Temperature Dependence of the Rate Coefficients for the Reactions of Br Atoms with Dimethyl Ether and Diethyl Ether

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The rate constants for the reactions of atomic bromine with dimethyl ether and diethyl ether were measured from approximately 300 to 350 K using the relative rate method. Both isooctane and isobutane were used as the reference reactants, and the rate constants for the reactions of these hydrocarbons were measured relative to each other over the same temperature range. The kinetic measurements were made by photolysis of dilute mixtures of bromine, the reference reactant, and the test reactant in mixtures of argon and oxygen at a total pressure of 1 atm. The resulting ratios of rate constants were combined with the absolute rate constant as a function of temperature for the reference reaction of Br with isobutane to calculate absolute rate constants for the reactions of Br with isooctane, dimethyl ether, and diethyl ether. The absolute rate constant, in the units cm^3 molecule^{-1} s^{-1}, for the reaction of Br with dimethyl ether was given by $k = (3.8 \pm 2.4) \times 10^{-10}$ exp($-(3.54 \pm 0.21) \times 10^3/T$) while for the reaction of Br with diethyl ether the rate constant is given by $k = (2.8 \pm 2.7) \times 10^{-10}$ exp($-(2.44 \pm 0.32) \times 10^3/T$). On the same basis, the rate constant for the reaction of Br with isooctane is given by $k = (3.34 \pm 0.59) \times 10^{-12}$ exp($-(1.80 \pm 0.11) \times 10^3/T$). In each case, the activation energy of the reaction is significantly smaller than the endothermicity of the reaction. This is discussed in terms of a complex mechanism for these reactions.

Introduction

Reactions of atomic bromine have been implicated in a range of atmospherically significant issues such as ozone depletion and this has been reviewed for both the troposphere and the stratosphere (e.g., refs 1 and 2). The detailed estimation of ambient concentrations of atomic bromine requires a quantitative assessment of its reactivity with available atmospheric sinks under the range of reaction conditions encountered in the atmosphere. While the rate constants for reactions of Br with organic compounds are generally smaller than those for the corresponding reactions of atomic chlorine, much less is known about the temperature dependence of reactions of atomic bromine than is known about the reactions of atomic chlorine.[3,4] The rate constants at ambient temperature of reactions of Br with a wide range of organic compounds have been correlated with the rate constants of the corresponding reactions of OH, NO_3, and O(^{3}P),[5] but such a correlation at a fixed temperature provides no indication of the relative importance of entropic and enthalpic effects in determining the relative reactivity. What is evident from this correlation is that the rate constants at ∼300 K for reactions of Br with organic compounds cover a significantly wider range of numerical values than those of OH, NO_3, and O(^{3}P), and examination of the data in refs 3 and 4 indicates that the same is true relative to the reactions of organic compounds with chlorine atoms. It is desirable to have more complete information about the temperature dependence of the rate constants for reactions of atomic bromine, both to permit their extrapolation to temperatures typical of the upper atmosphere and of the polar regions and to provide information that will enhance understanding of the dynamics of these reactions.

Measurement of the temperature dependence of the rate constants for reactions of halogen atoms with hydrocarbons has played an important role in establishing values of the enthalpies of formation of small hydrocarbon free radicals.[6,7] More recently, such data have been used in computational work that seeks to elucidate the dynamics of the reactions of halogen atoms with saturated organic compounds.[8,9] These calculations have demonstrated that, at least for reactions involving a polar reactant such as methanol, the reaction dynamics are complex involving the intervention of bound complexes of the reactant with the bromine atom. In reactions of Br with hydrocarbons, only the direct hydrogen abstraction path is possible although this could still involve formation of a long-lived complex which ultimately releases HBr. When the organic reactant contains an oxygen atom, as is the case in methanol and in the ethers whose reactions are investigated in the present work, a second abstraction path is possible. In this new path, the bromine atom forms a comparatively stable complex with the oxygen atom and then rearranges to form the complex which ultimately releases HBr. The likelihood of a complex mechanism for production of HBr in the reactions of Br with organic compounds makes it important to assess both the enthalpic and entropic effects on the rate constants of bromine atom reactions when attempting to understand the origins of reactivity trends in these reactions.

The work which we report here examines the temperature dependence of the rate constants for the reactions of atomic bromine with dimethyl ether and diethyl ether and compares the results with those for the reaction of Br with isooctane. While it is expected that only a single channel will operate in the reaction with isooctane, the ethers will have an additional channel available resulting from complex formation between the bromine atom and the oxygen atom. With both isooctane and dimethyl ether, only methyl hydrogens are present, while

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in diethyl ether there are two hydrogen abstraction processes, that from CH_3 and that from CH_2. In all cases, the rate constants are measured using the relative rate approach with isobutane as the reference reactant. Large concentrations of O_2 are present in most of the experiments to scavenge the free radicals formed in the initial attack by Br, thereby preventing their reaction with the parent organic reactant.

