Temperature Dependence of the Rate Coefficients for the Reactions of Atomic Bromine with Toluene, Tetrahydrofuran, and Tetrahydropyran

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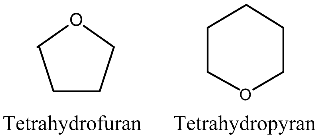
The rate coefficients for the reactions of atomic bromine with toluene, tetrahydrofuran, and tetrahydropyran were measured from approximately 295 to 362 K using the relative rate method. Iso-octane was used as the reference compound for the reaction with toluene, and iso-octane and toluene were used as the reference compounds for the reaction with tetrahydrofuran; tetrahydrofuran was used as the reference compound for the reaction with tetrahydropyran. The rate coefficients were found to be unaffected by changes in pressure and oxygen concentration. The rate coefficient ratios were converted to absolute values using the absolute rate coefficient for the reaction of Br with the reference compound. The absolute rate coefficients, in the units cm^3 $molecule^{-1}$ s^{-1}, for the reaction of Br with toluene are given by $k(T) = (3.7 \pm 1.7) \times 10^{-12} \exp(-(1.63 \pm 0.15) \times 10^3/T)$, for the reaction of Br with tetrahydrofuran by $k(T) = (3.7 \pm 2.7) \times 10^{-10} \exp(-(2.20 \pm 0.22) \times 10^3/T)$, and for the reaction of Br with tetrahydropyran by $k(T) = (3.6 \pm 1.8) \times 10^{-10} \exp(-(2.35 \pm 0.16) \times 10^3/T)$. The uncertainties represent one standard deviation. The Arrhenius parameters for these reactions are compared with results in the literature for dimethyl ether, diethyl ether, and a series of saturated hydrocarbons, and the effects of structural variation on these parameters are identified.

Introduction

Reactions of atomic bromine with organic compounds are potentially important in understanding the chemistry of our atmosphere,[1,2] particularly in the marine boundary layer where both natural and anthropogenic sources of bromine are significant. Rate coefficients at ambient temperature for a number of reactions of atomic bromine with organic substrates have been correlated with the rate coefficients for the reactions of OH, NO_3, and $O(^3P)$ with the same organic compounds.[3] However, such a correlation at a fixed temperature has limited value because it provides no information about the temperature dependence of these rate coefficients. This makes it impossible to extrapolate the rate coefficients reliably to higher and lower temperature regimes that might be of more relevance to understanding atmospheric phenomena. It also provides no information about the relative roles of entropy of activation and enthalpy of activation in controlling the chemical reactivity.

We recently began a program to systematically examine the separate roles of entropy and enthalpy of activation in regulating the reactivity of organic compounds with atomic bromine.[4,5] We chose to initially examine the reactions of ethers not only because these compounds are in common use industrially as solvents and refrigerants but also because less is known about their reactions with atomic bromine than is the case for hydrocarbons. The most striking feature of that work was the substantial difference in reactivity of dimethyl ether and diethyl ether. While dimethyl ether was slightly less reactive than the reference compound, iso-octane, the rate coefficient for diethyl ether was more than an order of magnitude larger than that for iso-octane. While the entropies of activation for the reactions of dimethyl ether and diethyl ether were virtually identical, even after making allowance for the statistical difference resulting from the different number of hydrogen atoms available for abstraction in these compounds, the enthalpies of activation for their reactions differed by approximately 10 kJ mol^{-1}. Comparison with published calculations of the transition state properties for the reaction of atomic bromine with methanol[6] led us to conclude[5] that two reaction channels exist. One channel leads to the formation of a relatively stable complex between the bromine atom and the oxygen atom of the ether and has a much larger activation energy for the production of HBr than for decomposition back to the reactants. The other channel bypasses this complex, forming HBr directly with a smaller activation energy than the first channel. Although our measurements[5] on dimethyl ether and diethyl ether did not provide clear information about the different reactivities of the CH_3 and CH_2 hydrogen atoms in diethyl ether, we concluded that the increased reactivity of diethyl ether was probably attributable to increased ease of abstraction of the CH_3 hydrogen atoms compared to those immediately adjacent to the ether oxygen.



In this manuscript we present the results of experiments on the determination of the temperature dependence of the rate coefficients for the reactions of atomic bromine with tetrahydrofuran and tetrahydropyran. These compounds were selected because, like dimethyl ether and diethyl ether, they contain a single ether oxygen and differ only in the relative distances of the CH_2 hydrogens from the oxygen atom, thereby systematically varying the probability that the attacking bromine atom will complex significantly with the oxygen atom. However,

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unlike the case of diethyl ether, the cyclic structure of these ethers removes the effects, present in diethyl ether, resulting from the rotation of the methyl groups into configurations in which the abstraction of their hydrogen atoms by bromine would be inhibited by the formation of an adduct between the Br and the ether oxygen. If the attacking bromine atom were to participate in complex formation with the ether oxygen in the transition state for the reaction channel being observed, this would be anticipated to significantly decrease the entropy of activation for the reaction. This would be reflected in a lowering of the Arrhenius pre-exponential factor for the reaction and probably of the activation energy for the reaction as well. The choice of five- and six-membered rings also ensures that ring strain will be significantly less important than would be the case with three- or four-membered ring systems. The strain energies for these compounds have been reported to be 25 kJ mol^{-1} for tetrahydrofuran and 2 kJ mol^{-1} for tetrahydropyran.[7] Consequently, the selection of tetrahydrofuran and tetrahydropyran is expected to provide a selective test of the importance of complex formation between the bromine atom and the ether oxygen in the transition state.

Experimental Section

The apparatus and experimental methods have been described in earlier work[4,5] and will be described only briefly here. The cylindrical Pyrex reaction vessel was surrounded by four fluorescent lamps and had a volume of approximately 70 L. It was enclosed in an insulated jacket through which hot or cold air could be circulated to maintain a temperature either above or below ambient temperature. The useful output of the lamps was from approximately 350 to 650 nm. Within this range, no photochemical decomposition of the organic reagents was observed, but photolysis of Br_2 provided a satisfactory source of atomic bromine. The temperature of the reactor was maintained at a constant value by a thermostat which controlled the temperature of the circulating air. The temperature inside the reactor was measured by three iron−constantan thermocouples positioned at different locations inside the reaction vessel along its long axis. Pressures were measured with a 10 Torr Baratron and a 1000 Torr piezoelectric pressure gauge. Reaction mixtures were prepared from dilute mixtures in argon of Br_2 and the organic reagents which were stored in separate Pyrex bulbs. The gas handling system was constructed of Pyrex, was mercury free, and used Teflon stopcocks.

Photolysis of Br_2 has several advantages over other Br precursors in relative rate experiments. Unlike other Br precursors, it produces only one reactive species, which eliminates the concern that a companion free radical might consume one or both organic reactants at a rate that would be competitive with the reaction of the organic reactant with Br. Br_2 also undergoes photolysis at wavelengths at which photolysis of an organic reactant is often negligible. Many potential photochemical Br precursors require shorter wavelengths than Br_2 and introduce the possibility that the organic reactants will be consumed significantly by photolysis as well as by a reaction with Br. In addition, Br_2 is an effective scavenger of free radicals. In all of our experiments, the concentration of Br_2 was sufficiently large that a significant amount was still present at the end of a series of experiments. This ensures that free radicals produced in the reaction of Br with the organic reactants will be scavenged effectively by Br_2. Since free radicals react with Br_2 to produce Br as the only free radical product, no new reactive free radical species are introduced by the use of Br_2 as a scavenger.

