^3\ cm^6$.

2.1. Enthalpy of Formation

The recommended value of enthalpy of formation of gaseous bromoacetic acid, $-(383.5 \pm 3.1)\ kJ\ mol^{-1}$, was obtained by Lagoa *et al.*[1] from experimental measurements. This value is the sum of the enthalpy of formation of bromoacetic acid in the crystalline state, $\Delta_f H°(C_2H_3BrO_2$, cr I, 298.15 K$) = -(466.98 \pm 1.08)\ kJ\ mol^{-1}$, determined from rotating bomb combustion calorimetry, and the enthalpy of sublimation, $\Delta_{sub}H°(C_2H_3BrO_2) = (83.50 \pm 2.95)\ kJ\ mol^{-1}$, determined from Knudsen effusion experiments. Note that the recommended value is close to the value predicted by the method of group equations:[2]

$$\begin{aligned}\Delta_f H^\circ(\mathrm{CH_2Br{-}COOH}) &= \Delta_f H^\circ(\mathrm{CH_2Cl{-}COOH}) + \Delta_f H^\circ(\mathrm{CH_2Br{-}CH_3}) \\ &\quad - \Delta_f H^\circ(\mathrm{CH_2Cl{-}CH_3}) = (-427.6) + (-61.9) \\ &\quad -(-112.1) = -377.4 \ \ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

(the $\Delta_f H^\circ$ values for CH_2BrCH_3, and CH_2ClCH_3 were taken from compilation by Pedley,[3] for $CH_2ClCOOH$—from Ref. 1). A somewhat lower estimate of the enthalpy of formation of bromoacetic acid, $-(395\pm6)$ kJ mol^{-1} was given by Lias *et al.*[4]

2.2. Heat Capacity and Entropy

From their microwave study, van Eijck *et al.*[5] determined the rotational constants of three isotopic species ($CH_2{}^{79}BrCOOH$, $CH_2{}^{81}BrCOOH$, and $CH_2{}^{79}BrCOOD$). Although no complete structure could be evaluated from the available data, the substitution coordinates of the Br atom and the carboxyl H atom were consistent only with the *trans* structure with respect to the atoms Br—C—C—O—H. This conformation is identical to lowest-energy form of chloroacetic acid named as *cis-syn* because of *cis* configuration for O═C—O—H and Cl—C—C═O groups. The *cis* structure with respect to the atoms Br—C—C—O—H was obtained by Chen *et al.*[6] from *ab initio* calculation. However, the geometry of chloroacetic acid calculated by Chen *et al.*[6] was also not consistent with that determined from experimental studies. The *trans* structure with respect to the atoms Br—C—C—O—H (C_s symmetry) is accepted in this work for lowest-energy conformer of bromoacetic acid in accord with the microwave data.[5] The isotope-weighted value of the product of the principal moments of inertia of bromoacetic acid is calculated in this work from the rotational constants for $CH_2{}^{79}BrCOOH$ and $CH_2{}^{81}BrCOOH$.[5] Structural parameters given above are those estimated by comparison with structural parameters of CH_3COOH,[7] CH_2ClCH_3,[8] $CH_2ClCOOH$,[9] and CH_2BrCH_3.[10] These structural parameters yield values for the rotational constants which are 1.2%–1.6% different from the observed values used in the calculations. The difference has a negligible effect on the thermodynamic functions.

There is no information on other stable conformers of bromoacetic acid arising from internal rotation around the C—C bond. van Eijck *et al.*[5] could only conclude that the *gauche* conformation, if present, is not significantly higher in energy than the *trans* conformation. Their rough estimate of the torsional frequency, 47 cm^{-1}, may be compared with 62 cm^{-1} for chloroacetic acid.[11] As in the case of chloroacetic acid, the simple potential,

$$V(\varphi)=\tfrac{1}{2}V_3(1-\cos 3\varphi),$$

where φ is the Br—C—C═O torsional angle, is used in this work to calculate the internal rotational contributions to the thermodynamic functions of bromoacetic acid. The barrier height for the rotation about the C—C bond is practically the same in CH_2ClCH_3 and CH_2BrCH_3 molecules.[12,13] For that reason, the value of V_3 for bromoacetic acid was accepted to be the same as that for chloroacetic acid. The value of the reduced moment of inertia for the CH_2Br top was derived from structural parameters adopted in this work (see above).

Vibrational spectra of bromoacetic acid were investigated only for a solid phase.[14–17] These vibrational assignments are incomplete and it may be expected that they are much different from a gaseous spectrum as in the case of chloroacetic acid. Fundamental frequencies of gaseous bromoacetic acid were estimated in this work by normal coordinate calculations using the force constants transferred from related compounds. Simplified force fields for CH_3COOH, CH_2ClCH_3, CH_2BrCH_3, and $CH_2ClCOOH$ were determined using experimental vibrational assignments for these molecules.[18–21] 37 force constants were used to calculate the vibrational frequencies of bromoacetic acid:

$f_{\rm O-H}$	7.092	$f_{\rm wag(C=O)}$	0.310	$f_{\rm C-C,C-C-H}$	0.199
$f_{\rm C-H}$	4.998	$f_{\rm tors(C-O)}$	0.183	$f_{\rm C-C,C-C-O}$	−0.425
$f_{\rm C=O}$	14.076	$f_{\rm tors(C-C)}$	0.028	$f_{\rm C-C,C-C-Br}$	−0.017
$f_{\rm C-C}$	4.101	$f_{\rm C-H,C-H}$	0.061	$f_{\rm C-C,O=C-C}=f_{\rm C-C,O=C-O}$	1.250
$f_{\rm C-O}$	3.891	$f_{\rm C-H,C-C}$	0.332	$f_{\rm C-O,C-O-H}$	0.041
$f_{\rm C-Br}$	3.531	$f_{\rm C-H,C-Br}$	−0.402	$f_{\rm C-O,C-C-O}$	0.296
$f_{\rm H-C-H}$	0.274	$f_{\rm C-C,C-Br}$	0.377	$f_{\rm C-O,O=C-C}=f_{\rm C-O,O=C-O}$	0.605
$f_{\rm C-C-H}$	0.793	$f_{\rm C-C,C-O}$	0.693	$f_{\rm C-Br,H-C-Br}$	0.148
$f_{\rm C-O-H}$	0.424	$f_{\rm C=O,C-O}$	2.221	$f_{\rm C-Br,C-C-Br}$	0.044
$f_{\rm C-C-O}$	2.465	$f_{\rm C=O,C-C}$	1.660	$f_{\rm C-H,H-C-Br}$	−0.533
$f_{\rm H-C-Br}$	0.547	$f_{\rm C=O,C-C-O}$	−1.365	$f_{\rm C-H,H-C-H}$	−0.184
$f_{\rm C-C-Br}$	1.042	$f_{\rm C=O,O=C-C}=f_{\rm C=O,O=C-O}$	0.687	$f_{\rm C-H,C-C-H}$	0.216
$f_{\rm O=C-C}=f_{\rm O=C-O}$	2.312				

(stretching and stretch–stretch interaction constants are in units of mdyn/Å; bend, wagging, and torsion constants are in units of mdyn Å; stretch–bend interaction constants are in units of mdyn). These constants were transferred from CH_3COOH and CH_2BrCH_3 molecules with corrections made by analyzing the trends in force constants of molecules CH_3COOH, CH_2ClCH_3, and $CH_2ClCOOH$.

The uncertainties in the calculated thermodynamic functions (Table 1) may reach (3–6) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $C_p°(T)$ and (5–12) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $S°(T)$. They are caused by the uncertainties in the adopted vibrational frequencies and the approximate treatment of internal rotation.

Ideal gas thermodynamic properties of bromoacetic acid have not been reported previously.

2.3. References

[1] A. L. C. Lagoa, H. P. Diogo, M. Pilar Dias, M. E. Minas da Piedade, L. M. P. F. Amaral, M. A. V. Ribeiro da Silva, J. A. Martinho Simões, R. C. Guedes, B. J. Costa Cabral, K. Schwarz, and M. Epple, Chem. Eur. J. **7**, 483 (2001).

[2] D. R. Stull, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Krieger, Malabar, FL, 1987); see also the ‘‘difference method,’’ N. Cohen, and S. W. Benson, Chem. Rev. **93**, 2419 (1993).

[3] J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds* (Thermodynamics Research Center, College Station, TX, 1994), Vol. I.

[4] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, J. Phys. Chem. Ref. Data **17**, Suppl. 1 (1988).

[5] B. P. van Eijck, H. A. Dijkerman, and J. Smits, J. Mol. Spectrosc. **73**, 305 (1978).

[6] L.-T. Chen, G.-J. Chen, and X.-Y. Fu, Chin. J. Chem. **13**, 10 (1995).

[7] B. P. van Eijck, J. van Opheusden, M. M. M. van Schaik, and E. van Zoeren, J. Mol. Spectrosc. **86**, 465 (1981).

[8] M. Hayashi and T. Inagusa, J. Mol. Struct. **220**, 103 (1990).

[9] J. L. Derissen, and J. M. J. M. Bijen, J. Mol. Struct. **29**, 153 (1975).

[10] T. Inagusa and M. Hayashi, J. Mol. Spectrosc. **129**, 160 (1988).

[11] B. P. van Eijck, A. A. J. Maagdenberg, and J. Wanrooy, J. Mol. Struct. **22**, 61 (1974).

[12] J. R. Durig, W. E. Bucy, L. A. Carreira, and C. J. Wurrey, J. Chem. Phys. **60**, 1754 (1974).

[13] J. Gripp, H. Dreizler, and R. Schwarz, Z. Naturforsch. A **40**, 575 (1985).

[14] J. E. Katon, T. P. Carll, and F. F. Bentley, Appl. Spectrosc. **25**, 229 (1971).

[15] J. E. Katon and D. Sinha, Appl. Spectrosc. **25**, 497 (1971).

[16] J. E. Katon and R. L. Kleinlein, Spectrochim. Acta A **29**, 791 (1973).

[17] P. F. Krause, J. E. Katon, and R. W. Mason, J. Phys. Chem. **82**, 690 (1978).

[18] H. Hollenstein and H. H. Günthard, J. Mol. Spectrosc. **84**, 457 (1980).

[19] S. Suzuki and A. B. Dempster, J. Mol. Struct. **32**, 339 (1976).

[20] S. Suzuki, J. L. Bribes, and R. Gaufres, J. Mol. Spectrosc. **47**, 118 (1973).

[21] J. Nieminen, M. Pettersson, and M. Räsänen, J. Phys. Chem. **97**, 10925 (1993).

TABLE 1. Ideal gas thermodynamic properties of bromoacetic acid $C_2H_3BrO_2$(g) at the standard state pressure, $p° = 0.1$ MPa $(T_r = 298.15$ K)

T (K)	$C_p°$ (J K^{-1} mol^{-1})	$S°$ (J K^{-1} mol^{-1})	$-[G° - H°(T_r)]/T$ (J K^{-1} mol^{-1})	$H° - H°(T_r)$ (kJ mol^{-1})	$\Delta_f H°$ (kJ mol^{-1})	$\Delta_f G°$ (kJ mol^{-1})	log $K_f°$
0	0.000	0.000	∞	−16.862	−364.616	−364.616	∞
25	36.587	211.762	852.075	−16.008	−365.365	−365.150	762.919
50	41.371	238.698	539.288	−15.029	−366.712	−364.466	380.746
75	45.202	256.212	442.164	−13.946	−368.184	−363.016	252.820
100	48.832	269.713	397.423	−12.771	−369.448	−361.099	188.614
150	56.415	290.927	358.541	−10.142	−371.701	−356.428	124.116
180	61.214	301.635	348.180	−8.378	−372.997	−353.251	102.508
190	62.843	304.988	345.818	−7.758	−373.427	−352.142	96.808
200	64.482	308.253	343.859	−7.121	−373.854	−351.012	91.672
210	66.128	311.439	342.239	−6.468	−374.281	−349.858	87.020
220	67.778	314.553	340.910	−5.799	−374.706	−348.686	82.786
230	69.431	317.602	339.831	−5.113	−375.130	−347.493	78.916
240	71.083	320.592	338.967	−4.410	−375.553	−346.282	75.364
250	72.731	323.527	338.291	−3.691	−375.975	−345.055	72.094
260	74.374	326.412	337.779	−2.955	−376.398	−343.809	69.070
270	76.007	329.250	337.411	−2.204	−382.140	−342.466	66.252
280	77.630	332.043	337.169	−1.435	−382.632	−340.987	63.610
290	79.240	334.795	337.040	−0.651	−383.115	−339.491	61.147
298.15	80.540	337.010	337.010	0.000	−383.500	−338.262	59.261
300	80.834	337.509	337.011	0.149	−383.587	−337.981	58.846
350	88.515	350.553	338.023	4.385	−400.269	−329.432	49.164
400	95.600	362.842	340.365	8.991	−401.362	−319.235	41.687
450	102.021	374.480	343.514	13.934	−402.305	−308.911	35.857
500	107.785	385.532	347.168	19.182	−403.114	−298.489	31.182
600	117.569	406.081	355.302	30.468	−404.395	−277.439	24.153
700	125.486	424.820	363.915	42.634	−405.305	−256.204	19.118
800	132.017	442.016	372.617	55.519	−405.904	−234.859	15.334
900	137.498	457.891	381.222	69.002	−406.239	−213.457	12.388
1000	142.157	472.625	389.634	82.991	−406.354	−192.028	10.030
1100	146.150	486.366	397.810	97.411	−406.281	−170.598	8.101
1200	149.592	499.234	405.732	112.203	−406.053	−149.181	6.494
1300	152.573	511.328	413.394	127.315	−405.702	−127.785	5.134
1400	155.164	522.732	420.800	142.704	−405.257	−106.425	3.971
1500	157.423	533.516	427.958	158.336	−404.734	−85.097	2.963
1600	159.399	543.741	434.879	174.180	−404.160	−63.786	2.082
1700	161.134	553.457	441.570	190.208	−403.549	−42.535	1.307
1800	162.662	562.712	448.045	206.400	−402.914	−21.313	0.618
1900	164.013	571.543	454.315	222.735	−402.270	−0.130	0.004
2000	165.210	579.987	460.389	239.197	−401.625	21.019	−0.549

3. Chloroacetic Acid, CH_2Cl—COOH

Chloroacetic acid ($C_2H_3ClO_2$) Ideal gas $M_r = 94.4975$

$\Delta_f H°(0\ \mathrm{K}) = -416.0 \pm 1.0$ kJ mol^{-1}

$S°(298.15\ \mathrm{K}) = 325.9 \pm 5.0$ J K^{-1} mol^{-1} $\Delta_f H°(298.15\ \mathrm{K}) = -427.6 \pm 1.0$ kJ mol^{-1}

Molecular constants

Point group: C_s Symmetry number: $\sigma = 1$

Ground electronic state: $\tilde{X}\ ^1A$ Energy: $\epsilon_X = 0$ cm^{-1} Quantum weight: $g_X = 1$

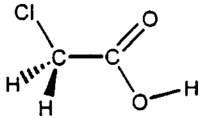
Vibrational frequencies, ν_i, and degeneracies g_i

Symmetry		ν_i, cm^{-1}	g_i	Symmetry		ν_i, cm^{-1}	g_i
A'	ν_1	3566	1		ν_{10}	596	1
	ν_2	3019	1		ν_{11}	397	1
	ν_3	1806	1		ν_{12}	216	1
	ν_4	1428	1	A''	ν_{13}	3076	1
	ν_5	1354	1		ν_{14}	1193	1
	ν_6	1274	1		ν_{15}	929	1
	ν_7	1111	1		ν_{16}	611	1
	ν_8	891	1		ν_{17}	492	1
	ν_9	792	1		ν_{18}	...[a]	1

[a] Instead of torsional mode $\nu_{18} = 62$ cm^{-1}, the contributions due to the internal rotation about C—C bond were calculated from the potential $V(\varphi) = \frac{1}{2}V_3(1-\cos 3\varphi)$, where φ is the torsional angle and $V_3 = 450$ cm^{-1}.

CH_2Cl top: Reduced moment of inertia, $I_r = 2.4514\times 10^{-39}$ g cm^2, Symmetry number, $\sigma_m = 1$.

Geometry



r(C—C) = 1.508 ± 0.006 Å
r(C═O) = 1.223 ± 0.004 Å
r(C—O) = 1.352 ± 0.005 Å
r(C—Cl) = 1.778 ± 0.005 Å

r(C—H) = 1.09 ± 0.02 Å
r(O—H) = 0.97 ± 0.015 Å
∠C—C═O = 126.1 ± 0.5°
∠C—C—O = 110.6 ± 0.4°
∠C—C—Cl = 112.5 ± 0.4°
∠C—C—H = 109.5 (assumed)
∠H—C—H = 109.5 (assumed)
∠C—O—H = 105.8 ± 1.1°
φ(O═C—C—Cl) = 0.0°
φ(O═C—O—H) = 0.0°

Rotational constants in cm^{-1}:

$A_0 = 0.350\,738 \quad B_0 = 0.078\,433 \quad C_0 = 0.064\,913$

Product of moments of inertia: $I_A I_B I_C = 12\,284\times 10^{-117}$ g^3 cm^6.

3.1. Enthalpy of Formation

The recommended value of the enthalpy of formation of gaseous chloroacetic acid at 298.15 K is the sum of the enthalpy of formation of the α form of the solid and the enthalpy of sublimation both at 298.15 K. The value of $\Delta_f H^\circ(298.15\,\mathrm{K}, \alpha\text{-cr}) = -(509.74 \pm 0.49)$ kJ mol^{-1} is from the work of Lagoa *et al.*[1] who measured the enthalpy of combustion of the α form of the solid with a rotating bomb calorimeter. Their result is in agreement with the result $\Delta_f H^\circ(298.15\,\mathrm{K,cr}) = -(510.5 \pm 8.3)$ kJ mol^{-1} of Smith *et al.*[2] from their re-evaluation of earlier static bomb calorimetry measurements.[3]

The enthalpy of sublimation, $\Delta_{\mathrm{sub}} H^\circ(298.15\,\mathrm{K}) = (82.19 \pm 0.92)$ kJ mol^{-1}, used here is also from Lagoa *et al.*,[1] and is derived from vapor pressures of the solid obtained from Knudsen effusion experiments. This value is supported by application of Hess's law where the enthalpy of sublimation is the sum of five processes at the standard pressure of 1 bar. Thus,

$$\begin{aligned}\Delta_{\mathrm{sub}} H^\circ \quad & (298.15\,\mathrm{K}) \\ &= [H^\circ(\mathrm{cr}, 334.8\,\mathrm{K}) - H^\circ(\mathrm{cr}, 298.15\,\mathrm{K})] \\ &\quad + \Delta_{\mathrm{fus}} H^\circ(334.8\,\mathrm{K}) + [H^\circ(1, 462\,\mathrm{K}) - H^\circ(1, 334.8\,\mathrm{K})] \\ &\quad + \Delta_{\mathrm{vap}} H^\circ(462\,\mathrm{K}) - [H^\circ(\mathrm{g}, 462\,\mathrm{K}) \\ &\quad - H^\circ(\mathrm{cr}, 298.15\,\mathrm{K})] = 80.9 \pm 2.3 \ \mathrm{kJ\,mol^{-1}}.\end{aligned}$$

The first and third terms $[H^\circ(T_2) - H^\circ(T_1)] \approx C_p{}^\circ(\mathrm{cr}) \times \Delta T$ are (3.9 ± 0.1) and (21.6 ± 0.5) kJ mol^{-1}, respectively, based on $C_p{}^\circ(\mathrm{cr}) = (106.7 \pm 2.0)$ J K^{-1} mol^{-1} from differential scanning calorimetery (DSC) measurements[1] and $C_p{}^\circ(1) = (168.9 \pm 4.0)$ J K^{-1} mol^{-1} from Pickering.[4] [This value of $C_p{}^\circ(\mathrm{cr})$ differs significantly from the average value of 144 J K^{-1} mol^{-1} over the range of 288–318 K reported in Pickering[4] and adopted in NIST Chemistry WebBook[5] and Donalski and Hearing.[6] The value of $C_p{}^\circ(1) = 179.9$ J K^{-1} mol^{-1} from Urazovskii and Sidorov[7] was not used.] $\Delta_{\mathrm{fus}} H^\circ(334.8\,\mathrm{K}) = 16.3 \pm 0.7$ kJ mol^{-1} from DSC measurements[1] while $\Delta_{\mathrm{vap}} H^\circ(462\,\mathrm{K}) = (54.5 \pm 2.0)$ kJ mol^{-1}

TABLE 2. Ideal gas thermodynamic properties of chloroacetic acid $C_2H_3ClO_2(g)$ at the standard state pressure, $p^\circ = 0.1$ MPa $(T_r = 298.15\ \mathrm{K})$

T (K)	C_p° ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	S° ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$-(G^\circ - H^\circ(T_r))/T$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$H^\circ - H^\circ(T_r)$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f H^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f G^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	$\log K_f^\circ$
0	0.000	0.000	∞	−16.514	−416.032	−416.032	∞
25	36.170	203.287	829.838	−15.664	−417.069	−414.897	866.858
50	40.498	229.818	523.832	−14.701	−418.460	−412.226	430.639
75	44.011	246.902	428.827	−13.644	−419.862	−408.793	284.702
100	47.641	260.056	385.047	−12.499	−420.999	−404.926	211.506
150	55.261	280.802	346.988	−9.928	−422.890	−396.468	138.059
180	59.960	291.292	336.846	−8.200	−423.925	−391.086	113.487
190	61.543	294.576	334.536	−7.592	−424.261	−389.252	107.010
200	63.133	297.773	332.618	−6.969	−424.594	−387.401	101.176
210	64.730	300.892	331.033	−6.330	−424.922	−385.533	95.894
220	66.332	303.940	329.733	−5.674	−425.246	−383.649	91.088
230	67.938	306.924	328.676	−5.003	−425.565	−381.752	86.696
240	69.546	309.849	327.831	−4.316	−425.880	−379.841	82.668
250	71.155	312.721	327.169	−3.612	−426.190	−377.915	78.959
260	72.762	315.543	326.668	−2.892	−426.493	−375.978	75.533
270	74.365	318.319	326.308	−2.157	−426.792	−374.030	72.359
280	75.962	321.053	326.072	−1.405	−427.085	−372.071	69.409
290	77.551	323.746	325.945	−0.638	−427.372	−370.101	66.661
298.15	78.838	325.913	325.913	0.000	−427.600	−368.487	64.556
300	79.129	326.402	325.916	0.146	−427.651	−368.121	64.094
350	86.790	339.180	326.908	4.296	−428.953	−358.094	53.441
400	93.933	351.242	329.202	8.816	−430.094	−347.892	45.429
450	100.456	362.689	332.293	13.678	−431.085	−337.556	39.181
500	106.342	373.583	335.881	18.851	−431.941	−327.116	34.173
600	116.373	393.891	343.883	30.005	−433.310	−306.019	26.641
700	124.509	412.462	352.372	42.063	−434.295	−284.721	21.246
800	131.218	429.540	360.965	54.859	−434.957	−263.304	17.192
900	136.840	445.329	369.473	68.270	−435.342	−241.822	14.035
1000	141.610	460.000	377.801	82.199	−435.499	−220.311	11.508
1100	145.691	473.693	385.903	96.569	−435.459	−198.792	9.440
1200	149.204	486.524	393.760	111.318	−435.259	−177.285	7.717
1300	152.241	498.590	401.364	126.394	−434.930	−155.797	6.260
1400	154.877	509.971	408.719	141.753	−434.500	−134.342	5.012
1500	157.173	520.736	415.831	157.358	−433.991	−112.918	3.932
1600	159.180	530.946	422.709	173.178	−433.426	−91.512	2.987
1700	160.940	540.650	429.364	189.186	−432.819	−70.164	2.156
1800	162.490	549.894	435.805	205.359	−432.185	−48.846	1.417
1900	163.858	558.716	442.044	221.678	−431.536	−27.566	0.758
2000	165.071	567.153	448.090	238.125	−430.883	−6.322	0.165

is derived from vapor pressure data over a temperature range from 385.45 K to the normal boiling point.[9,10] [Other values of $\Delta_{\mathrm{fus}}H^\circ(334.8\ \mathrm{K})$ are 16.3 $\mathrm{kJ\,mol^{-1}}$ from Pickering[4] and 12.3 $\mathrm{kJ\,mol^{-1}}$ from Acree.[8]] The value $[H^\circ(\mathrm{g},462\ \mathrm{K}) - H^\circ(\mathrm{cr},298.15\ \mathrm{K})] = (15.4 \pm 0.7)$ $\mathrm{kJ\,mol^{-1}}$ is interpolated from Table 2 of the present work. This corrects the estimate $\Delta_{\mathrm{sub}}H^\circ(298.15) = (75.3 \pm 4.2)$ $\mathrm{kJ\,mol^{-1}}$ by Cox and Pilcher[5,6,11] based on $\Delta_{\mathrm{fus}}H^\circ(334\ \mathrm{K}) = 19.4\ \mathrm{kJ\,mol^{-1}}$ from Steiner and Johnson[12] and $\Delta_{\mathrm{vap}}H^\circ(462\ \mathrm{K}) = 54.5\ \mathrm{kJ\,mol^{-1}}$ mentioned above. Cox and Pilcher also use Hess's law, but assume that the values of C_p° for the gas, liquid, and solid phases are equal.

