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Kinetic Studies of the Reaction of Cl Atoms with BrCH₂OCH₃Kyriakos G. Kambanis, Yannis G. Lazarou, Igor I. Morozov,[†] and Panos Papagiannakopoulos*

Department of Chemistry, University of Crete, Heraklion 714 09, Crete, Greece

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The reaction of chlorine atoms with bromomethyl methyl ether, BrCH₂OCH₃, was studied with the very low pressure reactor (VLPR) technique in the temperature range 273–363 K. The absolute rate constant was found to be independent of temperature and its value was $(2.61 \pm 0.46) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Conventional transition state theory suggests that the reaction proceeds mainly via the metathesis of a hydrogen atom from the substituted ether side.

Introduction

The increasing level of anthropogenic compounds in the atmosphere has led to the thorough consideration of their contribution in stratospheric ozone depletion, global warming, and climate changes.^{1,2} Chlorofluorocarbons (CFC), generally known as freons, are a major class of compounds that have been released into the atmosphere in considerable amounts.³ They have been widely used as refrigerants, all-purpose solvents, and propellants for aerosol containers. However, freons are gradually being removed from the market due to their contribution in the stratospheric ozone destruction, by their photolytic decomposition to halogen atoms. The most promising substitutes have been hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC). In general, these compounds are more friendly to the environment, and compatible with existing technologies. In addition, these alternatives should have a short lifetime in the lower troposphere, by reacting with hydroxyl radicals during daytime, so they could not drift up in the stratosphere. Furthermore, their tropospheric decomposition mechanisms should lead to environmentally acceptable products. Chlorine atoms, though less significant than hydroxyl radicals, are generated by photolytic decomposition of chlorinated compounds, which are emitted into the troposphere by several anthropogenic activities.³ Moreover, chlorine atoms are thought to be produced in coastal atmospheres via heterogeneous oxidative processes of sea salt.⁴

In the present paper, we studied the reactivity of a new class of replacement compounds, partially halogenated ethers. The reaction of chlorine atoms with a simple brominated ether, bromomethyl methyl ether, BrCH₂OCH₃ (BMME), was studied in the gas phase and over a relatively wide temperature range.

Experimental Section

The experiments were performed with the very low pressure reactor (VLPR) technique.^{5,6} It consists of a cylindrical Pyrex reactor ($V = 31 \text{ cm}^3$) attached to the first stage of a differentially pumped system. The reactor has two capillary inlets and is thermostated in the range 0–100 °C by a water jacket. The inner surface of the reactor is covered with halocarbon wax in order to prevent the wall recombination processes of atoms and radicals. The reactor has a circular escape aperture that is adjustable in diameter, in order to allow uninterrupted changes to the reactor escape rates and residence times. An aperture 5 mm wide was selected throughout the experiments. The gaseous

TABLE 1: Mass Spectral Relative Intensities of (a) Bromomethyl Methyl Ether (BrCH₂OCH₃) and (b) Radicals BrCHOCH₃/BrCH₂OCH₂, Both at 19 eV and $I_{\text{emission}} = 0.18 \text{ mA}$

| (a) BMME | | | | | | | | | | | |
|---|-----|-----|------|-----|------|----|-----|----|-----|-----|-----|
| <i>m/e</i> | 15 | 29 | 30 | 31 | 45 | 79 | 81 | 93 | 94 | 95 | 96 |
| <i>I</i> | 162 | 97 | 15 | 1 | 1000 | 2 | 2 | 6 | 23 | 6 | 23 |
| (b) Radicals BrCHOCH ₃ /BrCH ₂ OCH ₂ | | | | | | | | | | | |
| <i>m/e</i> | 15 | 29 | 30 | 31 | 44 | 93 | 94 | 95 | 96 | 109 | 111 |
| <i>I</i> | 714 | 710 | 1000 | 403 | 170 | 55 | 118 | 55 | 118 | 53 | 53 |