Typical reaction mixtures contained roughly 3×10^{16} molecules cm^{-3} of Br_2 with 10−100 times smaller concentrations of the organic reagents. Photolysis of Br_2 produced Br at substantially smaller concentrations than Br_2, so the concentration of Br was anticipated to remain essentially constant over the range of reaction times used in a given experiment. Under such conditions, the loss of an organic reactant is effectively first order with a pseudo first-order rate coefficient given by $k[\text{Br}]$ in which k is the second-order rate coefficient for the reaction. Good first-order plots were obtained for the loss of the organic reactants, verifying that the concentration of Br was indeed effectively constant and allowing the concentration of atomic bromine to be estimated once the numerical value of the second-order rate coefficient had been determined. Concentrations of atomic bromine estimated in this way were of the order of 10^{11}−10^{12} molecules cm^{-3}, roughly two to three orders of magnitude smaller than the concentrations of the organic reagents. These concentrations are similar to those found in our earlier work[4,5] from which we conclude that the light flux absorbed by the bromine was also similar to that in our earlier experiments. The concentrations of the unreacted organic reagents in the reaction chamber after varying exposure times were determined by direct injection of a sample of known pressure from a sample loop into a gas chromatograph equipped with a flame ionization detector. The chromatographic separation was achieved with an 8 ft. × 1/8 in. column packed with SP1000.

In preparation for a typical experiment, small, known pressures of the dilute mixtures of Br_2, the test reactant, and the reference reactant were introduced to the reaction vessel, and the pressure was brought up to the desired total pressure, usually about 1 atm, by adding measured pressures of either argon only or a mixture of argon and oxygen. After equilibrating for at least half an hour, a known pressure of the reaction mixture was introduced to a sample loop from the chamber, and a gas chromatogram of the initial reaction mixture was recorded to indicate the initial concentrations of the test and reference reactants. After exposure to radiation from the fluorescent lamps for a known period of time, a second gas chromatogram was obtained to determine the extent of consumption of each reactant. In a similar manner, subsequent chromatographic analyses were done until the desired extent of the reaction had been attained. Comparison of the peak areas of each organic reactant initially and after each successive irradiation, after normalizing to account for a small pressure drop in the sample loop for each successive experiment, allowed the calculation of the ratio of rate coefficients of the test and reference reactant. The amount of reaction mixture removed for each analysis was sufficiently small so that several successive irradiations could be done with a given reaction mixture without significantly changing the total pressure in the reaction vessel. The extent of consumption of the organic reactants was kept as small as practical to minimize any effects of secondary reactions.

In the kinetic analysis, it is assumed that the loss of the test and reference reactants occurs only by the reactions

$$\text{Br} + \text{RH}_x \rightarrow \text{HBr} + \text{R}_x^{\bullet} \qquad (1)$$

$$\text{Br} + \text{RH}_{\text{ref}} \rightarrow \text{HBr} + \text{R}_{\text{ref}}^{\bullet} \qquad (2)$$

Here, RH_x is the test reactant, and RH_{ref} is the reference reactant. The rate coefficient ratio is then given by

$$\ln\left\{\frac{[\mathrm{RH}_x]_{t_0}}{[\mathrm{RH}_x]_t}\right\} = \frac{k_1}{k_2}\ln\left\{\frac{[\mathrm{RH}_{\mathrm{ref}}]_{t_0}}{[\mathrm{RH}_{\mathrm{ref}}]_t}\right\} \qquad \text{(I)}$$

A plot of $\ln\{[\mathrm{RH}_x]_{t_0}/[\mathrm{RH}_x]_t\}$ against $\ln\{[\mathrm{RH}_{\mathrm{ref}}]_{t_0}/[\mathrm{RH}_{\mathrm{ref}}]_t\}$ should then be linear with the slope equal to k_1/k_2 and with a zero intercept. The peak areas in the gas chromatograms are proportional to the concentrations of the analytes, so the peak areas can be substituted for the indicated concentrations in eq I after normalization to the sample loop pressure used in the analysis of the reaction mixture before photolysis. The absolute rate coefficient for the test reaction, k_1, can then be calculated from the known value of the absolute rate coefficient for the reference reaction at the temperature of the experiment. These plots were found to be linear, giving confidence that the assumptions implicit in this analysis were correct and that secondary reactions did not influence the values obtained for the rate coefficients. Typical plots are found in Figure 1. Although eq I suggests that the intercepts of these plots should be zero, the plots were not forced through the origin, since a small systematic error in determining the initial concentration of either reactant would lead to a positive or negative intercept. Such an error would not affect the slope, but forcing the plots to pass through the origin would bias the slope. However, since 0,0 is a valid experimental data point, this value was included when calculating the slope and intercept. In all cases, the intercepts of these plots were less than the standard error of fitting the data.

Some discussion of the uncertainties implicit in this measurement technique is appropriate at this point. One advantage of the relative rate method is that the numerical values of the rate coefficient ratios depend principally on the precision of the chromatographic analyses. The pressure measurements that are used to compensate for small changes in pressure in the sample loop contribute an uncertainty of less than 0.2%, which is substantially less than the uncertainty contributed by the repeatability of measuring the peak areas in the chromatograms. The uncertainties in the chromatographic analyses include both instrumental uncertainties and “human error” from such activities as repeatability of sample injection. It is difficult to separate these contributions, and in any event, it is the composite uncertainty that determines the uncertainty in the rate constant ratios. Even with care and a favorable extent of reaction, it is difficult to obtain an uncertainty of less than ±1% in $\ln\{[\mathrm{RH}]_0/[\mathrm{RH}]_t\}$. If the reference and “test” reactant contribute equally to the slope, this leads to an uncertainty of approximately ±2% in the slopes of the relative rate plots. This situation is similar to that obtained in the measurement of the rate coefficient of the reaction of Br with tetrahydropyran using tetrahydrofuran as the reference reactant with the results indicated in Table 3. If the slope is fairly large, the less reactive reactant will dominate in determining the uncertainty because its extent of consumption will be smaller, leading to a comparatively large relative uncertainty in the value of $\ln\{[\mathrm{RH}]_0/[\mathrm{RH}]_t\}$. Table 1 indicates that the largest slopes obtained in measuring the rate coefficient for the reaction of Br with toluene using isobutane as the reference reactant were approaching 10. The uncertainty in the slope now increases to approximately ±10% under favorable conditions and can be larger than this. The largest slopes were obtained when measuring the rate coefficient for the reaction of Br with tetrahydrofuran using iso-octane as the reference compound. In this case, Table 2 indicates that some of the slopes were as large as 40. The uncertainty in the slope expected in these circumstances would be larger than ±10%. Clearly, the best results are expected if the reference reactant has a rate coefficient that is similar to that of the reaction whose rate coefficient is being measured. Examination of the slopes in Tables 1−3 indicates that the standard deviations in the slopes are typically of the magnitudes indicated above, although fortuitous compensation of uncertainties is also observed.