3.2. Heat Capacity and Entropy

According to the experimental[13–18] and theoretical[15,17–19] studies, the lowest-energy conformer of chloroacetic acid ($CH_2Cl—CO—OH$) has the *cis-syn* structure (C_s symmetry) with the *cis* configuration for the carboxylic group and with the chlorine atom lying in the carboxylic plane eclipsed with the carbonyl group. The second more stable form corresponds to the *cis-gauche* structure with a Cl—C—C═O angle of ~130° (C_1 symmetry). This form differs from *cis-syn* by internal rotation of the CH_2Cl group about the C—C bond. Structural parameters of the most stable conformer of chloroacetic acid were determined by gas phase electron diffraction.[14] These parameters are in good agreement with results from *ab initio*[18,19] and molecular mechanics[15] calculations. In this work, the product of the principal moments of inertia for the most stable *cis-syn* conformer of chloroacetic acid was calculated using rotational constants determined from the microwave study.[13] Structural parameters given above are those obtained from the electron diffraction study.[14] These parameters reproduce the product of the principal moments of inertia calculated above within 3%.

Three conformations with respect to internal rotation around the C—C bond were found from an electron diffraction investigation,[14] namely, 56% of a *cis-syn* conformation, 30% of a *cis-gauche* conformation with the CH_2Cl group rotated 131° from the former position, and the remaining 14% of a *cis-gauche* conformation with 79° rotation of the CH_2Cl group. Three conformers of chloroacetic acid were identified by vibrational spectroscopy.[15–18] Two of them were *cis-syn* and *cis-gauche* in agreement with the electron diffraction data. The third stable form was found to have the *trans* structure, in which the carboxylic hydrogen atom is in the *trans* position with respect to the C═O bond. *Trans* conformers arise from rotation of the OH group about the C—O bond. *Ab initio* calculations[17,18] and molecular mechanics studies[15] strongly suggest that the third stable form should be the *trans* form. The barrier height for the rotation of the OH group around the C—O bond is predicted to be 1700–3500 cm^{-1}.[16–18] Due to the height of this barrier and the temperature range of the present tabulation, this internal rotation was ignored in this work.

Two *cis* conformers with respect to internal rotation about the C—C bond were considered in this work: the *cis-syn* conformer of C_s symmetry and two enantiomeric forms of *cis-gauche* conformer of C_1 symmetry. The observed data and the calculations[14,16–18] consistently predict a slight energy preference for the *cis-syn* form and a small barrier of (400–450) cm^{-1} for its interconversion. The simple potential

$$V(\varphi)=\tfrac{1}{2}V_3(1-\cos 3\varphi),$$

where φ is the Cl—C—C═O torsional angle, is used here for a very approximate calculation of the internal rotational contributions to the thermodynamic functions of chloroacetic acid. The value of the reduced moment of inertia for the CH_2Cl top was derived from the electron diffraction structural parameters.[14]

Vibrational spectra of chloroacetic acid were studied in the liquid and solid phases,[15,20,21] in the vapor[22] and matrix.[16,18] The fundamental frequencies adopted in this work are those derived by Nieminen *et al.*[18] from matrix isolation infrared spectra $(\nu_1, \nu_3-\nu_5, \nu_7, \nu_8, \nu_9, \nu_{15}-\nu_{17})$ and *ab initio* calculation $(\nu_2, \nu_6, \nu_{10}-\nu_{14})$. These frequencies are in good agreement with results of normal coordinate analysis,[22] molecular mechanics,[15] and *ab initio*[17] calculations. The value for the torsional frequency, ν_{18}, was estimated from the microwave spectrum[13] and it coincides with the value calculated by the *ab initio* method.[18]

The uncertainties in the calculated thermodynamic functions (Table 2) may amount to as much as (3–5) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $C_p°(T)$ and 5–10 $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $S°(T)$. They are caused by the uncertainties in the adopted vibrational frequencies and the approximate treatment of the internal rotation.

Thermodynamic properties of chloroacetic acid were calculated earlier by Banerjee[23] using molecular constants known at that time. A value for the barrier height of ~1750 cm^{-1} was adopted for calculating the internal rotation contributions of the CH_2Cl and OH groups. The difference between the values of $C_p°(T)$ and $S°(T)$ given here and those by Banerjee[23] amounts to 57 and 35 $\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. Such a difference could not be due to the discrepancy in molecular constants used. The calculation of Banerjee[23] seems to be in error. The rough estimate by the method of group equations,

$$\begin{aligned} &C_p°(\mathrm{CH_2Cl—COOH})\\ &\quad=C_p°(\mathrm{CH_3—COOH})+C_p°(\mathrm{CH_2Cl—CH_3})\\ &\qquad-C_p°(\mathrm{CH_3—CH_3})\\ &\quad=63.4+62.6-52.5=73.5\ \ \mathrm{JK^{-1}\ \ mol^{-1}},\end{aligned}$$

is close to the value obtained in this work (78.8 $\mathrm{J\,K^{-1}\,mol^{-1}}$) and is very different from the value of Banerjee[23] (136.0 $\mathrm{J\,K^{-1}\,mol^{-1}}$). The calculation of Banerjee[23] is reproduced in the reference book of Frenkel *et al.*[24]

3.3. References

[1] A. L. C. Lagoa, H. P. Diogo, M. Pilar Dias, M. E. Minas da Piedade, L. M. P. F. Amaral, M. A. V. Ribeiro da Silva, J. A. Martinho Simões, R. C. Guedes, B. J. Costa Cabral, K. Schwarz, and M. Epple, Chem. Eur. J. **7**, 483 (2001).

[2] L. Smith, L. Bjellerup, S. Krook, and H. Westermark, Acta Chem. Scand. **7**, 65 (1953).

[3] E. Schjånberg, Z. Phys. Chem. Abt. A **172**, 197 (1935).

[4] S. U. Pickering, J. Chem. Soc. **67**, 664 (1895).

[5] *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by W. G. Mallard and P. J. Lindstrom (National Institute of Standards and Technology, Gaithersburg, MD, November 1998) (http://webbook.nist.gov/chemistry).

[6] E. S. Domalski and E. D. Hearing, J. Phys. Chem. Ref. Data **25**, 1 (1996).

[7] S. S. Urazovskii and I. A. Sidorov, Dokl. Akad. Nauk SSSR **70**, 859 (1950).

[8] W. E. Acree, Jr., Thermochim. Acta **189**, 37 (1991).

[9] R. R. Dreisbach and S. A. Shrader, Ind. Eng. Chem. **41**, 2879 (1949).

[10] D. R. Stull, Ind. Eng. Chem. **39**, 517 (1947).

[11] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic, London, 1970).

[12] L. E. Steiner and J. Johnston, J. Phys. Chem. **32**, 912 (1928).

[13] B. P. van Eijck, A. A. J. Maagdenberg, and J. Wanrooy, J. Mol. Struct. **22**, 61 (1974).

[14] J. L. Derissen and J. M. J. M. Bijen, J. Mol. Struct. **29**, 153 (1975).

[15] R. Fausto and J. J. C. Teixeira-Dias, J. Mol. Struct. **144**, 225 (1986).

[16] A. Kulbida and A. Nosov, J. Mol. Struct. **265**, 17 (1992).

[17] R. Fausto, J. J. C. Teixeira-Dias, and F. P. S. C. Gil, J. Chem. Soc., Faraday Trans. **89**, 3235 (1993).

[18] J. Nieminen, M. Pettersson, and M. Räsänen, J. Phys. Chem. **97**, 10925 (1993).

[19] K. E. Edgecombe and R. J. Boyd, Can. J. Chem. **62**, 2881 (1984).

[20] J. R. Barcelo, M. P. Jorge, and C. Otero, J. Chem. Phys. **28**, 1230 (1958).

[21] R. J. Jakobsen and J. E. Katon, Spectrochim. Acta A **29**, 1953 (1973).

[22] L. I. Kozhevina, V. M. Belobrov, V. A. Panichkina, and E. V. Titov, Zh. Strukt. Khim. **20**, 405 (1979).

[23] S. C. Banerjee, Br. Chem. Eng. **14**, 671 (1969).

[24] M. Frenkel, G. J. Kabo, K. N. Marsh, G. N. Roganov, and R. C. Wilhoit, *Thermodynamics of Organic Compounds in the Gas State* (Thermodynamics Research Center, College Station, TX, 1994), Vol. I, p. 341.

4. Oxopropanedinitrile, NC—CO—CN

Oxopropanedinitrile (C_3N_2O) Ideal gas $M_r = 80.0458$

$\Delta_f H°(0\ \mathrm{K}) = 246.5 \pm 6.4\ \ \mathrm{kJ\,mol^{-1}}$

$S°(298.15\ \mathrm{K}) = 310.0 \pm 1.0\ \ \mathrm{J\,K^{-1}\,mol^{-1}}$ $\Delta_f H°(298.15\ \mathrm{K}) = 247.5 \pm 6.4\ \ \mathrm{kJ\,mol^{-1}}$

Molecular constants

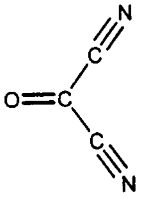
Point group: $C_{2\nu}$ Symmetry number: $\sigma = 2$

Ground electronic state: $\tilde{X}\ {}^1A_1$ Energy: $\epsilon_X = 0\ \ \mathrm{cm^{-1}}$ Quantum weight: $g_X = 1$

Vibrational frequencies, ν_i, and degeneracies g_i

Symmetry		ν_i, $\mathrm{cm^{-1}}$	g_i	Symmetry		ν_i, $\mathrm{cm^{-1}}$	g_i
A_1	ν_1	2230	1	B_1	ν_7	712	1
	ν_2	1711	1		ν_8	208.2	1
	ν_3	712	1	B_2	ν_9	2230	1
	ν_4	553	1		ν_{10}	1124	1
	ν_5	127.5	1		ν_{11}	550	1
A_2	ν_6	307	1		ν_{12}	245.2	1

Geometry



$r(\mathrm{C{=}O}) = 1.204 \pm 0.005\ \ \text{Å}$

$r(\mathrm{C{-}C}) = 1.461 \pm 0.005\ \ \text{Å}$

$r(\mathrm{C{\equiv}N}) = 1.159 \pm 0.015\ \ \text{Å}$

$\angle \mathrm{C{-}C{-}C} = 114.7 \pm 0.5°$

$\angle \mathrm{C{-}C{\equiv}N} = 179.2 \pm 0.5°$

Rotational constants in $\mathrm{cm^{-1}}$:

$A_0 = 0.225\,529 \quad B_0 = 0.097\,556 \quad C_0 = 0.067\,980.$

Product of moments of inertia: $I_A I_B I_C = 14\,666 \times 10^{-117}\ \ \mathrm{g^3\,cm^6}$.

4.1. Enthalpy of Formation

The recommended value of enthalpy of formation of oxopropanedinitrile is based on calorimetric measurements by von Glemser and Häusser[1] as evaluated by Cox and Pilcher.[2]

4.2. Heat Capacity and Entropy

Spectroscopic,[3–10] electron diffraction,[11] and theoretical[12–20] investigations have shown that oxopropanedinitrile, $CO(CN)_2$, is planar in its ground electronic state $\tilde{X}\ {}^1A_1$ and belongs to the $C_{2\nu}$ symmetry group. In this work, the product of the principal moments of inertia of $CO(CN)_2$ was calculated using the rotational constants determined by microwave spectroscopy.[4] In the absence of isotopic data, a unique set of geometrical parameters cannot be obtained from the microwave spectrum. Structural parameters given above are r_e parameters determined by combining the results of electron diffraction, microwave spectroscopy, and *ab initio* calculations.[20] These parameters give values for rotational constants which are only 0.3%–0.9% different from the observed values. The C—C≡N chain appears to be nearly linear, the deviation from linearity being 0.8°. A small inward bend (0.5°–2°) was also found by *ab initio* calculations[12,13,19] but is contradicted by *ab initio* calculations of Tyrrell[15] where the C—C≡N is bent outwards by 1.2°.

Vibrational spectra of oxopropanedinitrile were studied in the gas, liquid, and solid phase[5–10] but there are still several uncertainties in the assignment of the fundamentals. The vibrational frequencies accepted in this work are those assigned by Miller *et al.*[9] from infrared and Raman spectra of gaseous and liquid oxopropanedinitrile. Their assignment was supported by *ab initio* calculation.[15]

According to the semiempirical calculation,[21] the excited electronic states of $CO(CN)_2$ lie above 24 000 $\mathrm{cm^{-1}}$. They are not taken into account in the calculation of thermodynamic functions.

The uncertainties in the calculated thermodynamic functions (Table 3)are estimated to be (1–2) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $C_p°(T)$ and (1–2.5) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $S°(T)$.

Thermodynamic properties of $CO(CN)_2$ were calculated earlier by Natarajan and Rajendran[22] using electron diffraction structural parameters[11] and the vibrational assignment of Bates and Smith.[8] The numerical data in the four columns of the table of thermodynamic functions in Natarajan and Rajendran[22] are transposed. Moreover, these functions do not correspond to the molecular constants used by the authors. The difference between the $C_p°(T)$ and $S°(T)$ values given here and those by Natarajan and Rajendran[22] amounts to 20 $\mathrm{J\,K^{-1}\,mol^{-1}}$ and could not be due to the discrepancy in molecular constants used.

4.3. References

[1] O. von Glemser and V. Häusser, Z. Naturforsch. B **3**, 159 (1948).

[2] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic, London, 1970); see also J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds* (Thermodynamics Research Center, College Station, TX, 1994), Vol. I.

[3] J. F. Westerkamp, Bol. Acad. Nacl. Cienc. Argen. **42**, 191 (1961).

[4] R. M. Lees, Can, J. Chem. **49**, 367 (1971).

[5] A. Tramer and K. L. Wierzchowski, Bull. Acad. Pol. Sci., Classe III **5**, 411 (1957).

[6] A. Tramer and K. L. Wierzchowski, Bull. Acad. Pol. Sci., Classe III **5**, 417 (1957).

[7] J. Prochorov, A. Tramer, and K. L. Wierzchowski, J. Mol. Spectorsc. **19**, 45 (1966).

[8] J. B. Bates and W. H. Smith, Spectrochim. Acta A **26**, 455 (1970).

[9] F. A. Miller, B. M. Harney, and J. Tyrrell, Spectrochim. Acta A **27**, 1003 (1971).

[10] D. M. Thomas, J. B. Bates, E. R. Lippincott, Indian. J. Pure Appl. Phys. **9**, 969 (1971).

[11] V. Typke, M. Dakkouri, and F. Schlumberger, J. Mol. Struct. **62**, 111 (1980).

[12] W. Kosmus, K. Kalcher, and G. D. Fleming, J. Mol. Struct: THEOCHEM **89**, 317 (1982).

[13] K. Siam, M. Dakkouri, J. D. Ewbank, and L. Schäfer, J. Mol. Struct: THEOCHEM **204**, 291 (1990).

[14] M. Dakkouri, Struct. Chem. **1**, 179 (1990).

[15] J. Tyrrell, J. Mol. Struct.: THEOCHEM **231**, 87 (1991).

[16] M. Dakkouri, J. Mol. Struct.: THEOCHEM **258**, 401 (1992).

[17] J. Tyrrell, J. Mol. Struct.: THEOCHEM **258**, 403 (1992).

[18] J. L. G. De Paz and M. Yanez, J. Mol. Struct.: THEOCHEM **107**, 59 (1984).

[19] M. H. Palmer, J. Mol. Struct.: THEOCHEM **200**, 1 (1989).

[20] J. Demaison, G. Wlodarczak, H. Rück, K. H. Wiedenmann, and H. D. Rudolph, J. Mol. Struct.: **376**, 399 (1996).

[21] C. H. Warren and C. Ching, Theor. Chim. Acta **30**, 1 (1973).

[22] A. Natarajan and S. Rajendran, Can. J. Spectorsc. **26**, 229 (1981).

TABLE 3. Ideal gas thermodynamic properties of oxopropanedinitrile $C_3N_2O(g)$ at the standard state pressure, $p° = 0.1$ MPa ($T_r = 298.15$ K)

T (K)	$C_p°$ (J K^{-1} mol^{-1})	$S°$ (J K^{-1} mol^{-1})	$-(G° - H°(T_r))/T$ (J K^{-1} mol^{-1})	$H° - H°(T_r)$ (kJ mol^{-1})	$\Delta_f H°$ (kJ mol^{-1})	$\Delta_f G°$ (kJ mol^{-1})	$\log K_{fs}°$
0	0.000	0.000	∞	−17.147	246.525	246.525	∞
25	33.558	186.154	838.755	−16.315	246.274	246.273	−514.553
50	37.466	210.389	519.096	−15.435	246.040	246.369	−257.376
75	43.512	226.703	419.028	−14.424	245.902	246.567	−171.722
100	49.389	240.041	372.658	−13.262	245.872	246.796	−128.911
150	59.439	262.030	332.251	−10.533	246.052	247.230	−86.092
180	64.718	273.341	321.506	−8.670	246.268	247.447	−71.806
190	66.369	276.884	319.064	−8.014	246.354	247.510	−68.044
200	67.965	280.329	317.042	−7.342	246.444	247.569	−64.657
210	69.506	283.683	315.374	−6.655	246.539	247.623	−61.592
220	70.992	286.951	314.008	−5.953	246.639	247.672	−58.804
230	72.425	290.138	312.901	−5.235	246.742	247.716	−56.257
240	73.804	293.250	312.018	−4.504	246.848	247.756	−53.922
250	75.131	296.290	311.328	−3.760	246.956	247.792	−51.773
260	76.408	299.262	310.807	−3.002	247.067	247.823	−49.788
270	77.636	302.169	310.434	−2.232	247.179	247.851	−47.949
280	78.818	305.013	310.189	−1.449	247.292	247.873	−46.241
290	79.956	307.799	310.059	−0.655	247.407	247.892	−44.650
298.15	80.853	310.028	310.028	0.000	247.500	247.905	−43.431
300	81.052	310.529	310.029	0.150	247.521	247.907	−43.164
350	85.979	323.404	311.035	4.329	248.092	247.925	−37.000
400	90.165	335.165	313.327	8.735	248.634	247.864	−32.367
450	93.807	346.000	316.363	13.337	249.125	247.738	−28.756
500	97.037	356.054	319.835	18.109	249.559	247.560	−25.862
600	102.566	374.251	327.420	28.099	250.253	247.090	−21.511
700	107.123	390.415	335.286	38.590	250.757	246.521	−18.395
800	110.898	404.974	343.102	49.497	251.123	245.892	−16.055
900	114.022	418.222	350.724	60.748	251.390	245.219	−14.232
1000	116.608	430.373	358.090	72.284	251.851	244.520	−12.772
1100	118.754	441.591	365.177	84.055	251.719	243.809	−11.577
1200	120.542	452.003	371.984	96.023	251.810	243.084	−10.581
1300	122.038	461.712	378.517	108.154	251.862	242.358	−9.738
1400	123.297	470.804	384.788	120.422	251.871	241.623	−9.015
1500	124.364	479.348	390.810	132.807	251.846	240.895	−8.389
1600	125.273	487.404	396.598	145.290	251.779	240.197	−7.842
1700	126.052	495.022	402.165	157.857	251.679	239.474	−7.358
1800	126.724	502.247	407.526	170.497	251.541	238.765	−6.929
1900	127.307	509.114	412.694	183.199	251.366	238.058	−6.545
2000	127.815	515.658	417.680	195.956	251.156	237.363	−6.199

5. Glycolic Acid, HO—CH_2—COOH

Glycolic acid ($C_2H_4O_3$) Ideal gas $M_r = 76.0518$

$\Delta_f H°(0\ \mathrm{K}) = -567.9 \pm 10.0\ \ \mathrm{kJ\ mol^{-1}}$

$S°(298.15\ \mathrm{K}) = 318.6 \pm 5.0\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $\Delta_f H°(298.15\ \mathrm{K}) = -583.0 \pm 10.0\ \ \mathrm{kJ\ mol^{-1}}$

Molecular constants

Point group: C_1

Ground electronic state: $\tilde{X}\ {}^1A$

Symmetry number: $\sigma = 1$

Energy: $\epsilon_X = 0\ \mathrm{cm^{-1}}$

Number of optical isomers: $n = 2$

Quantum weight: $g_X = 1$

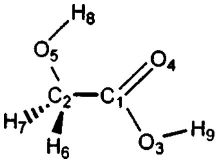
Vibrational frequencies, ν_i, and degeneracies g_i

Symmetry		ν_i, cm^{-1}	g_i	Symmetry		ν_i, cm^{-1}	g_i
A'	ν_1	3561	1		ν_{12}	642	1
	ν_2	3561	1		ν_{13}	468	1
	ν_3	2928	1		ν_{14}	270	1
	ν_4	1774	1	A''	ν_{15}	2919	1
	ν_5	1452	1		ν_{16}	1231	1
	ν_6	1439	1		ν_{17}	1019	1
	ν_7	1332	1		ν_{18}	621	1
	ν_8	1265	1		ν_{19}	495	1
	ν_9	1143	1		ν_{20}	281	1
	ν_{10}	1090	1		ν_{21}	…[a]	1
	ν_{11}	854	1				

[a] Instead of torsional mode $\nu_{21}=152\,\text{cm}^{-1}$, the contributions due to the internal rotation round the C—C bond were calculated from the potential $V(\varphi)=\frac{1}{2}\Sigma_{n=1}^{8}V_n(1-\cos n\varphi)$, where φ is the torsional angle, $V_1=971.1$, $V_2=1192.6$, $V_3=-196.0$, $V_4=-244.1$, $V_5=137.1$, $V_6=-173.5$, $V_7=118.8$, and $V_8=-48.0$ (in cm^{-1}).

