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A Kinetic Analysis of the Effect of O_2 on the Reactions of Atomic Bromine with Some Hydrocarbons and Ethers

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The kinetics of the reactions of atomic bromine with ethene, 2-methylpropane, dimethyl ether, and diethyl ether have been studied at 298 K in a 70-L photochemical reaction chamber with the relative rate method. Chemical analysis was by gas chromatography with a flame ionization detector. The effects of bromine and oxygen partial pressure and of the choice of reference reactant on the numerical values of the rate constants obtained have been evaluated. The results are analyzed to obtain limiting values of the rate constant ratio that are independent of the concentration of O_2 and do not depend on the mechanism used to represent the overall reaction. The following rate constants were obtained at 298 K by using the well-established rate constant for the reaction of Br with 2-methylpropane as the primary reference: Br + $(CH_3)_2O$, $k_{298} = 9.43 \times 10^5$ L mol^{-1} s^{-1} ± 2%; Br + $(C_2H_5)_2O$, $k_{298} = 1.41 \times 10^7$ L mol^{-1} s^{-1} ± 6%. With the rate constants for Br + $(CH_3)_2O$ as a secondary reference value, the rate constant at 298 K for Br + $(C_2H_5)_2O$ was 1.27×10^7 L mol^{-1} s^{-1} ± 8% calculated at a limiting high concentration of O_2. When Br + $(C_2H_5)_2O$ was measured relative to Br + C_2H_4, the rate constant at 298 K, calculated for limiting high concentrations of O_2, ranged from 4.7×10^7 to 1.2×10^7 L mol^{-1} s^{-1} depending on the rate constant chosen for the reference reaction. The sensitivity to oxygen concentration of the rate constant for the reaction of Br with ethene depends on the concentration of Br_2 used as the photolytic source of atomic bromine. When the reaction of Br with an organic reactant is sensitive to the presence of oxygen, measurements at O_2 concentrations much larger than those in synthetic air may be required to obtain reliable rate constants for the initial reaction of Br with the organic reactant.

Introduction

Kinetic study of reactions of atomic bromine has interested physical chemists for a long time, playing an important part in establishing the fundamentals of chemical kinetics.[1] Measurements of rate constants of halogen atom reactions have also played a significant role in determining the enthalpies of formation of small hydrocarbon free radicals.[2,3] Since the early 1980s, there has been a growing realization of the importance of atomic bromine in ozone destruction cycles in the atmosphere[4−8] and this has sparked considerable interest in obtaining improved experimental measurements of the rate constants of reactions of atomic bromine.

The range of experimental techniques available for use in studying reactions of atomic bromine with organic reactants includes thermal and photochemical methods, flash photolysis, and discharge-flow experiments with measurement of atomic bromine concentrations by resonance fluorescence or determination of loss of the organic reactant or formation of reaction products by gas chromatography, infrared spectrometry, or mass spectrometry. Details of the applications of these methods can be found in the numerous references provided in ref 9. Despite this range of available methods, most of the rate constants currently available have been determined by the relative rate method.[9−11] These relative rate measurements are often made in synthetic air,[10,11] partly because of the obvious relevance to atmospheric chemistry. However, air is also used on the principle that the presence of a large concentration of O_2 will result in scavenging organic free radicals, formed in the initial Br atom attack, converting them to peroxy radicals which are believed to be generally less reactive[12] than their precursors. These peroxy radicals then decompose, typically by self-reaction, to yield a wide range of products among which aldehydes and carboxylic acids are common.[11]

Despite the widespread use of synthetic air as a medium in which to study the kinetics of atomic bromine reactions, examination of the role of O_2 in their reaction mechanisms and kinetics has largely been restricted to experiments in synthetic air on the addition of Br to organic compounds containing double bonds. Two studies, however, have made a systematic evaluation of the effect of O_2 on the kinetics of the reaction of Br with ethene over a wide range of oxygen concentrations. Barnes et al.[13] used the relative rate method to measure the rate constants for reactions of Br with a series of alkenes and alkynes as a function of pressure, temperature, and O_2 concentration. They interpreted their results in terms of a two-step process in which the Br atom first adds reversibly to the organic reactant forming a complex that then decomposes to the observed reaction products. The presence of O_2 in the reaction mixture increased the numerical values of the measured rate constants relative to those which had been reported earlier. Yarwood et al.[14] also measured the rate constant for the reaction of Br with ethene as a function of O_2 concentration but did not quantitatively analyze the variation that they observed. Although there is some information about the effect of O_2 on the kinetics of reactions of Br with unsaturated compounds, we are unaware of a comparable study of the effect of O_2 on the kinetics and mechanisms of the reactions of Br with saturated organic compounds.

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The reactions of Br with organic compounds have a qualitative similarity to the corresponding reactions of other electrophilic reagents such as $O(^3P)$, NO_3, OH, and Cl. However, while the addition of Br to π bonds is rapid, the hydrogen abstraction reactions that are common for $O(^3P)$, OH, and Cl are often endothermic for Br. As a result, the reactions of Br with saturated hydrocarbons are generally slower than the corresponding reactions of $O(^3P)$, OH, and Cl. The presence of an electron-rich heteroatom such as oxygen appears to enhance the rate of hydrogen abstraction by Br as indicated in relative rate measurements for its reaction with diethyl ether.[15] A correlation of the rate constants for a large number of reactions of Br with organic compounds with the rate constants of the corresponding reactions of $O(^3P)$, OH, and NO_3 has also been reported.[16] An effort to construct a similar correlation with the rate constants for reactions of Cl atoms was not successful because these reactions are so rapid that the structural selectivity found in the reactions of $O(^3P)$, OH, NO_3, and Br is largely lost in the reactions of atomic chlorine. A recent application of the frontier molecular orbital approach to the addition reactions of $O(^3P)$, OH, Cl, Br, and NO_3 with chloroethenes[17] addresses the relationship of the reactivity of these species to the energy difference between the highest occupied molecular orbital of the olefin and the singly occupied molecular orbital of the adduct formed in the reactions with these atomic and free radical species. There is also an extensive literature on the theory of addition reactions of OH and Cl with systems containing π bonds and this has been well summarized in other recent publications.[18,19] However, little information is available on the effect of the presence in organic reagents of heteroatoms such as oxygen on the correlations of Br atom reactivity with that of other atomic and free radical species.

A frequent source of difficulty in making relative rate measurements of reactions of atomic bromine is the scarcity of reliable reference reactions with rate constants of appropriate magnitude. For best results, relative rate measurements require reliable reference rate constants within about a factor of 5 of the rate constant being measured. The rate constant for the reaction of Br with 2-methylpropane has been reasonably well established as a function of temperature by direct rather than relative measurement.[20] Ethene has also found use as a reference compound.[15] The value of its rate constant for reaction with Br was reported by Barnes et al.[13] to be 9.6×10^7 L mol^{-1} s^{-1} (1.6×10^{-13} cm^3 molecule^{-1} s^{-1}) based on an extensive relative rate study of the role of O_2 in the reactions of Br with a series of alkenes and alkynes. However, a lower value of 7.41×10^7 L mol^{-1} s^{-1} (1.23×10^{-13} cm^3 molecule^{-1} s^{-1}) has recently been reported[11] that agrees well with an earlier value[14] of 7.8×10^7 L mol^{-1} s^{-1} (1.3×10^{-13} cm^3 molecule^{-1} s^{-1}), both values measured in synthetic air. Bierbach et al. have compiled a useful list of reference rate constants[10] but it is desirable to have a wider range of appropriate reference values available both to serve as a cross check and to aid in resolving experimental difficulties such as chromatographic resolution.

We report here results obtained by using the relative rate method to evaluate the effect of O_2 on the rates and mechanisms of reactions of Br with a selection of hydrocarbons and ethers. The results are used to examine the validity of using large concentrations of O_2 to isolate the rate constant of the initial Br atom attack on the organic reactant. Rate constants are reported at 298 K, which will be useful as reference values in other experiments.

Experimental Section

The experiments were made in a cylindrical Pyrex reaction vessel with a volume of approximately 70 L. The reaction vessel was surrounded by four 40-W fluorescent lamps. The useful wavelength range of these lamps was from approximately 350 to 650 nm with maximum intensity at approximately 460 nm and four strong lines at 365, 405, 436, and 546 nm corresponding to emission from mercury present in the fluorescent lamps. This provided good overlap with the Br_2 absorption spectrum ($\sim$360 to 550 nm, $\lambda_{max} \sim 410$ nm) but was well removed from spectroscopic transitions of the organic substrates ensuring that only photolysis of Br_2 was likely to be significant.