Experiments such as ours are conventionally done in the presence of a significant concentration of oxygen. This is done both to simulate the concentration of oxygen in the atmosphere and on the assumption that oxygen will serve to scavenge free radicals generated in the initiation step of the reaction, hopefully avoiding interference from secondary reactions. However, reactions of O_2 with free radicals generated by the reaction of interest would be expected to generate new radical species, and an analysis of the likely result of this intervention by O_2 was discussed in a previous publication.[5] Briefly, the concern is that the reaction of O_2 with an organic radical would be expected to generate HO_2 radicals which would then react rapidly with Br forming OH. Since OH tends to be much more reactive toward organic reagents than Br, the presence of OH would then increase the rate of consumption of the organic reactants, leading to upward or downward curvature of the kinetic plots depending on whether the test or reference reactant is more reactive toward OH. Such curvature was, in fact, observed at large extents of reaction in one of our earlier publications,[4] and the extent of reaction was always kept sufficiently small that no curvature was observed. The observation that the numerical values of the rate coefficients obtained with varying concentrations of O_2 did not show a dependence on the concentration of oxygen gives further confidence that interference from secondary reactions of OH radicals has been largely avoided. The particularly large rate coefficient for the reaction of OH with Br_2[8] may have resulted in efficient scavenging of OH by the large concentrations of Br_2 used in our experiments. The effect of O_2 on the reaction of Cl with butanone has been very completely discussed in a recent publication,[9] and this should be representative of the effects of O_2 on the reactions of Cl with other organic compounds. Many of the reactions introduced in the reactions of Br in the presence of O_2 are expected to be similar to those in reactions of Cl with organic compounds. As long as the species formed in the new reactions in the presence of O_2 do not lead to additional loss routes for the organic reactants, the presence of O_2 should not affect the values obtained for the rate constants of the bromine atom reactions.

The organic reactants used in this study were toluene (ACP, >99.5%), tetrahydrofuran (Aldrich, anhydrous, ≥99.9%, inhibitor-free), tetrahydropyran (Aldrich, anhydrous, 99%), isobutane (Aldrich, 99.995%), and iso-octane (2,2,4-trimethylpentane) (Aldrich, 99+%). These were thoroughly degassed followed by distillation of the desired amount into its storage bulb. Bromine (ACP, 99.5%) was purified by freeze−pump−thaw cycles followed by distillation of the desired amount into its storage bulb. The other gases, He (Praxair, 99.9995%), Ar (Praxair, 99.9995%), and O_2 (Praxair, 99.9995%), were used without further purification.

As in our previous work,[4,5] the organic reactants were tested for possible interference due to photolysis and a dark reaction with Br_2. Each organic reactant was used to prepare a reaction mixture with a composition similar to that to be used in the experiments except that bromine was not added. Irradiation for periods of as much as four hours produced no measurable change in the concentration of the organic reactant. We conclude that under our conditions photolysis of the organic reactants