COOH top: Reduced moment of inertia, $I_r=1.9292\times10^{-39}$ g cm^2, Symmetry number, $\sigma_m=1$.

Geometry



$r(C_1—C_2)=1.495\pm0.006$ Å
$r(C_1—O_3)=1.349\pm0.006$ Å
$r(C_1═O_4)=1.210\pm0.006$ Å
$r(C_2—O_5)=1.406\pm0.004$ Å
$r(O_3—H_9)=0.989\pm0.019$ Å
$r(O_5—H_8)=0.956\pm0.003$ Å
$r(C_2—H_{6,7})=1.097\pm0.003$ Å

$\angle C_2—C_1—O_3=112.6\pm0.5°$
$\angle C_2—C_1═O_4=124.2\pm0.4°$
$\angle C_1—C_2—O_5=111.3\pm0.4°$
$\angle O_5—C_2—H_{6,7}=110.6\pm0.3°$
$\angle C_1—C_2—H_{6,7}=108.8\pm0.3°$
$\angle C_1—O_3—H_9=105.5\pm1.1°$
$\angle C_2—O_5—H_8=105.2\pm0.1°$

Rotational constants in cm^{-1}:
$A_0=0.356\,783 \quad B_0=0.135\,128 \quad C_0=0.099\,891$.

Product of moments of inertia: $I_AI_BI_C=4555\times10^{-117}$ g^3 cm^6.

Other stable conformers:	Point group	Symmetry number, σ	Number of optical isomers, n	Energy, cm^{-1}
	C_1	1	2	1200
	C_1	1	2	1300

5.1. Enthalpy of Formation

No experimental or theoretical data on enthalpy of formation of gaseous glycolic acid are known from the literature. The value accepted in this work, $\Delta_fH°$ (298.15 K) $=-(583\pm10)$ kJ mol^{-1}, is based on two estimates by additivity methods.

The first value was estimated by group additivity using the equation

$$\begin{aligned}\Delta_fH°(\text{HO—CH}_2\text{—COOH})\\ &=\Delta_fH°[\text{O—(H)(C)}]+\Delta_fH°[\text{C—(H)}_2\text{(CO)(O)}]\\ &\quad+\Delta_fH°[\text{CO—(C)(O)}]+\Delta_fH°[\text{O—(CO)(H)}]\\ &=(-158.6)+(-33.5)+(-147.3)+(-241.8)\\ &=-581.2\ \text{kJ mol}^{-1}\end{aligned}$$

with group values generated by Cohen[1] except for the missing value for the [C—(H)$_2$(CO)(O)] group. The latter was evaluated from values known for related groups:

$$\begin{aligned}\Delta_fH°[\text{C—(H)}_2\text{(CO)(O)}]\\ &=\Delta_fH°[\text{C—(H)}_2\text{(CO)(C)}]\\ &\quad+\Delta_fH°[\text{C—(H)(CO)(C)(O)}]\\ &\quad-\Delta_fH°[\text{C—(H)(CO)(C)}_2]\end{aligned}$$

$$=(-21.8)+(-18.8)$$
$$-(-7.1)=-33.5\ \ \mathrm{kJ\,mol^{-1}}.$$

The other $\Delta_f H°$ value of glycolic acid may be predicted by the method of group equations[2] using

$$\Delta_f H°(\mathrm{HO—CH_2—COOH})$$
$$=\Delta_f H°(\mathrm{CH_3—COOH})+\Delta_f H°(\mathrm{HO—CH_2—CH_3})$$
$$-\Delta_f H°(\mathrm{CH_3—CH_3})$$
$$=(-432.8)+(-235.2)$$
$$-(-83.8)=-584.2\ \ \mathrm{kJ\,mol^{-1}}.$$

Values for $\Delta_f H°$ for CH_3COOH, CH_3CH_2OH, and C_2H_6 were taken from a compilation by Pedley.[3] A value intermediate between the above two estimates was assigned to the enthalpy of formation of glycolic acid.

5.2. Heat Capacity and Entropy

From microwave spectroscopic studies,[4–6] the lowest-energy structure of glycolic acid was concluded to be of C_s symmetry with the alcoholic hydroxyl group pointing toward the carbonyl oxygen of carboxyl group. This structure involves the intramolecular bonding between the alcohol hydrogen and the carbonyl oxygen. With the exception of the methylene hydrogen all the atoms in the molecule were found to be coplanar. The pathways and energy barriers involved in possible conformational interconversions of glycolic acid were investigated by *ab initio* calculations.[7–12] Along with rotamers of *cis*-glycolic acid, where the carbonyl group has the *cis* conformation with its hydroxyl group, the conformers of *trans*-glycolic acid were predicted from theoretical studies. Based on electron diffraction data[13] the second lowest conformer has been assigned to a *cis*-glycolic acid with hydrogen bonding between two hydroxyl groups. The energy difference between these conformers was found to be 1470 $\mathrm{cm^{-1}}$ based on fitting to the diffraction data. However, this result is in conflict with theoretical data [8,10–12] predicting the energy difference for the two lowest conformers to be 530–880 $\mathrm{cm^{-1}}$. Moreover, it has been shown by Godfrey *et al.*[11] from *ab initio* calculations and a microwave study that the two experimentally observed glycolic acid species need not necessarily be the two of lowest energy. The authors in Ref. 11 have assigned the second conformer detected by microwave spectroscopy as the *trans*-glycolic acid with relative energy of ~1200 $\mathrm{cm^{-1}}$. This conformer was structurally quite similar to the *trans*-glycolic acid conformer detected earlier in an infrared matrix isolation study.[9]

The symmetries and relative stabilities of the conformers of glycolic acid adopted in this work are based on the detailed *ab initio* calculations of Godfrey *et al.*[11] who tested some of their predictions experimentally. The lowest energy conformer identified by *ab initio* calculation[11] was found to be the C_1 conformer which is a slightly twisted version of the C_s from detected by microwave spectroscopy.[4–6] A conformer of C_1 symmetry exists in two enantiomeric forms, and there is a small barrier (1.5 $\mathrm{cm^{-1}}$) between this conformer and its mirror image where the saddle point is of C_s symmetry. The ground vibrational state energy in these symmetric double wells may be greater than the height of the saddle point, in which case the effective structure of the observed conformer would closely match the C_s conformer of the saddle point. It should be noted that the decision between assigning C_s or C_1 symmetry is of great importance for the calculation of the thermodynamic functions. For C_1 symmetry the term $R\ln 2$ must be added to both the entropy and Gibbs energy function because two optically isomeric forms are present. C_1 symmetry was accepted in this work as the point group of the lowest-energy form of glycolic acid.

The product of the principal moments of inertia for the most stable conformer of glycolic acid was calculated using the rotational constants determined from microwave spectrum investigation.[4] Structural parameters given above were determined from the microwave spectra of normal and isotopically substituted species of glycolic acid.[5] In general, these geometric molecular parameters are close to those determined from electron diffraction analysis[13] and *ab initio* calculations.[7,8,10]

According to the *ab initio* calculation of Godfrey *et al.*[11] the C_1 conformer, a twisted version of *cis*-form with hydrogen bonding between the hydroxyl groups, is expected to be the second lowest conformer with relative energy of 693 $\mathrm{cm^{-1}}$. In this work, the energy profile between two lowest-energy C_1 conformers[11] was approximated by a potential energy function for internal rotation around the C—C bond,

$$V(\varphi)=\frac{1}{2}\sum_{n=1}^{8} V_n(1-\cos n\varphi),$$

where φ is the $O_4—C_1—C_2—C_5$ torsional angle. The eight coefficients (V_n) in the expansion for this moderately complex potential energy function were determined using data from the *ab initio* calculation by Godfrey *et al.*[11] The flat minimum at $\varphi=0°$ corresponds to the lowest-energy C_1 conformer of glycolic acid. Because of the small barrier height between its enantiomeric forms (1.5 $\mathrm{cm^{-1}}$), they are not represented by the above potential and their contribution was taken into account by adding the $R\ln 2$ to the entropy and Gibbs energy function. The barrier of 1658 $\mathrm{cm^{-1}}$ at $\phi=110°$ separates the lowest-energy conformer from the second C_1 stable conformer with an energy minimum of 693 $\mathrm{cm^{-1}}$ at $\phi=155°$. There is a barrier of 338 $\mathrm{cm^{-1}}$ at $\varphi=180°$ between this conformer and its mirror image. The value of the reduced moment of inertia I_r was calculated using the molecular structural parameters of Blom and Bauder.[5] The next most abundant C_1 conformers with relative energies of ~1200 and 1300 $\mathrm{cm^{-1}}$ (Goldfrey *et al.*[11]) were taken into account in this work ignoring their internal rotation and adopting their molecular constants to be the same as those of the basic conformer. The conformers with energies of about 2000 cm^{-1} and higher were ignored because of their negligible contribution to the thermodynamic functions.

Hollenstein *et al.*[14] have measured the infrared spectra of 11 isotopic modifications of glycolic acid isolated in an argon matrix and have evaluated the transferable valence force field that reproduced the observed frequencies and isotopic shifts very satisfactorily. The vibrational assignment by Hollenstein *et al.*[14] for C_s symmetry is adopted in this work. Fundamentals of glycolic acid calculated by an *ab initio* method[10] are close to experimental values except for the low-frequency torsional mode.

The uncertainties in the calculated thermodynamic functions (Table 4) may reach (3–5) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $C_p°(T)$ and (5–10) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $S°(T)$. They are essentially due to the approximate treatment of internal rotation in glycolic acid.

Ideal gas thermodynamic properties of glycolic acid have not been reported previously.

5.3. References

[1] N. Cohen, J. Phys. Chem. Ref. Data **25**, 1411 (1996).

[2] D. R. Stull, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Krieger, Malabar, FL, 1987); see also the ‘‘difference method,’’ N. Cohen and S. W. Benson, Chem. Rev. **93**, 2419 (1993).

[3] J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds* (Thermodynamics Research Center, College Station, TX, 1994), Vol. I.

[4] C. E. Blom and A. Bauder, Chem. Phys. Lett. **82**, 492 (1981).

[5] C. E. Blom and A. Bauder, J. Am. Chem. Soc. **104**, 2993 (1982).

[6] H. Hasegawa, O. Ohashi, and I. Yamaguchi, J. Mol. Struct. **82**, 205 (1982).

[7] M. D. Newton and G. A. Jeffrey, J. Am. Chem. Soc. **99**, 2413 (1977).

[8] T.-K. Ha, C. E. Blom, and H. H. Günthard, J. Mol. Struct.; THEOCHEM **85**, 285 (1981).

[9] H. Hollenstein, T.-K. Ha, and H. H. Günthard, J. Mol. Struct. **146**, 289 (1986).

[10] M. Flock and M. Ramek, Int. J. Quant. Chem. **26**, 505 (1992).

[11] P. D. Godfrey, F. M. Rodgers, and R. D. Brown, J. Am. Chem. Soc. **119**, 2232 (1997).

[12] F. Jensen, Acta Chem. Scand. **51**, 439 (1997).

[13] K. Iijima, M. Kato, and B. Beagley, J. Mol. Struct. **295**, 289 (1993).

[14] H. Hollenstein, R. W. Schär, N. Schwizgebel, G. Grassi, and H. H. Günthard, Spectrochim. Acta A **39**, 193 (1983).

TABLE 4. Ideal gas thermodynamic properties of glycolic acid $C_2H_4O_3$(g) at the standard state pressure, $p° = 0.1$ MPa ($T_r = 298.15$ K)

T (K)	$C_p°$ ($\mathrm{J\ K^{-1}\ mol^{-1}}$)	$S°$ ($\mathrm{J\ K^{-1}\ mol^{-1}}$)	$-(G° - H°(T_r))/T$ ($\mathrm{J\ K^{-1}\ mol^{-1}}$)	$H° - H°(T_r)$ ($\mathrm{kJ\ mol^{-1}}$)	$\Delta_f H°$ ($\mathrm{kJ\ mol^{-1}}$)	$\Delta_f G°$ ($\mathrm{kJ\ mol^{-1}}$)	$\log K_f°$
0	0.000	0.000	∞	−17.007	−567.940	−567.940	∞
25	37.880	194.730	839.900	−16.129	−569.214	−566.334	1183.274
50	39.654	221.605	524.756	−15.158	−571.011	−562.818	587.964
75	42.201	238.111	426.614	−14.138	−572.893	−558.300	388.829
100	46.011	250.752	381.121	−13.037	−574.448	−553.193	288.955
150	55.327	271.119	341.183	−10.510	−577.040	−541.987	188.734
180	61.435	281.742	330.402	−8.759	−578.430	−534.844	155.206
190	63.524	285.120	327.931	−8.134	−578.873	−532.410	146.368
200	65.636	288.431	325.873	−7.488	−579.308	−529.953	138.408
210	67.769	291.685	324.168	−6.821	−579.732	−527.475	131.200
220	69.920	294.888	322.764	−6.133	−580.147	−524.977	124.644
230	72.089	298.043	321.621	−5.423	−580.551	−522.460	118.653
240	74.272	301.158	320.704	−4.691	−580.945	−519.926	113.157
250	76.467	304.234	319.983	−3.937	−581.327	−517.376	108.098
260	78.669	307.276	319.436	−3.162	−581.698	−514.811	103.425
270	80.876	310.286	319.042	−2.364	−582.057	−512.231	99.096
280	83.082	313.267	318.782	−1.544	−582.403	−509.639	95.073
290	85.285	316.221	318.643	−0.702	−582.737	−507.034	91.325
298.15	87.074	318.610	318.610	0.000	−583.000	−504.902	88.456
300	87.480	319.150	318.611	0.161	−583.059	−504.418	87.826
350	98.188	333.446	319.716	4.806	−584.470	−491.195	73.306
400	108.146	347.217	322.298	9.968	−585.568	−477.792	62.392
450	117.092	360.482	325.809	15.603	−586.386	−464.267	53.890
500	124.943	373.235	329.918	21.658	−586.965	−450.666	47.080
600	137.622	397.192	339.162	34.818	−587.557	−423.343	36.855
700	147.128	419.154	349.044	49.077	−587.601	−395.964	29.547
800	154.453	439.298	359.085	64.171	−587.259	−368.606	24.067
900	160.307	457.840	369.041	79.919	−586.638	−341.310	19.809
1000	165.136	474.988	378.789	96.198	−585.808	−314.095	16.406
1100	169.214	490.923	388.267	112.921	−584.815	−286.970	13.627
1200	172.712	505.800	397.449	130.022	−583.696	−259.942	11.315
1300	175.742	519.747	406.326	147.448	−582.482	−233.008	9.362
1400	178.385	532.870	414.900	165.157	−581.200	−206.174	7.692
1500	180.703	545.258	423.182	183.114	−579.868	−179.431	6.248
1600	182.744	556.987	431.181	201.289	−578.508	−152.761	4.987
1700	184.547	568.121	438.912	219.655	−577.132	−126.198	3.878
1800	186.144	578.716	446.387	238.191	−575.750	−99.707	2.893
1900	187.564	588.818	453.620	256.878	−574.375	−73.299	2.015
2000	188.830	598.472	460.623	275.699	−573.016	−46.960	1.226

6. Glyoxal, O═CH—CH═O

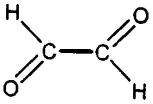
Glyoxal ($C_2H_2O_2$) Ideal gas $M_r = 58.0366$

$\Delta_f H°(0\ \mathrm{K}) = -206.4 \pm 0.5\ \mathrm{kJ\ mol^{-1}}$

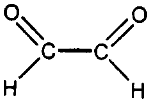
$S°(298.15\ \mathrm{K}) = 272.5 \pm 1.0\ \ \mathrm{J\ K^{-1}\ mol^{-1}}$ $\Delta_f H°(298.15\ \mathrm{K}) = -212.0 \pm 0.8\ \mathrm{kJ\ mol^{-1}}$

Molecular constants

trans-Glyoxal



cis-Glyoxal



	trans-Glyoxal	*cis*-Glyoxal
Point group:	C_{2h}	C_{2v}
Symmetry number, σ:	2	2
Ground electronic state:	$\tilde{X}\,{}^1A_g$	$\tilde{X}\,{}^1A_1$
Quantum weight, g_x:	1	1
Relative energy, ϵ_X, $\mathrm{cm^{-1}}$:	0	1555

Vibrational frequencies, ν_i, and degeneracies, g_i

	Symmetry	ν_i, $\mathrm{cm^{-1}}$	g_i	Symmetry	ν_i, $\mathrm{cm^{-1}}$	g_i
ν_1	A_g	2843.27	1	A_1	2841	1
ν_2		1744.12	1		1746	1
ν_3		1352.60	1		1369	1
ν_4		1065.81	1		827	1
ν_5		550.53	1		284.5	1
ν_6	A_u	801.36	1	A_2	1050	1
ν_7		...[a]	1		...[a]	1
ν_8	B_g	1047.81	1	B_1	750	1
ν_9	B_u	2835.07	1	B_2	2810	1
ν_{10}		1732.10	1		1761	1
ν_{11}		1312.38	1		1360	1
ν_{12}		338.55	1		825	1

	trans-Glyoxal	*cis*-Glyoxal
Geometry:		
r(C—C)	1.525 ± 0.003 Å	1.522 Å
r(C═O)	1.207 ± 0.002 Å	1.208 Å
r(C—H)	1.116 ± 0.008 Å	1.109 Å
∠C—C═O	121.2 ± 0.2°	123.1°
∠O═C—H	126.6 ± 1.7°	122.8°
Rotational constants, $\mathrm{cm^{-1}}$:		
A_0	1.844 319	0.891 062
B_0	0.160 021	0.206 503
C_0	0.147 351	0.167 864
Product of moments of inertia, $I_AI_BI_C \times 10^{117}$ $\mathrm{g^3\,cm^6}$:	504.42	710.17
Reduced moment of inertia for CHO top, $I_r \times 10^{39}$ $\mathrm{g\,cm^2}$:	0.8199	0.4807
Symmetry number for CHO top, σ_m:	1	1

[a] Instead of torsional mode ν_7 (126.7 $\mathrm{cm^{-1}}$ for *trans*- and 89.6 $\mathrm{cm^{-1}}$ for *cis*-glyoxal), the contributions due to the internal rotation were calculated from the potential $V(\varphi) = \frac{1}{2}\Sigma_{n=1}^{6} V_n(1-\cos n\varphi)$, where φ is the torsional angle, $V_1 = 1587.6$, $V_2 = 1139.5$, $V_3 = -59.0$, $V_4 = -110.9$, $V_5 = 40.0$, and $V_6 = 0.0$ (in $\mathrm{cm^{-1}}$). For the internal rotational constant B, the Fourier expansion coefficients were used $B = B_0 + \Sigma_{n=1}^{6} B_n \cos n\varphi$ where $B_0 = 4.213$, $B_1 = -1.117$, $B_2 = 0.421$, $B_3 = -0.126$, $B_4 = 0.040$, $B_5 = -0.015$, and $B_6 = 0$ (in $\mathrm{cm^{-1}}$).

6.1. Enthalpy of Formation

The value of $\Delta_f H°$ (298.15 K) for glyoxal accepted in this work was determined by Fletcher and Pilcher[1] from measurements of heat of combustion by flame calorimetry. A lower value of $-224.3\ \mathrm{kJ\,mol^{-1}}$ was obtained by Curtiss *et al.*[2] from *ab initio* calculation.

6.2. Heat Capacity and Entropy

It has been shown both spectroscopically[3–18] and theoretically[19–35] that glyoxal (O═CH—CH═O) undergoes rotational isomerization and exists in two planar, *trans* and *cis*, forms. The structure of the more stable *trans* conformer has been determined by a combination of electron diffraction and rotational data.[36] As *trans*-glyoxal has no dipole moment, there is no microwave spectrum, and accurate rotational constants for the ground state can only be obtained by rotational analysis of infrared or electronic absorption bands. The values obtained for the rotational constants of *trans*-glyoxal[4,5,13,14,37] are in good agreement with each other. Using the rotational constants for the five isotopic species, Birss *et al.*[11] have evaluated the structural parameters for *trans*-glyoxal. These parameters are in excellent agreement with electron diffraction results.[36] In general, these experimental geometries are in good agreement with theoretical results.[24,26,28,33–35,38–43] The product of the principal moments of inertia for the planar structure of *trans*-glyoxal of C_{2h} symmetry was calculated here using the rotational constants determined from a high-resolution Fourier-transform study of *trans*-glyoxal.[15] Structural parameters of *trans*-glyoxal given above are those obtained from an electron diffraction investigation.[36] These parameters reproduce the spectroscopic moments of inertia with in an accuracy of 0.2%–0.3%.

Rotational constants for the ground state of *cis*-glyoxal were obtained from rotational analysis of the 0–0 band[6,8] and by microwave spectroscopy.[7,10,12,17,18] The product of the principal moments of inertia for the planar structure of *cis*-glyoxal of C_{2v} symmetry was calculated in this work using the rotational constants determined from microwave studies.[17,18] Sets of possible structural parameters of *cis*-glyoxal were evaluated using the rotational constants for its isotopomers combined with assumptions of the values of some parameters.[7,8,10,28,44] The geometry of *cis*-glyoxal was also calculated by *ab initio*[22,24,26–29,31–33,35,38,39,41,42] and molecular mechanics[43] methods. Structural parameters of *cis*-glyoxal shown above were proposed by Tyulin *et al.*[44] from analysis of microwave data.[17]

Vibrational spectra of glyoxal were studied in the gas phase[4–8,10,13,15,16,45–55] and with matrix isolation techniques.[56–58] The experimental assignments have been confirmed by normal coordinate analyses[44,59–64] and theoretical calculations.[26,28,29,31,34,35,40,43,65–70] The adopted values for vibrational frequencies of *trans*-glyoxal were taken from the investigation of dispersed fluorescence spectra[53] ($\nu_1-\nu_5,\nu_8$), high-resolution infrared spectra[48] ($\nu_6,\nu_7,\nu_{11},\nu_{12}$), a rotational fine structure of the C–H stretching band[5] (ν_9) and a high-resolution infrared Fourier-transform study[15] (ν_{10}). The uncertainties in these values are within 0.5 $\mathrm{cm^{-1}}$. The adopted values of $\nu_1-\nu_7$ and ν_{10} fundamental frequencies of *cis*-glyoxal are those observed from gas and Ar-matrix spectra.[13,18,55,58] For unobserved frequencies ($\nu_8,\nu_9,\nu_{11},\nu_{12}$), the values were selected on the basis of *ab initio* calculations;[28,31,35,68] and their uncertainties are estimated to be 25–50 $\mathrm{cm^{-1}}$.