The experiments were at ambient temperature, 300 ± 2 K, and at total pressures close to atmospheric (92 to 97 kPa) except in those experiments which were intended to search for pressure dependence of the rate constants. Temperature uniformity and constancy during an experiment could be monitored by a set of three thermocouples evenly spaced along the axis of the reaction vessel. Pressures were measured by a 10-Torr Baratron capacitance manometer and a piezoelectric pressure transducer that was calibrated daily. We estimate the precision of the Baratron measurements to be ± 0.05 Torr and that of the piezoelectric transducer to be ± 5 Torr. Reaction mixtures were made from dilute mixtures of Br_2 and of the organic reactants prepared in argon and stored in 12-L Pyrex bulbs. The uncertainty in the concentrations of the reaction mixtures prepared in this way is estimated to be $\pm 1\%$. The entire gas handling system was grease-free and mercury-free and used Teflon stopcocks exclusively. In a typical experiment, small pressures of the Br_2 and organic reactant mixtures were added to the reaction chamber, followed by the desired amount of O_2, and the chamber was brought to a total pressure of approximately 1 atm by admitting argon rapidly to provide turbulent mixing. The system was allowed to stand for at least 15 min after filling to ensure thorough mixing. Experiments in which the mixture was allowed to stand for varying periods of time as long as an hour or more gave results that were indistinguishable from those obtained after 15 min.

Chemical analysis of the organic compounds was by gas chromatography employing a Perkin-Elmer Sigma 3 gas chromatograph equipped with a flame ionization detector and an 8 ft × 1/8 in. column packed with SP1000. Resolution of the analyte peaks was achieved by temperature programming (40 °C for 3 min, ramp to 100 °C at 30 °C per minute, hold at 100 °C). This program provided good separation in a convenient length of time and permitted measurement of the relevant peak areas under isothermal conditions, thereby avoiding the uncertainty associated with measurement of peak areas during the temperature ramp. Samples were removed to a gas sample loop for analysis. The amount of sample removed for analysis was sufficiently small that several consecutive photolysis experiments could be made on the same reaction mixture without appreciably altering the total pressure in the reaction chamber. Replicate gas chromatograms gave a typical reproducibility of $\pm 10\%$ or better, depending on the relative magnitudes of the analyte concentrations to be measured. Quartz windows mounted on the ends of the reaction chamber also allowed spectrophotometric measurement of the Br_2 concentration before and after an experiment. Infrared spectra, used for qualitative examination of the mixtures before and after reaction, were obtained with a Nicolet Magna 560 FTIR spectrometer. In these experiments, samples were removed from the reaction chamber to a standard infrared gas cell with a path length of 10 cm equipped with 2.5 cm diameter KBr windows and used in a single pass configuration. The spectral resolution was 2 cm^{-1} and as many as 200 interoferograms were summed to obtain an acceptable signal-to-noise ratio. Spectra were scanned from 4000 to 400 cm^{-1} but only the region from 4000 to 2000 cm^{-1} was used because the complexity of the spectra at smaller wavenumbers prevented their use to provide an unequivocal identification of the components of the mixtures. When more intense spectra were required, reaction mixtures were prepared directly in the gas cell, using ratios of reactant to Br_2 that were similar to those used in the photolysis chamber but with larger absolute concentrations. Spectra were then obtained before photolysis and after a series of increasing photolysis periods. These spectra were not used for quantitative analysis and their appearance was qualitatively the same as the spectra obtained with samples taken directly from the photolysis chamber. Typical spectra are presented in Figures 2 and 3.

All kinetic experiments were made with a sufficiently large partial pressure of Br_2 that its concentration remained nearly constant during an experiment as required to ensure a constant concentration of Br and consequent first-order consumption of the organic reactants. Typical concentrations of Br_2 and the organic reactant were of the order of 10^{-5} and 10^{-6} mol L^{-1}, respectively. This provided concentrations of atomic bromine of approximately 10^{-10} to 10^{-11} mol L^{-1} as estimated from the slopes of the measured pseudo-first-order plots for loss of the organic reactant and the numerical values of the relevant rate constants. Photolysis times ranged from about 1 min to over 1 h. Blank experiments were made for each reactant to determine whether there was a significant dark reaction and to verify that the organic reactant did not undergo measurable photolysis. The dark reactions required preparation of a mixture of the organic reactant and Br_2 at concentrations typical of a photolysis experiment. The concentrations of the organic reactant and of Br_2 were measured after mixing and again after the mixture had been allowed to stand in the dark reaction vessel for at least 1 h. The photolysis experiments required addition of the organic reactant and argon to the reaction vessel without Br_2 followed by irradiation with the fluorescent lamps for at least 1 h. The concentration of the organic reactant was measured before and after irradiation. None of the organic reactants examined showed photochemical decomposition and the only reactants tested which showed a significant dark reaction were isopropyl alcohol and diisopropyl ether. Consequently, kinetic data are not reported for these latter reactants.

Kinetic analysis is based on the assumption of loss of the organic reactants in the reactions

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

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

in which R_x is the compound whose rate constant it is desired to measure and R_{ref} is the reference reactant whose rate constant must be known to put k_1 on an absolute basis. On the assumption that these are the only reactions consuming Br, R_x, and R_{ref} and that R_x and R_{ref} are not regenerated, integration of the rate laws gives the following relation from which the rate constants k_1 can be calculated.

$$\ln\left\{\frac{[\mathrm{R}_x]_{t_0}}{[\mathrm{R}_x]_t}\right\} = \frac{k_1}{k_2}\ln\left\{\frac{[\mathrm{R}_{\mathrm{ref}}]_{t_0}}{[\mathrm{R}_{\mathrm{ref}}]_t}\right\} \tag{3}$$

A plot of $\ln\{[R_x]_{t0}/[R_x]_t\}$ against $\ln\{[R_{ref}]_{t0}/[R_{ref}]_t\}$ should then give a straight line with zero intercept and slope k_1/k_2 from which the value of k_1 is readily obtained by using the known value of the reference rate constant. Several assumptions are inherent in this approach. Free radical reactions are seldom one-step processes. There are situations in which the free radical products of a reaction may undergo relatively rapid reactions with the organic reactant so that more than one molecule of this reactant is consumed for each occurrence of the kinetically limiting step. The rate constant calculated in this case is a composite quantity incorporating parameters additional to the absolute rate constant. Since both the reference compound and the “unknown” undergo reaction simultaneously with Br, the use of eq 3 can produce rate constants that vary with reaction conditions such as pressure and chemical composition. There is also the possibility that the reaction products or intermediates in the reaction of one reactant with Br may interfere with the reaction of the other reactant with Br. It is assumed that the experimental conditions are such that these kinetic complications are negligible or that the method of data analysis is able to compensate for their effects. Investigation of the extent to which these assumptions are valid forms an important component of this work.

Experiments with mixtures of ethene and diethyl ether in which the extent of consumption of the organic reactant was large sometimes showed pronounced curvature of the relative rate plots such as those in Figure 1a. This effect was most noticeable at O_2 partial pressures greater than approximately 10% of the total and its severity increased with increasing partial pressure of O_2. We attribute this curvature to secondary reactions involving oxidation products and reaction conditions were selected that avoided this complication. In all experiments, the extent of reaction was restricted to much smaller values than those at which appreciable curvature of the relative rate plots was detected. The precision of the slopes of these plots was typically about ±10% or less although in a few instances the precision was closer to ±20%. This is indicated in Tables 1 to 3. A second factor affecting the accuracy of the results is our lack of a reference compound with a rate constant for its reaction with Br lying between those for the reaction of Br with diethyl ether and for the corresponding reaction with dimethyl ether. In the experiments in which mixtures of diethyl ether with dimethyl ether or with 2-methylpropane were used, the extent of consumption of dimethyl ether or of 2-methylpropane was only approximately 10% of the consumption of diethyl ether. This led to a much greater contribution of chromatographic uncertainty to the relative rate measurements made with those mixtures and this is reflected in the greater scatter in the results obtained with those mixtures compared with the precision of the results obtained with mixtures of diethyl ether with ethene or of dimethyl ether with 2-methylpropane in which the rate constants for reaction of Br with the organic reactants have more comparable numerical values.