reaction mixture is discharged through the escape aperture to the first vacuum chamber, collimated by means of a skimmer on the entrance of the second high vacuum chamber. Thus, an effusive molecular beam is formed that is modulated in the high vacuum chamber by means of a tuning fork chopper, vibrating at 200 Hz. A quadrupole mass spectrometer (BALZERS QMG511 with cross-beam ion source) located 5 cm downstream from chopper is used for the molecular beam chemical analysis. The ionizing electron energy is kept low at 19 eV in order to minimize fragmentation of HCl and its possible interference with chlorine atom measurements at *m/e* 35. Both modulated mass spectrometer output and chopper reference signal are fed to a lock-in amplifier (NF LI-570) in order to amplify the mass spectrometric signal. The lock-in amplifier output is directed to a computer (microPDP-11) which also controls the mass spectrometer operation. The precision of mass spectrometric intensity measurements was ca. 7%.

The steady-state concentrations of Cl atoms, BMME, and HCl were monitored by measuring the intensity of their primary mass peaks at *m/e* 35, 45, and 36, respectively. The mass spectrum peaks and their relative intensities of BrCH₂OCH₃ at an electron energy of 19 eV are presented in Table 1a. Its primary peak at *m/e* 45, due to methoxymethyl ion, CH₃OCH₂⁺, fragment, was measured several times during the course of each experiment in order to verify the constant sensitivity of the mass spectrometer. In addition, the peak intensity I_{45} was linear with BMME steady-state concentration and was given by the expression $I_{45} = Q_{45} k_{\text{esc,BMME}} V_{\text{cell}} [\text{BMME}]$ with an accuracy of ca. 10%, where Q_{45} is a stable calibration mass spectrometric factor. Finally, the *m/e* 45 peak of BMME did not have any contribution from possible reaction products, BrCHOCH₃ and BrCH₂OCH₂, since both radical species cannot produce the fragment CH₃OCH₂⁺.

Both Cl₂ and BMME gases were diluted in He (5% mixture) of high purity. Helium was previously passed through molecular sieves at liquid nitrogen temperature to remove traces of moisture. Bromomethyl methyl ether was supplied from Aldrich and was of technical purity (95%). It was subjected to several

[†] Permanent address: Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygin str. 4, Moscow, 117334, Russia.

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freeze–pump–thaw cycles in order to remove all volatile impurities. Molecular chlorine was of high purity (Linde 2.8, 99.8%) and was mixed with helium after degassing once at $T = 77$ K. Chlorine atoms were produced in a microwave discharge of the Cl_2/He mixture flowing through a quartz tube enclosed in a airflow-cooled cavity operating at 2450 MHz. The incident microwave power from a microwave generator (EMS Microtron 200 Mark 3) was adjusted to 35 W and was totally absorbed from the flowing mixture. The quartz tube inner surface was covered with a dried mixture of phosphoric and boric acid in order to inhibit chlorine atom recombination. Throughout the experiments complete Cl_2 dissociation (over 96%) was maintained as verified by the intensity of peak m/e 70 in the reaction mass spectra.

The flow of gases to the reactor was controlled by calibrated capillary gas resistances, and the back pressures were measured by capacitance manometers (Validyne DP-15). The escape rates of all species were determined from calibration curves, which were previously obtained by measuring the escape rates of several gases after a fast halt of their flow to the VLPR reactor. The expression $k_{\text{esc}} = 9.78(T/M)^{1/2}$ was employed, where T is the absolute temperature and M the molecular weight.

The VLPR apparatus was checked by measuring the rate of the well-known reaction between chlorine atoms and methanol. The rate constant value obtained at three different temperatures ($T = 303, 333$, and 363 K) was $(5.80 \pm 0.60) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (within a 2σ uncertainty), in excellent agreement with the literature value $5.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁷

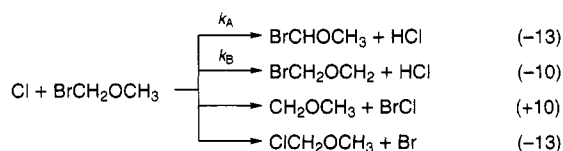
The steady-state concentration was measured on an absolute basis, by using the expression $I_{35} = Q_{35}k_{\text{esc,Cl}}V_{\text{cell}}[\text{Cl}]$. Q_{35} is a calibration factor for Cl atoms, which was previously determined by a titration method with the known reaction of Cl with methanol. In short, the steady-state assumption leads to the expression:

