AN *AB* INITIO-BASED SCREENING TOOL FOR THE ATMOSPHERIC LIFETIMES OF HALON REPLACEMENTS

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INTRODUCTION

The decision to phase out the use of halons due to their role in stratospheric ozone loss has led to accelerated efforts to find "environmentally friendly" replacements. Thus, the need has arisen for an efficient means to evaluate the large suite of proposed alternatives for environmental acceptability. In particular, this means obtaining one of the most important pieces of information relating to the atmospheric fate of volatile species: the reactivity towards the hydroxyl radical. The reaction with tropospheric OH typically controls the atmospheric lifetime of many substances and is thus a starting point in the evaluation of its acceptability. Carrying out laboratory measurements on all the proposed replacements is an expensive proposition. made worse by the fact that many of the compounds would have to be synthesized and provided in sufficient purity for kinetic measurements. Clearly, the development of screening tools capable *of* predicting the properties important in assessing environmental persistence would be beneficial to this process.

STATEMENT OF THE PROBLEM

Over the years. various structure-activity relationships have been used to estimate rate constants for chemical reactions, including those of the hydroxyl radical. These usually require a substantial amount of data on a suite of chemicals to provide reliable predictions for similar compounds. The magnitude and difficulty of this task is illustrated by the results of studies on hydrofluoroethers. Normally, it has been assumed that the presence of an ether linkage decreases the bond strength of adjacent C-H bonds and, thus, increases their reactivity. In comparing fluoroalkanes and the corresponding fluoroethers, however, both activation and deactivation are observed (Figure 1) [1]. An analysis of these results has not revealed any consistent pattern, suggesting that experimental kinetic studies for many more fluoroethers would need to be conducted.

Rather than taking this brute force approach, we have decided to explore the possibility of applying fundamental theory to the problem of predicting reactivity. We initiated a systematic study of the application of *ab initio* electronic structure calculations combined with transition state theory to the kinetics of hydrogen-atom abstractions by hydroxyl radicals. The objective was to develop efficient and reliable computational chemistry "screening tools" useful in predicting the fate *of* halon replacements once they are released into the atmosphere.

DEVELOPMENT OF THE METHODOLOGY

The initial study *[2]*focused on the reaction: $OH + CH_2Br_2 \rightarrow H_2O + CHBr_2$

Dibromomethane was chosen because (a) reliable experimental kinetic data are available and (b) because bromine is an important element in fire suppression. Further, the relatively large electronic system associated with the bromine atom makes this a stringent test of the proposed quantum chemical methodologies.

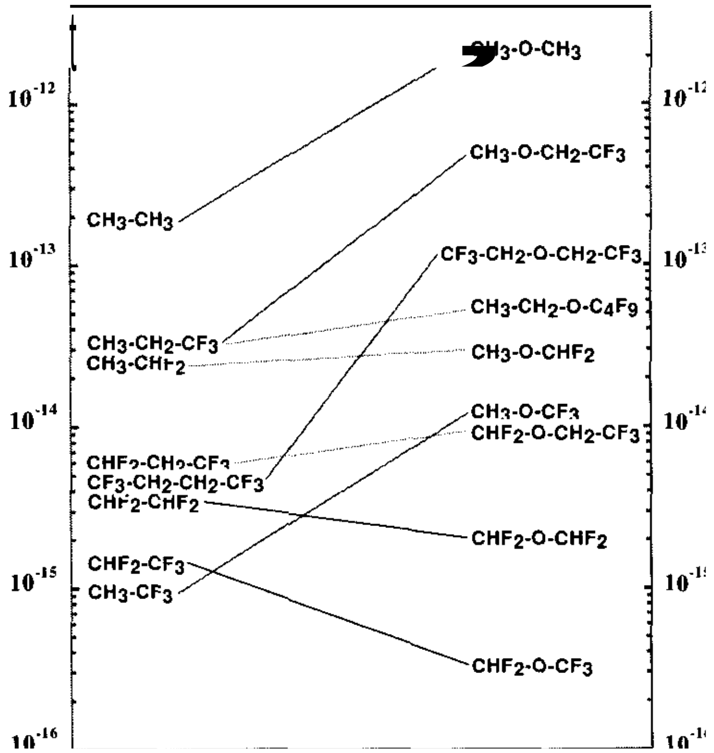

Figure 1. Graph of the relationship between the reactivity of OH towards fluoroalkanes and fluoroethers [1].

