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An ab Initio Study of the Kinetics of the Reactions of Halomethanes with the Hydroxyl Radical. 3. Kinetic Parameters Predictions for the Potential Halon Replacements CH_2FBr, $CHFBr_2$, CHFClBr, $CHCl_2Br$, and $CHClBr_2$[†]

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Ab initio PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) calculations, together with canonical transition state theory, were used in order to compute the energetics and predict the kinetics (in the temperature range 250−400 K) of the H atom abstraction reaction between the hydroxyl radical and the five halomethanes: CH_2FBr, $CHFBr_2$, CHFClBr, $CHCl_2Br$, and $CHClBr_2$. The procedure adopted in this study has been discussed and validated in our previous two publications (Louis, F.; Gonzalez, C. A.; Huie, R. E.; Kurylo, M. J. *J. Phys. Chem. A* **2000**, *104*, 2931. Louis, F.; Gonzalez, C. A.; Huie, R. E.; Kurylo, M. J. *J. Phys. Chem. A* **2000**, *104*, 8773.). In the present work, this computational procedure is extended to develop relations of the Evans−Polanyi type, which provide an alternate method to predict rate constants for other reactions where computational expense becomes a limiting factor. In addition, rate constants computed at 277 K were used in the estimation of the atmospheric lifetimes for the five halomethanes. The validity of these results is also discussed.

Introduction

In the first two papers[1,2] of this series (herein referred to as Paper I[1] and Paper II[2]), we presented an exhaustive and systematic study regarding the feasibility of applying relatively inexpensive ab initio electronic structure calculations together with canonical transition state theory, TST, leading to the generation of efficient and reliable computational tools that properly describe the kinetics of hydrogen-atom abstraction reactions by the hydroxyl radical from partially halogenated organic compounds. As explained in our previous work,[1,2] these reactions are of particular importance in the determination of the atmospheric lifetimes of compounds suggested as replacements for fully halogenated alkanes, widely used in industry.

By using a validation set of 13 hydrogen-atom abstraction reactions between the hydroxyl radical and a series of halomethanes of type CHXYZ, (X = F, Cl, or Br), we found that the relatively inexpensive level of theory PMP4(SDTQ)/6-311G-(3df,2p)//MP2/6-311G(2d,2p) combined with TST and the simple Wigner's tunneling correction formalism predicts kinetic parameters in quite reasonable agreement with the experimental data.[2] This can be appreciated by inspecting the results presented in Figure 1, where the temperature dependence of the ratio $k_{\text{theory}}/k_{\text{experiment}}$ in the range 250−400 K is shown for the thirteen reactions included in the validation set of Paper II.[2] As can be seen in this plot, even at low temperatures, most of the computed rate constants deviate from the corresponding experimental values by no more than a factor of 2. The only exception is the reaction OH + $CHCl_3$, where the predicted rate constants lie within a factor of 2 at 400 K and 4 at 250 K with respect the experimental results. As discussed in Paper II,[2] this is not surprising, given the low barrier this reaction exhibits, making the assumptions used by the canonical transition state theory questionable. The previously observed[1,2] reliability of the theoretical procedure used in this work can be attributed to a fortuitous but systematic cancellation of errors between the Møller−Plesset perturbation theory and the truncated basis sets employed. In Papers I and II, it was also shown that Wigner tunneling corrections predict Arrhenius plots in better agreement with experiment in the case of H atom abstractions from halocarbons by OH radicals, while an unsymmetrical Eckart correction leads to Arrhenius plots with the wrong shape. As explained in Paper I, these results can be explained by the significantly wide barriers exhibited by this class of reactions, for which the Wigner tunneling formulation seems to be a better model compared with Eckart's treatment. On the basis of these very encouraging results, we have recommended this methodology as a de facto computational procedure for a "screening tool"