The compounds whose reactions with Br were examined are ethene (Matheson, 99%), 2-methylpropane (Aldrich, 99.995%), dimethyl ether (Aldrich, 99+%), diethyl ether (ACP, 99.0%), methylene chloride (ACP, 99.5%), chloroform (Anachemia, 99.7%), methanol (Caledon, 99.8%), ethanol (Consolidated Alcohols, absolute), isopropyl alcohol (Caledon, 99.8%), diisopropyl ether (Fluka, 99%+), and 1,4-dioxane (Fluka, 99.8%). These were purified by thorough degassing of the liquids or freeze−pump−thaw cycles for the gases followed by distillation into the storage vessels. Of these, methylene chloride and chloroform reacted too slowly to measure with our apparatus and available reference compounds. We estimate an upper limit of the rate constant for the reactions of these compounds with atomic bromine to be approximately 10^4 L mol^{-1} s^{-1}. Methanol,

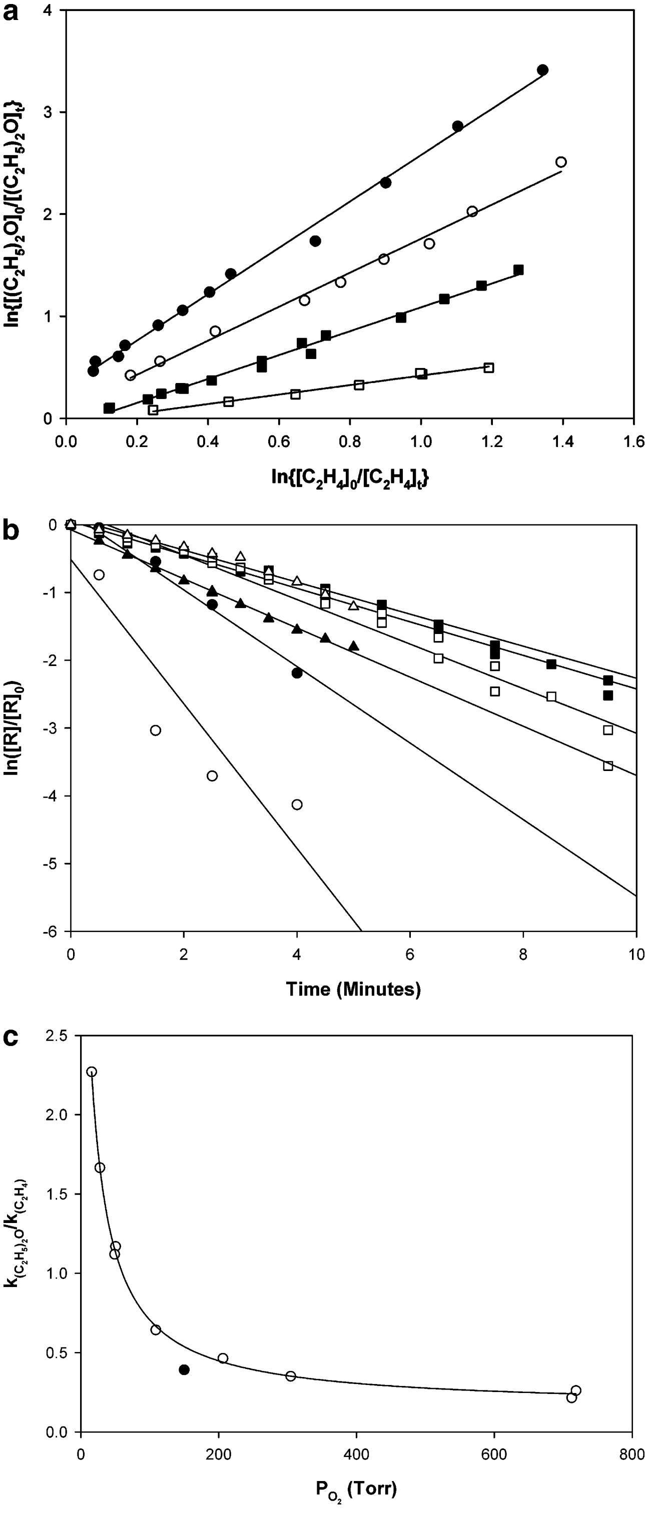

Figure 1. (a) Typical relative rate plots for the reactions of Br with diethyl ether and ethene. For all experiments, $[Br_2] \approx 2 \times 10^{-5}$ mol L^{-1}, $[C_2H_4]_0 \approx 1 \times 10^{-6}$ mol L^{-1}, $[(C_2H_5)_2O]_0 \approx 1 \times 10^{-6}$ mol L^{-1}, total pressure ≈ 720 Torr; (●) 15 Torr of O_2, (○) 30 Torr of O_2, (■) 50 Torr of O_2, (□) 200 Torr of O_2. (b) Typical pseudo-first-order plots of reactant loss at various O_2 partial pressures. For the open symbols, R is diethyl ether while the filled symbols represent ethene. For all experiments, $[Br_2] \approx 2 \times 10^{-5}$ mol L^{-1}, $[C_2H_4]_0 \approx 1 \times 10^{-6}$ mol L^{-1}, $[(C_2H_5)_2O]_0 \approx 1 \times 10^{-6}$ mol L^{-1}, total pressure ≈ 720 Torr; (●, ○) no added O_2, (■, □) 50 Torr of O_2 added, (▲, △) 200 Torr of O_2 added. (c) Variation of rate constant ratio with O_2 partial pressure. For all experiments, $[Br_2] \approx 2 \times 10^{-5}$ mol L^{-1}, $[C_2H_4]_0 \approx 1 \times 10^{-6}$ mol L^{-1}, $[(C_2H_5)_2O]_0 \approx 1 \times 10^{-6}$ mol L^{-1}, total pressure ≈ 720 Torr; (○) this work, (●) data reported in ref 16.

ethanol, and 1,4-dioxane presented difficulty in obtaining chromatographic resolution, and isopropyl alcohol and diisopropyl ether had an unacceptably large dark reaction with Br_2. These compounds were therefore excluded from the current investigation and the remaining compounds, ethene, 2-methylpropane, dimethyl ether, and diethyl ether, were selected for more thorough study. The Br_2 (ACP, 99.5%) was purified by freeze−pump−thaw cycles followed by distillation into the storage vessel. The other gases, He (Praxair, 99.9995%), O_2 (Praxair, 99.9995%), and Ar (Praxair, 99.9995%), were used without further purification.

Results

The kinetic data are presented in four pairs: diethyl ether measured relative to ethene, diethyl ether measured relative to dimethyl ether, dimethyl ether measured relative to 2-methylpropane, and diethyl ether measured relative to 2-methylpropane. In each case, relative rate plots are presented as a function of O_2 concentration and the pseudo-first-order loss of each organic reactant is verified. Since the concentration of atomic bromine is expected to remain constant for a given series of photolysis experiments made with use of the same reaction mixture, the pseudo-first-order rate constants measured for the individual organic reactants, R, are the product $k_R[Br]$ and variations in these first-order rate constants with varying reaction conditions, such as the concentration of O_2, reflect variations in either the concentration of atomic bromine or the effective rate constant k_R. This provides a means of assessing separately the effect of a change in reaction conditions on the values of [Br] and k_R since, for a given pair of reactants, changes in [Br] have no effect on the rate constant ratio while changes in k_R will affect the value of that ratio. Measurement of some of the rate constants relative to more than one reference reaction allows examination for a dependence of the rate constant ratio on the choice of reference reactant.

Diethyl Ether Measured Relative to Ethene. The good linearity of the log−log plots in Figure 1a of relative concentrations of diethyl ether and ethene suggests that eq 3 is followed over a wide range of O_2 concentrations. The slopes of these plots decrease systematically with increasing concentration of added O_2. As indicated in Figure 1b, both diethyl ether and ethene show pseudo-first-order behavior. In both cases, the first-order rate constant decreases with increasing O_2 concentration, the first-order rate constant for diethyl ether loss decreasing more rapidly and reaching a limiting value at smaller O_2 concentrations than that for ethene. The rate constant ratio for these reactions is plotted against partial pressure of O_2 in Figure 1c, in which the ratio reported by Wallington et al.[15] is also indicated. These results are also presented in Table 1. The limiting value of the rate constant ratio obtained in our experiments is clearly in good agreement with their reported value. The observation that the rate constant for the reaction of Br with diethyl ether decreases relative to that for the reaction of Br with ethene is qualitatively consistent with the oxygen dependence of the rate constant for the reaction of Br with ethene reported by Barnes et al.[13]

Diethyl Ether Measured Relative to Dimethyl Ether. The reaction of Br with C_2H_4 has been postulated to occur by formation of an unstable adduct that then yields products or decomposes back to reactants.[13] The effects of O_2 concentration and variation in pressure on the kinetics of this reaction have been interpreted via the reaction of O_2 with this adduct in competition with its other loss channels and this interpretation is still used to account for the O_2 dependence of the reactions of Br with alkenes and alkynes.[11] Measurement of the relative