***Ab** initio* calculations were carried out with Møller-Plesset second and fourth order perturbation theory (MP2 and MP4), and the coupled cluster method, in the space of singles, doubles and triple electronic excitations, CCSD(T). Full geometry optimization and vibrational frequency calculations at the MP2 level were performed on reactants, products, and the transition state using the 6-311G(d,p) and 6-311G(2d,2p) basis sets. The geometry parameters optimized at the MP2/ 6-311G(2d,2p) level of theory were used in single-point energy calculations with increasing basis set sizes, from 6-311G(2d,2p) to 6-311++G(3df,3pd) at both the MP2 and MP4(SDTQ) levels of theory. Canonical transition state theory was used to predict the rate constants as a function of the temperature (250-400 K) making use of the expression:

$$k(T)=\Gamma(T)\times\frac{k_B T}{h}\times\frac{Q^{TS}(T)}{Q^{OH}(T)Q^{alk}(T)}\times\exp\left(-\frac{\Delta E}{k_B T}\right)$$

where: $Q^{TS}(T)$, $Q^{OH}(T)$ and $Q^{alk}(T)$ are the total partition functions for the transition state, hydroxyl radical, and the haloalkane at temperature T; **AE** is the activation energy including thermal corrections to the internal energy and zero-point energy: k_B is Boltzman's constant; and h is Planck's constant. Γ(T) in the equation indicates the corresponding tunneling correction at temperature T.

Three different expressions were tested for the tunneling correction: the closed-form approximation by Wigner: and calculations based on the symmetrical and unsymmetrical Eckart potentials. These three expressions were then applied in two different ways to obtain Γ(T). The first approach is the normal way in which these corrections are calculated, making use of the imaginary frequency, $\nu^{\neq}$, calculated at the same level of theory as the forward and reverse reaction barriers. In the second approach, the reaction path was calculated by the intrinsic reaction coordinate (IRC) algorithm and fit to the Eckart potential in the region of the transition state. In this case, $\nu^{\neq}$ was an adjustable parameter in the fit. The results of these fits for the reaction of OH with CH_2Br_2 are shown in Figures 2 and 3 [3–6].

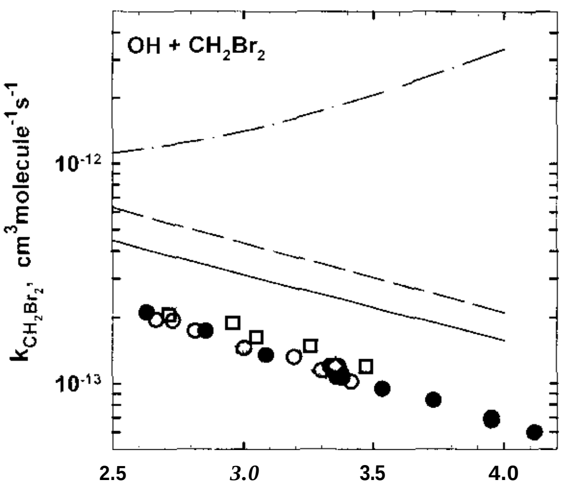

Figure 2. Temperature dependence of the rate constants for the reaction of CH_2Br_2 with OH computed at PMP4 (SDTQ)/6-311++G (3df,3pd)//MP2/6-311G(2d,2p) using the imaginary frequency computed at the MP2/6-311G (2d,2p) level. Solid line: Wigner tunneling correction; short dashed line: symmetrical Eckart tunneling correction; and dash-dotted line: unsymmetrical Eckart tunneling correction [2].