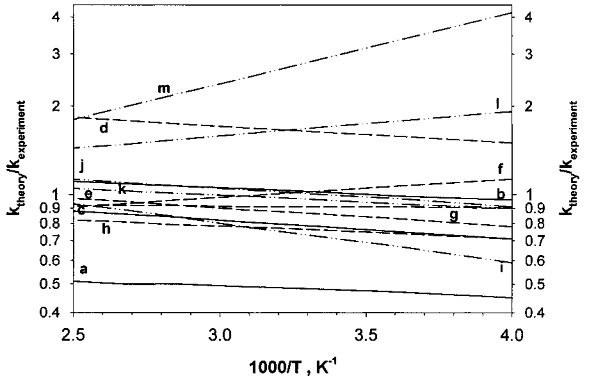

Figure 1. Evolution of the ratio $k_{\text{theory}}/k_{\text{experiment}}$ over the temperature range 250−400 K for the validation set of thirteen H atom abstraction reactions. a: CH_3F. b: CH_3Cl. c: CH_3Br. d: CH_2F_2. e: CH_2FCl. f: CH_2Cl_2. g: CH_2ClBr. h: CH_2Br_2. i: CHF_3. j: CHF_2Cl. k: CHF_2Br. l: $CHFCl_2$. m: $CHCl_3$.

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that can be used to help in establishing the environmental acceptability of partially halogenated organic compounds.

In this work, we apply the same methodology recommended in Paper II to compute the energetics and kinetic parameters of the following five H atom abstraction reactions:

$$OH + CH_2FBr \rightarrow H_2O + CHFBr \qquad (R1)$$

$$OH + CHFBr_2 \rightarrow H_2O + CFBr_2 \qquad (R2)$$

$$OH + CHFClBr \rightarrow H_2O + CFClBr \qquad (R3)$$

$$OH + CHCl_2Br \rightarrow H_2O + CCl_2Br \qquad (R4)$$

$$OH + CHClBr_2 \rightarrow H_2O + CClBr_2 \qquad (R5)$$

The main goal of this study is to utilize our theoretical procedure to provide Arrhenius parameters for these reactions. This is particularly relevant in view of the lack of experimental data available for these reactions, with the exception of OH + $CHCl_2$-Br for which the rate constant has been only measured at 298 K.[3] These reactants all contain bromine, which is a chemically active fire suppressant agent[4] and are thus potential halon replacements (ref 1 from Paper I). To our knowledge, no theoretical calculations dealing with the thermochemistry and kinetics of these reactions have been reported previously.

In this study we are also extending our computational approach to the problem of estimating these rate constants to include computationally less expensive methods. Specifically, we have explored predictive schemes, based on the enthalpies of the reactions, calculated at the same level of theory we have applied to the kinetics. Enthalpy calculations are much easier to carry out and lower levels of theory may possibly be adequate. We explore this approach now in anticipation of the difficulties we may face in calculating rate constants for larger molecules.

Computational Methods[5a]

All calculations described below were carried out with the Gaussian 94[5b] suite of programs on a Cray C90/6256 supercomputer and a 32-processor Silicon Graphics Origin 2000 parallel computer. Details with the methodology used in the present calculations have been discussed elsewhere.[1,2] Briefly, fully optimized geometries, harmonic frequencies, and zero-point energy corrections, ZPE, of reactants, transition structures, and products were computed with the second-order Møller−Plesset perturbation theory, UMP2, using the 6-311G(2d,2p) basis set. Electron correlation was calculated with the fourth-order Møller−Plesset perturbation theory in the space of single, double, triple, and quadruple excitations with full annihilation of spin contamination,[6] PMP4(SDTQ). These single-point energy calculations were carried out with the 6-311G(3df,2p) basis set using the geometries previously optimized at the MP2/6-311G(2d,2p) level. All relative energies quoted and discussed in this paper include zero-point energy corrections with unscaled frequencies obtained at the MP2/6-311G(2d,2p) level.

Rate constants, *k(T)*, were computed using the following transition state theory expression:[7]

$$k(T) = \Gamma(T)\frac{k_B T}{h}\frac{Q^{TS}(T)}{Q^{OH}(T)Q^{CHXYZ}(T)}\exp\left(-\frac{\Delta E}{k_B T}\right) \qquad (1)$$