The torsional potential function for glyoxal has been investigated experimentally[3,6,7,9,13,16,18,71] and theoretically[19–34,70,72] by many authors. An early infrared study[3] suggested a very high *trans-cis* rotation barrier (V_{rot}) of 4810 $\mathrm{cm^{-1}}$ based on a torsional frequency of 128 $\mathrm{cm^{-1}}$. Currie and Ramsay[6] provided the first estimate for *cis-trans* enthalpy difference, $\Delta H=(1125\pm100)\ \mathrm{cm^{-1}}$, from the temperature dependence of *cis* and *trans* absorption bands in the visible spectrum. Durig *et al.*[9] obtained the torsional potential function for glyoxal that fits the infrared data of the *trans* conformer and the microwave intensity data of the *cis* conformer and yields the $\Delta H=(1180\pm150)\ \mathrm{cm^{-1}}$ with a barrier height $V_{\mathrm{rot}}=1770\ \mathrm{cm^{-1}}$. The energy difference between the *cis* and *trans* conformers has been revised upwards twice by Butz *et al.*, first to $(1350\pm200)\ \mathrm{cm^{-1}}$ derived from a spectroscopic temperature study[13] and then to $(1688\pm100)\ \mathrm{cm^{-1}}$ by fitting spectroscopic data to a torsional potential.[16] The potential function obtained by Butz *et al.*[16] has a barrier to *trans-cis* rotation of 2077 $\mathrm{cm^{-1}}$. Recently Hübner *et al.*[18] have determined the *cis-trans* enthalpy difference, $\Delta H=(1555\pm48)\ \mathrm{cm^{-1}}$, from absorption intensities of glyoxal by microwave spectroscopy. This value is intermediate between the values reported by Butz *et al.*[13,16] Based on this value for ΔH, Hübner *et al.*[18] have recalculated the potential curve for internal rotation in glyoxal ($V_{\mathrm{rot}}=2003\ \mathrm{cm^{-1}}$). Numerous *ab initio* calculations yield different results for ΔH depending on the basis sets and levels of calculation (1050,[20] 1320–1970,[34] 1490,[29] 1500–1990,[31] 1504,[72] ∼1600,[26,27,32] 1700–2200,[23] ∼2000,[22,24,25,28,30] and 2422 $\mathrm{cm^{-1}}$).[70] Due to this wide range they are not of help in deciding among the available experimental data.

The torsional potential function determined by Hübner *et al.*[18] is accepted in this work in order to account for the internal rotation in glyoxal. The Fourier expansion coefficients for the internal rotation constant B were adopted to be the same as those used by Durig *et al.*[9] and later by other authors.[16,18] The values of the reduced moment of inertia, I_r, were calculated from accepted structural parameters (see above).

Experimentally observed absorption spectra of glyoxal have been identified with transitions to the excited electronic states $\tilde{a}\,{}^3A_u$ ($T_0=19\,199\ \mathrm{cm^{-1}}$) and $\tilde{A}\,{}^1A_u$ ($T_0=21\,973\ \mathrm{cm^{-1}}$).[45,73,74] These assignments agree with other experimental[75–79] and theoretical[35,80,81] studies. Dykstra and Schaefer[82] have predicted two low-lying (∼15 000 $\mathrm{cm^{-1}}$) unobserved triplet states from *ab initio* calculation. Because of high energies of excited electronic states of glyoxal, they are not considered in this work. These electronic states would only make an appreciable contribution to the thermo-

TABLE 5. Ideal gas thermodynamic properties of glyoxal $C_2H_2O_2$(g) at the standard state pressure, $p^\circ = 0.1$ MPa ($T_r = 298.15$ K)

T (K)	C_p° ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	S° ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$-(G^\circ - H^\circ(T_r))/T$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$H^\circ - H^\circ(T_r)$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f H^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f G^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	$\log K_f^\circ$
0	0.000	0.000	∞	−13.690	−206.432	−206.432	∞
25	33.558	168.135	682.424	−12.857	−206.857	−206.353	431.146
50	36.353	192.179	431.899	−11.986	−207.559	−205.605	214.791
75	39.053	207.448	354.677	−11.042	−208.268	−204.466	142.401
100	41.428	219.011	319.370	−10.306	−208.805	−203.114	106.095
150	45.964	236.671	289.008	−7.851	−209.665	−200.077	69.672
180	48.675	245.290	281.018	−6.431	−210.146	−198.114	57.490
190	49.594	247.947	279.209	−5.940	−210.306	−197.441	54.280
200	50.525	250.514	277.710	−5.439	−210.467	−196.761	51.388
210	51.471	253.002	276.474	−4.929	−210.627	−196.071	48.769
220	52.433	255.419	275.463	−4.410	−210.788	−195.374	46.387
230	53.414	257.771	274.643	−3.880	−210.948	−194.670	44.210
240	54.414	260.066	273.987	−3.341	−211.107	−193.959	42.213
250	55.434	262.307	273.476	−2.792	−211.265	−193.241	40.375
260	56.473	264.502	273.089	−2.233	−211.422	−192.517	38.677
270	57.533	266.653	272.810	−1.663	−211.576	−191.787	37.103
280	58.611	268.765	272.628	−1.082	−211.729	−191.051	35.641
290	59.707	270.841	272.531	−0.490	−211.880	−190.310	34.278
298.15	60.612	272.508	272.508	0.000	−212.000	−189.702	33.235
300	60.819	272.883	272.509	0.112	−212.027	−189.563	33.005
350	66.557	282.686	273.270	3.296	−212.711	−185.765	27.723
400	72.398	291.956	275.031	6.770	−213.294	−181.874	23.750
450	78.086	300.814	277.407	10.533	−213.765	−177.917	20.652
500	83.427	309.321	280.176	14.572	−214.126	−173.913	18.168
600	92.680	325.380	286.389	23.395	−214.547	−165.827	14.436
700	99.929	340.236	293.034	33.041	−214.638	−157.696	11.767
800	105.446	353.957	299.803	43.323	−214.488	−149.568	9.766
900	109.622	366.629	306.534	54.086	−214.174	−141.471	8.211
1000	112.807	378.351	313.137	65.214	−213.761	−133.416	6.969
1100	115.270	389.223	319.566	76.623	−213.288	−125.404	5.955
1200	117.204	399.339	325.797	88.251	−212.789	−117.436	5.112
1300	118.749	408.784	331.821	100.051	−212.289	−109.508	4.400
1400	120.001	417.631	337.638	111.991	−211.806	−101.621	3.791
1500	121.030	425.947	343.251	124.044	−211.349	−93.765	3.265
1600	121.887	433.786	348.667	136.191	−210.932	−85.921	2.805
1700	122.609	441.198	353.894	148.417	−210.556	−78.122	2.400
1800	123.223	448.224	358.941	160.709	−210.227	−70.337	2.041
1900	123.749	454.900	363.817	173.058	−209.948	−62.575	1.720
2000	124.204	461.260	368.531	185.457	−209.719	−54.823	1.432

dynamic functions at temperatures above 3000 K.

The uncertainties in the calculated thermodynamic functions (Table 5) are estimated to be (0.5–3.0) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $C_p^\circ(T)$ and (1.0–3.0) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $S^\circ(T)$.

The thermodynamic functions of glyoxal as an equilibrium mixture of *trans* and *cis* conformers were calculated by Compton.[83] The discrepancies between $C_p^\circ(T)$ and $S^\circ(T)$ values calculated in this work and in Compton[83] increase with temperature and reach 3.1 and 2.2 $\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively, at 1000 K. These discrepancies are due to different molecular constants used in the calculations and the noninclusion of internal rotation in glyoxal by Compton.[83] Values of $H^\circ(T) - H^\circ(0)$ given by Compton appear to be in error. Hollenstein *et al.*[84] derived the thermodynamic functions of glyoxal using the semiclassical approximation for the sum-over-states calculation for nonrigid molecules. The difference between their $C_p^\circ(T)$ and $S^\circ(T)$ values and those calculated in this work range from 0.1 to 8.8 $\mathrm{J\,K^{-1}\,mol^{-1}}$ depending on the level of approximation used. The discrepancies with the results of statistical calculations by Natarajan *et al.*[85] amount to (50–60) $\mathrm{J\,K^{-1}\,mol^{-1}}$ and cannot be due to differences in the molecular constants used.

6.3. References

[1] R. A. Fletcher and G. Pilcher, Trans. Faraday Soc. **66**, 794 (1970).
[2] L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. **106**, 1063 (1997).
[3] W. G. Fately, R. K. Harris, F. A. Miller, and R. E. Witkowski, Spectrochim. Acta **21**, 231 (1965).
[4] F. W. Birss, J. M. Brown, A. R. H. Cole, A. Lofthus, S. L. N. G. Krishnamachari, G. A. Osborne, J. Paldus, D. A. Ramsay, and L. Watmann, Can J. Phys. **48**, 1230 (1970).
[5] A. R. H. Cole and G. A. Osborne, J. Mol. Spectrosc. **36**, 376 (1970).
[6] G. N. Currie and D. A. Ramsay, Can. J. Phys. **49**, 317 (1971).
[7] J. R. Durig, C. C. Tong, and Y. S. Li, J. Chem. Phys. **57**, 4425 (1972).
[8] D. A. Ramsay and C. Zauli, Acta Phys. Acad. Sci. Hung. **35**, 79 (1974).
[9] J. R. Durig, W. E. Bucy, and A. R. H. Cole, Can. J. Phys. **53**, 1832 (1975).
[10] A. R. H. Cole, Y. S. Li, and J. R. Durig, J. Mol. Spectrosc. **61**, 346 (1976).
[11] F. W. Birss, D. B. Braund, A. R. H. Cole, R. Engleman, Jr., A. A. Green, S. M. Japar, R. Nanes, B. J. Orr, D. A. Ramsay, and J. Szyszka, Can. J. Phys. **55**, 390 (1977).
[12] A. Kh. Mamleev, R. G. Latypova, L. N. Gunderova, V. I. Tyulin, and N. M. Pozdeev, Zh. Strukt. Khim. **21**, 46 (1980).
[13] K. W. Butz, J. R. Johnson, D. J. Krajnovich, and C. S. Parmenter, J. Chem. Phys. **86**, 5923 (1987).
[14] E. Pebay Peyroula and R. Jost, J. Mol. Spectrosc. **121**, 167 (1987).
[15] J. Van der Auwera, M. Godefroid, M. Herman, T. R. Huet, and J. W. C. Johns, Can. J. Phys. **65**, 1636 (1987).
[16] K. W. Butz, D. J. Krajnovich, and C. S. Parmenter, J. Chem. Phys. **93**, 1557 (1990).
[17] N. M. Pozdeev, A. H. Mamleev, L. N. Gunderova, R. V. Galeev, G. R. Garipova, and V. I. Tyulin, Zh. Strukt. Khim. **36**, 418 (1995).
[18] H. Hübner, A. Leeser, A. Burkert, D. A. Ramsay, and W. Hüttner, J. Mol. Spectrosc. **184**, 221 (1997).
[19] U. Pincelli, B. Cadioli, and D. J. David, J. Mol. Struct. **9**, 173 (1971).
[20] T. K. Ha, J. Mol. Struct. **12**, 171 (1972).
[21] K. R. Sundberg and L. M. Cheung, Chem. Phys. Lett. **29**, 93 (1974).
[22] C. E. Dykstra and H. F. Shaefer III, J. Am. Chem. Soc. **97**, 7210 (1975).
[23] P. N. Skancke and S. Saebø, J. Mol. Struct. **28**, 279 (1975).
[24] Y. Osamura and H. F. Shaefer III, J. Chem. Phys. **74**, 4576 (1981).
[25] G. R. De Mare, J. Mol. Struct: THEOCHEM **107**, 127 (1984).
[26] T. J. Kakumoto, Sci. Hiroshima Univ. A **51**, 69 (1987).
[27] S. Saebǿ, Chem. Phys. **113**, 383 (1987).
[28] C. W. Bock, Y. N. Panchenko, and S. V. Krasnoshchiokov, Chem. Phys. **125**, 63 (1988).
[29] G. E. Scuseria and H. F. Schaefer III, J. Am. Chem. Soc. **111**, 7761 (1989).
[30] C. W. Bock and A. Toro-Labbe, J. Mol. Struct: THEOCHEM **232**, 239 (1991).
[31] G. R. De Mare, J. Mol. Struct: THEOCHEM **253**, 199 (1992).
[32] G. R. De Mare, Yu. N. Panchenko, and A. V. Abramenkov, J. Phys. Chem. **96**, 2111 (1992).
[33] J. Tyrrell, J. Mol. Struct: THEOCHEM **258**, 41 (1992).
[34] B. Mannfors, J. T. Koskinen, L.-O. Pietila, and L. Ahjopalo, J. Mol. Struct: THEOCHEM **393**, 39 (1997).
[35] J. F. Stanton and J. Gauss, Spectrochim. Acta A **53**, 1153 (1997).
[36] K. Kuchitsu, T. Fukuyama, and Y. Morino, J. Mol. Struct. **1**, 463 (1968).
[37] J. Paldus and D. A. Ramsay, Can. J. Phys. **45**, 1389 (1967).
[38] C. W. Bock, P. George, C. J. Mains, and M. Trachtman, J. Mol. Struct. **49**, 211 (1978).
[39] P. George, C. W. Bock, and M. Trachtman, J. Mol. Struct. **69**, 183 (1980).
[40] P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, and A. Vargha, J. Am. Chem. Soc. **105**, 7037 (1983).
[41] C. Van Alsenoy, V. J. Klimkowski, and L. Schäfer, J. Mol. Struct: THEOCHEM **109**, 321 (1984).
[42] N. L. Allinger, L. Schäfer, K. Siam, V. J. Klimkowski, and C. Van Alsenoy, J. Comput. Chem. **6**, 331 (1985).
[43] N. L. Allinger and Y. Fan, J. Comput. Chem. **15**, 251 (1994).
[44] V. I. Tyulin, G. M. Kuramshina, Y. A. Pentin, and L. H. Ho, Zh. Strukt. Khim. **38**, 287 (1997).
[45] J. C. D. Brand, Trans. Faraday Soc. **50**, 431 (1954).
[46] R. K. Harris, Spectrochim. Acta **20**, 1129 (1964).
[47] W. Holzer and D. A. Ramsay, Can. J. Phys. **48**, 1759 (1970).
[48] A. R. H. Cole and G. A. Osborne, Spectrochim. Acta A **27**, 2461 (1971).
[49] R. Y. Dong and D. A. Ramsay, Can. J. Phys. **51**, 1491 (1973).
[50] A. B. Duval, D. A. King, R. Haines, N. R. Isenor, and B. J. Orr, J. Raman Spectrosc. **17**, 177 (1986).
[51] G. A. Bickel and K. K. Innes, J. Chem. Phys. **86**, 1752 (1987).
[52] D. Frye, L. Dai, and H.-L. Lapierre, J. Chem. Phys. **89**, 2609 (1988).
[53] E. Pebay Peyroula, A. Delon, and R. Jost, J. Mol. Spectrosc. **132**, 123 (1988).
[54] W. G. Wickun and K. K. Innes, J. Mol. Spectrosc. **127**, 277 (1988).
[55] R. Y. Dong, R. Nanes, and D. A. Ramsay, Can. J. Chem. **71**, 1595 (1993).
[56] M. Diem, B. G. MacDonald, and E. K. C. Lee, J. Phys. Chem. **85**, 2227 (1981).
[57] L. J. Van IJzendoorn, L. J. Allamandola, F. Baas, S. Körnig, and J. M. Greenberg, J. Chem. Phys. **85**, 1812 (1986).
[58] A. Engdahl and B. Nelander, Chem. Phys. Lett. **148**, 264 (1988).
[59] T. Fukuyama, K. Kuchitsu, and Y. Morino, Bull. Chem. Soc. Jpn. **41**, 3019 (1968).
[60] C. Cossart-Magos, Spectrochim. Acta A **34**, 415 (1978).
[61] H. J. Oelichmann, D. Bougeard, and B. Schrader, J. Mol. Struct. **77**, 149 (1981).
[62] L. O. Pietila, K. Palmo, and B. Mannfors, J. Mol. Spectrosc. **112**, 104 (1985).
[63] L. O. Pietila, K. Palmo, and B. Mannfors, J. Mol. Spectrosc. **116**, 1 (1986).
[64] R. Sander and H. Bettermann, J. Mol. Struct. **263**, 123 (1991).
[65] Y. N. Panchenko, P. Pulay, and F. Torok, J. Mol. Struct. **34**, 283 (1976).
[66] H. Kato, K. Yamashita, and S. Kato, J. Phys. Chem. **82**, 2115 (1978).
[67] C. W. Bock, P. George, and M. Trachtman, J. Mol. Spectrosc. **78**, 248 (1979).
[68] Y. N. Panchenko, G. R. De Mare, and V. I. Pupyshev, J. Phys. Chem. **99**, 17544 (1995).
[69] X. Zhou, C. J. M. Wheeless, and R. Liu, Vib. Spectrosc. **12**, 53 (1996).
[70] M. L. Senent, J. Mol. Struct. **406**, 51 (1997).
[71] H. H. Le and V. I. Tyulin, Zh. Strukt. Khim. **16**, 63 (1975).
[72] E. L. Coitino and J. Tomasi, Chem. Phys. **204**, 391 (1996).
[73] G. W. King, J. Chem. Soc. 5054 (1957).
[74] D. A. Ramsay, M. Verloet, F. Vanhorenbeke, M. Godefroid, and M. Herman, J. Mol. Spectrosc. **149**, 348 (1991).
[75] W. Goetz, A. J. McHugh, and D. A. Ramsay, Can. J. Phys. **48**, 1 (1970).
[76] L. G. Anderson, C. S. Parmenter, H. M. Poland, and J. D. Rau, Chem. Phys. Lett. **8**, 232 (1971).
[77] L. G. Anderson, C. S. Parmenter, and H. M. Poland, Chem. Phys. **1**, 401 (1973).
[78] J. Kelder, H. Cerfontain, J. K. Eweg, and R. P. H. Rettschnick, Chem. Phys. Lett. **26**, 491 (1974).
[79] J. M. Leclercq, C. Mijoule, and F. Yvan, J. Chem. Phys. **64**, 1464 (1976).
[80] C. E. Dykstra, R. R. Lucchese, and H. F. Schaefer III, J. Chem. Phys. **67**, 2422 (1977).
[81] W. B. Mueller, J. F. Harrison, and P. J. Wagner, J. Am. Chem. Soc. **100**, 33 (1978).
[82] C. E. Dykstra and H. F. Schaefer III, J. Am. Chem. Soc. **98**, 401 (1976).
[83] D. A. C. Compton, J. Chem. Soc., Perkin Trans. 2, 1307 (1977).
[84] H. Hollenstein, A. Bauder, and H. H. Günthard, Chem. Phys. **47**, 269 (1980).
[85] A. Natarajan, P. Kolandaivelu, and A. Savarianandam, J. Indian Chem. Soc. **59**, 1155 (1982).

7. Cyanooxomethyl Radical, $O\dot{C}CN$

Cyanooxomethyl radical (C_2NO) Ideal gas $M_r = 54.0281$

$\Delta_f H°$ (0 K) $= 207.2 \pm 10.0$ kJ mol^{-1}

$S°(298.15\,K) = 278.2 \pm 1.5$ J K^{-1}mol^{-1} $\Delta_f H°$ (298.15 K) $= 210.0 \pm 10.0$ kJ mol^{-1}

Molecular Constants

Point group: C_s Symmetry number: $\sigma = 1$

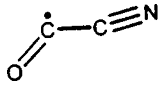
Ground electronic state: $\tilde{X}\,^2A'$ Energy: $\epsilon_X = 0$ cm^{-1} Quantum weight: $g_X = 2$

Excited electronic state: $\tilde{A}\,^2A''$ Energy: $\epsilon_A = 15\,500$ cm^{-1} Quantum weight: $g_A = 2$

Vibrational frequencies, ν_i, and degeneracies, g_i

Symmetry		ν_i, cm^{-1}	g_i	Symmetry		ν_i, cm^{-1}	g_i
A'	ν_1	2249	1		ν_4	488	
	ν_2	1703	1		ν_5	174	1
	ν_3	909	1	A''	ν_6	233	1

Geometry



$r(\mathrm{C{=}O}) = 1.19 \pm 0.02$ Å

$r(\mathrm{C{-}C}) = 1.47 \pm 0.02$ Å

$r(\mathrm{{\equiv}N}) = 1.16 \pm 0.02$ Å

$\angle \mathrm{O{=}C{-}C} = 128 \pm 3°$

$\angle \mathrm{C{-}C{\equiv}N} = 170 \pm 5°$

Product of moments of inertia: $I_A I_B I_C = 183 \times 10^{-117}$ g^3 cm^6.

7.1. Enthalpy of Formation

No experimental data are available for enthalpy of formation of the cyanooxomethyl radical. The value accepted in this work was estimated by Francisco and Liu[1] by using the isodesmic reaction approach with the following reaction:

$$O\dot{C}CN + HCN \rightarrow C_2N_2 + H\dot{C}O.$$

The relationship between the enthalpy of formation of $O\dot{C}CN$ and the enthalpy change of the above reaction is

$$\Delta_f H°(O\dot{C}CN) = \Delta_f H°(C_2N_2) + \Delta_f H°(H\dot{C}O) - \Delta_f H°(HCN) - \Delta_r H°.$$

Based on known experimental enthalpies of formation of HCN, C_2N_2, $H\dot{C}O$, and the $\Delta_r H°$ value predicted by *ab initio* calculations, Francisco and Liu[1] have estimated the enthalpy of formation for $O\dot{C}CN$ to be 207.5–210.0 kJ mol^{-1}.

7.2. Heat Capacity and Entropy

There are no experimental data on structure and vibrational spectra of $O\dot{C}CN$. According to *ab initio* calculations,[1,2] a bent structure of C_s symmetry is adopted in this work for $O\dot{C}CN$ in the ground electronic state $\tilde{X}\,^2A'$. The product of the principal moments of inertia was calculated using the structural parameters shown above. These values are based on the results of *ab initio* calculations[1,2] and comparison with structural parameters of $CO(CN)_2$, COX_2, and $X\dot{C}O$ (X=F, Cl) molecules.