TABLE 1: Rate Constant Ratios for the Reaction of Br with Diethyl Ether Measured Relative to the Reaction of Br with Ethene for Various Concentrations of O_2 at 300 ± 2 K and a Constant Pressure of 1 atm[a]

$[Br_2]_0$ (mol L^{-1})	$[(C_2H_5)_2O]_0$ (mol L^{-1})	$[C_2H_4]_0$ (mol L^{-1})	$[O_2]_0$ (mol L^{-1})	$k\{(C_2H_5)_2O\}/k\{C_2H_4\}$
1.65×10^{-5}	1.51×10^{-6}	1.12×10^{-6}	0	2.9 ± 0.5
1.36×10^{-5}	9.76×10^{-7}	1.05×10^{-6}	8.47×10^{-4}	2.27 ± 0.05
1.38×10^{-5}	1.02×10^{-6}	1.01×10^{-6}	1.49×10^{-3}	1.66 ± 0.05
1.32×10^{-5}	9.63×10^{-7}	1.06×10^{-6}	2.72×10^{-3}	1.17 ± 0.03
1.27×10^{-5}	9.97×10^{-7}	1.02×10^{-6}	2.64×10^{-3}	1.12 ± 0.04
1.38×10^{-5}	9.69×10^{-7}	1.05×10^{-6}	5.85×10^{-3}	0.64 ± 0.03
1.37×10^{-5}	9.74×10^{-7}	1.29×10^{-6}	1.11×10^{-2}	0.46 ± 0.02
1.49×10^{-5}	9.67×10^{-7}	9.94×10^{-7}	1.64×10^{-2}	0.35 ± 0.04
1.08×10^{-5}	1.54×10^{-6}	1.25×10^{-6}	3.83×10^{-2}	0.25 ± 0.08
1.18×10^{-5}	1.54×10^{-6}	8.61×10^{-7}	3.87×10^{-2}	0.26 ± 0.03

[a] Uncertainties are calculated at the 95% confidence level.

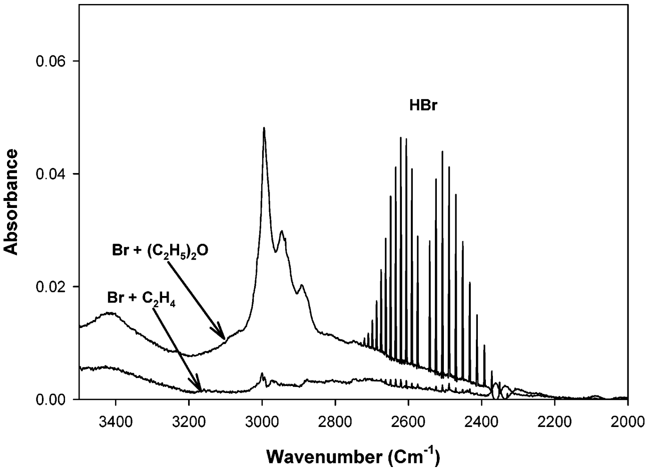

Figure 2. Infrared spectra of reaction products in the reaction of Br with ethene and with diethyl ether in the absence of O_2. For the reaction with ethene, $[C_2H_4]_0 = 4.6 \times 10^{-3}$ mol L^{-1} and $[Br_2]_0 = 1.5 \times 10^{-2}$ mol L^{-1}. For the reaction with diethyl ether, $[(C_2H_5)_2O]_0 = 3.2 \times 10^{-3}$ mol L^{-1} and $[Br_2]_0 = 1.8 \times 10^{-2}$ mol L^{-1}.

rate constants for the reactions of Br with dimethyl ether and diethyl ether provides a system in which, unlike the one just examined, both organic reactants are very similar and neither reactant contains double or triple bonds. Consequently, one might expect that the mechanisms of their reactions with Br would also show more similarity than the mechanisms for the reactions of Br with ethene and with diethyl ether and that the formation of an adduct would be much less important. Figure 2 indicates that the reaction of Br with ethene produced only a very small quantity of HBr, despite the nearly complete consumption of the ethene, while the reaction of Br with diethyl ether generated a substantial quantity of HBr. Figure 3 indicates that the reactions of Br with dimethyl ether and 2-methylpropane also generated a significant amount of HBr. Again, good linearity was obtained for the relative rate plots as indicated in Figure 4a. Good pseudo-first-order plots were also obtained for loss of both dimethyl ether and diethyl ether, as indicated in Figure 4b. The rate constant ratio for the reaction of Br with diethyl ether, relative to that for dimethyl ether, decreased with increasing O_2 concentration, as indicated in Figure 4c, although the decrease was not as dramatic as it was when the rate constant for $(C_2H_5)_2O$ was measured relative to that for C_2H_4. These results are also presented in Table 2. No dependence on total pressure was found over a range of 200 to 760 Torr in total pressure. Figure 4b indicates that the oxygen dependence is due to a modest decrease in the pseudo-first-order rate constant for the reactions of Br with both dimethyl ether and diethyl ether as the O_2 concentration increases, with the rate constant for the reaction of diethyl ether showing somewhat greater sensitivity to O_2 than that for the reaction of dimethyl ether. The much smaller sensitivity of the pseudo-first-order rate constants to O_2 compared to that observed for the mixtures of diethyl ether with ethene suggests that the rate constants measured for reactions of organic compounds with Br may depend on the nature of the reference reactant used for the determination.

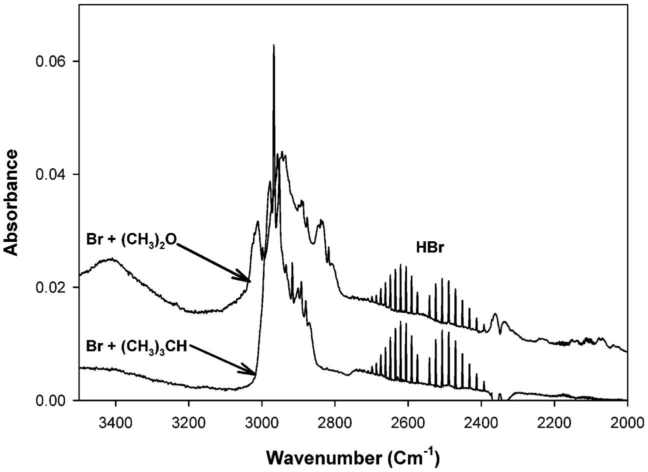

Figure 3. Infrared spectra of reaction products in the reaction of Br with dimethyl ether and with 2-methylpropane in the absence of O_2. For the reaction with dimethyl ether, $[(CH_3)_2O]_0 = 4.8 \times 10^{-4}$ mol L^{-1} and $[Br_2]_0 = 1.5 \times 10^{-2}$ mol L^{-1}. For the reaction with 2-methylpropane, $[(CH_3)_3CH]_0 = 4.7 \times 10^{-3}$ mol L^{-1} and $[Br_2]_0 = 1.7 \times 10^{-2}$ mol L^{-1}.

TABLE 2: Rate Constant Ratios for the Reaction of Br with Diethyl Ether Measured Relative to the Reaction of Br with Dimethyl Ether for Various Concentrations of O_2 at 300 ± 2 K and a Constant Pressure of 1 atm[a]

$[Br_2]_0$ (mol L^{-1})	$[(C_2H_5)_2O]_0$ (mol L^{-1})	$[(CH_3)_2O]_0$ (mol L^{-1})	$[O_2]_0$ (mol L^{-1})	$k\{(C_2H_5)_2O\}/k\{(CH_3)_2O\}$
2.37×10^{-5}	1.97×10^{-6}	3.19×10^{-6}	8.01×10^{-3}	18.7 ± 2.8
2.51×10^{-5}	2.42×10^{-6}	3.13×10^{-6}	7.78×10^{-3}	19.3 ± 2.3
8.31×10^{-5}	1.35×10^{-6}	8.81×10^{-6}	1.14×10^{-2}	20.1 ± 3.4
9.44×10^{-5}	2.31×10^{-6}	9.05×10^{-6}	1.15×10^{-2}	19.7 ± 1.4
9.35×10^{-5}	2.37×10^{-6}	9.20×10^{-6}	1.09×10^{-2}	17.4 ± 1.5
9.74×10^{-5}	2.56×10^{-6}	9.27×10^{-6}	2.71×10^{-3}	29.2 ± 3.2
1.04×10^{-4}	3.26×10^{-6}	9.20×10^{-6}	2.63×10^{-3}	28.4 ± 5.1
2.12×10^{-4}	3.08×10^{-6}	9.43×10^{-6}	1.09×10^{-2}	15.5 ± 1.4
5.23×10^{-5}	3.35×10^{-6}	9.56×10^{-6}	1.17×10^{-2}	15.1 ± 2.2
5.62×10^{-5}	3.41×10^{-6}	1.01×10^{-5}	1.13×10^{-2}	16.8 ± 2.0
1.19×10^{-4}	3.91×10^{-6}	1.01×10^{-5}	5.65×10^{-3}	23.2 ± 1.2
1.15×10^{-4}	3.72×10^{-6}	9.78×10^{-6}	1.70×10^{-2}	17.7 ± 1.6
1.12×10^{-4}	3.63×10^{-6}	9.67×10^{-6}	1.68×10^{-2}	16.2 ± 2.0
1.16×10^{-4}	3.49×10^{-6}	1.01×10^{-5}	9.69×10^{-4}	37.1 ± 5.1
1.15×10^{-4}	3.51×10^{-6}	9.61×10^{-6}	1.09×10^{-3}	35.2 ± 5.6

[a] Uncertainties are calculated at the 95% confidence level.