where $Q^{OH}(T)$, $Q^{CHXYZ}(T)$, and $Q^{TS}(T)$ are the total partition functions for the hydroxyl radical, halomethane of type CHXYZ, and transition state respectively at temperature T; ΔE is the activation energy including zero-point energy corrections; k_B is Boltzman's constant, and h is Planck's constant. For all species, the total partition function can be cast in terms of the translational ($Q^X{}_T$), rotational ($Q^X{}_R$), electronic ($Q^X{}_e$), and vibrational ($Q^X{}_v$) partition functions. In computing the electronic partition function for the OH radical $Q^{OH}{}_e$, the multiplicity of the states $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ and the energy gap of 139.7 cm^{-1} between the low-lying electronic states[8] have been taken into consideration. As in our previous work,[2] the tunneling correction $\Gamma(T)$ in eq 1 is computed by the simple Wigner's formalism:[9]

$$\Gamma(T) = 1 + \frac{1}{24}\left(\frac{h\nu^{\neq}}{k_B T}\right)^2 \qquad (2)$$

where $\nu^{\neq}$ is the imaginary frequency at the saddle point and the other terms have the same meaning as in eq 1. The rate constant calculations over the temperature range 250−400 K were carried out using the TURBO−RATE program.[10]

Results and Discussion

Transition Structures and Vibrational Frequencies. Table 1 lists all essential structural parameters as well as the imaginary frequencies computed at the UMP2/6-311G(2d,2p) level of theory for the transition structures corresponding to the five reactions (R1−R5). A complete list of all optimized geometrical parameters and vibrational frequencies corresponding to all reactants, transition structures, and products is shown in Tables 1S−5S provided in the Supporting Information.

The results shown in Table 1 indicate that, for all five transition states, the C−H bond being broken is elongated by approximately 10% while the H−O bond being formed is elongated by approximately 35% when compared to their equilibrium values. This is a clear indication of the "reactant-like" nature of these stationary points. These results seem to indicate relatively large exothermicities and low reaction barriers (see below), in keeping with Hammond's postulate.[11]

Direct inspection of the transition state low-frequency modes reported in Table 5S indicates that, in all cases, there is one mode consisting of an internal −OH rotation about the nearly linear C−H−O axis. Given that the barriers for these rotations were sufficiently small (Table 1), these modes were treated as hindered rotors instead of a vibration. As explained in our previous papers,[1,2] these modes were removed from the vibrational partition function for the transition state and the corresponding hindered rotor partition function $Q_{HR}(T)$, calculated by the method devised by Ayala and Schlegel,[12] was included in the expression for the rate constant.[1]

Reaction Enthalpies and Barriers. Table 2 summarizes the results for reaction enthalpies $\Delta_r H$(ISO) calculated at 298 K by a procedure similar to the one adopted in our earlier publications,[1−2] where the reaction enthalpies for the five reactions computed by direct subtraction of electronic energies between products and reactants are corrected by values of D_{298}(H−CXYZ) utilizing the following isodesmic reactions:

$$CH_3 + CHXYZ \rightarrow CH_4 + CXYZ (X,Y,Z = H, F, Cl, \text{ or } Br) \qquad (R6)$$

First, the reaction enthalpies of these reactions (R6) are computed at the same level of theory as that for the five abstraction reactions under study. These enthalpies are then used, in conjunction with the experimental value of D_{298}(H−CH_3) = 440 kJ mol^{-1},[13] to calculate the corresponding D_{298}(H−CXYZ) values. Finally, these D_{298}(H−CXYZ) quantities are used in the calculation of the reaction enthalpy for reactions R1−R5 by

TABLE 1: Essential Structural Parameters,[a] Imaginary Vibrational Frequencies for the Transition States of Each Reaction, and Internal Rotation Barrier of the −OH Group at the MP2/6-311G(2d,2p) Level of Theory

	r (C−H$_R$)	r (O−H$_R$)	θ (OH$_R$C)	$\nu^{\neq}$ cm^{-1}	V_0 kJ mol^{-1}	treatment of ν_{ROT} (HO···H···C)[b]
CH_2FBr	1.190	1.296	160.3	2184i	8.7	hindered rotor
$CHFBr_2$	1.186	1.296	162.0	2183i	7.8	hindered rotor
CHFClBr	1.189	1.291	162.7	2220i	7.3	hindered rotor
$CHCl_2Br$	1.183	1.299	170.8	2174i	3.4	hindered rotor
$CHClBr_2$	1.182	1.300	171.3	2173i	3.3	hindered rotor

[a] Bond lengths r are in angstroms, bond angles θ in degrees; the hydrogen atom involved in H atom abstraction is noted H$_R$. [b] Low-frequency mode associated with the −OH rotation around the axis along the C−H bond being broken.