$$\Delta[\text{CH}_3\text{OH}]k_{\text{esc,CH}_3\text{OH}} = \Delta[\text{Cl}]k_{\text{esc,Cl}}$$

where $\Delta[\text{CH}_3\text{OH}] = [\text{CH}_3\text{OH}]_0 - [\text{CH}_3\text{OH}]_t$ and $\Delta[\text{Cl}] = [\text{Cl}]_0 - [\text{Cl}]_t$ (subscript o refers to absence of chlorine or methanol reactants). The drop in chlorine signal intensity ΔI_{35} is correlated with $\Delta[\text{Cl}]$ that is derived by the above expression and the decrease in methanol concentration.

Results

The kinetic system under study could involve the following bimolecular reactions:



The reaction enthalpies (in kcal/mol) are estimated by employing Benson's additivity rules.⁸ The contribution of two unlisted groups, $\text{C}-(\text{H})_2(\text{O})(\text{Br})$ and $\text{C}-(\text{H})_2(\text{O})(\text{Cl})$, was extrapolated from values of groups with similar structure and was taken as -5.28 and -16.4 kcal/mol, respectively.

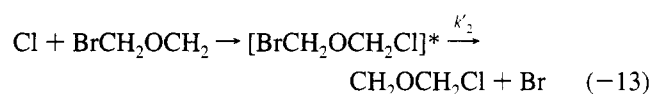
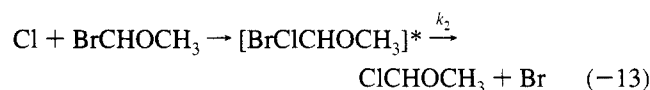
The last two channels are considered unlikely since the third one is highly endothermic and the fourth one involves an energetically unfavored transition state with a five-coordinated carbon atom and strong repulsions between the two halogen atoms.

Mass spectrometric analysis of the reaction products, following the subtraction of BMME contributions, reveals the appearance of major peaks at m/e 36, 44, 31, and 30, a relative

increase in peaks at m/e 15, 29, 93, 94, 95, and 96, and several new minor peaks at 80, 82, 109, and 111. The peak at m/e 36 is due to HCl , while the remaining major peaks at m/e 30 (CH_2O^+) and m/e 44 ($\text{CH}_2\text{OCH}_2^+$ or CH_3OCH^+) are assigned to both reaction primary products, BrCHOCH_3 and $\text{BrCH}_2\text{OCH}_2$ radicals. Their relative mass peak intensities are shown in Table 1b. The peaks at m/e 31 (CH_3O^+) and 15 (CH_3^+) are uniquely assigned to BrCHOCH_3 radical, and the peaks at m/e 109, 111 (BrCH_2O^+) and 93, 95 (BrCH_2^+) to $\text{BrCH}_2\text{OCH}_2$ radical. This analysis indicates the presence of both reaction channels but cannot provide their relative contribution. The minor peaks at m/e 80 and 82 are attributed to HBr molecules which are probably formed via secondary processes. However, their intensities correspond to negligible concentrations that do not affect the kinetic scheme. In addition, no mass spectroscopic indication of the formation of BrCl or $\text{ClCH}_2\text{OCH}_3$ was found, which complies with the exclusion of the last two reactions from the kinetic scheme.

Furthermore, the addition of substantial amounts of HCl ($[\text{HCl}] > 100[\text{BMME}]$) to the reaction mixture did not produce any change to the mass spectral intensities of the reaction products, which indicates the absence of the reverse reaction. Moreover, this reverse reaction is endothermic and is expected to have a room temperature rate ca. $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 2 orders of magnitude slower than the forward reaction (by analogy to the rate of OH radical with HCl).⁹