Dimethyl Ether Measured Relative to 2-Methylpropane. An accurate value of the absolute rate constant for the reaction of Br with 2-methylpropane is available[20,21] and has been used elsewhere as a reference value for relative rate measurements.[13,15] While the rate constant for this reaction at 300 K is too small to be useful as a reference for the reaction of Br with ethene, it is an excellent choice for use as a reference for the reaction of Br with dimethyl ether. As expected, the spectra of Figure 3 indicate that HBr is a major product of the reactions of both dimethyl ether and 2-methylpropane with atomic bromine. As Figure 5a illustrates, excellent linearity is again obtained for the relative rate plot. What is striking in comparison with the other systems studied is the observation that there is no detectable dependence of the rate constant ratio on the O_2

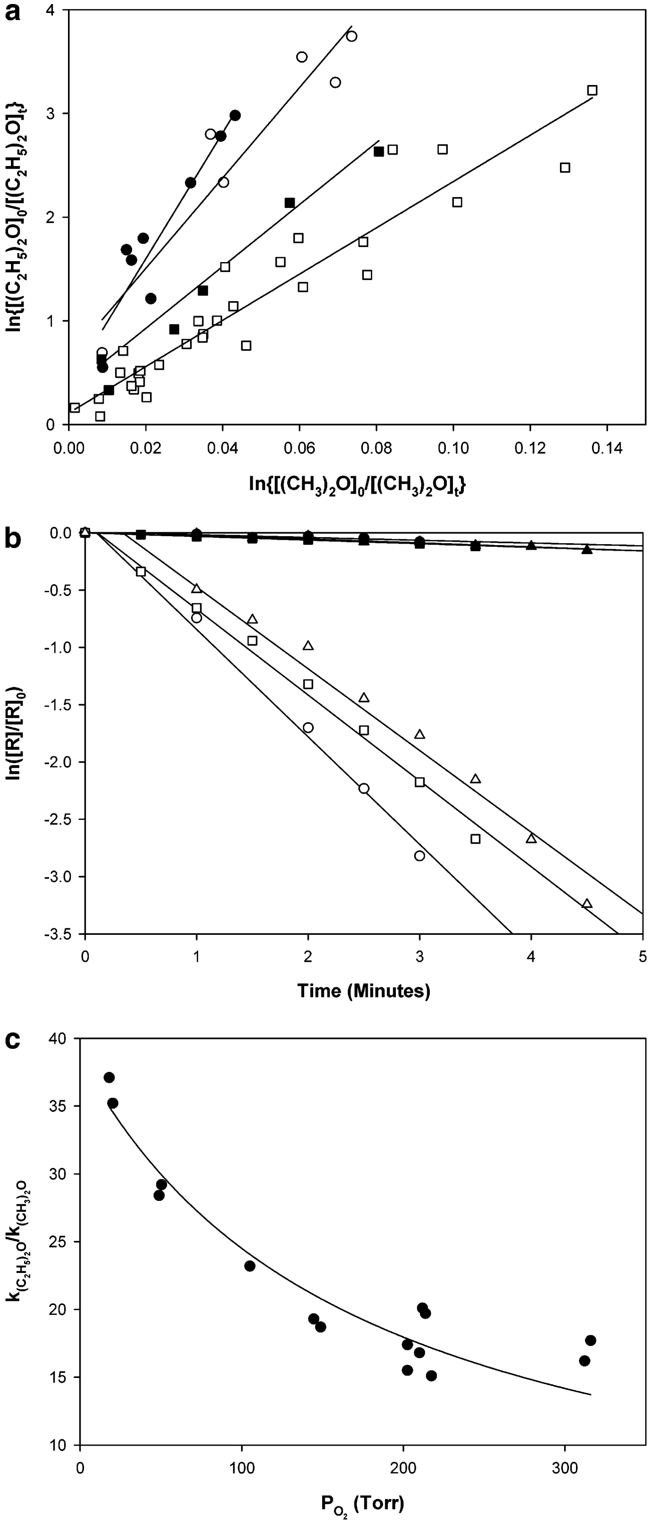

Figure 4. (a) Typical relative rate plots for the reactions of Br with dimethyl ether and diethyl ether. For all experiments, $[Br_2] \approx 2 \times 10^{-5}$ to 2×10^{-4} mol L^{-1}, $[(CH_3)_2O]_0 \approx 1 \times 10^{-5}$ mol L^{-1}, $[(C_2H_5)_2O]_0 \approx 2 \times 10^{-6}$ mol L^{-1}, total pressure ≈720 Torr; (●) 20 Torr of O_2, (○) 50 Torr of O_2, (■) 100 Torr of O_2, (□) 200 Torr of O_2. (b) Typical pseudo-first-order plots for reactant loss at various O_2 partial pressures. For the open symbols, R is diethyl ether while the filled symbols represent dimethyl ether. For all experiments, $[Br_2] \approx 2 \times 10^{-5}$ to 2×10^{-4} mol L^{-1}, $[(CH_3)_2O]_0 \approx 1 \times 10^{-5}$ mol L^{-1}, $[(C_2H_5)_2O]_0 \approx 2 \times 10^{-6}$ mol L^{-1}, total pressure ≈ 720 Torr; (●, ○) 20 Torr of O_2 added, (■, □) 100 Torr of O_2 added, (▲, △) 200 Torr of O_2 added. (c) Variation of rate constant ratio with O_2 partial pressure. For all experiments, $[Br_2] \approx 2 \times 10^{-5}$ to 2×10^{-4} mol L^{-1}, $[(CH_3)_2O]_0 \approx 1 \times 10^{-5}$ mol L^{-1}, $[(C_2H_5)_2O]_0 \approx 2 \times 10^{-6}$ mol L^{-1}, total pressure ≈ 720 Torr.