TABLE 2: Calculated Reaction Enthalpies Δ_rH(ISO) and Vibrationally Adiabatic Barriers at PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) Level of Theory

	Δ_rH(ISO)[a] (kJ mol^{-1})	V_a^G (kJ mol^{-1})[b]
OH + CH_2FBr	−81.9	13.1
OH + $CHFBr_2$	−92.5	7.7
OH + CHFClBr	−90.7	8.9
OH + $CHCl_2Br$	−105.3	4.5
OH + $CHClBr_2$	−105.7	3.8

[a] Including the sum of thermal energies (Δ*Z*PE + thermal energy corrections at 298 K). [b] Including the Δ*Z*PE correction.

TABLE 3: Summary of Kinetic Parameters Calculated at PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) Level of Theory Including Wigner's Tunneling Correction

	E_a/R (K)	A, 10^{-12} [a]	k (theory, 298 K), 10^{-14} [a]
OH + CH_2FBr	1440	3.8	3.0
OH + $CHFBr_2$	825	1.6	10.0
OH + CHFClBr	920	1.5	6.8
OH + $CHCl_2Br$	330	0.8	26.4
			12.0[b]
OH + $CHClBr_2$	250	0.8	34.6

[a] Units are cm^3 molecule^{-1} s^{-1}. [b] Experimental value measured by Bilde et al.[3]

means of the following relation:

$$\Delta_r H(\mathrm{ISO}) = D_{298}(\mathrm{H{-}CXYZ}) - D_{298}(\mathrm{H{-}OH}) \qquad (3)$$

As observed in Table 2, the five reactions are significantly exothermic with values of the reaction enthalpies varying from −81.9 to −105.7 kJ mol^{-1}.

Table 2 also lists the vibrationally adiabatic barriers V_a^G for the five reactions under study. The values of V_a^G are computed by the following relation:

$$V_a^G = E_{TS} - E_R + \mathrm{ZPE}_{TS} - \mathrm{ZPE}_R \qquad (4)$$

where E_{TS} and E_R are the computed ab initio total energies for the transition state and reactants, while ZPE$_{TS}$ and ZPE$_R$ are the corresponding zero-point energy corrections.

The results in Table 2 indicate that the substitution in the halomethane's structure of F atom by Cl or Br tends to decrease the barrier, but the substitution of Cl by Br does not seem to have a significant impact in the barrier height. Overall, reactions R1−R5 are characterized by large heats of reaction and relatively low barrier heights (3.8 to 13.1 kJ mol^{-1}), in keeping with the "reactant-like" nature of their corresponding transition states.

Kinetic Parameters. Table 3 shows the Arrhenius parameters obtained from a fit of the equation

$$k(T) = A \exp(-E_a/RT) \qquad (5)$$

to the reaction rate constants computed in the temperature range 250−400 K. In addition, the rate constants computed at 298 K are also shown. For the first three compounds, CH_2FBr, $CHFBr_2$, and CHFClBr, the *A*-factors per C−H bond, are the same. The *A*-factors for the compounds $CHCl_2Br$, and $CHClBr_2$ are about a factor of 2 lower. These latter compounds also have lower computed activation energies and higher rate constants at 298 K. Given the low barrier heights for these reactions, it is possible that canonical transition state theory might not be entirely appropriate and that the predicted rate constants might be just an upper bound to the real results. In these cases, more computationally expensive methodologies, such as the variational transition state theory formalism, VTST,[14] should be used in order to compute rate constants with a higher accuracy. On the basis of our previous results on the reaction between OH + $CHCl_3$[2], however, we believe that the TST results are accurate within a factor of 2−4 in the case of these two reactions. This is further confirmed by the computed k(298 K) for the reaction OH + $CHCl_2Br$ (Table 3), which is approximately 2.2 times higher that the value measured by Bilde et al.[3]

Evans−Polanyi Relations. Despite the success of the methodology used in this work in predicting kinetic parameters in reasonable agreement with experimental results for H atom abstraction reactions between OH radicals and halogenated methanes,[1,2] it is clear that the treatment of larger systems might be prohibitively expensive from a computational point of view. This is particularly true in the case of halogenated organic compounds with more than three carbon atoms, where the number of possible transition states could increase significantly. This situation gets worse in cases where a sizable number of halogens such as bromine are also present, given that the full ab initio treatment of the electronic structure problem could become unfeasible.