Experimental Section

The apparatus and experimental methods used have been described in detail previously[10] and are summarized briefly here. The experiments were made in a cylindrical Pyrex reaction chamber of ~70 L volume which was surrounded with fluorescent lamps. The useful wavelength range for photolysis was from approximately 350 to 650 nm, which provided efficient photolysis of Br_2, the atomic bromine precursor, and avoided photolysis of the organic reactants. The temperature of the reactor was adjusted by blowing heated air through the chamber surrounding it, and the temperature was controlled by using a thermostat to control the flow of heated air. The thermostat sensor was located inside the reaction vessel, and the temperature was monitored with three iron−constantan thermocouples located along the axis of the reaction vessel. Pressures were measured with a 10 Torr Baratron pressure gauge and a piezoelectric pressure gauge. Reaction mixtures were prepared from dilute mixtures in argon of Br_2 and the organic reagents which were stored in separate 12 L Pyrex bulbs. The entire gas handling system was made of Pyrex. It was mercury-free and used Teflon stopcocks exclusively. Typical reaction mixtures contained roughly 300 ppmv of Br_2 with significantly smaller amounts of the organic reactants. Photolysis of Br_2 will typically produce concentrations of Br that are far smaller than the concentration of Br_2 so the concentration of Br is anticipated to be small and approximately constant over the range of extents of consumption of the organic reactant encountered in our experiments. The rate of consumption of each reactant, R, in a second-order reaction with Br will be given by rate $= k[\mathrm{Br}][\mathrm{R}]$ so, with a virtually constant value of [Br], the consumption of each organic reactant will be pseudo-first-order. While pseudo-first-order behavior is not required for the kinetic analysis, it does permit estimation of the concentrations of atomic bromine in our experiments. Plots of the log of the concentration of organic reactant as a function of time were found to be linear, as indicated in Figure 1, verifying pseudo-first-order behavior. The slopes of these lines are the pseudo-first-order rate coefficient, k[Br]. Since the numerical value of the second-order rate constant, k, is known, the value of the pseudo-first-order rate coefficient permits estimation of the concentration of Br in a given experiment. Concentrations of atomic bromine estimated in this way were in the range 10^{11}−10^{12} molecules cm^{-3}. Chemical analysis of the mixtures in the chamber was by gas chromatography using a flame ionization detector and an 8 ft × $^{1}/_{8}$ in. column packed with SP1000.

In a typical experiment, small measured amounts of the stock mixtures of Br_2, the reference reactant, and the test reactant were added to the reaction chamber, and the pressure was brought to ~1 atm by adding known amounts of oxygen and argon. The mixture was allowed to stand for approximately half an hour to equilibrate, and a gas chromatogram of the initial mixture was obtained. The mixture was next exposed to irradiation from the fluorescent lamps for varying periods of time. After each irradiation period, the concentrations of the reference and test reactant were determined by removing a known pressure of sample from the reaction chamber to a gas sampling loop followed by injection into the gas chromatograph. Comparison of the peak areas initially and following irradiation, after normalization for small variations in the pressure of the sample loop, permitted calculation of the ratio of rate constants for the test and reference reactants. The amount of sample removed for analysis was so small that several consecutive irradiation experiments could be done without significantly altering the total pressure in the reaction vessel. Consumption of the organic reactants was kept as small as practicable to minimize the possibility of secondary reactions.

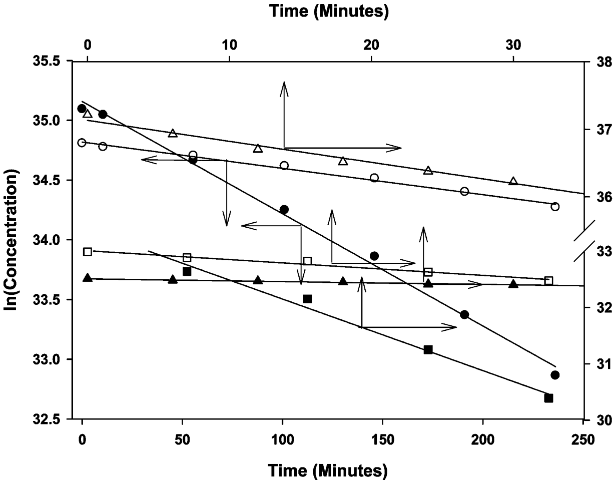


Figure 1. Filled symbols are for isooctane while open symbols are for the other organic reactant. (●, ○) $[Br_2]_0 = 1.00 \times 10^{16}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.74 \times 10^{15}$ molecules cm^{-3}, $[C_4H_{10}]_0 = 1.31 \times 10^{15}$ molecules cm^{-3}, temperature = 302 K; (■, □) $[Br_2]_0 = 1.02 \times 10^{16}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.52 \times 10^{14}$ molecules cm^{-3}, $[(CH_3)_2O]_0 = 2.12 \times 10^{14}$ molecules cm^{-3}, temperature = 296 K; (▲, △) $[Br_2]_0 = 6.31 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.32 \times 10^{14}$ molecules cm^{-3}, $[(C_2H_5)_2O]_0 = 1.45 \times 10^{16}$ molecules cm^{-3}, temperature = 321 K.

The kinetic analysis assumes that loss of the test and reference reactants occurs only by the reactions

$$\mathrm{Br} + \mathrm{RH}_x \rightarrow \text{products} \tag{1}$$

$$\mathrm{Br} + \mathrm{RH}_{\mathrm{ref}} \rightarrow \text{products} \tag{2}$$

in which RH_x is the test reactant and RH_{ref} is the reference reactant. The rate constant ratio is then given by

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

A plot of $\ln\{\{[\mathrm{RH}_x]_{t_0}\}/\{[\mathrm{RH}_x]_t\}\}$ against $\ln\{[\mathrm{RH}_{\mathrm{ref}}]_{t_0}/[\mathrm{RH}_{\mathrm{ref}}]_t\}$ is predicted to be linear with zero intercept and slope equal to k_1/k_2. Since the peak areas in the chromatograms are linearly proportional to the concentrations of RH_x and RH_{ref}, the peak areas can be substituted for concentrations in eq I. The absolute rate constant for the test reaction can then be calculated if the absolute rate constant for the reference reaction is accurately known at the temperature of the experiment. These plots were linear in all cases, suggesting that secondary reactions were not important, and typical examples for each reaction are presented in Figure 2. These plots were not forced through the origin since a small systematic analytical error in the concentration of either reactant would lead to a small positive or negative offset in the plots, and forcing the plot to pass through the origin would bias the slope. In any event, the intercepts of these plots were close to zero.