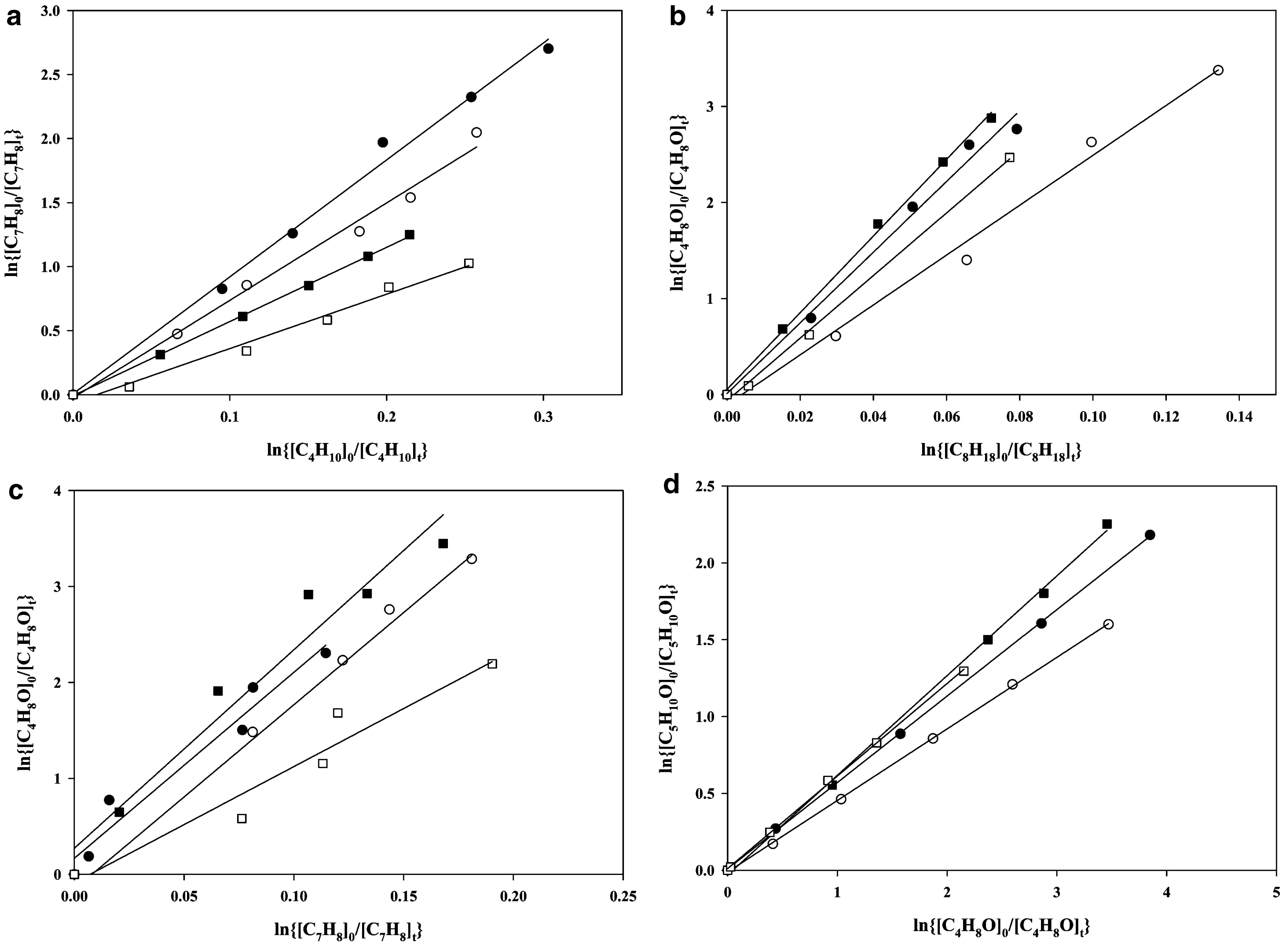

Figure 1. (a) Typical relative rate plots for the reaction of Br with toluene measured relative to the reaction of Br with isobutane. (●) $[Br_2] = 1.96 \times 10^{16}$ molecules cm^{-3}, $[C_7H_8] = 4.92 \times 10^{15}$ molecules cm^{-3}, $[C_4H_{10}] = 3.14 \times 10^{15}$ molecules cm^{-3}, $P(O_2) = 0$ Torr, total pressure = 760 Torr, temperature = 303.1 K; (○) $[Br_2] = 1.84 \times 10^{16}$ molecules cm^{-3}, $[C_7H_8] = 4.10 \times 10^{15}$ molecules cm^{-3}, $[C_4H_{10}] = 3.77 \times 10^{15}$ molecules cm^{-3}, $P(O_2) = 0$ Torr, total pressure = 759 Torr, temperature = 313.7 K; (■) $[Br_2] = 1.66 \times 10^{16}$ molecules cm^{-3}, $[C_7H_8] = 4.31 \times 10^{15}$ molecules cm^{-3}, $[C_4H_{10}] = 3.10 \times 10^{15}$ molecules cm^{-3}, $P(O_2) = 0$ Torr, total pressure = 758 Torr, temperature = 328.7 K; (□) $[Br_2] = 1.38 \times 10^{16}$ molecules cm^{-3}, $[C_7H_8] = 4.61 \times 10^{15}$ molecules cm^{-3}, $[C_4H_{10}] = 2.83 \times 10^{15}$ molecules cm^{-3}, $P(O_2) = 0$ Torr, total pressure = 759 Torr, temperature = 351.0 K. (b) Typical relative rate plots for the reaction of Br with tetrahydrofuran measured relative to the reaction of Br with iso-octane. (●) $[Br_2] = 1.01 \times 10^{16}$ molecules cm^{-3}, $[C_4H_8O] = 4.97 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}] = 1.12 \times 10^{15}$ molecules cm^{-3}, $P(O_2) = 81$ Torr, total pressure = 762 Torr, temperature = 304.7 K; (○) $[Br_2] = 1.02 \times 10^{16}$ molecules cm^{-3}, $[C_4H_8O] = 5.08 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}] = 1.06 \times 10^{15}$ molecules cm^{-3}, $P(O_2) = 76$ Torr, total pressure = 253 Torr, temperature = 303.8 K; (■) $[Br_2] = 9.21 \times 10^{15}$ molecules cm^{-3}, $[C_4H_8O] = 5.34 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}] = 8.02 \times 10^{14}$ molecules cm^{-3}, $P(O_2) = 74$ Torr, total pressure = 780 Torr, temperature = 304.5 K; (□) $[Br_2] = 1.09 \times 10^{16}$ molecules cm^{-3}, $[C_4H_8O] = 3.71 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}] = 6.94 \times 10^{14}$ molecules cm^{-3}, $P(O_2) = 76$ Torr, total pressure = 760 Torr, temperature = 329.0 K. (c) Typical relative rate plots for the reaction of Br with tetrahydrofuran measured relative to the reaction of Br with toluene. (●) $[Br_2] = 1.61 \times 10^{16}$ molecules cm^{-3}, $[C_4H_8O] = 1.24 \times 10^{16}$ molecules cm^{-3}, $[C_7H_8] = 8.19 \times 10^{14}$ molecules cm^{-3}, $P(O_2) = 191$ Torr, total pressure = 760 Torr, temperature = 315.6 K; (○) $[Br_2] = 1.81 \times 10^{16}$ molecules cm^{-3}, $[C_4H_8O] = 1.05 \times 10^{16}$ molecules cm^{-3}, $[C_7H_8] = 8.87 \times 10^{14}$ molecules cm^{-3}, $P(O_2) = 187$ Torr, total pressure = 762 Torr, temperature = 315.5 K; (■) $[Br_2] = 2.00 \times 10^{16}$ molecules cm^{-3}, $[C_4H_8O] = 1.01 \times 10^{16}$ molecules cm^{-3}, $[C_7H_8] = 8.17 \times 10^{14}$ molecules cm^{-3}, $P(O_2) = 216$ Torr, total pressure = 761 Torr, temperature = 328.5 K; (□) $[Br_2] = 1.58 \times 10^{16}$ molecules cm^{-3}, $[C_4H_8O] = 1.50 \times 10^{16}$ molecules cm^{-3}, $[C_7H_8] = 8.07 \times 10^{14}$ molecules cm^{-3}, $P(O_2) = 199$ Torr, total pressure = 759 Torr, temperature = 321.6 K. (d) Typical relative rate plots for the reaction of Br with tetrahydropyran measured relative to the reaction of Br with tetrahydrofuran. (●) $[Br_2] = 1.89 \times 10^{16}$ molecules cm^{-3}, $[C_5H_{10}O] = 3.38 \times 10^{15}$ molecules cm^{-3}, $[C_4H_8O] = 1.10 \times 10^{16}$ molecules cm^{-3}, $P(O_2) = 300$ Torr, total pressure = 766 Torr, temperature = 298.3 K; (○) $[Br_2] = 1.27 \times 10^{16}$ molecules cm^{-3}, $[C_5H_{10}O] = 3.61 \times 10^{15}$ molecules cm^{-3}, $[C_4H_8O] = 8.54 \times 10^{15}$ molecules cm^{-3}, $P(O_2) = 116$ Torr, total pressure = 763 Torr, temperature = 305.4 K; (■) $[Br_2] = 1.58 \times 10^{16}$ molecules cm^{-3}, $[C_5H_{10}O] = 3.20 \times 10^{15}$ molecules cm^{-3}, $[C_4H_8O] = 9.56 \times 10^{15}$ molecules cm^{-3}, $P(O_2) = 55$ Torr, total pressure = 760 Torr, temperature = 329.7 K; (□) $[Br_2] = 2.01 \times 10^{16}$ molecules cm^{-3}, $[C_5H_{10}O] = 3.50 \times 10^{15}$ molecules cm^{-3}, $[C_4H_8O] = 1.28 \times 10^{16}$ molecules cm^{-3}, $P(O_2) = 77$ Torr, total pressure = 765 Torr, temperature = 360.1 K.

does not interfere with their reactions with Br. To test for a dark reaction, each organic reactant was used to prepare a mixture having a composition similar to those used in the experiments. These mixtures were each allowed to stand in the reaction chamber for several hours with the lamps turned off. Again, no appreciable change in the concentration of the organic reactant was observed within a length of time typical of the duration of a set of kinetics experiments on a reaction mixture, leading to the conclusion that no significant reaction occurred between the organic reactants and the Br_2.

Results

We first present the results for the reaction of Br with toluene which we characterized to provide an alternative reference reaction for use in measuring the rate coefficients for the reaction

TABLE 1: Summary of Kinetic Data for the Reaction of Br with Toluene Measured Relative to the Reaction of Br with Isobutane[a]

absolute temperature	$[C_7H_8]_0 \times 10^{-15}$ (molecules cm^{-3})	$[C_4H_{10}]_0 \times 10^{-15}$ (molecules cm^{-3})	$[Br_2]_0 \times 10^{-15}$ (molecules cm^{-3})	$k_{C_7H_8}/k_{C_4H_{10}}$	$k_{C_7H_8} \times 10^{14}$ (cm^3 molecule^{-1} s^{-1})
302.4	5.07	3.55	18.4	9.2 ± 1.1	1.60 ± 0.19
303.1	4.92	3.14	19.6	9.13 ± 0.37	1.62 ± 0.07
309.7	5.45	2.93	15.9	10.1 ± 0.35	2.29 ± 0.08
313.7	4.12	3.77	18.4	7.61 ± 0.39	1.99 ± 0.10
318.3	4.43	3.27	16.2	7.16 ± 0.52	2.19 ± 0.16
322.8	4.66	3.46	16.0	7.22 ± 0.72	2.57 ± 0.26
328.7	4.31	3.10	16.6	5.79 ± 0.06	2.50 ± 0.03
336.0	5.13	3.14	15.4	5.87 ± 0.48	3.19 ± 0.26
344.3	5.04	3.04	13.4	4.83 ± 0.45	3.36 ± 0.31
351.0	4.61	2.83	13.8	4.24 ± 0.27	3.58 ± 0.23
352.4	3.88	4.20	13.8	3.87 ± 0.44	3.40 ± 0.39

[a] The reference rate coefficient is given[11] in cm^3 molecule^{-1} s^{-1} by the Arrhenius expression $k(T) = (1.61 \pm 0.60) \times 10^{-10} \exp(-(3.46 \pm 0.17) \times 10^3/T)$. The uncertainties in the table represent one standard deviation and do not include a contribution from the reference rate coefficient.