The most probable secondary reactions are



Application of the steady-state approximation to the reaction system yields the following expressions:

$$\Delta[\text{Cl}]k_{\text{esc,Cl}} = k_1[\text{Cl}][\text{BMME}] + k_2[\text{Cl}][\text{R}] \quad (1)$$

$$\Delta[\text{BMME}]k_{\text{esc,BMME}} = k_1[\text{Cl}][\text{BMME}] \quad (2)$$

$$k_1[\text{Cl}][\text{BMME}] = k_{\text{esc,R}}[\text{R}] + k_2[\text{Cl}][\text{R}] \quad (3)$$

where $[\text{R}]$ denotes the total concentration of BrCHOCH_3 and $\text{BrCH}_2\text{OCH}_2$ radicals, $\Delta[\text{Cl}] = [\text{Cl}]_0 - [\text{Cl}]_t$, $\Delta[\text{BMME}] = [\text{BMME}]_0 - [\text{BMME}]_t$, and $k_{\text{esc,Cl}}$, $k_{\text{esc,BMME}}$, and $k_{\text{esc,R}}$ are the escape constants.

Combination of (2) and (3) gives

$$\Delta[\text{BMME}]k_{\text{esc,BMME}}Q_{30}V_{\text{cell}}k_{\text{esc,R}}/I_{30} = k_{\text{esc,R}} + k_2[\text{Cl}]$$

where I_{30} the signal intensity and Q_{30} is a constant signal calibration factor for both radicals.

Plots of the ratio $\Delta[\text{BMME}]k_{\text{esc,BMME}}/I_{30}$ vs $[\text{Cl}]$ do not display any systematic trend and the points are scattered around a constant value, which implies the absence of the above secondary reaction. Moreover, there was no mass spectroscopic evidence of the secondary reaction products ClCHOCH_3 and $\text{CH}_2\text{OCH}_2\text{Cl}$, which should yield peaks at m/e 50 and 52 (CH_3Cl^+) and m/e 49, 51 (CH_2Cl^+), respectively.

Experiments were performed at four different temperatures 273, 303, 333, and 363 K, and typical experimental data of all relative parameters are presented in Table 2.

TABLE 2: Typical Steady State Concentrations of Carrier Gas He, Final Concentrations of Cl and BMME, Intensity Ratios $R_1 = I_{\text{Cl}_0}/I_{\text{Cl}_r}$, $R_2 = I_{\text{BMME}_0}/I_{\text{BMME}_r}$, Concentration Difference $\Delta[\text{BMME}] = ([\text{BMME}]_0 - [\text{BMME}]_r)$, and Signals Intensities of Radicals BrCHOCH₃/BrCH₂OCH₂ for the Four Temperatures Studied^a

| [He] ($\times 10^{13}$) | R_1 | [Cl] _r ($\times 10^{11}$) | R_2 | [BMME] _r ($\times 10^{11}$) | $\Delta[\text{BMME}]$ ($\times 10^{11}$) | I_{30} |
|------------------------------|-------|---|-------|---|---|----------|
| <i>T</i> = 273 K | | | | | | |
| 2.87 | 1.52 | 8.24 | 3.66 | 3.16 | 8.41 | 0.041 |
| 3.44 | 2.19 | 6.92 | 2.70 | 9.46 | 16.10 | 0.092 |
| 4.21 | 2.91 | 6.71 | 2.47 | 16.94 | 24.99 | 0.097 |
| 4.98 | 4.19 | 4.03 | 1.74 | 33.81 | 24.90 | 0.102 |
| 6.35 | 5.66 | 3.17 | 1.47 | 61.52 | 28.85 | 0.107 |
| <i>T</i> = 303 K | | | | | | |
| 2.58 | 2.07 | 3.84 | 1.83 | 9.62 | 8.00 | 0.011 |
| 2.72 | 2.24 | 4.86 | 1.97 | 12.13 | 11.82 | 0.059 |
| 2.95 | 3.14 | 3.88 | 1.78 | 20.72 | 16.20 | 0.094 |
| 3.64 | 4.83 | 3.65 | 1.61 | 44.68 | 27.29 | 0.102 |
| 3.85 | 5.16 | 3.67 | 1.56 | 53.56 | 29.83 | 0.126 |
| <i>T</i> = 333 K | | | | | | |
| 2.42 | 1.58 | 5.84 | 2.54 | 4.37 | 6.72 | 0.029 |
| 2.57 | 1.90 | 5.32 | 1.93 | 10.12 | 9.46 | 0.071 |
| 2.72 | 2.20 | 4.83 | 1.78 | 14.81 | 11.53 | 0.084 |
| 2.89 | 2.63 | 5.37 | 1.78 | 22.21 | 17.41 | 0.096 |
| 3.35 | 5.58 | 2.22 | 1.47 | 43.29 | 20.13 | 0.099 |
| <i>T</i> = 363 K | | | | | | |
| 2.56 | 1.43 | 7.99 | 2.74 | 4.20 | 7.30 | 0.042 |
| 3.08 | 1.55 | 10.76 | 2.42 | 8.83 | 12.59 | 0.077 |
| 3.67 | 1.98 | 7.01 | 1.74 | 20.05 | 14.73 | 0.093 |
| 4.72 | 2.57 | 7.11 | 1.70 | 33.95 | 23.82 | 0.117 |
| 5.52 | 3.12 | 6.92 | 1.68 | 45.87 | 31.36 | 0.153 |