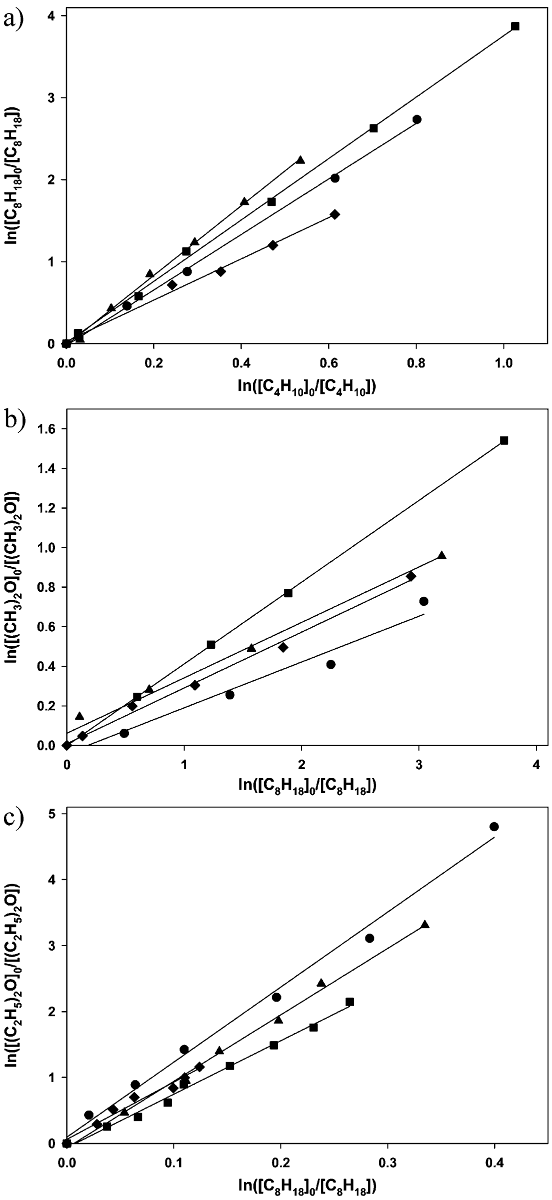


Figure 2. (a) (●) $[Br_2]_0 = 9.33 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.92 \times 10^{15}$ molecules cm^{-3}, $[C_4H_{10}]_0 = 1.22 \times 10^{15}$ molecules cm^{-3}, temperature = 316 K; (■) $[Br_2]_0 = 1.17 \times 10^{16}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 2.47 \times 10^{15}$ molecules cm^{-3}, $[C_4H_{10}]_0 = 8.37 \times 10^{14}$ molecules cm^{-3}, temperature = 312 K; (▲) $[Br_2]_0 = 1.00 \times 10^{16}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.74 \times 10^{15}$ molecules cm^{-3}, $[C_4H_{10}]_0 = 1.31 \times 10^{15}$ molecules cm^{-3}, temperature = 302 K; (◆) $[Br_2]_0 = 7.77 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.25 \times 10^{15}$ molecules cm^{-3}, $[C_4H_{10}]_0 = 1.60 \times 10^{15}$ molecules cm^{-3}, temperature = 338 K. **(b)** (●) $[Br_2]_0 = 1.02 \times 10^{16}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.52 \times 10^{14}$ molecules cm^{-3}, $[(CH_3)_2O]_0 = 2.12 \times 10^{14}$ molecules cm^{-3}, temperature = 296 K; (■) $[Br_2]_0 = 7.95 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.72 \times 10^{14}$ molecules cm^{-3}, $[(CH_3)_2O]_0 = 8.67 \times 10^{14}$ molecules cm^{-3}, temperature = 312 K; (▲) $[Br_2]_0 = 1.04 \times 10^{16}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.10 \times 10^{15}$ molecules cm^{-3}, $[(CH_3)_2O]_0 = 1.10 \times 10^{15}$ molecules cm^{-3}, temperature = 311 K; (◆) $[Br_2]_0 = 9.76 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.05 \times 10^{15}$ molecules cm^{-3}, $[(CH_3)_2O]_0 = 1.36 \times 10^{15}$ molecules cm^{-3}, temperature = 312 K. **(c)** (●) $[Br_2]_0 = 7.46 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 2.51 \times 10^{14}$ molecules cm^{-3}, $[(C_2H_5)_2O]_0 = 1.83 \times 10^{15}$ molecules cm^{-3}, temperature = 348 K; (■) $[Br_2]_0 = 8.08 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 3.20 \times 10^{14}$ molecules cm^{-3}, $[(C_2H_5)_2O]_0 = 5.80 \times 10^{15}$ molecules cm^{-3}, temperature = 307 K; (▲) $[Br_2]_0 = 6.86 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 3.36 \times 10^{14}$ molecules cm^{-3}, $[(C_2H_5)_2O]_0 = 8.70 \times 10^{15}$ molecules cm^{-3}, temperature = 316 K; (◆) $[Br_2]_0 = 6.31 \times 10^{15}$ molecules cm^{-3}, $[C_8H_{18}]_0 = 1.32 \times 10^{14}$ molecules cm^{-3}, $[(C_2H_5)_2O]_0 = 1.45 \times 10^{16}$ molecules cm^{-3}, temperature = 321 K.

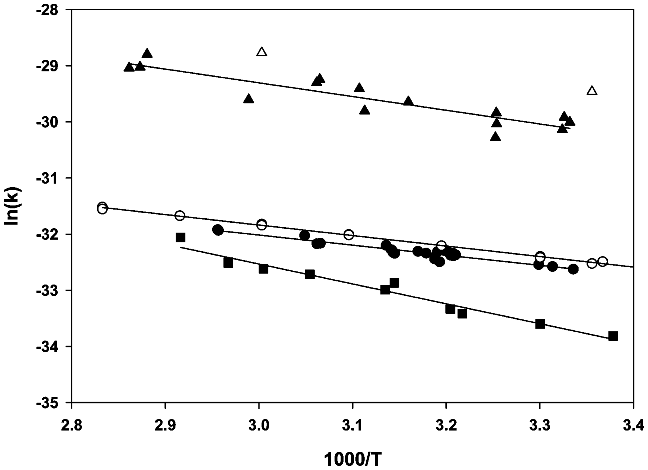


Figure 3. (●) Br + isooctane, this work; (○) Br + isooctane, ref 11; (■) Br + $(CH_3)_2O$, this work; (▲) Br + $(C_2H_5)_2O$, this work; (△) Br + $(C_2H_5)_2O$, ref 16.