TABLE 2: Summary of Kinetic Data for the Reaction of Br with Tetrahydrofuran Measured Relative to the Reaction of Br with (a) Iso-octane[a] **and (b) Toluene**[b]

(a) Iso-octane

absolute temperature	$[C_8H_{18}]_0 \times 10^{-15}$ (molecules cm^{-3})	$[C_4H_8O]_0 \times 10^{-15}$ (molecules cm^{-3})	$[Br_2]_0 \times 10^{-15}$ (molecules cm^{-3})	$k_{C_4H_8O}/k_{C_8H_{18}}$	$k_{C_4H_8O} \times 10^{13}$ (cm^3 molecule^{-1} s^{-1})
294.8	1.11	4.64	12.4	23.5 ± 1.8	1.75 ± 0.13
296.1	1.13	5.07	12.4	22.8 ± 2.8	1.75 ± 0.21
302.1	0.83	5.42	9.78	24.9 ± 5.2	2.15 ± 0.45
302.7	1.03	5.61	9.21	27.6 ± 1.9	2.41 ± 0.17
303.2	0.74	5.00	10.1	35.2 ± 4.8	3.11 ± 0.42
303.3	0.81	5.39	9.20	33.4 ± 2.7	2.95 ± 0.24
303.8	1.06	5.08	10.2	26.0 ± 1.5	2.32 ± 0.13
304.5	0.80	5.34	9.21	39.9 ± 1.1	3.61 ± 0.10
304.7	1.12	4.97	10.1	36.8 ± 2.2	3.34 ± 0.20
305.1	1.04	11.1	6.9	30.3 ± 4.0	2.77 ± 0.37
328.4	0.61	4.82	11.3	39.7 ± 4.4	5.52 ± 0.61
329.0	0.69	3.71	10.9	32.6 ± 1.0	4.58 ± 0.14
329.2	0.82	4.84	11.3	29.7 ± 5.7	4.18 ± 0.80
349.5	0.85	4.50	10.2	36.3 ± 4.4	7.03 ± 0.85
349.5	0.65	4.74	7.99	31.8 ± 8.2	6.17 ± 1.59
350.1	0.81	4.54	10.2	37.3 ± 2.3	7.29 ± 0.45

(b) Toluene

absolute temperature	$[C_7H_8]_0 \times 10^{-15}$ (molecules cm^{-3})	$[C_4H_8O]_0 \times 10^{-15}$ (molecules cm^{-3})	$[Br_2]_0 \times 10^{-15}$ (molecules cm^{-3})	$k_{C_4H_8O}/k_{C_7H_8}$	$k_{C_4H_8O} \times 10^{13}$ (cm^3 molecule^{-1} s^{-1})
300.7	0.853	9.03	15.0	12.7 ± 1.6	2.10 ± 0.26
301.0	0.890	12.0	21.2	15.0 ± 2.1	2.50 ± 0.35
305.2	0.814	10.6	16.0	13.8 ± 2.1	2.47 ± 0.38
310.1	0.832	24.4	38.7	20.2 ± 3.5	3.95 ± 0.68
315.5	0.887	10.5	18.1	19.2 ± 1.6	4.10 ± 0.34
315.6	0.819	12.4	16.1	19.4 ± 2.1	4.14 ± 0.45
322.7	0.769	10.4	19.8	21.0 ± 3.9	5.04 ± 0.94
328.5	0.817	10.1	20.0	20.7 ± 2.3	5.41 ± 0.60
338.4	0.762	8.68	20.0	21.8 ± 3.4	6.60 ± 1.03

[a] The reference rate coefficient is given[5] in cm^3 molecule^{-1} s^{-1} by the Arrhenius expression $k(T) = (3.34 \pm 0.59) \times 10^{-12} \exp(-(1.80 \pm 0.11) \times 10^3/T)$. The uncertainties in the table represent one standard deviation and do not include a contribution from the reference rate coefficient. [b] The reference rate coefficient is given in cm^3 molecule^{-1} s^{-1} by the Arrhenius expression $k(T) = (3.7 \pm 1.7) \times 10^{-12} \exp(-(1.63 \pm 0.15) \times 10^3/T)$ on the basis of the results in Table 1. The uncertainties in the table represent one standard deviation and do not include a contribution from the reference rate coefficient.

of Br with tetrahydrofuran. The results for tetrahydrofuran and tetrahydropyran are then presented separately. In each case, the results obtained by application of eq I are presented. This is followed by an Arrhenius plot of the absolute rate coefficients derived from the relative rate measurements. In the Arrhenius expressions, the uncertainties represent one standard deviation. In all of these reactions, FTIR spectra of the reaction products indicated that formation of HBr was the dominant reaction channel. This is consistent with our previous experiments on the reactions of Br with ethers.[4,5]

Toluene Measured Relative to Isobutane. It became evident that the rate coefficients for the reaction of Br with tetrahydrofuran were so large that it was difficult to obtain adequate precision in measuring them using the reaction of Br with iso-octane as the reference reaction. Consequently, we selected the reaction of Br with toluene as a potentially better reference

TABLE 3: Summary of Kinetic Data for the Reaction of Br with Tetrahydropyran Measured Relative to the Reaction of Br with Tetrahydrofuran[a]

absolute temperature	$[C_4H_8O]_0 \times 10^{-15}$ (molecules cm^{-3})	$[C_5H_{10}O]_0 \times 10^{-15}$ (molecules cm^{-3})	$[Br_2]_0 \times 10^{-15}$ (molecules cm^{-3})	$k_{C_5H_{10}O}/k_{C_4H_8O}$	$k_{C_5H_{10}O} \times 10^{13}$ (cm^3 molecule^{-1} s^{-1})
297.7	10.6	3.21	17.4	0.626 ± 0.009	1.42 ± 0.02
298.3	11.0	3.38	18.9	0.562 ± 0.004	1.30 ± 0.01
300.2	10.6	3.55	17.3	0.783 ± 0.019	1.89 ± 0.05
300.8	11.0	3.26	17.2	0.693 ± 0.048	1.70 ± 0.12
301.9	11.3	3.49	17.6	0.640 ± 0.025	1.61 ± 0.06
302.4	8.76	6.92	13.2	0.505 ± 0.016	1.29 ± 0.04
304.5	8.23	4.58	13.8	0.596 ± 0.023	1.60 ± 0.06
305.1	8.66	3.14	13.4	0.542 ± 0.036	1.48 ± 0.10
305.4	8.54	3.61	12.7	0.466 ± 0.004	1.27 ± 0.01
305.4	8.36	4.38	13.0	0.589 ± 0.024	1.61 ± 0.07
306.7	8.11	3.00	14.1	0.646 ± 0.022	1.82 ± 0.06
307.0	7.44	3.38	11.0	0.511 ± 0.033	1.45 ± 0.09
320.7	10.5	2.93	15.4	0.551 ± 0.011	2.13 ± 0.04
322.2	9.26	2.95	15.8	0.557 ± 0.022	2.22 ± 0.09
327.8	9.95	3.05	12.0	0.721 ± 0.015	3.23 ± 0.07
329.7	9.56	3.20	15.8	0.649 ± 0.014	3.02 ± 0.07
330.4	10.1	2.90	17.1	0.688 ± 0.016	3.25 ± 0.08
351.4	20.1	4.95	40.3	0.680 ± 0.044	4.79 ± 0.31
360.1	12.8	3.50	20.1	0.602 ± 0.007	4.93 ± 0.06
362.1	14.9	4.22	27.3	0.624 ± 0.027	5.29 ± 0.23

[a] The reference rate coefficient is given in cm^3 molecule^{-1} s^{-1} by the Arrhenius expression $k(T) = (3.7 \pm 2.7) \times 10^{-10} \exp(-(2.20 \pm 0.22) \times 10^3/T)$ on the basis of the results in Table 2. The uncertainties in the table represent one standard deviation and do not include a contribution from the reference rate coefficient.