^a Steady-state concentrations are in molecules cm⁻³. Signal intensities are in arbitrary units normalized relative to the mass spectrometer and lock-in amplifier sensitivities used.

Application of the steady-state approximation to the chlorine atom concentrations leads to the expression

$$[\text{Cl}]_0 k_{\text{esc,Cl}} = [\text{Cl}]_r k_{\text{esc,Cl}} + k_1 [\text{Cl}]_r [\text{BMME}]_r$$

which rearranges to

$$([\text{Cl}]_0/[\text{Cl}]_r - 1) k_{\text{esc,Cl}} = k_1 [\text{BMME}]_r$$

The rate constant was determined from the above equation by substituting the concentration ratio with the mass spectrometric intensity ratio and using the final expression

$$(R_1 - 1) k_{\text{esc,Cl}} = k_1 [\text{BMME}]_r$$

where R_1 is $I_{\text{Cl}_0}/I_{\text{Cl}_r}$ (subscripts o and r specify absence and presence of BMME, respectively). A typical plot of the above equation at $T = 303$ K is presented in Figure 1. The linear least-squares fits to the data yield the rate constant k_1 with a precision ca. 20% (2σ). Intercepts of all plots are nearly zero which supports the validity of the proposed kinetic scheme.

The rate constants obtained at various temperatures are listed in Table 3. An Arrhenius plot of all experimental data is presented in Figure 2. Within experimental error the rate constant k_1 is independent of temperature and takes the average value $k_1 = (2.61 \pm 0.46) (2\sigma) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Thus the reaction proceeds with a zero activation energy.

Discussion

To our knowledge, there has been only one previous study on the reaction of chlorine atoms with brominated ethers. Using a relative rate technique, the rate of Cl atoms with 2-bromoethyl methyl ether, BrCH₂CH₂OCH₃, was found to be $k_{300} = (16.3 \pm 5.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁰

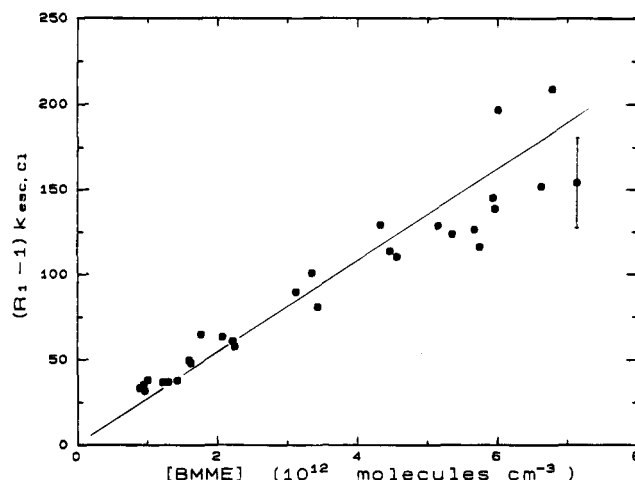


Figure 1. Plot of $(R_1 - 1) k_{\text{esc,Cl}}$ vs $[\text{BMME}]$ at 303 K. Error bar reflects the propagated errors (2σ).