Some discussion of the role of O_2 is required at this point since its presence could generate new radical species that might affect the measured values of the rate constants. As indicated earlier, the use of O_2 in the bath gas is anticipated to scavenge the free radicals generated by the attack of Br on the parent organic compound. While it is usual to assume that the products of these scavenging reactions do not interfere with the measurement of the rate constants (e.g., ref 11), some justification of this assumption is appropriate. The initial reaction of atomic bromine is indicated below together with the main anticipated subsequent reactions of the organic free radical formed in the initial reaction. In order to interfere with measurement of the rate constant for the reaction of Br with the parent organic reactant, a new reactive species would need to be produced which would compete efficiently with Br for RH.

$$Br + RH \rightarrow HBr + R^{\bullet}$$

$$R^{\bullet} + Br_2 \rightarrow RBr + Br$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \rightarrow HO_2 + \text{product}$$

The last reaction in this sequence can take place either via the peroxy radical, as shown, or in a single step,[12] and the nature of the products of this reaction other than HO_2 will be determined by the identity of the parent organic reactant, RH. The HO_2 radical would then produce OH radicals, primarily by reaction with atomic bromine. The reaction of OH with the parent organic reactant would be anticipated to be much faster than the corresponding reactions of Br (e.g., refs 3 and 4), leading to significant additional consumption of the parent organic reactant once the concentration of OH becomes significant. This could potentially result in curvature of the relative rate plots. In our earlier work,[10] we indicated that pronounced curvature of the relative rate plots was sometimes observed at comparatively large extents of reaction when the O_2 concentration was relatively large. We attributed this to secondary reactions resulting from oxidation and restricted the kinetic analysis to extents of reaction that were sufficiently small to avoid this curvature. The same practice was exercised here, and the observation that the relative rate plots exhibited good linearity and produced rate constants which did not show a measurable dependence on the concentration of either Br_2 or O_2 suggests that the complications resulting from the production of reactive intermediates such as OH were largely avoided.

TABLE 1: Summary of Kinetic Data for the Reaction of Br with Isooctane Measured Relative to the Reaction of Br with Isobutane

absolute temp (K)	$[C_8H_{18}]_0 \times 10^{-15}$ (molecules cm^{-3})	$[C_4H_{10}]_0 \times 10^{-15}$ (molecules cm^{-3})	$[Br_2]_0 \times 10^{-15}$ (molecules cm^{-3})	$k_{C_8H_{18}}/k_{C_4H_{10}}$	$k_{C_8H_{18}} \times 10^{15}$ (cm^3 molecule^{-1} s^{-1})
299.8	1.86	1.26	9.94	4.40	6.77
301.8	1.74	1.31	10.0	4.28	7.11
303.1	1.73	1.08	9.33	4.20	7.35
311.5	1.78	1.23	9.51	3.67	8.74
311.8	1.98	1.22	9.33	3.59	8.60
311.8	2.47	0.837	11.7	3.74	8.97
312.0	1.85	1.25	9.33	3.59	8.69
312.2	1.79	1.23	8.97	3.72	9.08
313.2	1.70	1.24	9.09	3.06	7.73
313.7	1.90	1.27	8.67	3.16	8.13
314.6	1.94	1.23	10.4	3.40	9.02
315.5	1.92	1.22	9.33	3.41	9.32
318.0	0.241	0.614	2.93	3.02	8.99
318.1	0.226	0.765	2.11	3.05	9.14
318.3	0.220	0.674	3.04	3.18	9.58
318.3	0.939	3.53	12.8	3.16	9.53
318.9	0.897	4.40	7.35	3.37	10.4
326.2	0.292	3.38	10.8	2.74	10.8
326.6	0.517	3.02	9.45	2.68	10.6
328.0	0.266	1.70	10.7	2.96	12.3
338.2	1.25	1.60	7.77	2.36	13.5
338.3	1.70	0.964	8.01	2.39	13.7

TABLE 2: Summary of Kinetic Data for the Reaction of Br with Dimethyl Ether Measured Relative to the Reaction of Br with Iso-octane

absolute temp (K)	$[C_8H_{18}]_0 \times 10^{-14}$ (molecules cm^{-3})	$[C_2H_6O]_0 \times 10^{-14}$ (molecules cm^{-3})	$[Br_2]_0 \times 10^{-14}$ (molecules cm^{-3})	$k_{C_2H_6O}/k_{C_8H_{18}}$	$k_{C_2H_6O} \times 10^{15}$ (cm^3 molecule^{-1} s^{-1})
296.0	1.52	2.12	102	0.240	2.06
303.0	2.03	2.07	96.4	0.257	2.56
310.8	11.0	11.0	104	0.264	3.07
312.1	10.5	13.6	97.6	0.280	3.33
318.0	4.56	5.34	172	0.401	5.34
319.0	4.09	6.50	127	0.347	4.70
327.4	0.650	9.15	88.5	0.393	6.20
332.8	1.28	8.85	78.3	0.395	6.83
337.3	1.72	8.67	79.5	0.414	7.67
337.9	17.2	10.8	79.5	0.408	7.57
342.9	2.79	0.323	67.4	0.585	11.9