reaction. There is only one reported measurement of the rate coefficient for this reaction and this provided a value of 1.3×10^{-14} cm^3 molecule^{-1} s^{-1} at a single temperature of 300 K.[10] We measured the rate coefficient of the reaction of Br with toluene as a function of temperature so that it could be used as a reference reaction in the hope of obtaining more precise measurements of the rate coefficient for the reaction of Br with tetrahydrofuran over the accessible temperature range. The reaction of isobutane with Br was selected as the reference reaction because its absolute rate coefficient has been well-characterized as a function of temperature;[11,12] its value is within about a factor of 10 of the reported rate coefficient for the reaction of Br with toluene at 300 K. We previously measured the rate coefficient for the reaction of Br with iso-octane (2,2,4-trimethylpentane) as a secondary reference reaction using isobutane as the primary reference.[5] For consistency with that previous work, we have used the Arrhenius expression $k(T) = (1.61 \pm 0.60) \times 10^{-10} \exp(-(3.46 \pm 0.17) \times 10^3/T)$ for the reaction of Br with isobutane, reported by Seakins et al.,[11] in calculating the rate coefficients for the reaction of Br with toluene. Typical relative rate plots are provided in Figure 1a, and the temperature dependence of the absolute rate coefficients is presented in Figure 2. Also included in Figure 2 is the value of the rate coefficient for the reaction of Br with toluene determined by Bierbach et al.[10] at 300 K. Their result lies very close to the value that would be calculated from our Arrhenius parameters. The results for this reaction are summarized in Table 1. The Arrhenius expression for the reaction of Br with toluene derived from these rate coefficients is $k(T) = (3.7 \pm 1.7) \times 10^{-12} \exp(-(1.63 \pm 0.15) \times 10^3/T)$.

Tetrahydrofuran Measured Relative to Iso-octane. Iso-octane (2,2,4-trimethylpentane) was used as the reference compound for the experiments with tetrahydrofuran. While the rate coefficient for the reaction of iso-octane with Br is somewhat smaller than would have been desirable for this measurement, its use provides consistency with our recently published work on dimethyl ether and diethyl ether,[5] in which iso-octane was also used as the reference compound, and does not introduce the additional level of uncertainty that would result from calibration of a different reference reaction relative to iso-octane. This situation is no more difficult than was the case with diethyl ether in the previous experiments.[5] Since the rate of reaction of tetrahydrofuran was comparable to that of diethyl ether and the absolute rate coefficient for the reaction of iso-octane with Br is better established than that for the reaction of diethyl ether with Br, the use of iso-octane as the reference compound facilitated comparison of the Arrhenius parameters for tetrahydrofuran and diethyl ether. The rate coefficients for the reference reaction were calculated from the Arrhenius parameters reported in our earlier work[5] and are traceable to the absolute rate coefficients for the reaction of Br with isobutane reported by Seakins et al.[11] The Arrhenius expression used for the reference reaction of Br with iso-octane is $k(T) = (3.34 \pm 0.59) \times 10^{-12} \exp(-(1.80 \pm 0.11) \times 10^3/T)$. Typical

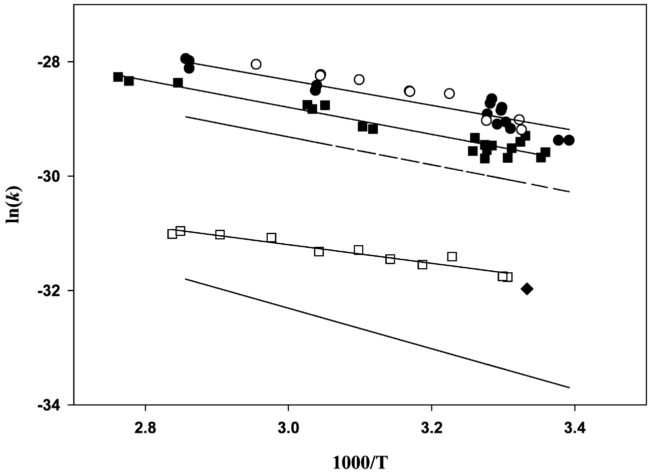

Figure 2. Arrhenius plots for various ethers. (●) Br + tetrahydrofuran relative to iso-octane, this work; (○) Br + tetrahydrofuran relative to toluene, this work; (■) Br + tetrahydropyran relative to tetrahydrofuran, this work; (□) Br + toluene relative to isobutane, this work; (◆) Br + toluene, ref 10; solid line, calculated for dimethyl ether from ref 5; dashed line, calculated for diethyl ether from ref 5.

relative rate plots are provided in Figure 1b, and the temperature dependence of the absolute rate coefficients is presented in Figure 2. The results for this reaction are summarized in Table 2. The rate coefficients were independent of the partial pressure of O_2 from 70 to 500 Torr. They were also independent of total pressure from 200 to 760 Torr, as would be expected for a bimolecular hydrogen abstraction reaction. The temperature dependence of the absolute rate coefficient in the units cm^3 $molecule^{-1}$ s^{-1} for the reaction of Br with tetrahydrofuran, based on these experiments, is given by the relation $k(T) = (4.9 \pm 3.4) \times 10^{-10} \exp(-(2.29 \pm 0.22) \times 10^3/T)$ in which the uncertainties represent one standard deviation. As is often found, the uncertainty in the intercept is large as a result of the long extrapolation to the origin based on data obtained over the small temperature range accessible in our apparatus. The scatter of the measured rate coefficients at a given temperature was approximately ±10% which was comparable to the uncertainties in the relative rate slopes listed in Table 2. We conclude that within our experimental temperature range this is probably a better estimate of the precision of our values of the rate coefficients than the least-squares estimate of the uncertainty in the intercept of the Arrhenius plot. In an effort to improve the precision of the Arrhenius parameters for this reaction, we made a second series of measurements of the temperature dependence of the rate coefficients of the reaction of tetrahydrofuran with atomic bromine, this time using toluene as the reference reactant. Toluene should be a better reference reactant than iso-octane because the rate coefficients for its reaction with Br are more comparable to those for the reaction of Br with tetrahydrofuran.

Tetrahydrofuran Measured Relative to Toluene. The rate coefficients for the reaction of Br with toluene are approximately a factor of two larger than those for the reaction of Br with iso-octane over the range of temperatures covered by our measurements. Use of toluene as a reference reactant for measuring the rate coefficients for the reaction of Br with tetrahydrofuran should provide improved precision as an alternative source of these rate coefficients by providing relative rate slopes that are approximately half the values measured using iso-octane as a reference reactant. The results of these measurements are provided in Table 2b and are presented in Figure 2. It is evident from the Arrhenius plot in Figure 2 that the rate coefficients for the reaction of Br with tetrahydrofuran obtained using toluene as a reference reactant are effectively the same as the rate coefficients obtained using iso-octane as the reference reactant. It is also evident that the results obtained relative to toluene show better precision than those obtained using iso-octane as the reference. When the two sets of rate coefficients for the reaction of Br with tetrahydrofuran are combined, the temperature dependence is given by $k(T) = (3.7 \pm 2.7) \times 10^{-10} \exp(-(2.20 \pm 0.22) \times 10^3/T)$. The Arrhenius parameters are within the quoted uncertainties of their values calculated from the experiments in which iso-octane was used as the reference reactant. However, the precision of the pre-exponential factor has improved as a result of the overall improvement of the precision of the measurements.