TABLE 3: Measured Values of Rate Constant k_1 at Various Temperatures

| <i>T</i> (K) | $k_1 \pm 1\sigma$ $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | [BMME] _r range $10^{12} \text{ molecules cm}^{-3}$ | points |
|-----------------|---|--|--------|
| 273 | 2.90 ± 0.45 | 0.6 – 4.5 | 20 |
| | 2.67 ± 0.65 | 0.5 – 5.5 | 11 |
| | 2.37 ± 0.18 | 1.0 – 6.7 | 26 |
| 303 | 2.78 ± 0.21 | 0.2 – 9.0 | 28 |
| | 2.80 ± 0.24 | 0.5 – 4.0 | 28 |
| | 2.53 ± 0.17 | 0.2 – 7.7 | 29 |
| 333 | 2.60 ± 0.52 | 0.5 – 7.0 | 34 |
| | 2.58 ± 0.18 | 0.2 – 6.3 | 26 |
| | 2.98 ± 0.13 | 0.5 – 5.0 | 23 |
| 363 | 2.40 ± 0.56 | 0.3 – 9.0 | 27 |
| | 2.50 ± 0.22 | 0.2 – 4.5 | 17 |
| | 2.22 ± 0.52 | 0.7 – 4.0 | 16 |

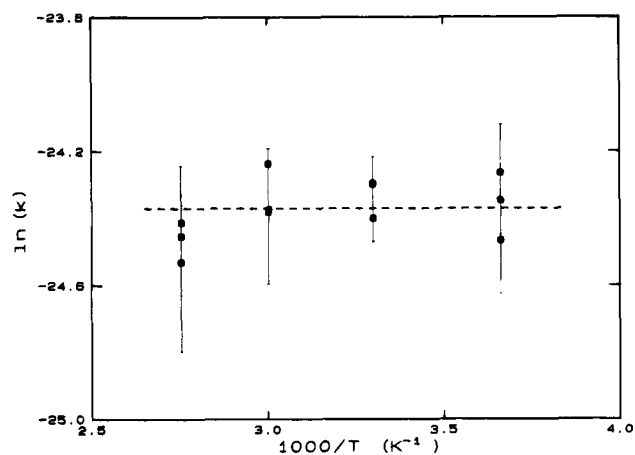


Figure 2. Arrhenius plot of $\ln k_1$ vs $1000/T$. Error bars reflect the total propagated errors (2σ) to the mean value which is indicated by the broken line.

The only known rates of chlorine atoms with brominated alkanes are those with CH₃Br, CH₂Br₂, and CH₂ClBr, and their room-temperature rate constants are rather low in the range of $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as listed in Table 4. The much faster rate of BMME implies that α -hydrogens are activated (weaker C–H bonds) via inductive effects due to the presence of oxygen, as in the case of fluoroethers.¹²

There have been a number of kinetic measurements for the reactions of chlorine atoms with unsubstituted ethers, and their data are presented in Table 4. The rate with dimethyl ether is ca. $1.78 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is the average value of five separate investigations^{13–17} and is an order of magnitude faster than that of BMME.

TABLE 4: Relevant Room Temperature Rate Constants of Cl Atoms with Ethers and Bromine- or/and Chlorine-Containing Alkanes