Vibrational frequencies of $O\dot{C}CN$ were calculated in this work using the following force constants:

$$f_{\mathrm{C{=}O}} = 11.413 \text{ mdyn/Å}, \quad f_{\mathrm{C{-}C{\equiv}N}} = 0.110 \text{ mdyn Å},$$

$$f_{\mathrm{C{-}C}} = 7.225 \text{ mdyn/Å}, \quad f_{\mathrm{CC,CO}} = 0.513 \text{ mdyn/Å},$$

$$f_{\mathrm{C{\equiv}N}} = 13.674 \text{ mdyn/Å}, \quad f_{\mathrm{CC,CN}} = -1.543 \text{ mdyn/Å},$$

$$f_{\mathrm{C{-}C{=}O}} = 0.750 \text{ mdyn Å}, \quad f_{\mathrm{CC,CCO}} = 0.585 \text{ mdyn}.$$

These constants were transferred from the $CO(CN)_2$ molecule except for $f_{\mathrm{C{-}C{=}O}}$ and $f_{\mathrm{C{-}C{\equiv}N}}$ whose values were reduced by comparison with the bending force constants in COX_2 and $X\dot{C}O$ (X=F, Cl, Br). Normal coordinate analysis for $CO(CN)_2$ was carried using the vibrational assignment of Miller *et al.*[3] The uncertainties in the calculated frequencies of $O\dot{C}CN$ can reach 50 cm^{-1}. These frequencies agree overall with those resulting from the *ab initio* calculation.[1]

The first excited electronic state $\tilde{A}\,^2A''$ of $O\dot{C}CN$ was predicted at an energy of ~15 500 cm^{-1} by an *ab initio* calculation[1] and was included in the calculations in this work. Structural parameters and vibrational frequencies for the $\tilde{A}\,^2A''$ state were accepted as identical to those of the ground state.

The uncertainties in the calculated thermodynamic functions (Table 6) are estimated to be (1.5–2.0) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $C_p°(T)$ and (1.5–3.0) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $S°(T)$.

Ideal gas thermodynamic properties of the cyanooxomethyl radical have not been reported previously.

7.3. References

[1] J. S. Francisco and R. Liu, J. Chem. Phys. **107**, 3840 (1997).

[2] A. L. Cooksy, J. Am. Chem. Soc. **117**, 1098 (1995).

[3] F. A. Miller, B. M. Harney, and J. Tyrrell, Spectrochim. Acta A **27**, 1003 (1971).

TABLE 6. Ideal gas thermodynamic properties of the cyanooxomethyl radical $C_2NO(g)$ at the standard state pressure, $p° = 0.1$ MPa ($T_r = 298.15$ K)

T (K)	$C_p°$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$S°$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$-(G° - H°(T_r))/T$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$H° - H°(T_r)$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f H°$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f G°$ ($\mathrm{kJ\,mol^{-1}}$)	$\log K_f°$
0	0.000	0.000	∞	−13.594	207.190	207.190	∞
25	33.297	174.512	685.016	−12.763	207.298	206.094	−430.604
50	35.132	197.975	436.251	−11.914	207.405	204.851	−214.003
75	38.803	212.901	359.439	−10.990	207.563	203.542	−141.757
100	42.195	224.543	324.309	−9.977	207.781	202.171	−105.602
150	47.280	242.677	294.223	−7.732	208.327	199.251	−69.384
180	49.604	251.509	286.384	−6.278	208.683	197.403	−57.284
190	50.296	254.210	284.620	−5.778	208.802	196.773	−54.096
200	50.955	256.807	283.165	−5.272	208.921	196.137	−51.225
210	51.582	259.308	281.970	−4.759	209.039	195.495	−48.626
220	52.182	261.721	280.995	−4.240	209.156	194.847	−46.262
230	52.757	264.054	280.208	−3.715	209.271	194.194	−44.102
240	53.309	266.311	279.582	−3.185	209.384	193.536	−42.121
250	53.839	268.498	279.095	−2.649	209.496	192.873	−40.298
260	54.350	270.620	278.729	−2.108	209.605	192.206	−38.614
270	54.842	272.680	278.467	−1.562	209.712	191.535	−37.054
280	55.318	274.683	278.296	−1.012	209.817	190.860	−35.605
290	55.779	276.632	278.205	−0.456	209.919	190.181	−34.255
298.15	56.145	278.183	278.183	0.000	210.000	189.625	−33.221
300	56.226	278.531	278.184	0.104	210.018	189.499	−32.994
350	58.286	287.356	278.877	2.968	210.473	186.041	−27.765
400	60.126	295.262	280.439	5.929	210.852	182.524	−23.835
450	61.811	302.442	282.491	8.978	211.153	178.965	−20.773
500	63.373	309.036	284.820	12.108	211.379	175.376	−18.321
600	66.186	320.845	289.863	18.589	211.634	168.146	−14.638
700	68.609	331.235	295.046	25.332	211.683	160.892	−12.006
800	70.666	340.534	300.161	32.299	211.585	153.643	−10.032
900	72.395	348.960	305.122	39.454	211.379	146.410	−8.497
1000	73.839	356.665	309.897	46.768	211.093	139.204	−7.271
1100	75.044	363.761	314.475	54.214	210.748	132.033	−6.270
1200	76.051	370.335	318.860	61.770	210.353	124.893	−5.436
1300	76.896	376.457	323.057	69.419	209.918	117.792	−4.733
1400	77.609	382.182	327.078	77.145	209.441	110.720	−4.131
1500	78.214	387.558	330.933	84.937	208.931	103.689	−3.611
1600	78.731	392.622	334.632	92.785	208.384	96.710	−3.157
1700	79.175	397.409	338.185	100.681	207.808	89.746	−2.758
1800	79.559	401.946	341.602	108.618	207.199	82.823	−2.403
1900	79.894	406.257	344.893	116.591	206.559	75.929	−2.087
2000	80.189	410.362	348.064	124.596	205.890	69.071	−1.804

8. Oxalic Acid, HO—CO—CO—OH

Oxalic acid ($C_2H_2O_4$) Ideal gas $M_r = 90.0354$

$\Delta_f H°(0\text{ K}) = -721.2 \pm 2.0\ \text{kJ mol}^{-1}$

$S°(298.15\text{ K}) = 320.6 \pm 5.0\ \text{J K}^{-1}\text{mol}^{-1}$ $\Delta_f H°(298.15\text{ K}) = -731.8 \pm 2.0\ \text{kJ mol}^{-1}$

Molecular constants

Point group: C_{2h} Symmetry number: $\sigma = 2$

Ground electronic state: $\tilde{X}\,^1A_g$ Energy: $\epsilon_X = 0\ \text{cm}^{-1}$ Quantum weight: $g_X = 1$

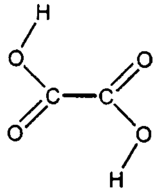
Vibrational frequencies, ν_i, and degeneracies, g_i

Symmetry		ν_i, cm^{-1}	g_i	Symmetry		ν_i, cm^{-1}	g_i
A_g	ν_1	3484	1		ν_{10}	–[a]	1
	ν_2	1800	1	B_g	ν_{11}	851	1
	ν_3	1423	1		ν_{12}	563	1
	ν_4	1195	1	B_u	ν_{13}	3484	1
	ν_5	815	1		ν_{14}	1826	1
	ν_6	608	1		ν_{15}	1278	1
	ν_7	405	1		ν_{16}	1127	1
A_u	ν_8	666	1		ν_{17}	651	1
	ν_9	460	1		ν_{18}	264	1

[a] Instead of torsional mode $\nu_{10} \sim 90\ \text{cm}^{-1}$, the contributions due to the internal rotation about C–C bond were calculated from the potential $V(\varphi) = \frac{1}{2}V_1(1 - \cos\varphi)$, where φ is the torsional angle and $V_1 = 700\ \text{cm}^{-1}$.

COOH top: Reduced moment of inertia, $I_r = 3.6454 \times 10^{-39}\ \text{g cm}^2$, Symmetry number, $\sigma_m = 1$

Geometry



$r(\text{C—C}) = 1.548 \pm 0.004$ Å
$r(\text{C═O}) = 1.208 \pm 0.001$ Å
$r(\text{C—O}) = 1.339 \pm 0.002$ Å
$r(\text{O—H}) = 1.056 \pm 0.014$ Å
$\angle\text{C—C═O} = 123.1 \pm 0.9°$
$\angle\text{O═C—O} = 125.0 \pm 0.2°$
$\angle\text{C—O—H} = 104.4 \pm 2.3°$

Product of moments of inertia: $I_A I_B I_C = 11\,950 \times 10^{-117}\ \text{g}^3\text{cm}^6$.

8.1. Enthalpy of Formation

Wilhoit and Shiao[1] have measured the enthalpy of combustion of solid oxalic acid in a rotating platinum bomb calorimeter and have calculated $\Delta_f H°(C_2H_2O_4, \text{cr}, 298.15\text{ K}) = -(829.9 \pm 1.0)\ \text{kJ mol}^{-1}$. The enthalpy of formation of gaseous oxalic acid is calculated from this value by adding the enthalpy of sublimation, $\Delta_{\text{sub}}H° = 98.1\ \text{kJ mol}^{-1}$, obtained from vapor pressure measurements.[2]

8.2. Heat Capacity and Entropy

Nahlovska *et al.*[3] carried out an electron diffraction and an IR study of oxalic acid indicating that the structure was in a planar *trans* conformation (C_{2h} symmetry) in which the hydrogen atom of one COOH group participated in intramolecular hydrogen bonding with the carbonyl oxygen of the other COOH group (''hydrogen bonded'' *trans* conformer). Infrared matrix-isolation spectra of oxalic acid[4] were interpreted in terms of the same model and the tentative conclusion was made that a second conformer of oxalic acid exists in the vapor phase. This conformer was suggested to be a *trans* form (C_{2h} symmetry) with the hydrogen atom of each COOH group oriented towards the carbonyl oxygen of the same COOH group (''free'' *trans* form). Oxalic acid was determined to be in its *trans* conformation from x-ray crystallographic studies[5] and no other conformers were observed. Studies of oxalic acid in solution[6] favored almost free rotation, which would include a range of possible conformations. *Ab initio* studies of oxalic acid[7–9] have obtained a most stable hydrogen bonded *trans* planar structure in agreement with the results of an electron diffraction investigation.[3] The hydrogen bonded or free *trans* form was found to be lowest energy depending on the basis set used in the *ab initio* calculations.[10] The free *trans* conformer was reported to be most stable by an earlier *ab initio* study.[11]

The hydrogen bonded *trans* form (C_{2h} symmetry) is accepted for oxalic acid in this work. Its product of principal moments of inertia was calculated using the structural parameters determined from the electron diffraction study.[3] Following the results of a theoretical calculation by Tyrrell,[9] it was assumed that there is a slight energy preference for this conformer and only a small barrier of about 2 kcal mol^{-1} (700 cm^{-1}) separating it from other stable conformers. The simple approximate potential,

$$V(\varphi)=\tfrac{1}{2}V_1(1-\cos\varphi),$$

where φ is the OC—CO torsional angle, was used here for the calculation of internal rotational contributions to the thermodynamic functions of oxalic acid. The value of the reduced moment of inertia for the COOH top was derived from the molecular constants shown above.

There are several studies of the vibrational spectra of the free $C_2H_2O_4$ molecule[3,4,12–14] but some fundamentals are still unobserved. Stace and Oralratmanee[14] have reported the infrared vapor phase measurements and the first vapor phase Raman spectra. They have proposed a new vibrational frequencies assignment based on their experimental results as well as calculated in-plane frequencies using an Urey–Bradley force field derived from formic and acetic acid. Redington and Redington[4] have investigated the infrared spectra of oxalic acid vapor and the infrared spectra of matrix-isolated $C_2H_2O_4$, C_2HDO_4, and $C_2D_2O_4$ and have carried out a normal coordinate analysis using a general valence force field for the in-plane infrared-active modes. None of the above studies, however, gives a complete vibrational assignment for oxalic acid. De Villepin and Novak[15] have developed a general valence force field for both infrared and Raman frequencies using the relatively small number of experimentally observed fundamentals. Their force field reproduces the experimental vibrational spectra of oxalic and is comparable with force fields already known for other carboxylic acids. The fundamental frequencies $\nu_2-\nu_5$ and ν_7 adopted here were observed in the Raman spectra of gaseous oxalic acid.[14] The 405 cm^{-1} mode was subsequently reassigned to ν_7.[4] The values of ν_8, ν_9, $\nu_{13}-\nu_{16}$, and ν_{18} are those determined from gas-phase infrared spectra.[4] The value for ν_{17} was obtained from spectra of neon matrix-isolated oxalic acid.[4] The uncertainties in these experimental frequencies are in the range of 5–10 cm^{-1}.

Redington and Redington[4] have suggested tentative values for $\nu_6(A_g)=538$ cm^{-1}, $\nu_{11}(B_g)=590$ cm^{-1}, and $\nu_{12}(B_g)=512$ cm^{-1} fundamentals using possible combination bands. The adopted values of these frequencies were taken from normal coordinate calculations.[15] Calculations for the other frequencies are in good agreement with experimental results. The value of the symmetric O—H stretching frequency ν_1 was accepted to be the same as the value of antisymmetric O—H stretching (ν_{13}) and it coincides with the calculated value.[15] The uncertainties in these frequencies are estimated to be 25–50 cm^{-1}.

Evidently due to its weak intensity, the C—C torsion mode $\nu_{10}(A_u)$ was not observed in a vapor phase spectra search that extended down to 35 cm^{-1}.[4] *Ab initio* calculations[8,10] have suggested the value of 160 cm^{-1} for the torsional mode, however, it should be noted that all other calculated values are much greater than those from experiment. Cyvin and Alfheim[16] have calculated $\nu_{10}=90$ cm^{-1} using force constants transferred from formic and acetic acids. The value of 110 cm^{-1} was obtained from other normal coordinate calculation.[15] The corresponding torsional mode for oxalyl fluoride (F—CO—CO—F) was observed in the gas phase at 54 cm^{-1} and in the solid phase at 94 cm^{-1}.[17] From the ratio of $\nu_{\text{tors}}(C_2F_2O_2,\ \text{solid})/\nu_{\text{tors}}(C_2F_2O_2,\ \text{gas})=1.74$ and the value of 138 cm^{-1} for the torsional mode of solid oxalic acid,[15,18] the value of $\sim$80 cm^{-1} for the torsional mode of gaseous oxalic acid is expected.

The uncertainties in the calculated thermodynamic functions (Table 7) may be as much as (5–7) J K^{-1} mol^{-1} for $C_p°(T)$ and (5–10) J K^{-1} mol^{-1} for $S°(T)$. These uncertainties arise from the uncertainties in the adopted values of the vibrational frequencies and the simple and approximate model for internal rotation.

Ideal gas thermodynamic properties of oxalic acid have not been reported previously.

8.3. References

[1] R. C. Wilhoit and D. Shiao, J. Chem. Eng. Data **9**, 595 (1964).

[2] R. S. Bradley and S. Cotson, J. Chem. Soc. 1684 (1953).

[3] Z. Nahlovska, B. Nahlovsky, and T. G. Strand, Acta Chem. Scand. **24**, 2617 (1970).

[4] R. L. Redington and T. E. Redington, J. Mol. Struct. **48**, 165 (1978).

[5] J. L. Derissen and P. H. Smit, Acta Crystallogr. Sect. B: Struct. Crystollgr. Cryst. Chem. **30**, 2240 (1974).

[6] T. A. Shippey, J. Mol. Struct. **65**, 71 (1980).

[7] C. Van Alsenoy, V. J. Klimkowski, and L. Schäfer, J. Mol. Struct: THEOCHEM **109**, 321 (1984).

[8] T. Kakumoto, J. Sci. Hiroshima Univ. A **51**, 69 (1987).

[9] J. Tyrrell, J. Mol. Struct: THEOCHEM **258**, 389 (1992).

[10] T. Kakumoto, K. Saito, and A. Imamura, J. Phys. Chem. **91**, 2366 (1987).

[11] D. Ajo, G. Condorelli, I. Fragala, and G. Granozzi, J. Mol. Struct. **37**, 160 (1977).

[12] M. Pava Bruce and F. E. Stafford, J. Phys. Chem. **72**, 4628 (1968).

[13] L. Bardet, G. Fleury, and V. Tabacik, C. R. Acad. Sci. B **270**, 1277 (1970).

[14] B. C. Stace and C. Oralratmanee, J. Mol. Struct. **18**, 339 (1973).

[15] J. De Villepin, A. Novak, and D. Bougeard, Chem. Phys. **73**, 291 (1982).

[16] S. J. Cyvin and I. Alfheim, Acta Chem. Scand. **24**, 2648 (1970).

[17] J. R. Durig, S. C. Brown, and S. E. Hannum, J. Chem. Phys. **54**, 4428 (1971).

[18] J. De Villepin, A. Novak, and F. Romain, Spectrochim. Acta A **34**, 1009 (1978).

TABLE 7. Ideal gas thermodynamic properties of oxalic acid $C_2H_2O_4$(g) at the standard state pressure, $p° = 0.1$ MPa ($T_r = 298.15$ K)

T (K)	$C_p°$ (J K^{-1} mol^{-1})	$S°$ (J K^{-1} mol^{-1})	$-(G° - H°(T_r))/T$ (J K^{-1} mol^{-1})	$H° - H°(T_r)$ (kJ mol^{-1})	$\Delta_f H°$ (kJ mol^{-1})	$\Delta_f G°$ (kJ mol^{-1})	$\log K_f°$
0	0.000	0.000	∞	−17.321	−721.180	−721.180	∞
25	40.556	193.337	848.905	−16.389	−722.227	−719.030	1502.311
50	41.771	221.869	529.039	−15.359	−723.498	−715.371	747.333
75	43.565	239.102	429.695	−14.295	−724.813	−711.016	495.189
100	46.685	252.031	383.721	−13.169	−725.959	−706.240	368.897
150	56.008	272.618	343.382	−10.615	−727.905	−695.943	242.346
180	62.509	283.401	332.497	−8.837	−728.902	−689.455	200.072
190	64.693	286.839	330.004	−8.201	−729.209	−687.255	188.937
200	66.861	290.213	327.931	−7.544	−729.504	−685.040	178.912
210	69.005	293.527	326.214	−6.864	−729.786	−682.809	169.837
220	71.116	296.786	324.802	−6.164	−730.057	−680.566	161.585
230	73.190	299.993	323.654	−5.442	−730.316	−678.311	154.047
240	75.223	303.151	322.734	−4.700	−730.564	−676.044	147.135
250	77.213	306.262	322.013	−3.938	−730.801	−673.768	140.774
260	79.160	309.329	321.466	−3.156	−731.027	−671.482	134.901
270	81.061	312.352	321.073	−2.355	−731.243	−669.187	129.460
280	82.918	315.334	320.815	−1.535	−731.450	−666.886	124.407
290	84.731	318.275	320.677	−0.696	−731.646	−664.576	119.701
298.15	86.176	320.644	320.644	0.000	−731.800	−662.689	116.099
300	86.501	321.178	320.645	0.160	−731.834	−662.260	115.308
350	94.724	335.142	321.729	4.695	−732.644	−650.598	97.095
400	101.995	348.276	324.235	9.616	−733.273	−638.832	83.422
450	108.424	360.668	327.601	14.880	−733.761	−626.996	72.779
500	114.112	372.392	331.499	20.446	−734.137	−615.113	64.260
600	123.628	394.073	340.152	32.352	−734.633	−591.258	51.473
700	131.195	413.720	349.281	45.107	−734.871	−567.341	42.335
800	137.323	431.652	358.473	58.543	−734.902	−543.401	35.480
900	142.375	448.127	367.531	72.536	−734.765	−519.472	30.149
1000	146.605	463.353	376.362	86.991	−734.487	−495.566	25.885
1100	150.187	477.499	384.921	101.836	−734.087	−471.692	22.398
1200	153.247	490.701	393.192	117.011	−733.590	−447.859	19.495
1300	155.880	503.074	401.173	132.471	−733.013	−424.068	17.039
1400	158.158	514.711	408.872	148.175	−732.379	−400.327	14.936
1500	160.137	525.692	416.297	164.092	−731.700	−376.632	13.115
1600	161.866	536.084	423.462	180.195	−730.994	−352.965	11.523
1700	163.381	545.943	430.379	196.458	−730.273	−329.363	10.120
1800	164.714	555.320	437.062	212.865	−729.544	−305.796	8.874
1900	165.891	564.258	443.523	229.396	−728.823	−282.276	7.760
2000	166.934	572.794	449.775	246.038	−728.113	−258.789	6.759

9. Methyl Hydroperoxide, CH_3—O—O—H

Methyl hydroperoxide (CH_4O_2) Ideal gas $M_r = 48.0414$

$\Delta_f H°(0\ \mathrm{K}) = -126.2 \pm 5.0$ kJ mol^{-1}

$S°(298.15\ \mathrm{K}) = 276.5 \pm 3.0$ J K^{-1} mol^{-1} $\Delta_f H°(298.15\ \mathrm{K}) = -139.0 \pm 5.0$ kJ mol^{-1}

Molecular constants

Point group: C_1

Symmetry number: $\sigma = 1$

Number of optical isomers: $n = 2$

Ground electronic state: $\tilde{X}\ {}^1A$

Energy: $\epsilon_X = 0$ cm^{-1}

Quantum weight: $g_X = 1$

Vibrational frequencies, ν_i, and degeneracies, g_i

Symmetry		ν_i, cm^{-1}	g_i	Symmetry		ν_i, cm^{-1}	g_i
A	ν_1	3604	1		ν_9	1145	1
	ν_2	2957	1		ν_{10}	1115	1
	ν_3	2955	1		ν_{11}	1003	1

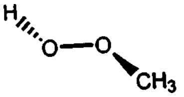
ν_4	2861	1	ν_{12}	800	1
ν_5	1509	1	ν_{13}	415	1
ν_6	1453	1	ν_{14}	...[a]	1
ν_7	1450	1	ν_{15}	...[b]	1
ν_8	1348	1			

[a] Instead of torsional mode $\nu_{14}=240\ \mathrm{cm}^{-1}$, the contributions due to the internal rotation of CH_3 group around the C—O bond were calculated from the potential $V(\varphi)=\frac{1}{2}V_3(1-\cos 3\varphi)$, where φ is the H—C—O—O torsional angle and $V_3=1120\ \mathrm{cm}^{-1}$.

[b] Instead of torsional mode $\nu_{15}=149\ \mathrm{cm}^{-1}$, the contributions due to the internal rotation of OH group around the O-O bond were calculated from the potential: $V(\varphi)=V_0+V_1\cos\varphi+V_2\cos 2\varphi+V_3\cos 3\varphi$, where φ is the C—O—O—H torsional angle, $V_0=780.7$, $V_1=1111.1$, $V_2=555.6$, and $V_3=52.6$ (in cm^{-1}).

CH_3 top: Reduced moment of inertia, $I_r=0.4282\times 10^{-39}\ \mathrm{g\,cm}^2$, Symmetry number, $\sigma_m=3$.

OH top: Reduced moment of inertia, $I_r=0.138\times 10^{-39}\ \mathrm{g\,cm}^2$, Symmetry number, $\sigma_m=1$.