Tetrahydropyran Measured Relative to Tetrahydrofuran. Tetrahydrofuran was used as the reference compound for the experiments with tetrahydropyran to facilitate comparison of the rate coefficients for these two reactants. The two compounds have very similar rate coefficients which also makes tetrahydrofuran a more suitable reference compound than either iso-octane or toluene for these measurements. Typical relative rate plots are provided in Figure 1d, and the temperature dependence of the absolute rate coefficients is presented in Figure 2. The results for this reaction are summarized in Table 3 and were calculated using the Arrhenius expression $k(T) = (3.7 \pm 2.7) \times 10^{-10} \exp(-(2.20 \pm 0.22) \times 10^3/T)$ as indicated above for the reference reaction with tetrahydrofuran. The temperature dependence of the rate constant ratio for tetrahydropyran and tetrahydrofuran is given by the expression $k_{\text{tetrahydropyran}}/k_{\text{tetrahydrofuran}} = (0.95 \pm 0.47) \exp(-(155 \pm 155)/T)$. The indication is that the rate coefficients for the reaction of Br with tetrahydropyran are only slightly smaller than the values for the reaction of Br with tetrahydrofuran at a given temperature and that this ratio does not have a statistically significant temperature dependence over our available temperature range. The conclusion is that the reactions of Br with tetrahydrofuran and tetrahydropyran have slightly different pre-exponential factors but effectively the same activation energy. The absolute rate coefficient in the units cm^3 $molecule^{-1}$ s^{-1} for the reaction of Br with tetrahydropyran, derived from these results using the Arrhenius expression for the reference reaction of Br with tetrahydrofuran, is given by the relation $k(T) = (3.6 \pm 1.8) \times 10^{-10} \exp(-(2.35 \pm 0.16) \times 10^3/T)$. In this expression, the indicated uncertainties represent one standard deviation and relate only to the measurements made relative to tetrahydrofuran. They do not include the uncertainties in the Arrhenius parameters for the reference reaction of Br with tetrahydrofuran. While the numerical values of both the pre-exponential factor and the activation energy for the reactions of Br with tetrahydrofuran and tetrahydropyran are the same within their statistical uncertainties, it is clear from Figure 2 that the rate coefficients for tetrahydropyran are consistently smaller than those for tetrahydrofuran over our experimental temperature range. Comparison of the relative rate plots in Figure 1d indicates that the ratio of the rate coefficients for tetrahydrofuran and tetrahydropyran shows only a small variation over our experimental temperature range. The slopes of the relative rate plots over our range of experimental conditions suggest that the rate coefficient for the reaction of Br with tetrahydropyran is between 60% and 70% of the value for the reaction with tetrahydrofuran.

Discussion

The temperature dependence of the rate coefficients for the reactions of Br with dimethyl ether, diethyl ether, tetrahydrofuran, and tetrahydropyran is presented in Figure 2. It is clear from these data that the reaction of Br with dimethyl ether is very much slower over our temperature range than in the other three reactions. In the reaction with dimethyl ether, all of the available hydrogen atoms are adjacent to the ether oxygen. However, in the other three ethers there is hydrogen attached to carbon atoms that are farther removed from the ether oxygen. This raises the possibility of at least two channels for hydrogen abstraction by Br in its reactions with diethyl ether, tetrahydrofuran, and tetrahydropyran. The channel with the lower activation energy would be anticipated to be the abstraction of hydrogen from the carbon atom adjacent to the ether oxygen as a result of the electron withdrawing effect of that oxygen atom. The abstraction of hydrogen from carbon atoms more distant from the ether oxygen would be expected to have a somewhat larger activation energy because the activating influence of the ether oxygen would be greatly reduced. However, the relative importance of this second reaction channel is not immediately evident. Comparison of the data in Table 4 for these four ethers suggests that the smaller rate coefficients for dimethyl ether can be attributed mainly to a larger enthalpy of activation for that reaction. The enthalpies of activation for

TABLE 4: Transition State Theory Parameters for the Reactions of Atomic Bromine with Tetrahydrofuran and Tetrahydropyran Compared to Dimethyl Ether, Diethyl Ether, Methanol, Toluene, and Some Alkanes[a]

reaction	enthalpy of activation ($kJ\ mol^{-1}$)	entropy of activation ($J\ K^{-1}\ mol^{-1}$)	entropy of activation per reactive C−H bond ($J\ K^{-1}\ mol^{-1}$)
$Br + C_4H_8O \rightarrow HBr + C_4H_7O$	16 ± 2	−94 ± 6	−104 ± 6
$Br + C_5H_{10}O \rightarrow HBr + C_5H_9O$	17 ± 1	−94 ± 4	−104 ± 4
$Br + (CH_3)_2O \rightarrow HBr + CH_2OCH_3$	27 ± 2	−96 ± 6	−111 ± 6
$Br + (C_2H_5)_2O \rightarrow HBr + C_2H_4OC_2H_5$	18 ± 3	−96 ± 8	−104 ± 8
$Br + CH_3OH \rightarrow HBr + CH_2OH$	33 ± 1	−98 ± 2	−107 ± 2
$Br + iso\text{-}C_4H_{10} \rightarrow HBr + C_4H_9$	24.5 ± 1.8	−105 ± 4	−105 ± 4
$Br + n\text{-}C_4H_{10} \rightarrow HBr + C_4H_9$	33.1 ± 1.1	−101 ± 2	−113 ± 2
$Br + C_3H_8 \rightarrow HBr + C_3H_7$	29.3 ± 1.0	−114 ± 2	−120 ± 2
$Br + C_2H_6 \rightarrow HBr + C_2H_5$	48.3 ± 2.1	−103 ± 4	−118 ± 4
$Br + iso\text{-}C_8H_{18} \rightarrow HBr + C_8H_{17}$	12.5 ± 0.9	−134 ± 3	−158 ± 3
$Br + C_6H_5CH_3 \rightarrow HBr + C_6H_5CH_2$	10.8 ± 1.3	−132 ± 4	−141 ± 4[b]

[a] The parameters for the reaction with methanol are calculated from the kinetic data of ref 6, while those for iso-octane, dimethyl ether, and diethyl ether are from ref 5. The parameters for ethane, propane, *n*-butane, and isobutane are calculated from the data in ref 11. The uncertainties in the table represent one standard deviation and do not include a contribution from the reference rate coefficient. [b] It is assumed that only the CH_3 hydrogen atoms are abstracted.

the reactions of Br with the other three ethers are smaller and more nearly comparable suggesting that the kind of hydrogen atom being abstracted in these reactions is the same and that such hydrogen atoms are energetically easier to remove than those in dimethyl ether. In the case of dimethyl ether, the expected activating effect of the ether oxygen atom is spread among six C−H bonds, while in each of the other ethers this activating effect is distributed among only four C−H bonds adjacent to the ether oxygen. This should result in lower enthalpies of activation for the abstraction of hydrogen in the reactions of Br with ethers having CH_2 groups adjacent to the ether oxygen compared to the situation that exists in dimethyl ether. If the contribution of hydrogen abstraction from the other carbon atoms in these ethers is unimportant compared to that of the abstraction from the CH_2 groups adjacent to the ether oxygen, the activation energies for the reactions of Br with diethyl ether, tetrahydrofuran, and tetrahydropyran should be comparable with no evident trend with the variation in the number and type of the other CH bonds in these compounds. The data in Table 4 indicate that the enthalpies of activation for the reactions of these three ethers with Br are the same within their statistical uncertainties and are approximately 10 kJ mol^{-1} smaller than the enthalpy of activation of the reaction of Br with dimethyl ether. This leads to the conclusion that the dominant reaction channel in the reactions of Br with these ethers is the abstraction of hydrogen from the carbon atom adjacent to the ether oxygen atom.