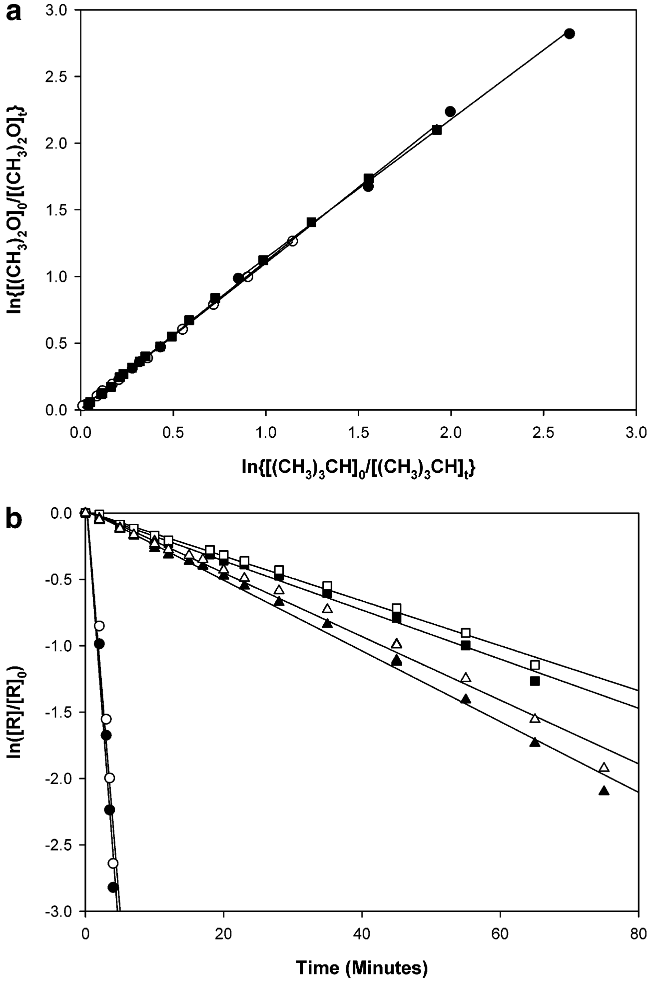

Figure 5. (a) Typical relative rate plots for the reactions of Br with dimethyl ether and 2-methylpropane. For all experiments, $[Br_2] \approx 1 \times 10^{-4}$ mol L^{-1}, $[(CH_3)_2O]_0 \approx 5 \times 10^{-6}$ mol L^{-1}, $[(CH_3)_3CH]_0 \approx 5 \times 10^{-6}$ mol L^{-1}, total pressure ≈ 720 Torr; (●) no O_2, (○) 50 Torr of O_2, (■) 200 Torr of O_2. (b) Typical pseudo-first-order plots for reactant loss at various O_2 partial pressures. For the open symbols, R is 2-methylpropane while the filled symbols represent dimethyl ether. For all experiments, $[Br_2] \approx 1 \times 10^{-4}$ mol L^{-1}, $[(CH_3)_2O]_0 \approx 5 \times 10^{-6}$ mol L^{-1}, $[(CH_3)_3CH]_0 \approx 5 \times 10^{-6}$ mol L^{-1}, total pressure ≈ 720 Torr; (●, ○) no O_2, (■, □) 50 Torr of O_2, (▲, △) 200 Torr of O_2.

concentration for this pair of reactants up to a partial pressure of 200 Torr of O_2. Again, no dependence on total pressure was observed over the range 200 to 760 Torr. While the pseudo-first-order rate constants for loss of dimethyl ether and of 2-methylpropane presented in Figure 5b now both decrease rapidly as the concentration of O_2 increases, this decrease has about the same sensitivity to O_2 for each reactant so that the rate constant ratio now shows no appreciable dependence on O_2. This behavior would be consistent with a decrease in the concentration of atomic bromine with increasing O_2 concentration as a result of scavenging by O_2 of organic free radicals that would otherwise react with Br_2 to produce an alkyl bromide and a bromine atom. This difference in behavior of the rate constant for the reaction of dimethyl ether with atomic bromine confirms the conclusion reached earlier that the kinetic behavior in these relative rate measurements can be sensitive to the choice of reference reactant.

Diethyl Ether Measured Relative to 2-Methylpropane. As Figure 6a indicates, the rate constant ratios for the reaction of atomic bromine with diethyl ether relative to 2-methylpropane also show no detectable dependence on O_2 concentration. However, unlike the case of dimethyl ether measured relative

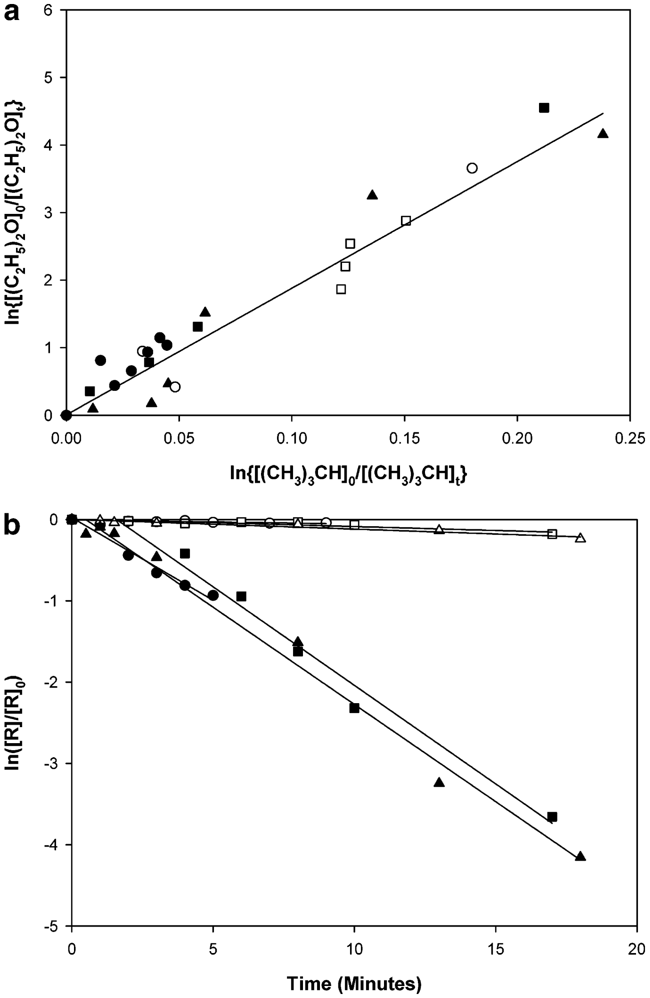

Figure 6. (a) Typical relative rate plots for the reactions of Br with diethyl ether and 2-methylpropane. For all experiments, $[Br_2] \approx 1 \times 10^{-5}$ mol L^{-1}, $[(C_2H_5)_2O]_0 \approx 1 \times 10^{-6}$ mol L^{-1}, $[(CH_3)_3CH]_0 \approx 4 \times 10^{-7}$ mol L^{-1}, total pressure ≈ 720 Torr; (●) no O_2, (○) 68 Torr of O_2, (■) 75 Torr of O_2, (□) 313 Torr of O_2, (▲) 717 Torr of O_2. (b) Typical pseudo-first-order plots for reactant loss at various O_2 partial pressures. For the open symbols, R is 2-methylpropane while the filled symbols represent diethyl ether. For all experiments, $[Br_2] \approx 1 \times 10^{-5}$ mol L^{-1}, $[(C_2H_5)_2O]_0 \approx 1 \times 10^{-6}$ mol L^{-1}, $[(CH_3)_3CH]_0 \approx 4 \times 10^{-7}$ mol L^{-1}, total pressure ≈ 720 Torr; (●, ○) no O_2, (■, □) 68 Torr of O_2, (▲, △) 717 Torr of O_2.

to 2-methylpropane, Figure 6b indicates that the individual pseudo-first-order rate constants for diethyl ether and for 2-methylpropane also show virtually no dependence on the concentration of O_2. These results imply that neither the effective rate constants of these reactions nor the steady-state bromine atom concentration varies significantly with O_2 concentration in these mixtures. Again, it is clear that the detailed chemical behavior of mixtures of organic reactants in these experiments is sensitive to the specific combination of organic compounds used in the mixture. We now turn to a kinetic analysis of the data to determine whether these detailed effects have a measurable influence on the rate constants calculated from the relative rates of disappearance of the organic reactants.

Kinetic Analysis. It is clear, particularly from the O_2 dependence of the relative rates for the mixture of ethers, that the rate constant ratio measured in synthetic air is not necessarily the limiting value of that ratio. It is therefore desirable to employ a method of analysis that derives a reliable value of the limiting rate constant ratio at high O_2 concentrations. Such a method should also be independent of the mechanism used to describe the reaction system since improvements in the mechanistic description of a reaction can necessitate revisions to the values of rate constants deduced from a mechanistic analysis. It should also be based on a representation of the data that produces minimal curvature, particularly close to the limiting value, and as short an extrapolation as possible in reaching the limiting value at high O_2 concentration.

TABLE 3: Relative Rate Constants at 298 K for the Reactions of Atomic Bromine with Dimethyl Ether Measured Relative to 2-Methylpropane[a]

total pressure (Torr)	oxygen partial pressure (Torr)	$[Br_2]$ (mol L^{-1})	$k\{(CH_3)_2O\}/k\{(CH_3)_3CH\}$
707	204	1.24×10^{-4}	1.16 ± 0.04
230	204	1.28×10^{-4}	1.107 ± 0.008
715	53.3	1.23×10^{-4}	1.095 ± 0.006
727	0.0	1.44×10^{-5}	1.07 ± 0.03

[a] Uncertainties are calculated at the 95% confidence level.