Given that the ab initio computation of heats of reaction are far less expensive (and less laborious) than the theoretical prediction of the kinetics, it would seem logical to look for other less expensive alternatives that involve only the treatment of the thermochemistry. In this work, we have adopted relations of the Evans−Polanyi type where properties such as vibrationally adiabatic barriers and/or reaction rate constants are related to the corresponding heats of reaction.

As a first approach, we have plotted the natural logarithm of the rate constant obtained experimentally at 298 K, ln k_{exp}(298 K), as a function of the calculated Δ_rH(ISO) at the same temperature for the 13 H atom abstraction reactions included in the validation set used in Paper II.[2] The resulting Evans−Polanyi plot is shown in Figure 2. A least-squares polynomial fit of the data leads to the following quadratic relation:

$$\ln k_{exp}(298\ \mathrm{K}) = -2.003 \times 10^{-3}\, \Delta_r H(\mathrm{ISO})^2 - 0.435\, \Delta_r H(\mathrm{ISO}) - 53.29 \qquad (6)$$

This relation can now be used together with the calculated reaction enthalpies for the five reactions presented in this study in order to predict their corresponding ln k_{exp}(298 K) values. The predicted results using this approach are also depicted in

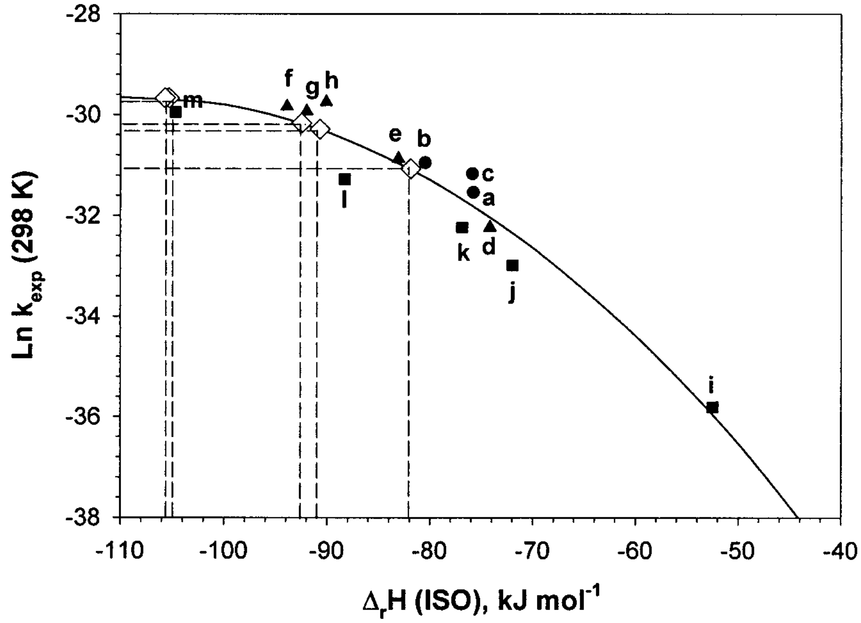

Figure 2. Quadratic variation of the ln k_{exp}(298 K) versus Δ_rH(ISO) in kJ mol^{-1}. a: CH_3F. b: CH_3Cl. c: CH_3Br. d: CH_2F_2. e: CH_2FCl. f: CH_2Cl_2. g: CH_2ClBr. h: CH_2Br_2. i: CHF_3. j: CHF_2Cl. k: CHF_2Br. l: $CHFCl_2$. m: $CHCl_3$.