The compounds whose reactions with Br were examined were isobutane (Aldrich, 99.995%), isooctane (Aldrich, 99+%), dimethyl ether (Aldrich, 99+%), and diethyl ether (ACP, 99.0%). These were purified by thorough degassing of the liquids or by freeze−pump−thaw cycles for the gases, followed by distillation of the desired amount into the storage bulb. The Br_2 (ACP, 99.5%) was purified by freeze−pump−thaw cycles followed by distillation into its storage bulb. The other gases, He (Praxair, 99.9995%), argon (Praxair 99.9995%), and O_2 (Praxair, 99.9995%), were used without further purification. As in our previous work,[10] these reactants were tested for interference due to photolysis and due to dark reaction with Br_2. To test for photolysis of the organic reactant, a mixture was prepared in the same manner as for a kinetic experiment, except that no Br_2 was added. The mixture was then irradiated for ~1 h. No evidence of loss of the organic reactant was observed. We conclude from this that loss of organic reactant either by photolysis or by removal at the walls of the reaction vessel was not significant. To test for dark reaction, a mixture with composition typical of our reaction conditions was prepared and allowed to stand in the dark for ~1 h. No loss of reactant was observed in these experiments, and it was concluded that loss of the organic reactant due to dark reaction or by loss at the walls was not significant.

Results

The results are presented in three sets: isooctane relative to isobutane, dimethyl ether relative to isooctane, and diethyl ether relative to isooctane. In each case, log−log plots typical of those used to determine the rate constant ratio via eq I are provided. Typical pseudo-first-order plots are given in Figure 1, and Arrhenius plots of the data for all the reactions investigated are collected in Figure 3. As noted in the Experimental Section, the first-order plots provide an estimate of the concentration of atomic bromine in the reaction chamber.

Isooctane Measured Relative to Isobutane. The rate of the reference reaction used in a relative rate experiment needs to be comparable to that of the test reaction for best precision. Operationally, this generally requires that the rate constant of the reference reaction should be within about a factor of 5 of that of the test reaction. The reaction of isooctane with Br meets this operational requirement acceptably for our experiments with dimethyl ether and diethyl ether, but its rate constant has only been measured once as a function of temperature, relative to isobutane.[13] While the absolute rate constant for the reaction of Br with isobutane has been measured as a function of temperature with good precision by two groups,[14,15] its rate constant is less well suited to our measurements of the reactions of Br with dimethyl ether or with diethyl ether than that of the reaction of Br with isooctane. We therefore measured the rate

TABLE 3: Summary of Kinetic Data for the Reaction of Br with Diethyl Ether Measured Relative to the Reaction of Br with Isooctane

absolute temp (K)	$[C_8H_{18}]_0 \times 10^{-14}$ (molecules cm^{-3})	$[C_4H_{10}O]_0 \times 10^{-14}$ (molecules cm^{-3})	$[Br_2]_0 \times 10^{-14}$ (molecules cm^{-3})	$k_{C_4H_{10}O}/k_{C_8H_{18}}$	$k_{C_4H_{10}O} \times 10^{15}$ (cm^3 $molecule^{-1}$ s^{-1})
300.1	2.30	21.0	87.3	9.92	93.0
300.7	2.31	57.5	88.8	10.7	101
300.8	2.05	59.3	85.1	8.55	81.4
307.3	3.20	58.0	80.8	8.30	90.1
307.4	4.95	80.8	67.9	6.49	70.6
308.3	4.40	92.9	79.1	10.1	110
316.5	3.37	87.0	68.6	10.3	134
321.2	1.32	145	63.1	8.05	114
321.8	2.09	141	62.5	11.8	169
326.3	1.22	137	75.4	12.9	199
326.6	1.88	141	95.2	12.1	188
334.6	0.524	88.8	69.1	7.79	139
347.2	2.25	17.8	76.2	14.2	311
348.1	2.51	15.8	74.6	11.2	248
349.5	1.86	29.5	73.1	10.8	244

constant for the reaction of isooctane with Br relative to the corresponding reaction of isobutane to provide an internally consistent reference rate constant for use in the experiments with the ethers. The results are presented in Table 1 and in Figures 2a and 3. We have used the absolute rate constant of ref 15 in calculating the absolute rate constants for the reaction of Br with isooctane. While the results of refs 14 and 15 are in excellent agreement, those of ref 15 have been selected on the basis that they are likely to be less susceptible to interference from heterogeneous effects. The temperature dependence of the reference rate constant for the reaction of Br with isobutane is then given in the units cm^3 $molecule^{-1}$ s^{-1} by the relation $k = (1.61 \pm 0.60) \times 10^{-10} \exp(-(3.46 \pm 0.17) \times 10^3/T)$. In Figure 3, the rate constants for the reaction of Br with isooctane calculated on this basis from the relative values reported in ref 13 are also presented for comparison. In general, our values are displaced by ~16% below those of ref 13. While this difference is within the combined uncertainties of the two measurements, it is clear from the plot that the discrepancy is systematic. It could be due to a variety of small differences in the details of the apparatus and methods used and illustrates the desirability of using an internally consistent reference rate constant determination in order to minimize the accumulation of differences arising from the methods used in different laboratories. The absolute rate constant for the reaction of Br with isooctane, based on our measurements relative to isobutane and the reference values calculated from the data of ref 15, is given by $k = (3.34 \pm 0.59) \times 10^{-12} \exp(-(1.80 \pm 0.11) \times 10^3)$, again in the units cm^3 $molecule^{-1}$ s^{-1}. In this and the other experimental work reported here, the uncertainties reflect only the standard deviation at the 95% confidence level resulting from our experimental scatter.