We begin with the experiments on the mixtures of 2-methylpropane with dimethyl ether since the rate constant for the reaction of Br with 2-methylpropane is to be used as the primary reference value and the rate constant ratio for this mixture was independent of O_2 concentration. The numerical values of the rate constant ratio are summarized in Table 3. The absolute rate constant at 298 K for the reaction of Br with 2-methylpropane may be calculated from the Arrhenius parameters of Seakins et al.[20] as 8.65×10^5 L mol^{-1} s^{-1} while the Arrhenius parameters of Russell et al.[21] lead to a value of 1.02×10^6 L mol^{-1} s^{-1}. We will use the lower value, 8.65×10^5 L mol^{-1} s^{-1}, in our calculations on the basis that it is derived from experiments which should be less susceptible to heterogeneous atom loss. However, the two values are in good agreement and use of the mean value of 9.42×10^5 L mol^{-1} s^{-1} would contribute an additional uncertainty of only about 8% in our calculated rate constants. Taking the average value of the measured rate constant ratio, 1.09 ± 0.02, from the values in the table and using the value of the reference rate constant identified above, we calculate an absolute rate constant at 298 K for the reaction of Br with $(CH_3)_2O$ of 9.43×10^5 L mol^{-1} s^{-1} ± 2%.

The rate constant for the reaction of diethyl ether with atomic bromine is much larger than that for the corresponding reaction of 2-methylpropane. However, it is still possible to use 2-methylpropane as a reference reactant although this leads to somewhat more scatter in Figure 6a than was obtained in Figure 5a from the experiments with dimethyl ether in which the test and reference reactants had nearly equal rate constants. The results of Figure 6a give a rate constant ratio $k\{(C_2H_5)_2O\}/k\{(CH_3)_3CH\}$ of 16.3 ± 6%. Again using a reference rate constant of 8.65×10^5 L mol^{-1} s^{-1}, we obtain a rate constant of 1.41×10^7 L mol^{-1} s^{-1} ± 6% for the reaction of Br with $(C_2H_5)_2O$, independent of the concentration of O_2.

The rate constant determined above for the reaction of Br with $(CH_3)_2O$ will now be used as a secondary reference value in the experiments with mixtures of $(CH_3)_2O$ and $(C_2H_5)_2O$. These experiments indicate a clear dependence of the relative rate constant on O_2 concentration. The format used to represent the experimental data in Figure 4c is not well suited to determination of a limiting value of the rate constant ratio at high O_2 concentrations because the very gradual slope of the asymptotic tail of the curve is difficult to characterize accurately and to extrapolate to obtain the value of the rate constant ratio at a limiting high concentration of O_2. A more useful representation is the reciprocal plot in Figure 7. A variety of functions were tested for use in fitting the data but the best results

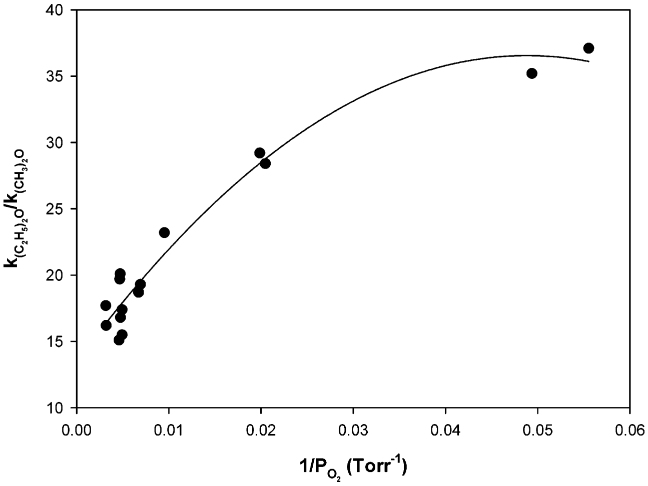

Figure 7. Analysis of the O_2 dependence of the rate constant ratio for mixtures of $(CH_3)_2O$ and $(C_2H_5)_2O$. Plotting symbols are the experimental data and the solid line represents a quadratic fit.

statistically were obtained with simple polynomial fits. A quadratic gave the best fit, particularly in the important region near the *y*-axis from which the accuracy of extrapolation to the vertical axis is determined, providing an intercept of 13.5 with a standard error of 0.9 and $r^2 = 0.956$. These results may be compared with the value of the rate constant ratio, 18.7, interpolated to the O_2 pressure of synthetic air by using the experimental data points on either side of that oxygen concentration. It is clear that even a rough attempt to find a limiting value of the ratio, using a reciprocal plot, is superior to the value that would be obtained from measurements restricted to the O_2 content of synthetic air. On the basis of this analysis, we derive a value of 13.5 ± 7% for the limiting ratio $k\{(C_2H_5)_2O\}/k\{(CH_3)_2O\}$ at high $[O_2]$ from which we calculate a rate constant at 298 K of 1.27×10^7 L mol^{-1} s^{-1} ± 8% for the reaction of Br with $(C_2H_5)_2O$ using the rate constant for Br + $(CH_3)_2O$ above measured relative to 2-methylpropane. This compares well with the more direct measurement of this rate constant, 1.41×10^7 L mol^{-1} s^{-1} ± 6% obtained with mixtures of diethyl ether and the primary reference compound 2-methylpropane, indicating that our extrapolation procedure has been effective in determining the limiting rate constant for this reaction at high concentrations of O_2. These results also suggest that the limiting high concentration of O_2 has removed the interferences that led to the observed variation in the calculated rate constant ratio at smaller O_2 concentrations.

We now analyze the O_2 dependence of the rate constant ratios for mixtures of diethyl ether and ethene in the same way as for the mixtures of the two ethers. The results are presented in Figure 8. Again, the best results were obtained with a quadratic fit, giving an intercept of 0.158 with a standard error of 0.03 and a correlation coefficient of 0.995. On this basis, we derive a limiting value of 0.158 ± 19% for the ratio $k\{(C_2H_5)_2O\}/k\{C_2H_4\}$ at high $[O_2]$ and 298 K. Again, the rate constant ratio interpolated to the synthetic air composition is 0.564 suggesting that the rate constant for the reaction of Br with ethene would incur significant error if only a rate constant ratio in synthetic air had been determined. When this limiting value of the rate constant ratio is combined with the average of the rate constants determined above for the reaction of Br with $(C_2H_5)_2O$, we calculate a rate constant at 298 K of 8×10^7 L mol^{-1} s^{-1} ± 30% for the reaction of Br with ethene.

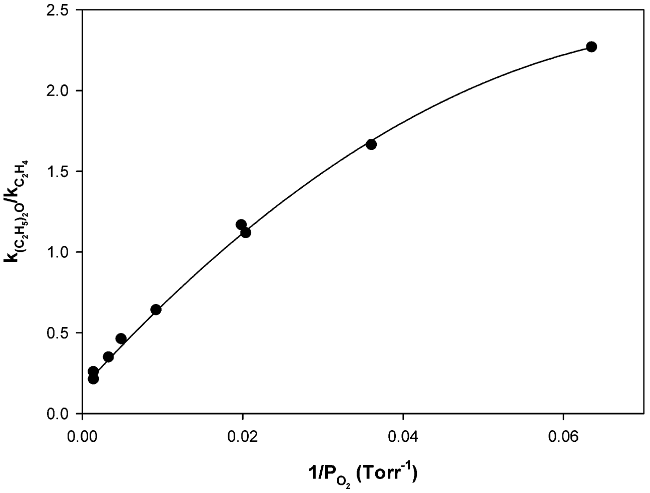

Figure 8. Analysis of the O_2 dependence of the rate constant ratio for mixtures of $(C_2H_5)_2O$ and C_2H_4. Plotting symbols are the experimental data and the solid line represents a quadratic fit.

Discussion

We begin with discussion of the results for the reaction of ethene with Br since there is information in the literature with which our measurements of oxygen dependence can be compared. The suitability of the kinetic analysis presented above can be examined with reference to this previous work and a mechanism will be developed that accounts for these results. The available data are summarized in Table 4. While all the rate constants were obtained with the relative rate approach, it is clear that different methods have been used to analyze the effect of oxygen. The results from refs 13 and 14 are sufficiently complete that their data can be reevaluated by using our approach, thereby providing an independent assessment of the impact of the method of analysis on the rate constant derived from the measurements. Results for temperatures close to 298 K from refs 13 and 14 are presented in Figure 9, together with our data. In all cases, it has been assumed that the rate constant used for the reference reaction does not depend on the O_2 concentration. When the reaction of Br with formaldehyde is the reference reaction and a value of 6.98×10^8 L mol^{-1} s^{-1} is used for the reference rate constant,[9] a limiting value of 2.86×10^8 L mol^{-1} s^{-1} ± 16% is obtained for the rate constant of the reaction of Br with ethene at 296 K and a total pressure of 700 Torr. When the reaction of Br with 2,2,4-trimethylpentane (TMP) is used as the reference and the ratio *k*(TMP)/*k*(2-methylpropane) from ref 13 is combined with the rate constant, 8.65×10^5 L mol^{-1} s^{-1}, for the reaction of Br with 2-methylpropane,[20] we obtain a value of 4.11×10^6 L mol^{-1} s^{-1} from the data at 293 K from ref 13 for the reaction of Br with TMP. This, in turn, leads to a rate constant of 3.14×10^8 L mol^{-1} s^{-1} ± 15% for the rate constant at 293 K of the reaction of Br with ethene based on the data of ref 13. In these calculations, the uncertainty is the standard error associated with the nonlinear least-squares analysis of the data. What is clear from this analysis is that these values for the rate constant of the reaction of Br with ethene, which have been claimed to be in significant discord,[11] are actually in good agreement with each other when the limiting rate constants extrapolated to high O_2 concentration are compared. It is also clear that the limiting values of this rate constant are much larger than the values calculated from the relative rates measured in synthetic air.