TABLE 4: Vibrational Adiabatic Barriers V_a^G in kJ mol^{-1} and Rate Constants at 298 K in cm^3 molecule^{-1} s^{-1}

compound	V_a^G (theory)[a]	$V_a^G(E-P)$[b]	k_{E-P}^{theory}[c] × 10^{13}	k_{E-P}^{exp}[d] × 10^{13}	$k_{ab\ initio}$[e] × 10^{13}
CH_2FBr	13.1	13.2	0.29	0.32	0.30
$CHFBr_2$	7.7	9.5	1.00	0.79	1.00
CHFClBr	8.9	10.1	0.83	0.70	0.68
$CHCl_2Br$	4.5	5.3	2.90	1.30	2.60
$CHClBr_2$	3.8	5.1	3.00	1.30	3.50

[a] Computed with the full ab initio treatment. [b] Predicted from the Evans−Polanyi eq 8. [c] Predicted from the Evans−Polanyi eq 7. [d] Predicted from the Evans−Polanyi eq 6. [e] Computed with the full ab initio treatment.

Figure 2. In addition, the results in Table 4 show that the predicted k(298)'s are in reasonable good agreement with the computed values obtained by the full ab initio treatment previously discussed.

Although the previous approach seems to work very well, it is rather limited in scope since it requires the knowledge of the experimental rate constants for a suitable validation set of reactions. This information might not be available, especially in instances where proposed partially halogenated organic compounds are being screened as potential replacements for their fully halogenated counterparts. In these cases, the prediction of the reaction rate constants based on purely theoretical calculations might be the best course of action. Figure 3 shows an Evans−Polanyi plot (using the same validation set) where the natural logarithm of the rate constant calculated at 298 K, ln k_{theory}(298 K), is plotted vs the corresponding calculated Δ_rH(ISO) values. As with the previous approach, a quadratic relation is obtained:

$$\ln k_{theory}(298\ \mathrm{K}) = -1.368 \times 10^{-3}\Delta_rH(\mathrm{ISO})^2 - 0.354\Delta_rH(\mathrm{ISO}) - 50.96 \quad (7)$$

Again, the results for the five reactions discussed in this work (see Table 4) show an excellent agreement between the predicted values using eq 7 and the k(298)'s computed by the full ab initio treatment. The Evans−Polanyi relations discussed above are general and can be applied to temperatures other than 298 K.

Sometimes, information regarding the adiabatic vibrational barrier for a particular reaction is needed. Figure 4 shows the plot of V_a^G vs Δ_rH(ISO) for the validation set of reactions. As in the previous two approaches, a polynomial fit of the data gives the following Evans−Polanyi relation for V_a^G (in kJ mol^{-1}):

$$V_a^G = 1.025 \times 10^{-3}\Delta_rH(\mathrm{ISO})^2 + 0.533\Delta_rH(\mathrm{ISO}) + 49.98 \quad (8)$$

As can be observed in Table 4, the five V_a^G's predicted by eq 8 are in excellent agreement with the corresponding values computed by the full ab initio formalism.

Atmospheric Lifetimes. Reactions with hydroxyl radicals in the troposphere constitute the main removal pathways of hydrogen-containing compounds. Following Prather and Spivakovsky,[15] we can estimate the atmospheric lifetime of a halomethane of the type CHXYZ due to reactions with hydroxyl radicals in the troposphere as

$$\tau_{CHXYZ}^{OH} = \frac{k_{CH_3CCl_3}^{OH}(277\ \mathrm{K})}{k_{CHXYZ}^{OH}(277\ \mathrm{K})}\tau_{CH_3CCl_3}^{OH} \quad (9)$$

Where τ_{CHXYZ}^{OH} and $\tau_{CH_3CCl_3}^{OH}$ are the atmospheric lifetimes of the halomethane CHXYZ and methyl chloroform (CH_3CCl_3), respectively, due to reactions with hydroxyl radicals in the troposphere only. In eq 9, k_{CHXYZ}^{OH} (277 K) and $k_{CH_3CCl_3}^{OH}$ (277 K) = 6.69 × 10^{-15} cm^3 molecule^{-1} s^{-1} [16] are the rate constants for the reactions of OH with these compounds at T = 277 K. A value of $\tau_{CH_3CCl_3}^{OH}$ equal to 5.9 years was used, which was obtained following the procedure used by Prinn et al.[17] from the measured lifetime of CH_3CCl_3, $\tau_{CH_3CCl_3}$ = 4.8 years, taking