Dimethyl Ether Measured Relative to Isooctane. The results obtained for the reaction of Br with dimethyl ether are presented in Table 2 and in Figures 2b and 3. The absolute rate constant for this reaction, based on the measured reference rate constants for the reaction of Br with isooctane, are given by $k = (3.8 \pm 2.4) \times 10^{-10} \exp(-(3.54 \pm 0.21) \times 10^3/T)$ in the units cm^3 $molecule^{-1}$ s^{-1}. The Arrhenius plot for the reaction of dimethyl ether is clearly steeper than that for the reaction of isooctane, indicating a somewhat larger activation energy for hydrogen abstraction from dimethyl ether. Although the rate constants for the reaction of Br with dimethyl ether are consistently smaller than those for the reaction of Br with isooctane over our experimental temperature range, it is clear that the reverse is expected to occur at temperatures that are only moderately higher than those accessible in our apparatus as a result of the significantly larger preexponential factor for the reaction of Br with dimethyl ether. Since the number of chemically equivalent methyl hydrogen atoms is significantly larger in isooctane than in dimethyl ether, there is evidently an entropic effect in addition to the simple statistical variation in the number of chemically equivalent hydrogen atoms available for abstraction. The results also suggest that the oxygen atom in dimethyl ether increases the energy required for hydrogen abstraction relative to the situation in isooctane.

Diethyl Ether Measured Relative to Isooctane. The results obtained for the reaction of Br with diethyl ether are presented in Table 3 and in Figures 2c and 3. The absolute rate constant for this reaction, based on the measured reference rate constants for the reaction of Br with isooctane, are given by $k = (2.8 \pm 2.7) \times 10^{-10} \exp(-(2.44 \pm 0.32) \times 10^3/T)$ in the units cm^3 $molecule^{-1}$ s^{-1}. The Arrhenius plot in Figure 3 for the reaction of Br with diethyl ether is clearly well above those for the other reactions in our experimental temperature range. Its slope is less than that for the reaction of dimethyl ether with atomic bromine, and the preexponential factor is clearly very different from the value that would be predicted from a simple statistical consideration of the number of hydrogen atoms available for abstraction. The smaller activation energy suggests that the oxygen atom in diethyl ether has less effect on the energy needed for hydrogen abstraction than was the case in the reaction of Br with dimethyl ether. Also indicated in Figure 3 are two rate constants measured for this reaction by Kondo and Benson[16] using the VLPR technique. These lead to the expression $k = 1.05 \times 10^{-10} \exp(-1.96 \times 10^3/T)$. Given the very different methods employed and the limited number of temperatures examined in this earlier work, the extent of agreement with our results is encouraging.

Discussion

The main reactions taking place in the reaction chamber are expected to be

$$RH_x + Br \rightarrow HBr + R_x^{\bullet} \tag{1}$$

$$RH_{ref} + Br \rightarrow HBr + R_{ref}^{\bullet} \tag{2}$$

$$R_x^{\bullet} + Br_2 \rightarrow R_xBr + Br \tag{3}$$

$$R_{ref}^{\bullet} + Br_2 \rightarrow R_{ref}Br + Br \quad (4)$$

$$R_x^{\bullet} + O_2 \rightarrow \text{products} \quad (5)$$

$$R_{ref}^{\bullet} + O_2 \rightarrow \text{products} \quad (6)$$

$$Br + \text{wall} \rightarrow Br\ \text{removal} \quad (7)$$

$$R_x^{\bullet} + \text{wall} \rightarrow R_x^{\bullet}\ \text{removal} \quad (8)$$

$$R_{ref}^{\bullet} + \text{wall} \rightarrow R_{ref}^{\bullet}\ \text{removal} \quad (9)$$

The assumption in the kinetic analysis is that reactions 1 and 2 are independent and are the only loss routes for RH_x and RH_{ref}. We verified in earlier work[10] that HBr is a major product of the reaction. Reactions of the free radicals $R_x^{\bullet}$ and $R_{ref}^{\bullet}$ with the parent compounds, RH_x and RH_{ref}, are expected to be simple hydrogen abstractions which would regenerate the parent reactant and replace the free radical reactant with another one. Thus, these reactions would have no net effect on the concentration of RH_x or RH_{ref}. Reactions 3 and 4 regenerate Br and so function both to scavenge organic free radicals and to maintain a constant concentration of Br. They provide no new reactions with the parent reactants and would not be expected to alter the rate of loss of RH_x relative to RH_{ref}. The molecular products of reactions 3−6 are not expected to react with the parent reactants, RH_x and RH_{ref}, although they might react with Br. While this would decrease the concentration of Br, it should not affect the relative rates of removal of RH_x and RH_{ref} and would therefore not affect the measured relative values of the rate constants. Similarly, the heterogeneous reactions 7−9 should not affect the relative rates of removal of the parent reactants. Reactions 5 and 6 are expected to be the dominant sinks for organic free radicals under most of our conditions, and their potential to produce OH radicals which could affect the relative rate measurements has been discussed in the Experimental Section. As indicated there, the extent of reaction was kept sufficiently small that the intervention of such secondary reactions leading to additional consumption of the organic reactant was not evident.

The number of channels available to reactions 1 and 2 will depend on the nature of the organic reactant in several ways which require discussion. The primary reference reaction is that of Br with isobutane. Isobutane has two kinds of abstractable hydrogen atoms; the CH_3 hydrogens which are primary and the CH hydrogen which is tertiary. While this would provide two channels for reaction with different rate constants, the sole purpose of the reaction of Br with isobutane is to provide an accurately characterized reference reaction to enable calculation of absolute rate constants from the measured relative rate constants. While the reported rate constants for the reaction of Br with isobutane are composite values for two channels, the accuracy of their application here in calculating absolute rate constants for other reactions does not depend on the mechanistic details of the reaction.