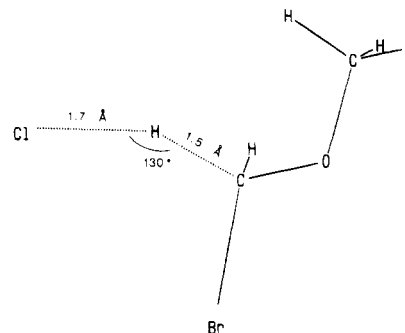
| reactant | rate constant (cm ³ molecule ⁻¹ s ⁻¹) | ref |
|---|--|-----|
| CH ₃ OCH ₃ | 1.76 × 10 ⁻¹⁰ | 13 |
| | 1.70 × 10 ⁻¹⁰ | 14 |
| | 2.05 × 10 ⁻¹⁰ | 15 |
| | 1.51 × 10 ⁻¹⁰ | 16 |
| | 1.90 × 10 ⁻¹⁰ | 17 |
| CH ₃ CH ₂ OCH ₂ CH ₃ | 3.56 × 10 ⁻¹⁰ | 15 |
| | 2.54 × 10 ⁻¹⁰ | 16 |
| | 2.58 × 10 ⁻¹⁰ | 10 |
| | 1.66 × 10 ⁻¹⁰ | 15 |
| CH ₃ OC(CH ₃) ₃ | 3.62 × 10 ⁻¹⁰ | 16 |
| (CH ₃ CH ₂ CH ₂) ₂ O | 1.63 × 10 ⁻¹⁰ | 10 |
| (CH ₃) ₂ CHOCH(CH ₃) ₂ | 1.51 × 10 ⁻¹⁰ | 16 |
| (CH ₃ CH ₂ CH ₂ CH ₂) ₂ O | 4.41 × 10 ⁻¹⁰ | 16 |
| (CH ₃ CH ₂ CH ₂ CH ₂ CH ₂) ₂ O | 4.97 × 10 ⁻¹⁰ | 16 |
| ClCH ₂ CH ₂ OCH ₃ | 1.44 × 10 ⁻¹⁰ | 10 |
| Cl ₂ CHCH ₂ OCH ₃ | 4.4 × 10 ⁻¹¹ | 10 |
| BrCH ₂ CH ₂ OCH ₃ | 1.63 × 10 ⁻¹⁰ | 10 |
| ClCH ₂ CH ₂ OCH ₂ CF ₃ | 3.0 × 10 ⁻¹² | 10 |
| CH ₃ Br | 5.53 × 10 ⁻¹³ | 11 |
| CH ₂ Br ₂ | 5.30 × 10 ⁻¹³ | 11 |
| CH ₂ BrCl | 4.18 × 10 ⁻¹³ | 11 |

TABLE 5: Estimation of the ΔS[‡](298) for the Reaction BrCH₂OCH₃ + Cl^a

| degrees of freedom | ΔS [‡] (diff), cal mol ⁻¹ K ⁻¹ | |
|---|--|--------------|
| | pathway A | pathway B |
| translational ΔS _{tr} = (3/2)R ln(M [‡] /M) | 0.742 | |
| rotational ΔS _{rot} = (1/2)R ln((I _A I _B I _C) [‡] /(I _A I _B I _C)) | 3.75 | 3.82 |
| electronic ΔS _{el} = R ln(2S+1) | 1.38 | |
| symmetry ΔS _σ = R ln(σ/σ [‡]) = R ln(2) | 1.38 | |
| internal rotations | | |
| about the C...H bond (new) | 8.55 | 8.65 |
| about the O-CH ₃ bond, ΔS _f = (1/2)R ln(I _f [‡] /I _f) | 0.017 | 5.42 |
| about the O-CH ₂ Br bond | 0.038 | 1.89 |
| ν(H...Cl) (new 2100 cm ⁻¹) | 0.001 | 0.001 |
| δ(C...H...Cl) (new 700 cm ⁻¹) | 0.32 | |
| ν(C...H) (2900 → 2100 cm ⁻¹) | r.c. | |
| δ(H-C...H) (1450 → 1000 cm ⁻¹) | 0.084 | 0.084 × 2 |
| δ(Br-C...H) (900 → 600 cm ⁻¹) | 0.319 | |
| δ(O-C...H) (1100 → 700 cm ⁻¹) | 0.253 | |
| ν(C-O) (1100 → 900 cm ⁻¹) | 0.08 | |
| | 16.91 | 24.10 |
| ΔS [‡] (298) = 16.91 - 39.5 = -22.59 cal mol ⁻¹ K ⁻¹ (pathway A) | | |
| ΔS [‡] (298) = 24.10 - 39.5 = -15.40 cal mol ⁻¹ K ⁻¹ (pathway B) | | |
| A ₃₀₀ (cm ³ molecule ⁻¹ s ⁻¹) = 10 ^{-5.72(T/298)²} exp(ΔS [‡] /R) = 2.31 × 10 ⁻¹¹ (pathway A) | | |
| A ₃₀₀ (cm ³ molecule ⁻¹ s ⁻¹) = 10 ^{-5.72(T/298)²} exp(ΔS [‡] /R) = 8.58 × 10 ⁻¹⁰ (pathway B) | | |

^a Pathway A corresponds to BrCH₂-approach and pathway B to CH₃-approach.