Geometry

$r(\text{C—H})=1.090\pm 0.010$ Å
$r(\text{O—H})=0.970\pm 0.005$ Å
$\angle\text{C—O—O}=105.3\pm 0.5$ Å
$\angle\text{O—O—H}=100.0\pm 2.0°$
$\angle\text{H—C—O}=109.5\pm 4.0°$
$\varphi(\text{C—O—O—H})=120\pm 5°$
$r(\text{C—O})=1.420\pm 0.005$ Å
$r(\text{O—O})=1.460\pm 0.010$ Å

Rotational constants in cm^{-1}:
$A_0=1.434\,544\quad B_0=0.350\,826\quad C_0=0.301\,985$.

Product of moments of inertia: $I_AI_BI_C=144.3\times 10^{-117}\ \mathrm{g}^3\,\mathrm{cm}^6$.

9.1. Enthalpy of Formation

Experimental data on enthalpy of formation are not available for methyl hydroperoxide. Values of $\Delta_f H°(CH_3OOH,\text{g},298.15\ \text{K})$ between -122 and $-138\ \mathrm{kJ\,mol^{-1}}$ were estimated from semiempirical,[1–3] molecular mechanics,[4–6] *ab initio*,[7] and group additivity[8–10] calculations. Lay *et al.*[11] have estimated $\Delta_f H°$ (298.15 K) to be $(139.7\pm 5.0)\ \mathrm{kJ\,mol^{-1}}$ using the experimentally determined value of $\Delta_f H°(CH_3OO)$ with an average bond energy for the O–H bond in ROOH compounds. Based on the experimental values of $\Delta_f H°(CH_3O)$, $\Delta_f H°(OH)$,[12] and the bond energy of the O–O bond in CH_3OOH,[13] the value of -134.3 kJ $\mathrm{mol^{-1}}$ may be obtained for the enthalpy of formation of methyl hydroperoxide. Benassi *et al.*[5] proposed $\Delta_f H°(298.15\ \text{K})=-138.1\ \mathrm{kJ\,mol^{-1}}$ by employing theoretical and empirical approaches. Similar values of $\Delta_f H°$ are predicted by the method of group equations from

$$\begin{aligned}\Delta_f H°(CH_3OOH)&=\Delta_f H°(CH_3OOCH_3)+\Delta_f H°(CH_3OH)\\&\quad-\Delta_f H°(CH_3OCH_3)\\&=(-125.5)+(-201.5)-(-184.1)\\&=-142.9\ \mathrm{kJ\,mol^{-1}},\end{aligned}$$

$$\begin{aligned}\Delta_f H°(CH_3OOH)&=\Delta_f H°(CH_3CH_2OOH)+\Delta_f H°(CH_3OH)\\&\quad-\Delta_f H°(CH_3CH_2OH)\\&=(-173.6)+(-201.5)-(-235.2)\\&=-139.9\ \mathrm{kJ\,mol^{-1}},\end{aligned}$$

(the $\Delta_f H°$ values were taken from Pedley[14] (CH_3OH, CH_3OCH_3, and CH_3CH_2OH), Baker *et al.*[15] (CH_3OOCH_3), and Lay *et al.*[11] (CH_3CH_2OOH). The average of these estimates, -139 ± 5.0 kJ mol^{-1}, is accepted in this work for the enthalpy of formation of methyl hydroperoxide at 298.15 K.

9.2. Heat Capacity and Entropy

The microwave spectrum of methyl hydroperoxide, CH_3OOH, has been investigated by Tyblewski *et al.*[16] However, the assignment of the spectrum was complicated because of the widespread effects of the internal rotation around the O—O bond. The experimental results provide definitive evidence that the minimum of the potential energy relative to internal rotation around the O—O bond corresponds to a *skew* conformation. The adjustment to the observed data resulted in a small *trans* barrier of 172.5 cm^{-1}. This barrier separates two equivalent potential minima associated with two enantiomeric *skew* forms. From a preliminary interpretation of microwave data, Tyblewski *et al.*[17] reported almost all the structural parameters of the CH_3OOH molecule. In a more detailed study, Tyblewski *et al.*[16] gave only one parameter adjusted to the observed data, $\angle$C—C—O$=105.3°$. All other structural parameters were adopted by those authors from *ab initio* calculations. Conformational properties of methyl hydroperoxide have been investigated theoretically.[1,2,4–6,11,16,18–22] *Ab initio*[5,16,19–22] and molecular mechanics[4,6] calculations provide an equilibrium molecular structure and *trans* barrier in close agreement with the conclusions of experimental study of Tyblewski *et al.*[16]

The product of the principal moments of inertia of methyl hydroperoxide was calculated in this work using the rotational constants determined from a microwave study.[16] Structural parameters for the *skew* C_1 symmetry conformation given above are based on the experimental[16] and theoretical[4–6,16,19–22] data for CH_3OOH and from comparison with the structural parameters of CH_3OOCH_3.[23] These parameters give values for the rotational constants which differ by only 0.4%–0.6% from the observed values.

Methyl hydroperoxide contains OH and CH_3 groups, which rotate around O—O and C—O bonds. Contributions to the thermodynamic functions from these hindered rotors were evaluated in this work based on available data on rotational barriers in CH_3OOH. The value of $V_3=1120\,\mathrm{cm}^{-1}$ was accepted for the barrier to internal rotation of the methyl group around the C—O bond. This value was found from the microwave study[16] and agrees closely with values obtained from *ab initio* calculations.[4,16] The double-minimum potential energy function,

$$V(\varphi)=V_0+V_1\cos\varphi+V_2\cos2\varphi+V_3\cos3\varphi,$$

was used in this work for the O—O internal rotation. This function was chosen earlier for the hindered rotation potential function in hydrogen peroxide.[24] The expansion coefficients V_0, V_1, V_2, and V_3 can be expressed in terms of the *trans* barrier height V_{trans}, the *cis* barrier height V_{cis}, and the COOH dihedral angle φ_e corresponding to a minimum of the potential function.[24] The values of V_0, V_1, V_2, and V_3 were calculated in this work assuming $V_{trans}=172.5\,\mathrm{cm}^{-1}$, $V_{cis}=2500\,\mathrm{cm}^{-1}$, and $\varphi_e=120°$. The value of $V_{trans}=172.5\,\mathrm{cm}^{-1}(\angle\mathrm{C—O—O—H}=180°)$ was taken from the microwave study.[16] It should be noted that substantially lower values of V_{trans} from 80 to 126 cm^{-1} were predicted by *ab initio*[5,16,19,20] and molecular mechanics[6] calculations, whereas high V_{trans} values of 240–590 cm^{-1} were found from other molecular mechanics studies.[4,5] No experimental data for the V_{cis} rotational barrier have been published. Its value accepted in this work is based on theoretical results[4–6,16,25] which agree closely with each other. The equilibrium COOH dihedral angle, $\varphi_e=120°$, was estimated in this work (see above). The values of the reduced moments of inertia for CH_3 and OH tops were calculated from structural parameters given above.

Experimental data on the vibrational spectra of methyl hydroperoxide are unknown. Vibrational frequencies of CH_3OOH were predicted from *ab initio* calculations.[16,22] In this work, fundamental frequencies of methyl hydroperoxide were estimated by normal coordinate calculations using force constants transferred from the CH_3OOCH_3 and H_2O_2 molecules:

$f_{\mathrm{O—O}}$	5.000	$f_{\mathrm{O—O—H}}$	0.940	$f_{\mathrm{C—H,H—C—O}}$	−0.056
$f_{\mathrm{C—O}}$	5.529	$f_{\mathrm{tors\ (C—O)}}$	0.094	$f_{\mathrm{C—H,H—C—H}}$	0.090
$f_{\mathrm{C—H}}$	4.692	$f_{\mathrm{tors\ (O—O)}}$	0.011	$f_{\mathrm{C—O,H—C—O}}$	0.240
$f_{\mathrm{O—H}}$	7.173	$f_{\mathrm{C—H,C—H}}$	0.041	$f_{\mathrm{C—O,C—O—O}}$	1.735
$f_{\mathrm{C—O—O}}$	1.512	$f_{\mathrm{C—H,C—O}}$	0.250	$f_{\mathrm{O—O,C—O—O}}$	0.617
$f_{\mathrm{H—C—O}}$	0.820	$f_{\mathrm{C—O,O—O}}$	0.267	$f_{\mathrm{O—O,O—O—H}}$	0.919
$f_{\mathrm{H—C—H}}$	0.516	$f_{\mathrm{O—O,O—H}}$	−0.317	$f_{\mathrm{O—H,O—O—H}}$	0.925

(stretching and stretch-stretch interaction constants are in units of mdyn/Å; bend and torsion constants are in units of mdyn Å; stretch-bend interaction constants are in units of mdyn). The valence force fields for CH_3OOCH_3 and H_2O_2 were obtained from normal coordinate calculations using known vibrational assignments.[6,26] Comparison of our frequencies with those obtained in *ab initio* calculations[16,22] shows satisfactory agreement taking into account the fact that the *ab initio* frequencies are unscaled and the anharmonicity contributions are neglected.

The uncertainties in the calculated thermodynamic functions (Table 8) may reach (2–4) J K^{-1} mol^{-1} for $C_p°(T)$ and (3–5) J K^{-1} mol^{-1} for $S°(T)$. They are caused by the uncertainties in the adopted vibrational frequencies and the approximate model used for internal rotation.

Ideal gas thermodynamic properties of methyl hydroperoxide have not been reported previously.

9.3. References

[1] C. Glidewell, J. Mol. Struct. **67**, 35 (1980).
[2] V. N. Kokorev, N. N. Vyshinskii, V. P. Maslennikov, I. A. Abronin, G. M. Zhidomirov, and Yu. A. Aleksandrov, Zh. Strukt. Khim. **22**, 9 (1981).
[3] M. Jonsson, J. Phys. Chem. **100**, 6814 (1996).
[4] L. Carballeira, R. A. Mosquera, and M. A. Rios, J. Comput. Chem. **9**, 851 (1988).
[5] R. Benassi, U. Folli, S. Sbardellati, and F. Taddei, J. Comput. Chem. **14**, 379 (1993).
[6] K. Chen and N. L. Allinger, J. Comput. Chem. **14**, 755 (1993).
[7] T. P. W. Jungkamp and J. H. Seinfeld, Chem. Phys. Lett. **257**, 15 (1996).

[8] S. W. Benson, J. Chem. Phys. **40**, 1007 (1964).

[9] S. W. Benson, J. Am. Chem. Soc. **86**, 3922 (1964).

[10] P. S. Nangia and S. W. Benson, J. Phys. Chem. **83**, 1138 (1979).

[11] T. H. Lay, L. N. Krasnoperov, C. A. Venanzi, J. W. Bozzelli, and N. V. Shokhirev, J. Phys. Chem. **100**, 8240 (1996).

[12] L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.

[13] R. D. Bach, P. Y. Ayala, and H. B. Schlegel, J. Am. Chem. Soc **118**, 12758 (1996).

[14] J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds* (Thermodynamics Research Center, College Station, TX, 1994), Vol. I.

[15] G. Baker, J. H. Littlefair, R. Shaw, and J. C. J. Thynne, J. Chem. Soc. 6970 (1965).

[16] M. Tyblewski, T. K. Ha, R. Meyer, A. Bauder, and C. E. Blom, J. Chem. Phys. **97**, 6168 (1992).

[17] M. Tyblewski, R. Meyer, and A. Bauder, 8th Colloquium on High Resolution Molecular Spectroscopy, Tours, France, 1983.

[18] K. Ohkubo, T. Fujita, and H. Sato, J. Mol. Struct. **36**, 101 (1977).

[19] R. A. Bair and W. A. Goddard III, J. Am. Chem. Soc. **104**, 2719 (1982).

[20] D. Christen, H. G. Mack, and H. Oberhammer, Tetrahedron **44**, 7363 (1988).

[21] J. Koller, M. Hodoscek, and B. Plesnicar, J. Am. Chem. Soc. **112**, 2124 (1990).

[22] R. Benassi and F. Taddei, Tetrahedron **50**, 4795 (1994).

[23] B. Haas and H. Oberhammer, J. Am. Chem. Soc. **106**, 6146 (1984).

[24] R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, J. Chem. Phys. **42**, 1931 (1965).

[25] L. Radom, W. J. Hehre, and J. A. Pople, J. Am. Chem. Soc. **94**, 2371 (1972).

[26] P. G. Giguere and T. K. K. Srinivasan, J. Raman Spectrosc. **2**, 125 (1974).

TABLE 8. Ideal gas thermodynamic properties of methyl hydroperoxide CH_4O_2(g) at the standard state pressure, $p° = 0.1$ MPa ($T_r = 298.15$ K)

T (K)	$C_p°$ ($J K^{-1} mol^{-1}$)	$S°$ ($J K^{-1} mol^{-1}$)	$-(G° - H°(T_r))/T$ ($J K^{-1} mol^{-1}$)	$H° - H°(T_r)$ ($kJ mol^{-1}$)	$\Delta_f H°$ ($kJ mol^{-1}$)	$\Delta_f G°$ ($kJ mol^{-1}$)	$\log K_f°$
0	0.000	0.000	∞	−13.919	−126.247	−126.247	∞
25	34.489	171.468	692.887	−13.036	−127.153	−125.355	261.912
50	35.540	195.488	438.841	−12.168	−128.683	−123.025	128.522
75	38.512	210.437	360.349	−11.243	−130.278	−119.836	83.460
100	41.627	221.948	324.360	−10.241	−131.534	−116.158	60.674
150	46.975	239.876	293.352	−8.021	−133.584	−108.013	37.613
180	49.820	248.694	285.189	−6.569	−134.723	−102.791	29.829
190	50.758	251.413	283.340	−6.066	−135.098	−101.007	27.768
200	51.703	254.040	281.810	−5.554	−135.472	−99.203	25.909
210	52.659	256.586	280.549	−5.032	−135.845	−97.380	24.222
220	53.627	259.058	279.516	−4.501	−136.215	−95.540	22.684
230	54.610	261.463	278.679	−3.960	−136.583	−93.683	21.276
240	55.609	263.808	278.011	−3.408	−136.949	−91.810	19.982
250	56.624	266.099	277.489	−2.847	−137.312	−89.922	18.788
260	57.653	268.340	277.094	−2.276	−137.671	−88.019	17.683
270	58.696	270.535	276.810	−1.694	−138.026	−86.103	16.657
280	59.751	272.689	276.625	−1.102	−138.376	−84.173	15.703
290	60.816	274.804	276.526	−0.499	−138.722	−82.231	14.811
298.15	61.690	276.502	276.502	0.000	−139.000	−80.640	14.128
300	61.889	276.884	276.503	0.114	−139.063	−80.277	13.977
350	67.290	286.830	277.276	3.344	−140.679	−70.350	10.499
400	72.583	296.163	279.059	6.841	−142.143	−60.202	7.861
450	77.604	305.005	281.455	10.597	−143.453	−49.879	5.790
500	82.279	313.427	284.234	14.596	−144.620	−39.418	4.118
600	90.573	329.181	290.432	23.250	−146.559	−18.190	1.584
700	97.633	343.688	297.017	32.670	−148.043	3.328	−0.248
800	103.693	357.130	303.701	42.743	−149.133	25.032	−1.634
900	108.935	369.654	310.342	53.381	−149.884	46.850	−2.719
1000	113.485	381.372	316.865	64.507	−150.352	68.737	−3.590
1100	117.439	392.378	323.235	76.058	−150.582	90.659	−4.305
1200	120.878	402.748	329.433	87.978	−150.618	112.593	−4.901
1300	123.871	412.544	335.453	100.219	−150.500	134.525	−5.405
1400	126.478	421.822	341.294	112.739	−150.261	156.442	−5.837
1500	128.752	430.627	346.958	125.503	−149.928	178.338	−6.210
1600	130.741	439.001	352.451	138.480	−149.526	200.219	−6.536
1700	132.485	446.981	357.779	151.643	−149.075	222.061	−6.823
1800	134.018	454.598	362.948	164.970	−148.588	243.882	−7.077
1900	135.369	461.881	367.965	178.441	−148.080	265.672	−7.304
2000	136.564	468.855	372.836	192.039	−147.563	287.436	−7.507

10. Dimethyl Peroxide, $CH_3—O—O—CH_3$

Dimethyl peroxide ($C_2H_6O_2$) Ideal gas $M_r = 62.0682$

$\Delta_f H°(0\ K) = -106.5 \pm 5.0\ kJ\ mol^{-1}$

$S°(298.15\ K) = 308.4 \pm 3.0\ J\ K^{-1}\ mol^{-1}$ $\Delta_f H°(298.15\ K) = -125.5 \pm 5.0\ kJ\ mol^{-1}$

Molecular constants

Point group: C_2 Symmetry number: $\sigma = 2$ Number of optical isomers: $n = 2$

Ground electronic state: $\tilde{X}\ ^1A$ Energy: $\epsilon_X = 0\ cm^{-1}$ Quantum weight: $g_X = 1$

Vibrational frequencies, ν_i, and degeneracies, g_i

Symmetry		ν_i, cm^{-1}	g_i	Symmetry		ν_i, cm^{-1}	g_i
A	ν_1	2945	1		ν_{13}	...[b]	1
	ν_2	2917	1	B	ν_{14}	3000	1
	ν_3	2900	1		ν_{15}	2965	1
	ν_4	1487	1		ν_{16}	2818	1
	ν_5	1474	1		ν_{17}	1483	1
	ν_6	1433	1		ν_{18}	1433	1
	ν_7	1198	1		ν_{19}	1430	1
	ν_8	1165	1		ν_{20}	1119	1
	ν_9	1020	1		ν_{21}	1112	1
	ν_{10}	786	1		ν_{22}	1032	1
	ν_{11}	448	1		ν_{23}	376	1
	ν_{12}	...[a]	1		ν_{24}	...[a]	1

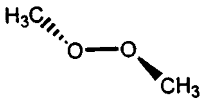
[a] Instead of torsional modes $\nu_{12} = 218\ cm^{-1}$ and $\nu_{24} = 231\ cm^{-1}$, the contributions due to the internal rotation of CH_3 groups around C—O bonds were calculated from the potential $V(\varphi) = \frac{1}{2}V_3(1 - \cos 3\varphi)$, where φ is the H—C—O—O torsional angle and $V_3 = 900\ cm^{-1}$.

[b] Instead of torsional mode $\nu_{13} = 73\ cm^{-1}$, the contributions due to the internal rotation of OCH_3 group around O—O bond were calculated from the potential $V(\varphi) = V_0 + V_1 \cos\varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi$, where φ is the C—O—O—C torsional angle, $V_0 = 1341.3$, $V_1 = 2081.0$, $V_2 = 1052.2$, and $V_3 = 225.5$ (in cm^{-1}).

CH_3 top: Reduced moment of inertia, $I_r = 0.4910 \times 10^{-39}\ g\ cm^2$, Symmetry number, $\sigma_m = 3$.

OCH_3 top: Reduced moment of inertia, $I_r = 1.5928 \times 10^{-39}\ g\ cm^2$, Symmetry number, $\sigma_m = 1$.

Geometry



$r(C—O) = 1.420 \pm 0.007\ Å$

$r(O—O) = 1.457 \pm 0.012\ Å$

$r(C—H) = 1.099 \pm 0.004\ Å$

$\angle C—O—O = 105.2 \pm 0.5°$

$\angle H—C—H = 110.1 \pm 0.7°$

$\phi(C—O—O—C) = 119 \pm 4°$

Product of moments of inertia: $I_A I_B I_C = 1123 \times 10^{-117}\ g^3\ cm^6$.

10.1. Enthalpy of Formation

The enthalpy of formation of dimethyl peroxide recommended in this work ($-125.5\ kJ\ mol^{-1}$) was determined by Baker *et al.*[1] from calorimetric measurements of the enthalpy of combustion. Slightly lower values of $\Delta_f H°$ (298.15 K) from $-129.3\ kJ\ mol^{-1}$ to $-133.9\ kJ\ mol^{-1}$ were estimated by group additivity[2,3] and molecular mechanics calculations.[4,5] A lower value is estimated from the experimental value of $\Delta_f H°(CH_3O)$ Gurvich *et al.*[6] and the bond energy for the O—O bond in CH_3OOCH_3:[7]

$$\begin{aligned}\Delta_f H^\circ(\mathrm{CH_3OOCH_3}) &= 2\Delta_f H^\circ(\mathrm{CH_3O}) \\ &\quad - D^\circ(\mathrm{CH_3O{-}OCH_3}) \\ &= 2\times 13-160 = -134\ \mathrm{kJ\,mol^{-1}}.\end{aligned}$$

A still more negative value, $-138.1\ \mathrm{kJ\,mol^{-1}}$, was proposed by Benassi *et al.*[8] employing theoretical and empirical approaches. Semiempirical MINDO[9,10] and molecular mechanics[11] calculations provide $\Delta_f H^\circ$ (298.15 K) values, -105.1 to $-121.6\ \mathrm{kJ\,mol^{-1}}$, which are greater than the experimental value. The available theoretical and empirical evaluations are grounds to believe that the experimental value of $\Delta_f H^\circ$ (298.15 K) may be overestimated. Thus, its uncertainty was increased in this work.

10.2. Heat Capacity and Entropy

The molecular structure of dimethyl peroxide, $\mathrm{CH_3OOCH_3}$, was studied by electron diffraction.[12] The molecular intensities were analyzed using a model which considered the internal rotation about the O—O bond. The equilibrium geometry was determined to be the *skew* conformation with a C—O—O—C dihedral angle of 119°. The barrier in the *trans* configuration ($\angle$C—O—O—C $=180^\circ$) was found to be $87^{+87}/_{-52}\ \mathrm{cm^{-1}}$. This result agrees with an analysis of infrared and Raman spectra[13] and a normal coordinate analysis based on the these data[14] as well as with results of semiempirical,[9,10,15,16] *ab initio*[17–19] and molecular mechanics[4,5,8] calculations. Photoelectron spectra investigations[20,21] and *ab initio* calculations[8,22–24] support an exactly planar or nearly planar *trans* configuration. However, it should be noted that the value of a dihedral angle depends strongly on the basis set and method used.[19] Hamada and Morishita[25] have described the Raman and infrared spectra of $\mathrm{CH_3OOCH_3}$ in terms of planar structure of D_{3h} symmetry. In this work, the product of the principal moments of inertia of dimethyl peroxide for *skew* conformation of C_2 symmetry was calculated using the structural parameters determined from electron diffraction study.[12]

The dimethyl peroxide molecule undergoes three large-amplitude motions: an internal rotation of the $\mathrm{OCH_3}$ groups about the O—O bond and internal rotation of the $\mathrm{CH_3}$ groups about two C—O bonds. Contributions to the thermodynamic properties from these hindered rotors were calculated in this work based on available data on the rotational barriers in $\mathrm{CH_3OOCH_3}$. The value of $V_3=900\ \mathrm{cm^{-1}}$ was accepted for the internal rotation barrier of methyl groups around the C-O bonds. This value was used by Koput[26] in his theoretical model describing the internal rotation in dimethyl peroxide and it is the average of the results of molecular mechanics calculations.[4] The double-minimum potential energy function,

$$V(\varphi)=V_0+V_1\cos\varphi+V_2\cos 2\varphi+V_3\cos 3\varphi,$$

was used in this work for the internal rotation around the O—O bond. This function was chosen earlier for the hindered rotation potential function in hydrogen peroxide.[27] The expansion coefficients V_0, V_1, V_2, and V_3 can be expressed in terms of the *trans* barrier height V_{trans}, the *cis* barrier height V_{cis}, and the COOC dihedral angle φ_e corresponding to a minimum of the potential function.[27] The values of V_0, V_1, V_2, and V_3 were calculated in this work assuming $V_{trans}=87\ \mathrm{cm^{-1}}$, $V_{cis}=4700\ \mathrm{cm^{-1}}$, and $\varphi_e=119^\circ$. The value of V_{trans} was taken from the electron diffraction study.[12] It agrees with results of theoretical calculations[4,5,8,19] within the limits of experimental accuracy. The adopted value of V_{cis} is based on results of *ab initio*[8,18] and molecular mechanics[4,5] calculations. The values of the reduced moments of inertia for $\mathrm{CH_3}$ and $\mathrm{OCH_3}$ tops were calculated from structural parameters given above.