In the reaction of Br with isooctane, all the methyl groups are equivalent so there is only one channel available for reaction. The temperature dependence of the rate constant for this reaction therefore provides Arrhenius parameters as well as entropies and enthalpies of activation for a single, well-defined reaction channel. Consequently, this reaction is very useful as a reference point for comparison with the other reactions studied. By contrast, dimethyl ether contains two equivalent methyl groups but provides as well the possibility of complex formation via the oxygen atom as will be discussed shortly. The result is the possibility of two reaction channels: one involving direct abstraction of a hydrogen atom and a second in which hydrogen abstraction is mediated by complex formation involving the oxygen atom. The reaction of Br with diethyl ether presents the additional complication of two kinds of C−H bonds. Abstraction of the CH_2 hydrogen atoms adjacent to the ether oxygen is likely to be both direct and mediated by complex formation. Abstraction of the CH_3 hydrogen atoms is less likely to be mediated by complex formation since these hydrogen atoms are located farther from the oxygen atom, although there are conformations in which complex formation might also be possible. As many as four reaction channels could be involved in the reaction of Br with diethyl ether.

The reaction of Br with CH_3OH provides a useful system for comparison with the reactions of Br with the ethers. The reaction with methanol has received both careful experimental study as a function of temperature[17] and detailed theoretical analysis.[8] While there are in principle two kinds of hydrogen atom that might be abstracted by a bromine atom, it is clear from experiment that at temperatures reasonably close to 300 K as in our experiments the dominant path by far is abstraction of the C−H hydrogen atoms. There are, however, two channels by which this might take place: direct abstraction of a C−H hydrogen and abstraction mediated by complex formation via the oxygen atom. In some respects, the ethers investigated in our experiments might be regarded as substituted alcohols. One advantage of dimethyl ether compared to methanol is that there is only one kind of hydrogen atom available for abstraction, and there is no O−H hydrogen available for hydrogen bonding. The usefulness of the reaction of Br with methanol for comparison with the reactions of the ethers is clear. We will therefore examine the trends in entropies and enthalpies of activation for the four reactions Br + isooctane, Br + methanol, Br + dimethyl ether, and Br + diethyl ether. These parameters are presented in Table 4. The values for the reaction of Br with methanol have been calculated from the work of ref 17 while the other values are based on our experimental work.

Two trends are evident in the parameters presented in Table 4. The smallest activation energy is for isooctane with the values increasing in the order diethyl ether < dimethyl ether < methanol. Evidently, increasing the size of the alkyl group attached to the oxygen atom decreases the activation energy of the reaction. The entropies of activation are very similar for the reactions of methanol, dimethyl ether, and diethyl ether and are significantly less negative than the entropy of activation for the reaction with isooctane. Although the preexponential factors were not normalized for the varying number of C−H bonds in the reactant, when the preexponential factor is divided by the number of C−H bonds, as in the last column of the table, the trend persists. It is clear that the presence of an oxygen atom in the organic reactant makes the entropy of activation less negative than was the case in the reaction of atomic bromine with isooctane. This implies that there are structural differences between the transition states of a hydrocarbon such as isooctane and an oxygenated organic compound such as an alcohol or an ether.

It was noted earlier that the reaction of atomic bromine with methanol has received a thorough theoretical analysis,[8] and the results of that work are now reviewed briefly. The energies of a series of molecular complexes and transition states for Br + CH_3OH were evaluated, and the schematic energy profile for abstraction of a hydrogen atom from CH_3, based on their calculations, is presented in Figure 4. In this picture, two

TABLE 4: Transition-State Theory Parameters for the Reactions of Atomic Bromine with Isooctane, Dimethyl Ether, Diethyl Ether, and Methanol[a]

reaction	enthalpy of activation (kJ mol^{-1})	entropy of activation (J K^{-1} mol^{-1})	entropy of activation per C−H bond (J K^{-1} mol^{-1})
$Br + iso\text{-}C_8H_{18} \rightarrow HBr + C_8H_{17}$	12.5 ± 0.9	−134 ± 3	−158 ± 3
$Br + (CH_3)_2O \rightarrow HBr + CH_2OCH_3$	27 ± 2	−96 ± 6	−114 ± 6
$Br + (C_2H_5)_2O \rightarrow HBr + C_2H_4OC_2H_5$	18 ± 3	−96 ± 8	−115 ± 8
$Br + CH_3OH \rightarrow HBr + CH_2OH$	33 ± 1	−98 ± 2	−107 ± 2

[a] The parameters for the reaction with methanol are calculated from the kinetic data of ref 17.

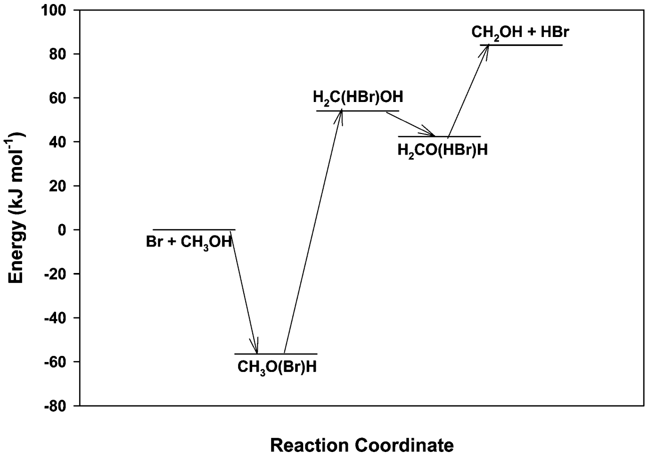
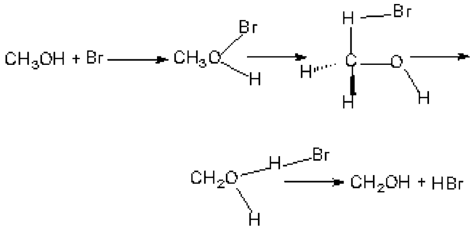


Figure 4. Schematic energy profile for the reaction of CH_3OH with atomic bromine, taken from ref 8.

channels are possible for the interaction of a bromine atom with methanol. In one channel, the bromine atom first attaches to the oxygen atom forming a comparatively stable complex $CH_3O(Br)H$. Next, the bromine atom transfers to one of the methyl hydrogen atoms, giving the transition state which then forms a relatively weakly bound complex $CH_2O(HBr)H$. Finally, this complex eliminates HBr giving the products HBr + CH_2OH. This sequence of reactions involving the $CH_3O(Br)H$ complex is



indicating in a general way the structural changes that are proposed to take place. In the second channel, the reaction bypasses this complex and proceeds directly to the transition state. The rate of loss of reactants in the first channel will depend on the rate of rearrangement of the $CH_3O(Br)H$ complex which has a large activation energy. On the other hand, the second channel produces the transition state directly and has a significantly smaller activation energy. The observation that the energy barrier for decomposition of the $CH_3O(Br)H$ complex to reactants is significantly less than that for its rearrangement to give the transition state leads to the conclusion that formation of this complex is not an effective route to reaction products.