The thermochemical version of conventional TST⁸ has been applied in the reaction of BMME with Cl for each of the possible two hydrogen abstraction pathways (A, BrCH₂-attack, and B, CH₃-attack), and the detailed entropy calculations are presented in Table 5. The geometry of BrCH₂OCH₃ was taken as the corresponding of CH₃OCH₃¹⁸ with the H--CHBr bonds shortened by 0.03 Å and the C--Br bond taken as that of CH₃Br.¹⁸ The main features of the adopted transition-state configuration are common to both models. The critical C...H and H...Cl bonds were extended by 0.4 Å relative to the corresponding normal bond lengths in ether and HCl molecules. The incoming chlorine atom was placed in an arrangement that permits the

**Figure 3.** Transition state geometry for pathway A.

maximization of the reduced moment of inertia on rotation around the C--H axis, with minimal van der Waals contacts of Cl with neighboring atoms, and the C--H--Cl angle was ca. 130°. The transition state geometry for pathway A is presented in Figure 3. The vibrational frequency values were decreased ca. 70% from their values in the stable molecules, implying a loosening of the corresponding force constants by one-half of their initial values.

The entropy calculations indicate that the preexponential Arrhenius factors for the two pathways differ by almost an order of magnitude. The A factor value for the methyl group attack was much higher than the experimental value, even if transition state parameters were pushed to their extremes. In contrast, the A factor value for the bromomethyl group attack was in excellent agreement with the experimental results, which suggests that this is the primary reaction pathway. Hence, the regioselectivity of the reaction depends mainly on the C--H bond strength, since the H--CHBrOCH₃ bond is expected to be weaker than the H--CH₂OCH₂Br bond, as in the case of H--CH₂Br (102.0 ± 2 kcal/mol) and H--CH₃ (105.1 ± 0.2 kcal/mol).¹⁹

The above suggestion is further strengthened by semiempirical calculations of the heats of formation of both reaction products BrCHOCH₃ and BrCH₂OCH₂ radicals. These calculations employ the Austin Model 1 (AM1) Hamiltonian, and including configuration interaction (CI) terms,^{20,21} and the values obtained were -15.1 and -10.0 kcal/mol, respectively. Similarly, the AM1 computed heat of formation of BMME was found to be -42.6 kcal/mol, which is 4 kcal/mol lower than the value obtained by additivity rules.⁸ Furthermore, the enthalpies of H--CHBrOCH₃ and H--CH₂OCH₂Br bonds were also calculated by employing the above method and the values obtained were 79.6 and 84.7 kcal/mol, respectively, with an accuracy ca ±10 kcal/mol.²⁰ However, considering that the strength of the H--CH₂OCH₃ bond is 93 ± 1 kcal/mol,¹³ the strengths of H--CHBrOCH₃ and H--CH₂OCH₂Br bonds are expected to be ca. 90 ± 2 and 92 ± 2 kcal/mol, respectively, which are in the range of calculated values. These semiempirical calculations are not sufficiently accurate but provide relative estimates of several parameters.

Considering the rate of the reaction of BrCH₂CH₂OCH₃ with Cl,¹⁰ this has been found to be about 6 times faster than that of BMME. This may be explained by the fact that methylene hydrogens are more easily abstracted, due to the activating effects of the vicinal methoxy and bromomethyl groups. Thus, the preexponential factor is expected to be high, due mainly to the large overall and internal moments of inertia for the activated complex (heavy Br and Cl atoms are far from each other). In the case of BMME, the thermochemically favorable attack of Cl atom on the bromomethyl group results to lower rotational contributions to the transition state entropy, translated into a small preexponential factor. These differences are directly reflected on the corresponding rates, since in all cases the activation barriers are expected to be negligible.

The reaction of OH with BMME is expected to have a rate constant of about $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is an order of magnitude slower than the relative reaction with chlorine atoms, as in the case of CH₄ and CH₃Cl.⁷ This rate is moderately fast, which indicates that tropospheric degradation of BMME is rather efficient compared with that of hydrochlorofluorocarbons²² and fluorinated ethers.¹² Hence, partially brominated ethers are a better choice than hydrochlorofluorocarbons considering their estimated tropospheric sink rates.

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