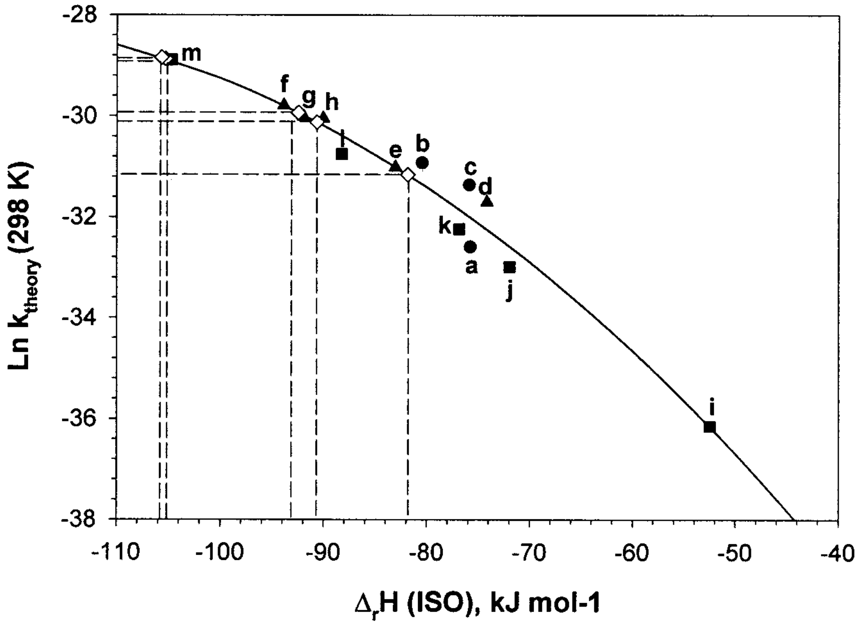

Figure 3. Quadratic variation of the Ln k_{theory}(298 K) versus Δ_rH(ISO) in kJ mol^{-1}. a: CH_3F. b: CH_3Cl. c: CH_3Br. d: CH_2F_2. e: CH_2FCl. f: CH_2Cl_2. g: CH_2ClBr. h: CH_2Br_2. i: CHF_3. j: CHF_2Cl. k: CHF_2Br. l: $CHFCl_2$. m: $CHCl_3$.

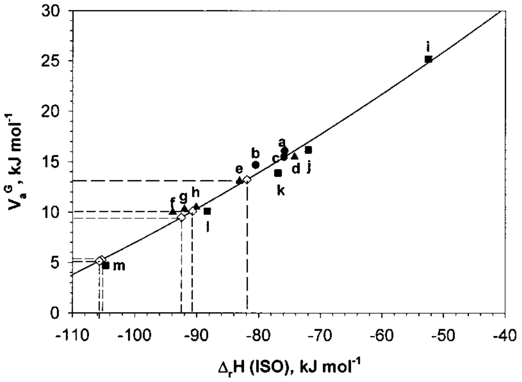

Figure 4. Quadratic variation of the vibrationally adiabatic barriers V_a^G versus Δ_rH(ISO) in kJ mol^{-1}. a: CH_3F. b: CH_3Cl. c: CH_3Br. d: CH_2F_2. e: CH_2FCl. f: CH_2Cl_2. g: CH_2ClBr. h: CH_2Br_2. i: CHF_3. j: CHF_2Cl. k: CHF_2Br. l: $CHFCl_2$. m: $CHCl_3$.

into account partial lifetimes due to ocean loss of 85 years and to stratospheric loss of 37 years.

Table 5 shows the results of these predictions as well as the results obtained using the experimental rate constants for the validation set of thirteen H atom abstraction reactions discussed in Paper II.[2] The atmospheric lifetimes estimated by these calculations are in quite reasonable agreement with those estimated by the experimental data. As can be seen in Table 5, the theoretical atmospheric lifetimes deviate from their experimental counterparts by no more than a factor of 2, except in the case of the reaction of OH with chloroform ($CHCl_3$) for which a factor of 3.4 is obtained.