Christe[13] has investigated the infrared spectra of $\mathrm{CH_3OOCH_3}$ and $\mathrm{CD_3OOCD_3}$ both in the gas phase and in an Ar matrix and the Raman spectra of these molecules in the liquid phase. The vibrational assignment proposed by Christe[13] has considerable uncertainty for a number of the vibrations, and the low-frequency modes were not assigned at all. Bell and Laane[14] have carried out a normal coordinate analysis of dimethyl peroxide using the experimental data of Christe.[13] Hamada and Morishita[25] have described the vibrational spectra of $\mathrm{CH_3OOCH_3}$ in terms of D_{3h} symmetry. However, this assignment is in conflict with available information on dimethyl peroxide. There are two *ab initio* calculations of vibrational frequencies of $\mathrm{CH_3OOCH_3}$.[23,28] Results of Benassi and Taddei[23] show overall agreement with experimental data taking into account the fact that the *ab initio* frequencies are unscaled and the anharmonicity contributions are neglected. Chen and Allinger[5] have carried out the molecular mechanics calculation of vibrational frequencies of dimethyl peroxide. Their results are in agreement with the available, but somewhat tentative and incomplete, experimental data.[13] The assignment proposed by Chen and Allinger[5] is accepted in this work.

The uncertainties in the calculated thermodynamic functions (Table 9) may reach (2–4) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $C_p^\circ(T)$ and (3–5) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $S^\circ(T)$. They are caused by uncertainties in the adopted vibrational frequencies and the approximate treatment of internal rotation.

Ideal gas thermodynamic properties of dimethyl peroxide have not been reported previously.

10.3. References

[1] G. Baker, J. H. Littlefair, R. Shaw, and J. C. J. Thynne, J. Chem. Soc. 6970 (1965).

[2] S. W. Benson, J. Chem. Phys. **40**, 1007 (1964).

[3] S. W. Benson, J. Am. Chem. Soc. **86**, 3922 (1964).

[4] L. Carballeira, R. A. Mosquera, and M. A. Rios, J. Comput. Chem. **9**, 851 (1988).

[5] K. Chen and N. L. Allinger, J. Comput. Chem. **14**, 755 (1993).

[6] L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.

[7] R. D. Bach, P. Y. Ayala, and H. B. Schlegel, J. Am. Chem. Soc. **118**, 12758 (1996).

[8] R. Benassi, U. Folli, S. Sbardellati, and F. Taddei, J. Comput. Chem. **14**, 379 (1993).

[9] C. Glidewell, J. Mol. Struct. **67**, 35 (1980).

[10] V. N. Kokorev, N. N. Vyshinskii, V. P. Maslennikov, I. A. Abronin, G. M. Zhidomirov, and Yu. A. Aleksandrov, Zh. Strukt. Khim. **22**, 9 (1981).

[11] W. H. Richardson, J. Org. Chem. **54**, 4677 (1989).

[12] B. Haas and H. Oberhammer, J. Am. Chem. Soc. **106**, 6146 (1984).

[13] K. O. Christe, Spectrochim. Acta A **27**, 463 (1971).

[14] M. E. B. Bell and J. Laane, Spectrochim. Acta A **28**, 2239 (1972).

[15] R. M. Minyaev, V. I. Minkin, I. I. Zakharov, and I. D. Sadekov, Teor. Eksp. Khim. **9**, 816 (1973).

[16] K. Ohkubo, T. Fujita, and H. Sato, J. Mol. Struct. **36**, 101 (1977).

[17] B. Plesnicar, D. Kocjan, S. Murovec, and A. Azman, J. Am. Chem. Soc. **98**, 3143 (1976).

[18] W. Gase and J. E. Boggs, J. Mol. Struct. **116**, 207 (1984).

[19] D. Christen, H. G. Mack, and H. Oberhammer, Tetrahedron **44**, 7363 (1988).

[20] K. Kimura and K. Osafune, Bull. Chem. Soc. Jpn. **48**, 2421 (1975).

[21] P. Rademacher and W. Elling, Liebigs Ann. Chem. 1473 (1979).

[22] R. A. Bair and W. A. Goddard III, J. Am. Chem. Soc. **104**, 2719 (1982).

[23] R. Benassi and F. Taddei, Tetrahedron **50**, 4795 (1994).

[24] M.-B. Huang and H. U. Suter, J. Mol. Struct: THEOCHEM **337**, 173 (1995).

[25] K. Hamada and H. Morishita, Spectrosc. Lett. **13**, 185 (1980).

[26] J. Koput, J. Mol. Spectrosc. **141**, 118 (1990).

[27] R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, J. Chem. Phys. **42**, 1931 (1965).

[28] G. A. Pitsevich, V. I. Gogolinskii, and I. P. Zyatkov, Zh. Prikl. Spektrosk. **56**, 643 (1992).

TABLE 9. Ideal gas thermodynamic properties of dimethyl peroxide $C_2H_6O_2$(g) at the standard state pressure, $p° = 0.1$ MPa ($T_r = 298.15$ K)

T (K)	$C_p°$ (J K^{-1} mol^{-1})	$S°$ (J K^{-1} mol^{-1})	$-(G°-H°(T_r))/T$ (J K^{-1} mol^{-1})	$H°-H°(T_r)$ (kJ mol^{-1})	$\Delta_f H°$ (kJ mol^{-1})	$\Delta_f G°$ (kJ mol^{-1})	log $K_f°$
0	0.000	0.000	∞	−17.153	−106.460	−106.460	∞
25	38.665	180.406	831.484	−16.277	−107.908	−104.953	219.284
50	42.071	208.414	513.657	−15.262	−110.130	−101.224	105.747
75	45.713	226.123	415.019	−14.167	−112.460	−96.245	67.030
100	49.953	239.851	369.568	−12.972	−114.304	−90.552	47.299
150	58.133	261.681	330.120	−10.266	−117.336	−78.000	27.162
180	62.664	272.683	319.647	−8.453	−119.030	−69.973	20.305
190	64.145	276.111	317.266	−7.819	−119.590	−67.232	18.483
200	65.624	279.439	315.292	−7.171	−120.149	−64.462	16.836
210	67.105	282.676	313.662	−6.507	−120.707	−61.664	15.338
220	68.594	285.832	312.325	−5.828	−121.264	−58.840	13.970
230	70.095	288.915	311.241	−5.135	−121.818	−55.990	12.716
240	71.609	291.930	310.374	−4.426	−122.370	−53.116	11.560
250	73.139	294.884	309.695	−3.703	−122.919	−50.219	10.493
260	74.685	297.783	309.181	−2.964	−123.465	−47.301	9.503
270	76.247	300.630	308.812	−2.209	−124.006	−44.360	8.582
280	77.823	303.432	308.570	−1.439	−124.542	−41.401	7.723
290	79.413	306.190	308.441	−0.652	−125.072	−38.422	6.921
298.15	80.717	308.409	308.409	0.000	−125.500	−35.981	6.304
300	81.014	308.910	308.411	0.150	−125.597	−35.425	6.168
350	89.107	322.005	309.427	4.402	−128.110	−20.196	3.014
400	97.131	334.429	311.782	9.059	−130.424	−4.619	0.603
450	104.858	346.320	314.963	14.110	−132.528	11.235	−1.304
500	112.164	357.750	318.674	19.538	−134.426	27.313	−2.853
600	125.390	379.396	327.012	31.431	−137.633	59.970	−5.221
700	136.887	399.609	335.955	44.558	−140.119	93.110	−6.948
800	146.892	418.557	345.108	58.759	−141.956	126.561	−8.263
900	155.605	436.373	354.269	73.893	−143.219	160.207	−9.298
1000	163.187	453.169	363.327	89.842	−143.993	193.966	−10.132
1100	169.774	469.039	372.223	106.498	−144.351	227.782	−10.816
1200	175.490	484.062	380.922	123.768	−144.366	261.615	−11.388
1300	180.449	498.309	389.409	141.570	−144.105	295.441	−11.871
1400	184.752	511.843	397.673	159.536	−143.625	329.235	−12.284
1500	188.491	524.721	405.719	178.502	−142.971	362.990	−12.640
1600	191.746	536.992	413.543	197.518	−142.187	396.716	−12.951
1700	194.585	548.703	421.152	216.838	−141.305	430.365	−13.223
1800	197.069	559.898	428.551	236.423	−140.351	463.971	−13.464
1900	199.247	570.612	435.748	256.241	−139.347	497.516	−13.677
2000	201.164	580.882	442.750	276.264	−138.314	531.010	−13.868

11. Diacetyl Peroxide, $CH_3—CO—O—O—CO—CH_3$

Diacetyl peroxide ($C_4H_6O_4$) Ideal gas $M_r = 118.089$

$\Delta_f H°(0\ \mathrm{K}) = -(477.0 \pm 10.0)\ \mathrm{kJ\ mol^{-1}}$

$S°(298.15\ \mathrm{K}) = (390.7 \pm 6.0)\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $\Delta_f H°(298.15\ \mathrm{K}) = -(500.0 \pm 10.0)\ \mathrm{kJ\ mol^{-1}}$

Molecular constants

Point group: C_2 Symmetry number: $\sigma = 2$ Number of optical isomers: $n = 2$

Ground electronic state: $\tilde{X}\ {}^1A$ Energy: $\epsilon_X = 0\ \mathrm{cm^{-1}}$ Quantum weight: $g_X = 1$

Vibrational frequencies, ν_i, and degeneracies g_i

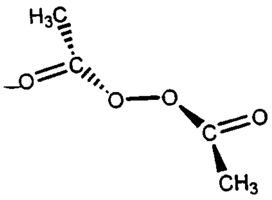
Symmetry		ν_i, $\mathrm{cm^{-1}}$	g_i	Symmetry		ν_i, $\mathrm{cm^{-1}}$	g_i
A	ν_1	3001	1		ν_{19}	…[b]	1
	ν_2	2998	1	B	ν_{20}	3001	1
	ν_3	2934	1		ν_{21}	2998	1
	ν_4	1762	1		ν_{22}	2934	1
	ν_5	1466	1		ν_{23}	1749	1
	ν_6	1428	1		ν_{24}	1457	1
	ν_7	1426	1		ν_{25}	1427	1
	ν_8	1290	1		ν_{26}	1426	1
	ν_9	1087	1		ν_{27}	1285	1
	ν_{10}	927	1		ν_{28}	962	1
	ν_{11}	875	1		ν_{29}	922	1
	ν_{12}	850	1		ν_{30}	808	1
	ν_{13}	648	1		ν_{31}	639	1
	ν_{14}	631	1		ν_{32}	619	1
	ν_{15}	392	1		ν_{33}	545	1
	ν_{16}	285	1		ν_{34}	328	1
	ν_{17}	151	1		ν_{35}	140	1
	ν_{18}	…[a]	1		ν_{36}	…[b]	1

[a] Instead of torsional mode $\nu_{18} \sim 70\ \mathrm{cm^{-1}}$, the contributions due to the internal rotation of $O—CO—CH_3$ group around O—O bond were calculated from the potential $V(\varphi) = V_0 + V_1 \cos\varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi$, where φ is the C—O—O—C torsional angle, $V_0 = 1433.9$, $V_1 = 2222.2$, $V_2 = 1111.1$, and $V_3 = 232.8$ (in $\mathrm{cm^{-1}}$).

[b] Instead of torsional modes ν_{19} and $\nu_{36} \sim 60\ \mathrm{cm^{-1}}$, the contributions due to the internal rotation of CH_3 groups around C—C bonds were calculated from the potential $V(\varphi) = \frac{1}{2} V_3 (1 - \cos 3\varphi)$, where φ is the H—C—C—O torsional angle and $V_3 = 80\ \mathrm{cm^{-1}}$.

$O—CO—CH_3$ top: Reduced moment of inertia, $I_r = 4.5200 \times 10^{-39}\ \mathrm{g\ cm^2}$, Symmetry number, $\sigma_m = 1$.

CH_3 top: Reduced moment of inertia, $I_r = 0.5182 \times 10^{-39}\ \mathrm{g\ cm^2}$, Symmetry number, $\sigma_m = 3$.



Geometry

$r(C—C) = 1.495 \pm 0.01\ \text{Å}$

$r(C{=}O) = 1.21 \pm 0.02\ \text{Å}$

$r(C—O) = 1.34 \pm 0.02\ \text{Å}$

$r(O—O) = 1.46 \pm 0.02\ \text{Å}$

$r(C—H) = 1.09 \pm 0.01\ \text{Å}$

$\angle C—C{=}O = 128 \pm 3°$

$\angle O{=}C—O = 122 \pm 3°$

$\angle C—O—O = 113 \pm 3°$

$\angle H—C—H = 109.5 \pm 2.0°$

$\varphi(C—O—O—C) = 120 \pm 10°$

$\varphi(O{=}C—O—O) = 0°$

Product of moments of inertia: $I_A I_B I_C = 96075 \times 10^{-117}\ \mathrm{g^3\ cm^6}$.

11.1. Enthalpy of Formation

Jaffe *et al.*[1] determined the enthalpy of formation for liquid diacetyl peroxide ($CH_3CO—OO—COCH_3$) from calorimetric measurements. Assuming the enthalpy of vaporization of diacetyl peroxide to be equal to the enthalpy of vaporization of acetic anhydride ($CH_3CO—O—COCH_3$), the authors obtained the value of $-498\ \mathrm{kJ\,mol^{-1}}$ for the enthalpy of formation of gaseous diacetyl peroxide. A similar value of $\Delta_f H°(298.15\ \mathrm{K}) = -502\ \mathrm{kJ\,mol^{-1}}$ may be derived from the group additivity contributions for peroxyacids and peroxyesters obtained by Benassi and Taddei[2] using empirical approaches and *ab initio* calculations. The value predicted by the method of group equations,

$$\begin{aligned}&\Delta_f H°(CH_3CO—OO—COCH_3)\\ &\quad = \Delta_f H°(CH_3CO—O—COCH_3) + \Delta_f H°(CH_3OOCH_3)\\ &\qquad - \Delta_f H°(CH_3OCH_3) = (-572.5) + (-125.5)\\ &\qquad - (-184.1) = -513.9\end{aligned}$$

(the $\Delta_f H°$ values for the related compounds were taken from the compilation by Pedley[3]), agrees with the two above estimates within the limits of the combined errors of those determinations. Considerably lower values of $\Delta_f H°$ for diacetyl peroxide were estimated from a group additivity approximation ($-540\ \mathrm{kJ\,mol^{-1}}$)[4] and a semiempirical calculation ($\sim -585\ \mathrm{kJ\,mol^{-1}}$).[5,6] The value recommended in this work, $-(500 \pm 10)\ \mathrm{kJ\,mol^{-1}}$, is based on the estimates.[1,2]

11.2. Heat Capacity and Entropy

Experimental data on molecular structure and vibrational frequencies of diacetyl peroxide, $CH_3CO—OO—COCH_3$, are unknown. Semiempirical MINDO calculations[5] predict that the *skew* conformation of C_2 symmetry with a C—O—O—C dihedral angle of 108° is the most stable. Although a planar structure was suggested for the peroxy acid group in peroxyacetic acid from a microwave study,[7] the *skew* conformation of C_2 symmetry is accepted in this work for diacetyl peroxide in accord with a semiempirical calculation[5] and by analogy with dimethyl peroxide.[8] The product of the principal moments of inertia was calculated from structural parameters estimated by comparison with structural parameters of $CH_3CO—OOH$,[7] $CH_3CO—O—COCH_3$,[9] and CH_3OOCH_3.[8]

The diacetyl peroxide molecule undergoes five large-amplitude motions: an internal rotation about a central O—O bond and about two C—C and two C—O bonds. Contributions to the thermodynamic functions due to internal rotation of CH_3 groups were calculated in this work assuming the V_3 barrier height to be the same as that in peroxyacetic acid.[7] The double-minimum potential energy function,

$$V(\varphi) = V_0 + V_1 \cos\varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi,$$

was used for the internal rotation about the O—O bond. This function was chosen earlier for the hindered rotation potential function in hydrogen peroxide.[10] The expansion coefficients V_0, V_1, V_2, and V_3 can be expressed in terms of the *trans* barrier height V_{trans}, the *cis* barrier height V_{cis}, and the COOC dihedral angle φ_e corresponding to a minimum of the potential function.[10] The values of V_0, V_1, V_2, and V_3 were calculated in this work assuming $V_{trans} = 90\ \mathrm{cm^{-1}}$, $V_{cis} = 5000\ \mathrm{cm^{-1}}$, and $\varphi_e = 120°$. The values of V_{trans} and V_{cis} are derived from the results of a MINDO calculation[5] taking into account that the same calculation overestimated the V_{trans} and underestimated the V_{cis} barriers for the CH_3OOH and CH_3OOCH_3 molecules. The values of the reduced moments of inertia for CH_3 and CH_3COO tops were calculated from structural parameters given above. There are no data on barriers hindering the internal rotation of CH_3CO groups about the C-O bonds. Frequencies $\nu_{17} = 151$ and $\nu_{35} = 140\ \mathrm{cm^{-1}}$ were accepted in this work for the torsional motion about the C-O bonds.

Zyatkov *et al.*[11] have calculated vibrational frequencies of diacetyl peroxide using a theoretical simulation of the force field. In this work, vibrational frequencies of $CH_3CO—OO—COCH_3$ were calculated using force constants transferred from the $CH_3CO—OOH$ molecule. The simplified valence force field for that molecule was obtained by normal coordinate calculations for the vibrational assignment of Cugley *et al.*[12] The calculated force constants reproduce the observed vibrational wave numbers of $CH_3CO—OOH$ with a root mean square deviation of 0.6 $\mathrm{cm^{-1}}$. The following 18 force constants were used for calculating the vibrational frequencies of diacetyl peroxide:

$f_{O—O}$	3.821	$f_{C—C—O}$	2.363	$f_{tors(C—O)}$	0.430
$f_{C—O}$	3.827	$f_{O═C—O} = f_{O═C—C}$	1.972	$f_{tors(O—O)}$	0.104
$f_{C═O}$	11.382	$f_{C—C—H}$	0.497	$f_{C═O,C—C} = f_{C═O,C—O}$	1.679
$f_{C—C}$	3.480	$f_{H—C—H}$	0.523	$f_{C—C,C—O}$	−0.356
$f_{C—H}$	4.836	$f_{wag(C═O)}$	0.515	$f_{C—H,C—C—H}$	0.415
$f_{C—O—O}$	1.659	$f_{tors(C—C)}$	0.006	$f_{C—O,O═C—O}$	0.232

(stretching and stretch-stretch interaction constants are in units of mdyn/Å; bending, wagging, and torsion constants are in units of mdyn Å; stretch-bend interaction constants are in units of mdyn).

The uncertainties in the calculated thermodynamic functions (Table 10) may reach (8–12) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $C_p°(T)$ and (6–10) $\mathrm{J\,K^{-1}\,mol^{-1}}$ for $S°(T)$. They are caused by the uncertainties in the adopted vibrational frequencies and the approximate treatment of internal rotation.

Ideal gas thermodynamic properties of diacetyl peroxide have not been reported previously.

11.3. References

[1] L. Jaffe, E. L. Prosen, and M. Szware, J. Chem. Phys. **27**, 416 (1957).
[2] R. Benassi and F. Taddei, J. Mol. Struct.: THEOCHEM **303**, 101 (1994).
[3] J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds* (Thermodynamics Research Center, College Station, TX, 1994), Vol. I.
[4] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, Chem. Rev. **69**, 279 (1969).
[5] C. Glidewell, J. Mol. Struct. **67**, 35 (1980).
[6] V. N. Kokorev, N. N. Vyshinskii, V. P. Maslennikov, I. A. Abronin, G. M. Zhidomirov, and Yu. A. Aleksandrov, Zh. Strukt. Khim. **22**, 9 (1981).
[7] J. A. Cugley, W. Bossert, A. Bauder, and H. H. Günthard, Chem. Phys. **16**, 229 (1976).
[8] B. Haas and H. Oberhammer, J. Am. Chem. Soc. **106**, 6146 (1984).
[9] H. J. Vledder, F. C. Mijlhoff, J. C. Leyte, and C. Romers, J. Mol. Struct. **7**, 421 (1971).
[10] R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, J. Chem. Phys. **42**, 1931 (1965).
[11] I. P. Zyatkov, V. I. Gogolinskii, V. V. Sivchik, and D. I. Sagaidak, Zh. Prikl. Spektrosk. **29**, 652 (1978).
[12] J. A. Cugley, R. Meyer, and H. H. Günthard, Chem. Phys. **18**, 281 (1976).