It seems reasonable to assume that the reactions of the ethers with atomic bromine are at least qualitatively similar to the corresponding reaction of methanol. In that case, the activation energy for direct formation of the transition state would also be significantly smaller than that for the channel in which the bromine atom first forms a complex with the oxygen atom. In the discussion which follows, it will be assumed that the measured rate constants refer only to the channel in which the transition state is formed directly. In comparing the reactions of methanol and the ethers, the activation energies of the reactions of Br with methanol and with dimethyl ether are nearly the same, with that for methanol being slightly larger than that for dimethyl ether. In both cases, only abstraction of a CH_3 hydrogen atom is possible. The transition state in the reaction of Br with methanol is viewed as being a configuration somewhat earlier on the reaction coordinate than the $CH_2O(HBr)H$ complex. This complex is regarded as a species in which HBr is hydrogen bonded to the oxygen atom of methanol, and it may be that there is already some hydrogen bonding in the transition state. The extent of this hydrogen bonding would affect the energy of the transition state and therefore the activation energy. The influence of hydrogen bonding between the forming HBr molecule and the oxygen atom in dimethyl ether would be similar to that in methanol. However, in the reaction of diethyl ether with atomic bromine the interaction of HBr with the oxygen in the transition state is expected to have only a small effect on the energy of the transition state for those interactions in which a CH_3 hydrogen atom is removed. This hydrogen-bonding interaction is expected to be stronger for abstraction of the CH_2 hydrogen atoms, but these C−H bonds are also expected to be somewhat weaker than those in dimethyl ether. The activation energy for the reaction with diethyl ether is significantly smaller than that for the reactions of methanol and dimethyl ether, possibly reflecting in part a combination of a smaller activation energy for the channel in which a CH_2 hydrogen is removed and weaker hydrogen bonding between HBr and the oxygen atom in the transition state for the channel in which a CH_3 hydrogen is removed. The smallest activation energy is found for the reaction of atomic bromine with isooctane. In this case, there is no possibility of enhanced stability of the transition state by interaction with an oxygen atom. The small activation energy relative to the reactions of Br with smaller alkanes reflects the established trend of decreasing activation energy with increasing number of carbon atoms in the alkane.[4]

A similar situation exists in comparison of the entropies of activation for these reactions. In this case, the situation is complicated by the availability of several C−H bonds which could participate in the reaction. If the number of hydrogen atoms available for abstraction by Br is n, then the preexponential factor for the reaction would be $n(kT/h)\exp(\Delta S^{\ddagger}/R)$. For methanol, $n = 3$ while for dimethyl ether it is 6 and for isooctane it is 18. In those cases, the entropy of activation per C−H bond would be calculated by subtracting $R \ln(n)$ from the overall entropy of activation. In the case of diethyl ether, the situation is less clear because there are two different kinds of C−H bond and therefore two different reaction channels. Nevertheless, since the calculation involves the logarithm of the number of C−H bonds, the difference between assuming ten C−H bonds or six C−H bonds is within the uncertainty of the measurements. Table 4 provides both the total entropy of activation and the entropy of activation based on the rate constant for attack on one C−H bond. The entropies of activation are similar for methanol and the ethers, but the entropy of activation for the reaction of isooctane is significantly more negative than the values for the other reactions. This suggests that the compounds containing an oxygen atom have transition states of similar structures while the transition state for the reaction of isooctane has a tighter structure (more negative entropy change) relative to the reactants than those for the compounds containing the oxygen atoms. This is consistent with the conclusion reached by Kondo and Benson,[16] on the basis of thermodynamic arguments, that the transition state in the reaction of Br with diethyl ether is relatively loose.

Reactions of atomic bromine with organic compounds typically have small rate constants compared to the corresponding reactions of other atmospherically relevant reactive species such as Cl and OH. This has often been attributed to the endothermicity of the reactions of atomic bromine as opposed to the exothermicity of the reactions of these other species. The reactions of the smaller alkanes with Br are typically endothermic by roughly 30−40 kJ mol^{-1}, as are the reactions of alcohols and ethers, suggesting that the activation energies of these reactions should be of at least this order of magnitude. In the case of reactions of Br with aldehydes, the reactions are endothermic by only a few kJ mol^{-1}, and the activation energies of these reactions are apparently of about the same magnitude as the endothermicity.[18] As Table 4 suggests, the activation energies for the reactions of atomic bromine with methanol and with the ethers studied in our experiments are much less than the endothermicity of these reactions. This would be consistent with a complex mechanism in which the rate-determining step has an activation energy that is significantly smaller than the endothermicity of the reaction. The results in Table 4 indicate that the reaction of atomic bromine with isooctane has an activation energy that is significantly smaller than that of the other reactions in the table and that the entropy of activation for the reaction of isooctane is significantly more negative than the approximately constant value of the entropy of activation for the other reactions in the table. This suggests that the mechanism for the reaction of atomic bromine with isooctane is different from that for the other reactions. In the case of the reaction with isooctane, formation of complexes analogous to those described for the reaction of Br with methanol and with the ethers is not possible.

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