It is instructive to compare the data in Table 4 for the reactions of Br with ethers and the reactions of Br with hydrocarbons. The data for the small alkanes in the table were calculated from the rate coefficients reported in ref 11. For these compounds, the enthalpy of activation for the reaction of Br with ethane is the largest, followed by the enthalpies of activation of the reactions of Br with propane and *n*-butane which are smaller and of similar magnitude, followed by the enthalpy of activation for the reaction of Br with isobutane which is the smallest. This has been interpreted[11] in the following way. In ethane only CH_3 hydrogens are available for the reaction, and only a primary free radical (C_2H_5) is formed, leading to a comparatively large activation energy. In both propane and *n*-butane, both CH_3 and CH_2 hydrogens are available for abstraction. Removal of a CH_2 hydrogen produces a more stable free radical (CH_3CHCH_3 or $CH_3CHCH_2CH_3$), and the activation energies for the reactions of these hydrocarbons with Br are smaller and are also of comparable magnitude. Finally, in isobutane both CH_3 and CH hydrogens are available for abstraction. Despite the steric hindrance due to the CH_3 groups, it is in this case the CH hydrogen that is removed because it forms a free radical ($(CH_3)_3C$) which is more stable than the free radical products in the reactions of Br with propane and *n*-butane, and this is reflected by a still smaller enthalpy of activation (see Table 4). As a result, the reaction of Br with isobutane has the smallest activation energy. This reflects the same trend observed in the reactions of Br with the ethers and supports the interpretation that it is the hydrogen atoms adjacent to the ether oxygen that are abstracted. The enthalpies of activation for the reactions of Br with the ethers are smaller than those for the abstraction of hydrogen from CH_3 and CH_2 sites in the reactions of Br with the hydrocarbons, reflecting the activating effect of the ether oxygen atom. If one assumes that the activating effect of the ether oxygen is largely restricted to H-abstraction from the α-carbon atom, it would be expected that, as the number of $-CH_2-$ groups increases, the additional $-CH_2-$ groups will have virtually the same reactivity as those in the *n*-alkanes. On this assumption, one would expect that the activation energy for the abstraction of a CH_3 hydrogen from diethyl ether would be similar to that for the abstraction of a CH_3 hydrogen from ethane. The lower value of the enthalpy of activation found for the reaction of diethyl ether, compared to that for the reaction of the ethane (Table 4), supports the postulate that the only significant channel for hydrogen abstraction by Br in its reactions with the ethers is the removal of a hydrogen atom adjacent to the ether oxygen.

The data in Table 4 indicate that the enthalpies of activation for the reaction of Br with the ethers are significantly smaller than that for the reaction of Br with methanol in which the formation of a hydrogen-bonded complex between the bromine atom and the OH group of the alcohol[6] results in an indirect abstraction mechanism. However, the entropies of activation for the reactions of Br with the ethers are virtually the same as that for the reaction of Br with methanol. The effect of complex formation seems to be felt primarily in the enthalpy of activation rather than in the entropy of activation. Table 4 indicates that the reactions of Br with small alkanes have entropies of activation that are only slightly more negative than those for the reactions of Br with the ethers and with methanol. While entropic effects do not appear to vary significantly in the reactions of Br with the smaller organic reactants in Table 4, the results for iso-octane and toluene stand out as being different. In the reaction of Br with iso-octane, the enthalpy of activation is much smaller than those obtained for the reactions of Br with the small alkanes and with the ethers. The entropy of activation is also significantly more negative than the values calculated for those reactions. The same is true of the reaction of Br with toluene. In the latter case, the low value of enthalpy of activation can be attributed to the particular stability of the benzyl radical which is formed on hydrogen abstraction from the CH_3 group. The more negative entropy of activation can be attributed to the more restrictive geometry associated with removal specifically of a CH_3 hydrogen as opposed to those on the benzene ring. In iso-octane, the bromine atom presumably removes the CH hydrogen in preference to the CH_2 or CH_3 hydrogen atoms. While this would be expected to result in an enthalpy of activation that is comparable to that found for isobutane, the value for the reaction of Br with iso-octane is approximately 12 kJ/mol smaller than the value for the reaction of Br with isobutane. The entropy of activation for the reaction of Br with iso-octane is also significantly more negative than that for the reaction of Br with isobutane, suggesting that the approach of Br to the CH hydrogen atom is sterically more difficult than in the abstraction of the CH hydrogen in isobutane.

Finally, we compare the results for the reactions of Br with ethers to the general behavior of other atmospherically significant oxidants. While OH is generally considered to be the most important atmospheric oxidant, both Br and Cl initiate oxidation of volatile organic compounds through their production of organic free radicals which then react with atmospheric oxygen to produce peroxy radicals and ultimately HO_2 and OH radicals.[5,9,10,13,14] NO_3 is important, particularly at night, in polluted urban atmospheres,[15] and $O(^3P)$ is a significant daytime atmospheric oxidant in atmospheres containing high concentrations of nitrogen oxides.[16] All of these species react with volatile organic compounds by both addition and hydrogen abstraction. A correlation of the rate coefficients at 298 K for reactions of Br with a wide range of volatile organic compounds relative to their reactions with OH, Cl, NO_3, and $O(^3P)$ was made several years ago,[3] and the general conclusions of that correlation are relevant to the current work. In each case, the correlations produced two linear components: one corresponding to reactions that proceed by hydrogen abstraction and one corresponding to addition reactions. The rate coefficients measured in the current work would fall near the intersection of the two linear components of these correlations. The rate coefficients for the reactions of Br with volatile organic compounds cover a much wider range of values than those of OH, Cl, NO_3, and $O(^3P)$, particularly in the case of hydrogen abstraction, and their values tend to be the smallest, while those of OH and Cl are the largest. While the rate coefficients for the reactions of Cl with organic compounds tend to be near the gas kinetic limit,[17,18] making their correlation with the rate coefficients of reactions of atomic bromine difficult, correlation of the bromine atom rate coefficients with those of OH, the dominant atmospheric oxidant, is possible.

The kinetics of the reactions of OH with a range of volatile organic compounds has been reviewed,[19] and the rate coefficients of the reactions of OH with the ethers whose reactions with Br are reported here have been measured.[20] The reactions of OH are consistent with attack at the hydrogen α to the ether oxygen. In this respect, the mechanism is the same as that proposed for the bromine atom reactions examined in our work. The reported[20] trend in the reactivity of OH with tetrahydropyran and tetrahydrofuran is consistent with our observed relative reactivity of atomic bromine with these cyclic ethers. The similarity of our results to those reported for the corresponding reactions of OH radicals provides support for the postulate that the Br and OH reactions with the ethers proceed by abstraction of the same hydrogen atom in the ether. The relative values of the rate coefficients are therefore controlled by the strengths of these bonds in the ethers.

Conclusions

The reactions of Br with ethers occur primarily by the abstraction of hydrogen from a carbon atom adjacent to the ether oxygen. Unlike the reaction of Br with methanol, the reactions with the ethers do not seem to involve formation of a hydrogen-bonded complex. Instead, the reaction appears to proceed by direct hydrogen abstraction. The activating effect of the ether oxygen atom provides a reduction of roughly 10 kJ/mol in the enthalpy of activation, compared to that of the abstraction of the same kind of hydrogen atom (CH_2 or CH_3) in the reactions of Br with small alkanes. While the entropies of activation for the reactions of Br with the ethers and with small alkanes have quite similar values, these values for the reactions of Br with toluene and with iso-octane are significantly more negative than those for the reactions of the ethers and the small alkanes with atomic bromine. It is evident that, while in many cases the variation in reactivity of a series of compounds toward Br may be dominated by enthalpic effects, there are situations in which differences in the entropy of activation can also contribute significantly to variation in reactivity.

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