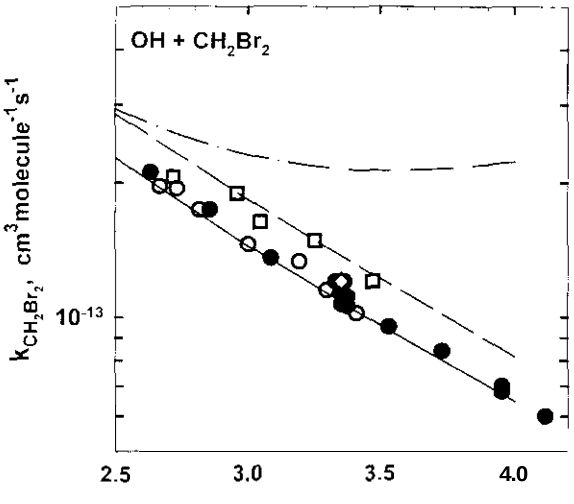

Figure 3. Temperature dependence of the rate constants for the reaction of CH_2Br_2 with OH computed at PMP4 (SDTQ)/ 6-311++G (3df, 3pd)//MP2/ 6-311G (2d,2p). Solid line: Wigner tunneling correction; short dashed line: symmetrical Eckart tunneling correction; and dash-dotted line: unsymmetrical Eckart tunneling correction. In all cases, the imaginary frequency was obtained by the fitting of the Eckart function to the results of the MP2/6-311G (2d,2p) IRC [2].

It is clear that calculations with the unsymmetrical Eckart treatment for tunneling not only do not reproduce the magnitude of the rate constants well, they do not even reproduce the shape of the Arrhenius plot. Interestingly, the best fits are obtained when the Wigner correction is utilized. Although excellent agreement with experiment is obtained when the imaginary frequency was derived from a fit to the IRC, reasonable agreement, within a factor of two, was obtained when $\nu^{\neq}$ was obtained directly from the transition state calculations. This is a considerably less expensive approach and will be employed in the subsequent calculations.

In the second phase of the project, kinetic parameters were calculated for a series of 12 partially halogenated methanes for which reliable experimental data exist [7]. Following the results for dibromomethane, geometry optimization and vibrational frequency calculations were perfomied for reactants, transition states, and products at the MP2/6-311G(2d,2p) level of theory. Single-point energy calculations were carried out at the PMP4(SDTQ) level with both 6-311G (3df,2p), and 6-311++G(3df,3pd) basis sets. Then, canonical transition state theory with Wigner's tunneling correction was used to predict the rate constants as function of temperature. The results of these calculations at 298 K are presented in Figure 4.

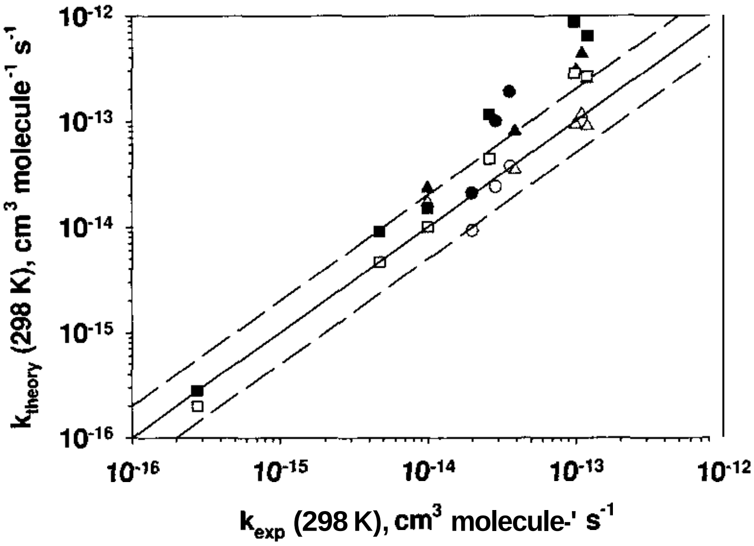

Figure 4. Comparison of experimental and calculated rate constants. Open symbols, PMP4 (SDTQ)/6-311G(3df,2p); closed symbols, PMP4(SDTQ)/6-311++G(3df,3pd). Circles, monosubstituted; triangles, disubstituted; squares, trisubstituted.