For the reactions of OH with CH_2FBr, $CHFBr_2$, and CHFClBr, we estimate the atmospheric lifetimes to be 1.88, 0.49, and 0.73 years, respectively. On the basis of the agreement between the rate constants calculated for the validation set and the measurements, we estimate an uncertainty of less than a factor of 2 in the rate constants from which these are derived. For the bromochloromethanes $CHCl_2Br$, and $CHClBr_2$, the corresponding atmospheric lifetimes estimated by our calculations are 58 and 43 days. We estimate an uncertainty of no more than a factor of 4 for the rate constants from which these are derived. The rate constants for their reaction with OH are indeed likely to be very similar to that of $CHCl_3$ and $CHBr_3$.

TABLE 5: Atmospheric Lifetimes in Years for a Series of Halomethanes of Type CHXYZ

compound	$\tau_{\text{CHXYZ}}^{\text{OH}}$ (theory)[a]	$\tau_{\text{CHXYZ}}^{\text{OH}}$ (experiment)[b]
CH_3F	6.37	2.92
CH_3Cl	1.55	1.55
CH_3Br	2.47	1.97
CH_2F_2	3.59	5.60
CH_2FCl	1.68	1.38
CH_2Cl_2	0.43	0.46
CH_2ClBr	0.54	0.49
CH_2Br_2	0.57	0.42
CHF_3	397	263
CHF_2Cl	13.16	12.73
CHF_2Br	6.03	5.64
$CHFCl_2$	1.18	2.13
$CHCl_3$	0.15	0.51
CH_2FBr	1.88	unknown
$CHFBr_2$	0.49	unknown
CHFClBr	0.73	unknown
$CHCl_2Br$	0.16	unknown
$CHClBr_2$	0.12	unknown

[a] Computed with the full ab initio treatment. [b] Experimental values of the rate constant at 277 K are calculated from the Arrhenius expressions reported in ref 16, and in ref 18 for the reaction OH + CH_2ClBr.

Note that the estimates of the lifetimes of these compounds do not include loss mechanisms due to photolysis or to hydrolysis. Any contribution from these sources will lead to a lower actual lifetime. In addition, the above estimates assume a uniform distribution of the gas throughout the troposphere. This assumption is probably reasonable for longer-lived compounds such as CH_2FBr, somewhat questionable for $CHFBr_2$ and CHFClBr, and is probably not valid for the short-lived compounds $CHCl_2Br$ and $CHClBr_2$, which are not likely to have a uniform distribution over the troposphere. Atmospheric modeling calculations are probably required to obtain more valid estimates. Nevertheless, from the point of view of a screening tool, the important information is that these compounds are predicted to be short-lived and are thus potentially suitable replacement compounds.

Conclusions

PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) molecular orbital calculations combined with transition state theory have been used in order to study the kinetics of the H atom abstraction reactions between the radical OH and a series of five bromine-containing halomethanes for which no experimental data are available. Given the previous success of this methodology[2] in predicting rate constants within a factor of 2 for similar reactions, we believe the kinetic parameters for the five reactions in this study are predicted with similar accuracy. The results presented in this work also show the feasibility of using relationships of the Evans−Polanyi type in order to predict the kinetics of other H atom abstraction reactions by OH radicals using only theoretical calculations of the reaction thermodynamics. These Evans−Polanyi relations provide a powerful addition to the computational "screening tool" proposed in our previous publications[1,2] aimed at the implementation of inexpensive semiquantitative methodologies that could aid scientists in the understanding of the kinetics processes similar to the ones discussed in this work. Finally, rate constants computed at 277 K were used in order to provide estimates of the atmospheric lifetimes for the five halomethanes: CH_2FBr, $CHFBr_2$, CHFClBr, $CHCl_2Br$, and $CHClBr_2$. It is observed that the species CH_2FBr, $CHFBr_2$, and CHFClBr exhibit considerably larger atmospheric lifetimes (from 0.5 to 1.9 years) when compared to the bromochloromethanes $CHCl_2Br$, and $CHClBr_2$ (in the order of days). As explained in the Discussion section, these numbers should be used only as a semiquantitative guide given that more sophisticated models are needed in order to get accurate atmospheric lifetimes.

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Supporting Information Available: Tables of (i) the optimized geometry parameters of the halomethanes, halomethyl radicals, and transition states (Tables 1S−3S), and (ii) their vibrational frequencies (Tables 4S and 5S).

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