TABLE 10. Ideal gas thermodynamic properties of diacetyl peroxide, $C_4H_6O_4$(g) at the standard state pressure, $p° = 0.1$ MPa ($T_r = 298.15$ K)

T (K)	$C_p°$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$S°$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$-(G°-H°(T_r))/T$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$H°-H°(T_r)$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f H°$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f G°$ ($\mathrm{kJ\,mol^{-1}}$)	$\log K_f°$
0	0.000	0.000	∞	−23.944	−476.961	−476.961	∞
25	50.640	213.740	1130.731	−22.925	−478.990	−473.540	989.395
50	58.035	251.723	682.615	−21.545	−481.588	−467.166	488.038
75	62.084	276.009	543.259	−20.044	−484.278	−459.352	319.917
100	66.834	294.500	478.840	−18.434	−486.503	−450.697	235.417
150	78.569	323.725	422.461	−14.810	−490.316	−431.949	150.416
180	86.766	338.764	407.276	−12.332	−492.443	−420.074	121.901
190	89.636	343.532	403.796	−11.450	−493.135	−416.035	114.374
200	92.559	348.204	400.900	−10.539	−493.820	−411.959	107.591
210	95.524	352.791	398.500	−9.599	−494.496	−407.849	101.446
220	98.523	357.304	396.525	−8.629	−495.163	−403.707	95.851
230	101.547	361.750	394.917	−7.628	−495.821	−399.536	90.736
240	104.588	366.136	393.626	−6.598	−496.468	−395.336	86.041
250	107.640	370.468	392.614	−5.536	−497.104	−391.109	81.717
260	110.696	374.749	391.844	−4.445	−497.729	−386.857	77.720
270	113.750	378.984	391.290	−3.323	−498.342	−382.581	74.014
280	116.796	383.176	390.925	−2.170	−498.943	−378.283	70.569
290	119.830	387.327	390.730	−0.987	−499.530	−373.963	67.357
298.15	122.291	390.682	390.682	0.000	−500.000	−370.427	64.896
300	122.848	391.441	390.685	0.227	−500.105	−369.622	64.356
350	137.551	411.491	392.235	6.740	−502.777	−347.661	51.885
400	151.377	430.772	395.855	13.967	−505.120	−325.337	42.484
450	164.144	449.350	400.773	21.860	−507.157	−302.738	35.141
500	175.813	467.258	406.531	30.363	−508.918	−279.929	29.244
600	196.085	501.163	419.512	48.990	−511.704	−233.859	20.359
700	212.888	532.691	433.456	69.465	−513.643	−187.388	13.983
800	226.936	562.062	447.717	91.476	−514.847	−140.688	9.186
900	238.778	589.495	461.963	114.778	−515.418	−93.879	5.449
1000	248.823	615.187	476.014	139.172	−515.458	−47.036	2.457
1100	257.379	639.314	489.774	164.493	−515.048	−0.210	0.010
1200	264.693	662.031	503.192	190.606	−514.271	46.561	−2.027
1300	270.965	683.471	516.243	217.397	−513.201	93.260	−3.747
1400	276.360	703.754	528.919	244.770	−511.906	139.862	−5.218
1500	281.017	722.984	541.221	272.645	−510.431	186.370	−6.490
1600	285.051	741.252	553.157	300.953	−508.834	232.810	−7.600
1700	288.556	758.641	564.737	329.637	−507.144	279.105	−8.576
1800	291.613	775.223	575.973	358.649	−505.392	325.314	−9.440
1900	294.288	791.063	586.880	387.947	−503.606	371.413	−10.211
2000	296.638	806.219	597.471	417.496	−501.807	417.423	−10.902

TABLE 11. Summary of the thermodynamic properties at 298.15 K and the standard state pressure, $p° = 0.1$ MPa

Molecule	$S°$ (298.15 K) ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$C_p°$ (298.15 K) ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$\Delta_f H°$ (298.15 K) ($\mathrm{kJ\,mol^{-1}}$)
Bromoacetic acid	337.0 ± 5.0	80.5 ± 3.0	−383.5 ± 3.1
Chloroacetic acid	325.9 ± 5.0	78.8 ± 3.0	−427.6 ± 1.0
Oxopropanedinitrile	310.0 ± 1.0	80.8 ± 1.0	247.5 ± 6.4
Glycolic acid	318.6 ± 5.0	87.1 ± 3.0	−583.0 ± 10.0
Glyoxal	272.5 ± 1.0	60.6 ± 0.5	−212.0 ± 0.8
Cyanooxomethyl radical	278.2 ± 1.5	56.1 ± 1.5	210.0 ± 10.0
Oxalic acid	320.6 ± 5.0	86.2 ± 5.0	−731.8 ± 2.0
Methyl hydroperoxide	276.5 ± 3.0	61.7 ± 2.0	−139.0 ± 5.0
Dimethyl peroxide	308.4 ± 3.0	80.7 ± 2.0	−125.5 ± 5.0
Diacetyl peroxide	390.7 ± 6.0	122.3 ± 8.0	−500.0 ± 10.0

12. Conclusions

The thermodynamic properties of 10 organic molecules have been calculated, based on the critical evaluation of available thermodynamic and spectroscopic information. Where no data were available, estimation techniques were used. Recommended values for the entropy, heat capacity, and the enthalpy of formation at 298.15 K are summarized in Table 11.

For a first round of new experimental studies, substantially improved formation properties could be obtained with new or confirming measurements for the enthalpy of formation for bromoacetic acid, glycolic acid, the cyanooxomethyl radical, and the three peroxides—methyl hydroperoxide, dimethyl peroxide, and diacetyl peroxide. In order to calculate significantly more reliable thermal functions, the structure and the vibrational frequencies are needed for the cyanooxomethyl radical and diacetyl peroxide, since these data were estimated for these two compounds.

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14. Extended Bibliographies

The following bibliography lists articles that were found in the literature pertaining to the molecules discussed above but were not used as sources of information in the evaluations.

14.1. Extended Bibliography for Bromoacetic Acid, $C_2H_3BrO_2$

71KIN/GOL King, K. D., Golden, D. M., and Benson, S. W., ''Thermochemistry of the gas-phase equilibrium $CH_3COCH_3+Br_2=CH_3COCH_2+HBr$,'' J. Chem. Thermodyn. **3**, 129–134 (1971).

78VAN/BRA Van Eijck, B. P., Brandts, P., Maas, J. P. M., ''Microwave spectra and molecular structures of rotational isomers of fluoroacetic acid and fluoroacetyl fluoride,'' J. Mol. Struct. **44**, 1–13 (1978).

93CAR/LAY Carson, A. S., Laye, P. G., Pedley, J. B., Welsby, A. M., ''The enthalpies of formation of iodomethane, diiodomethane, triiodomethane, and tetraiodomethane by rotating combustion calorimetry,'' J. Chem. Thermodyn. **25**, 261–269 (1993).

14.2. Extended Bibliography for Chloroacetic Acid, $C_2H_3ClO_2$

64JOH Johansen, H., ''Normal coordinate analysis of polyatomic molecules and statistical thermodynamics of isotopic molecules,'' Z. Phys. Chem. **227**, 305–328 (1964).

75CHA/DEV Chandramani, R., Devaraj, N., ''Torsional-vibration frequency in α-$CH_2ClCOOH$ and its temperature dependence from pure quadrupole resonance measurements,'' Indian J. Pure Appl. Phys. **13**, 637–638 (1975).

75SIN/KAT Sinha, D., Katon, J. E., Jakobsen, R. J., ''The vibrational spectra and structure of β- and γ-chloroacetic acid,'' J. Mol. Struct. **24**, 279–291 (1975).

86FAU/TEI2 Fausto, R., Teixeira-Dias, J. J. C., ‘‘Conformational and vibrational spectroscopic analysis of $CHCl_2COX$ and CCl_3COX ($X{=}Cl$, OH, OCH_3),’’ J. Mol. Struct. **144**, 241–263 (1986).

93KUL/FAU Kulbida, A., Fausto, R., ‘‘Conformers, vibrational spectra and infrared-induced rotamerization of dichloroacetic acid in argon and krypton matrixes,’’ J. Chem. Soc., Faraday Trans. **89**, 4257–4266 (1993).

96NYQ/CLA Nyquist, R. A., Clark, T. D., ‘‘Infrared study of α-haloacetic acids in solution,’’ Vib. Spectrosc. **10**, 203–228 (1996).

14.3. Extended Bibliography for Oxopropanedinitrile, C_3N_2O

53KEM/TRA Kemula, W., Tramer, A., ‘‘Vibrational specrum of carbonyl cyanide,’’ Roczniki Chem. **27**, 522–523 (1953).

70NAY/ARU Nayar, V. U., Aruldhas, G., ‘‘Force field and Coriolis coupling coefficients of carbonyl cyanide,’’ Indian J. Pure Appl. Phys. **8**, 840–841 (1970).

71DUN/WHI Duncan, A. B. F., Whitlock, R. F., ‘‘Vacuum ultraviolet absorption spectrum of carbonyl cyanide,’’ Spectrochim. Acta A **27**, 2539–2541 (1971).

72NAY/ARU Nayar, V. U., Aruldhas, G., Joseph, K. B., Cyvin, S. J., ‘‘Vibrational analyses and mean amplitudes for some simple molecules. III. Carbonyl cyanide,’’ Mol. Struct. Vib. 237–242 (1972).

97LER/DEW Leroy, G., Dewispelaere, J. P., Wilante, C., Benkadour, H., ‘‘A theoretical approach to the thermochemistry of the polymerization of some derivatives of the monomers $CH_2{=}X$ ($X{=}CH_2$, NH, O),’’ Macromol. Theory Simul. **6**, 729–739 (1997).

97MED/BHA Medhi, C., Bhattacharyya, S. P., ‘‘Transcription of the results of quantum calculations in terms of the classical notion of molecular structures: The cases of some small carbonyls in the ground and excited states,’’ Proc. Indian Acad. Sci., Chem. Sci. **109**, 61–70 (1997).

14.4. Extended Bibliography for Glycolic Acid, $C_2H_4O_3$

87KAK Kakumoto, T., ‘‘A theoretical study on the unimolecular decomposition of some α-dicarbonyl compounds: glyoxal, oxalic acid and glycolic acid,’’ J. Sci. Hiroshima Univ. A **51**, 69–111 (1987).

93DOM/HEA Domalski, E. S., Hearing, E. D., ‘‘Estimation of the thermodynamic properties of C-H-N-O-S-halogen compounds at 298.15 K,’’ J. Phys. Chem. Ref. Data **22**, 805–1159 (1993).

14.5. Extended Bibliography for Glyoxal, $C_2H_2O_2$

39LUV/SCH LuValle, J. E., Schomaker, V., ‘‘The molecular structures of glyoxal and dimethyl glyoxal by the electron diffraction method,’’ J. Am. Chem. Soc. **61**, 3520–3525 (1939).

49COL/THO Cole, A. R. H., Thompson, H. W., ‘‘Vibration-rotation bands of some polyatomic molecules,’’ Proc. R. Soc. London, Ser. A, **200**, 10–20 (1949).

54BRA/MIN Brand, J. C. D., Minkoff, G. J., ‘‘The infrared spectrum of dideuteroglyoxal,’’ J. Chem. Soc. 2970–2971 (1954).

64COL/OSB Cole, A. R. H., Osborne, G. A., ‘‘Fundamental ν_{12} of glyoxal,’’ J. Chem. Soc. 1532 (1964).

69JEN/HAG Jensen, H. H., Hagen, G., Cyvin, S. J., ‘‘Mean amplitudes of vibration for some conjugated carbonyl compounds: glyoxal, acrolein, and *p*-benzoquinone,’’ J. Mol. Struct. **4**, 51–58 (1969).

71AGA/BAI Agar, D. M., Bair, E. J., Birss, F. W., Borrell, P., Chen, P. C., Currie, G. N., McHugh, A. J., Orr, B. J., Ramsay, D. A., Roncin, J. Y.,‘‘The 4550 Å band system of glyoxal. III. Vibration-rotational analyses for 11 bands of $C_2D_2O_2$,’’ Can. J. Phys. **49**, 323–327 (1971).

73DON/RAM Dong, R. Y., Ramsay, D. A., ‘‘A band system of glyoxal-d_1 and glyoxal-d_2,’’ Can. J. Phys. **51**, 1463–1465 (1973).

73GLE/MCC Gleghorn, J. T., McConkey, F. W., ‘‘The structure and properties of carbonyl compounds,’’ J. Mol. Struct. **18**, 219–225 (1973).

73LE/TYU Le, H. H., Tyulin, V. I., ‘‘Raman spectrum of liquid glyoxal ($C_2O_2H_2$),’’ Opt. Spektrosk. **35**, 770–772 (1973).

75COL/DUR Cole, A. R. H., Durig, J. R., ‘‘Raman and infrared spectra of solid glyoxal-d_1 and glyoxal-d_2,’’ J. Raman Spectrosc. **4**, 31–39 (1975).

75GUT/BAU Gut, M., Bauder, A., Günthard H. H., ‘‘Solution of the rotation-internal rotation problem of glyoxal type molecules by infinite matrix technique,’’ Chem. Phys. **8**, 252–271 (1975).

75PAN Pancir, J., ‘‘*Cis-trans* isomerization of glyoxal. A contribution to the rehabilitation of semiempirical methods,’’ Theor. Chim. Acta **40**, 81–83 (1975).

76COL/CRO Cole, A. R. H., Cross, K. J., Ramsay, D. A., ‘‘Rotational structure of the (0–0) visible band of glyoxal-d_1. A reanalysis,’’ J. Phys. Chem. **80**, 1221–1223 (1976).

76DEV/TOW Devaquet, A. J. P., Townshend, R. E., Hehre, W. J., ''Conformational studies of 1,3-dienes,'' J. Am. Chem. Soc. **98**, 4068–4076 (1976).

77VON Von Niessen, W., ''*Trans*- and *cis*-glyoxal: A Green's function calculation on their photoelectron spectra,'' J. Am. Chem. Soc. **99**, 7151–7153 (1977).

78COS/FRA Cossart-Magos, C., Frad, A., Tramer, A., ''Fluorescence and phosphorescence spectra of glyoxal-h_2 and -d_2 from single vibronic levels of ^1A_u and ^3A_u states,'' Spectrochim. Acta A **34**, 195 (1978)

78LUC/SCH Lucchese, R. R., Schaefer, H. F., III, ''Formulation of the direct configuration interaction method for triplet spin states. Application to glyoxal,'' J. Chem. Phys. **68**, 769–774 (1978).

78PAR/ROR Parmenter, C. S., Rordorf, B. F., ''Fluorescence from selected rotational levels of S_1 glyoxal,'' Chem. Phys. **27**, 1–9 (1978).

79MOR/MAK Morozov, A. A., Makhnev, A. S., Panchenko, Y. N., Stepanov, N. F., ''Calculation of some molecular parameters of glyoxal,'' Vestn. Mosk. Univ., Ser. 2: Khim. **20**, 326–331 (1979).

81NGU/TRO Nguyen-Xuan, T., Tronchet, J. M. J., Bill, H., ''Conformational equilibriums of carbohydrates on the level of σC(sp^2),C(sp^3) bonding. IX. Study of the factors affecting the conformational equilibrium of E-1,3-disubstituted propenes using energy partitioning techniques,'' Helv. Chim. Acta **64**, 1949–1958 (1981).

81OSA/SHA Osamura, Y., Shaefer, H. F. III, Dupuis, M., Lester, W. A., Jr., ''A unimolecular reaction ABC→A+B+C involving three product molecules and a single transition state. Photodissociation of glyoxal: HCO—HCO→H_2+CO+CO,'' J. Chem. Phys. **75**, 5828–5836 (1981).

82BOC/TRA Bock, C. W., Trachtman, M., George, P., ''An *ab initio* study of the geometry of the C—C(H)═O group, the $f_{\mathrm{C—C^2}}$ stretching force constant, and the $f_{\mathrm{C═O,C—C}}$ coupling constant in conjugated monosubstituted carbonyl compounds,'' Chem. Phys. **68**, 143–154 (1982).

83PAN/MOC Panchenko, Y. N., Mochalov, V. I., Pentin, Y. A., ''Calculation of potential curves of the internal rotation of glyoxal and its fluoro derivatives in the CNDO/2 approximation taking into account a change in geometry,'' Vestn. Mosk. Univ., Ser. 2: Khim. **24**, 357–360 (1983).

85MUS/FIG Musso, G. F., Figari, G., Magnasco, V., ''Improved bond-orbital calculations of rotation barriers in molecules containing conjugated double bonds and/or π lone pairs,'' J. Chem. Soc., Faraday Trans. 2 **81**, 1243–1258 (1985).

86DUV/KIN Duval, A. B., King, D. A., Haines, R., Isenor, N. R., Orr, B. J., ''Coherent Raman spectroscopy of glyoxal vapor,'' J. Raman Spectrosc. **17**, 177–182 (1986).

86SPA/PRA Spangler, L. H., Pratt, D. W., Birss, F. W., ''Rotational analysis of some vibronic bands in the $^3A_u-{}^1A_g$ transition of glyoxal. Spin splittings in the lowest triplet state of the isolated molecule,'' J. Chem. Phys. **85**, 3229–3236 (1986).

86YAM/YAM Yamanouchi, K., Yamada, H., Tsuchiya, S., ''Rotationally resolved stimulated emission pumping spectra of glyoxal cooled in supersonic free jet,'' Chem. Phys. Lett. **132**, 361–364 (1986).

87PEB/JOS Pebay Peyroula, E., Jost, R., ''$S_1 \leftarrow S_0$ laser excitation spectra of glyoxal in a supersonic jet: Vibrational analysis,'' J. Mol. Spectrosc. **121**, 177–188 (1987).

87ROD/OLD Rodler, M., Oldani, M., Grassi, G., Bauder, A., ''Rotational spectra of s-*trans* and s-*cis* glyoxal-d_1 (CHO—CDO) observed by microwave Fourier transform spectroscopy,'' J. Chem. Phys. **87**, 5365–5369 (1987).

88FAB Fabian, W. M. F., ''AM1 calculations of rotation around essential single bonds and preferred conformations in conjugated molecules,'' J. Comput. Chem. **9**, 369–377 (1988).

89BRI Brinn, I. M., ''Fundamental vibrational frequency correlation. IV. $C_{2v}-C_{2h}$ in-plane trends,'' Spectrochim. Acta A **45**, 653–659 (1989).

89MOH/PAY Mohan, S., Payami, F., Kuttiappan, P., ''Laser Raman spectrum of glyoxal and its vibrational analysis,'' Proc. Indian Natl. Sci. Acad. A **55**, 598–601 (1989).

92WIB/RAB Wiberg, K. B., Rablen, P. R., Marquez, M., ''Resonance interactions in acyclic systems. 5. Structures, charge distributions, and energies of some hetrobutadiene rotamers,'' J. Am. Chem. Soc. **114**, 8654–8668 (1992).

95MO/ZHA Mo, Y., Zhang, Q., ''Why N_2O_2 is *cis* while $(CHO)_2$ is *trans*: MO and VB studies,'' Int. J. Quantum Chem. **56**, 19–26 (1995).

96PRO/SHO Promyslov, V. M., Shorygin, P. P., ''Quantum-chemical study of conjugation in molecules containing conjugated C═C and C═O bonds,'' Izv. Akad. Nauk, Ser. Khim. 1648–1652 (1996).

97REM/WAT Rempe, S. B., Watts, R. O., ''The convergence properties of hindered rotor energy levels,'' Chem. Phys. Lett. **269**, 455–463 (1997).

14.6. Extended Bibliography for Cyanooxomethyl Radical, NC_2O

91GUR/VEY Gurvich, L. V., Veyts, I. V., Alcock, C. B., *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.

92DOR/GUR Dorofeeva, O. V., Gurvich, L. V., ‘‘Thermodynamic properties of linear carbon chain molecules with conjugated triple bonds. Part 2. Free radicals C_nH ($n = 2-12$) and C_nN ($n = 2-11$),’’ Thermochim. Acta **197**, 53–68 (1992).

94PED Pedley, J. B., *Thermochemical Data and Structures of Organic Compounds* (Thermodynamics Research Center, College Station, TX, 1994), Vol. I.

14.7. Extended Bibliography for Oxalic Acid, $C_2H_2O_4$

26VER/HAR Verkade, P. E., Hartman, H., Coops, J., ‘‘Calorimetric researches. X. Heats of combustion of successive terms of homologous series: Dicarboxylic acids of the oxalic acid series,’’ Recl. Trav. Chim. **45**, 373–393 (1926).

78DEV/NOV De Villepin, J., Novak, A., Romain, F., ‘‘Vibrational spectra of oxalic acids. II. IR and Raman spectra of the α-phase of oxalic acid, and its deuterium and oxygen-18 derivatives,’’ Spectrochim. Acta A **34**, 1019–1024 (1978).

80SHI Shippey, T. A., ‘‘Vibrational studies in aqueous solutions. Part I. The oxalate ion,’’ J. Mol. Struct. **65**, 61–70 (1980).

95CHE/CHE Chen, L.-T., Chen, G.-J., Fu, X.-Y., ‘‘Theoretical studies on the mechanism of the thermal decarboxylation and decarbonylation of a number of α-ketoacids,’’ Chin. J. Chem. **13**, 487–492 (1995).

14.8. Extended Bibliography for Methyl Hydroperoxide, CH_4O_2

79MOL/ARG Molina, M. J., Arguello, G., ‘‘Ultraviolet absorption spectrum of methyl hydroperoxide vapor,’’ Geophys. Res. Lett. **6**, 953–955 (1979).

96GRE/COL Grela, M. A., Colussi, A. J., ‘‘Quantitative structure-stability relationships for oxides and peroxides of potential atmospheric significance,’’ J. Phys. Chem. **100**, 10150–10158 (1996).

96JUR/MAR Jursic, B. S., Martin, R. M., ‘‘Calculation of bond dissociation energies for oxygen containing molecules by *ab initio* and density functional theory methods,’’ Int. J. Quantum Chem. **59**, 495–501 (1996).

97JAC/WEH Jacob, P., Wehling, B., Hill, W., Klockow, D., ‘‘Feasibility study of Raman spectroscopy as a tool to investigate the liquid-phase chemistry of aliphatic organic peroxides,’’ Appl. Spectrosc. **51**, 74–80 (1997).

14.9. Extended Bibliography for Dimethyl Peroxide, $C_2H_6O_2$

82BAT/WAL Batt, L., Walsh, R., ‘‘A reexamination of the pyrolysis of bis trifluoromethyl peroxide,’’ Int. J. Chem. Kinet. **14**, 933–944 (1982).

92ZYA/KNY Zyatkov, I. P., Knyazhevich, N. D., Gogolinskii, V. I., Pitsevich, G. A., ‘‘Quantum-chemical calculations on structure and conformations of organosilicon peroxides,’’ Vestn. Beloruss. Gos. Univ., Ser. 1, No. 2, 33–37 (1992).

96LEE/SHI Lee, S.-Y., Shin, Y.-J., ‘‘Estimation of thermodynamic properties in the pyrolysis of dialkyl peroxides in helium gas,’’ Hwahak Konghak **34**, 592–596 (1996).

14.10. Extended Bibliography for Diacetyl Peroxide, $C_4H_6O_4$

71VLE/MIJ Vledder, H. J., Mijlhoff, F. C., Leyte, J. C., Romers, C., ‘‘Electron diffraction investigation of the molecular structure of gaseous acetic anhydride,’’ J. Mol. Struct. **7**, 421–429 (1971).

80HOL/GUN Hollenstein, H., Günthard, H. H., ‘‘A transferable valence force field for polyatomic molecules. A scheme for a series of molecules containing carbon:oxygen groups,’’ J. Mol. Spectrosc. **84**, 457–477 (1980).

81VAN/VAN Van Eijck, B. P., van Opheusden, J., van Schaik, M. M. M., van Zoeren, E., ‘‘Acetic acid: Microwave spectra, internal rotation and substitution structure,’’ J. Mol. Spectrosc. **86**, 465–479 (1981).

93CHE/ALL Chen, K., Allinger, N. L., ‘‘A molecular mechanics study of alkyl peroxides,’’ J. Comput. Chem. **14**, 755–768 (1993).

94BEN/TAD Benassi, R., Taddei, F., ‘‘Conformational properties of peroxyacids, peroxyesters and structurally related radicals: A theoretical *ab initio* MO approach,’’ J. Mol. Struct.: THEOCHEM **303**, 83–100 (1994).

96JON Jonsson, M., ‘‘Thermochemical properties of peroxides and peroxyl radicals,’’ J. Phys. Chem. **100**, 6814–6818 (1996).