Interestingly, the rate constants calculated with the smaller basis set were found to be in better agreement with experimental values than those calculated with the larger basis set. The A-factors computed at both levels of theory are very close, and they are found to be within a factor of 1.0 - 2.5 of the values reported in the literature. As with the rate constants at 298 K, the values of E_a/R computed with the smaller basis set are closer to the experimental values (max. deviation = 15.6%, average deviation of 9.4%) when compared to the corresponding E_a/R's computed with the larger basis sets (max. deviation = 51.4%, average deviation = 19.4%). Overall, these results suggest that PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) is a good compromise between accuracy and computational expense in the theoretical treatment of hydrogen abstraction reactions between OH radicals and halomethanes, possibly as a result of a systematic cancellation of errors between the convergence rate of the perturbation theory and the size of the basis sets used.

APPLICATION OF THE METHODOLOGY

In the third phase of the project, we have calculated rate constants for a series of bromine-containing halomethanes for which experimental data do not exist [8]. These calculations have resulted in the following rate constants at 298 K:

Bromoalkane	k x 10^{14} cm^3 s^{-1}
CH_2FBr	3.0
$CHFBr_2$	10.0
$CHFClBr$	6.8
$CHCl_2Br$	26
$CHClBr_2$	35

In general, we consider these rate constants to be accurate to within a factor of 2 to **3.** although it was apparent from the set of 12 halomethanes originally tested that the level of agreement with measurements worsened with increasing reactivity. From the point of view of a screening tool, this is not a problem since these reactions are already quite fast and hence environmental persistence is diminished.

Finally, the reason we started this project was the difficulty in rationalizing the behavior ofthe hydrofluoroethers by simple structure-activity concepts. Therefore, we have carried out some preliminary calculations on the reactions of three selected ethers and their corresponding alkanes. These calculations are not yet complete in that we have not yet applied hindered rotor corrections to the transition state partition functions, nor have we taken into account all possible rotational conformers. Yet the calculations are sufficient to ascertain if this level of theory will correctly predict the observed reactivity patterns. Below we present the ratio of the rate constants for the alkane relative to those of the ethers at 298K:

Ethane/Ether	Theorv	Experiment
CH_3CF_3/CH_3OCF_3	14.3	**10.0**
CHF_2CF_3/CHF_2OCF_3	0.3	***0.2***
CHF_2CHF_2/CHF_2OCHF_2	***0.2***	0.4

These results demonstrate that this basic approach is a viable method of predicting the reactivity of new functional groups towards the hydroxyl radical and thus can form a component of a screening tool for the environmental acceptability of proposed fire suppressants.

CONCLUSIONS

These studies have been quite successful, and we have been able to demonstrate that a relatively reasonable level of theory is sufficient to predict rate constants to a degree of accuracy sufficient for a screening tool. These full transition state calculations are still difficult, however, for larger systems. Therefore, we have been exploring additional strategies for the prediction of rate constants. Since the thermodynamics are far easier to calculate than reaction kinetics, we have begun looking into applying the simple relationship between rate constant and reaction enthalpy and the rate constant embodied in the Evans-Polanyi equation. We have found that there is a simple quadratic relationship between the logarithm of the rate constant and the calculated reaction enthalpy for the haloniethanes. It remains to be seen if we can make this concept work beyond a simple homologous series.

ACKNOWLEDGMENT

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