TABLE 4: Rate Constants at 298 ± 2 K for the Reaction of Br with C_2H_4

rate constant (L mol^{-1} s^{-1})	method	ref
$9.63 \times 10^7 \pm 19\%$	photolysis of Br_2; rates measured relative to 2,2,4-trimethylpentane as a function of O_2; value obtained by steady-state analysis	13
$7.83 \times 10^7 \pm 8\%$	photolysis of Br_2; rates measured relative to formaldehyde as a function of O_2; value quoted for synthetic air	14
$7.41 \times 10^7 \pm 7\%$	photolysis of Br_2; rates measured relative to formaldehyde and acetaldehyde in synthetic air	11
$8.48 \times 10^7 \pm 30\%$	Photolysis of Br_2; rates measured relative to $(C_2H_5)_2O$ as a function of O_2 and referenced to $(CH_3)_3CH$; limiting value at infinite O_2	this work
$2.50 \times 10^7 \pm 10\%$	photolysis of Br_2; rates measured relative to $(C_2H_5)_2O$ as a function of O_2 and referenced to $(CH_3)_3CH$; ratio interpolated to synthetic air	this work

We may now use the average of the two values, calculated above, for the rate constant of the reaction of Br with ethene as a reference value for use with our measured limiting value of the rate constant ratio from mixtures of ethene with diethyl ether. This leads to a rate constant at 298 K for the reaction of Br with diethyl ether of 4.7×10^7 L mol^{-1} s^{-1} ± 30%. This value is approximately a factor of 3 larger than those measured relative to dimethyl ether or 2-methylpropane. On the other hand, use of the rate constant 7.41×10^7 L mol^{-1} s^{-1}, reported more recently[11] for the rate constant of the reaction of Br with C_2H_4, leads to a rate constant for Br + $(C_2H_5)_2O$ of 1.2×10^7 L mol^{-1} s^{-1}, which is close to our value of this rate constant measured relative to both $(CH_3)_2O$ and $(CH_3)_3CH$. Unfortunately, the work of ref 11 was done in synthetic air and there is insufficient information available to determine how far their rate constant is from the limiting value at high O_2 concentrations.

The measurements of the rate constant for the reaction of diethyl ether with Br are subject to a number of possible systematic errors in addition to the random uncertainties measured by the standard deviations. Both 2-methylpropane and dimethyl ether react at least a factor of 10 more slowly with Br than is the case with diethyl ether. This large difference in reactivity leads to potentially large uncertainties in the measured rate constant ratio due to the difficulty in accurately measuring very small changes in concentration of 2-methylpropane or dimethyl ether while avoiding unduly large extents of reaction of diethyl ether with the consequent possibility of interference from secondary reactions. This situation is clear from the ranges of the axes in Figures 4a and 6a, as well as from the scatter of the data points in those figures. While the data in Figure 6a seem to accurately pass through the origin, those in Figure 4a seem to have a positive *y*-intercept that could be attributed to a systematic analytical error in the quite small values on the *x*-axis. Secondary reactions would affect the measured rate constant ratios if they resulted in additional consumption of one of the reactants or regeneration of one of the reactants. The plots in Figures 4a and 6a show no indication of such intervention by secondary reactions at the larger conversions of $(C_2H_5)_2O$. The most likely result of such intervention would be to make the ratio k_{ether}/k_{ref} too large, resulting in curvature of the plots in Figures 4a and 6a at the larger extents of reaction. However, no curvature was evident in these experiments and our rate constants calculated from the mixtures of diethyl ether with dimethyl ether and with 2-methylpropane are smaller than the value calculated from experiments in which ethene is the reference compound. Ethene reacts with Br at a rate that is much more comparable to that of the corresponding reaction of diethyl ether making it in principle a more suitable reference reactant for measuring the rate constant of the reaction of Br with diethyl ether. In this case, allowance for the significant oxygen dependence of the rate constant for the reaction of Br with C_2H_4 provides a reference rate constant from the data in refs 13 and 14, which leads to a rate constant for the reaction of Br with diethyl ether that is substantially larger than the value we measure relative to both 2-methylpropane and dimethyl ether. The apparently good agreement obtained by using the rate constant for Br + C_2H_4 reported in ref 11 could be fortuitous since allowance for a continued increase in that rate constant as the oxygen concentration is increased beyond the value for synthetic air would lead to a value closer to that obtained in our analysis of the data from refs 13 and 14. If our values of the ratio k_{ether}/k_{ethene} are too large, the most likely cause would be secondary reactions consuming diethyl ether and it might be expected that these secondary reactions would also have been present in the experiments with mixtures containing dimethyl ether and 2-methylpropane. It is also possible that our extrapolation procedure for estimating the limiting rate constant for the reaction of Br with ethene has produced too large a value of this rate constant from the data of refs 13 and 14. The origin of this discrepancy in the measured values of the rate constant of the reaction of Br with diethyl ether is unclear and determination of an accurate value for its rate constant will require additional experiments with other reference reactants whose rate constants for reaction with Br are comparable to that of the reaction of Br with diethyl ether.

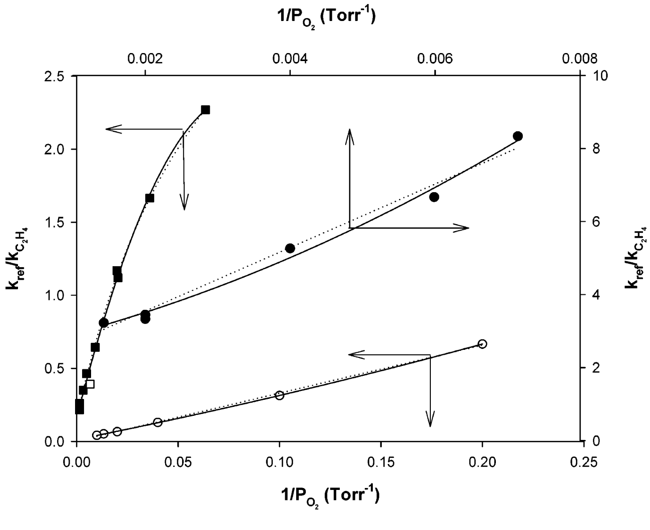

Figure 9. Analysis of the O_2 dependence of the rate constants for the reaction of Br with C_2H_4 based on this work relative to diethyl ether (■) as well as on experiments reported in the literature with mixtures of formaldehyde[14] (●) or 2,2,4-trimethylpentane[13] (○) with C_2H_4. Plotting symbols are the experimental data, the solid line represents a quadratic fit, and the dotted line represents the fit obtained with eq 10 in the text.

In the case of reactions of Br with alkenes and alkynes, the mechanism postulated by Barnes et al.[13] and represented by the reactions below permits a steady-state analysis that culminates in a function that represents the O_2 dependence of their data quite well.

$$Br + C_2H_4 + M \leftrightarrows C_2H_4Br + M \tag{4}$$

$$C_2H_4Br + O_2 \rightarrow C_2H_4BrO_2 \tag{5}$$

$$C_2H_4BrO_2 \rightarrow \text{oxidation products} \tag{6}$$

In their measurements of the reaction of Br with ethene relative to that with 2,2,4-trimethylpentane, they were able to show that the rate constant for their reference reaction was independent of the concentration of O_2 and they attributed the effect of O_2, which they measured to its intervention only in the mechanism for the reaction of Br with ethene. However, reactions such as that of the free radical C_2H_4Br with Br_2 or decomposition of this free radical, both of which could be required to account for the reaction products formed in the absence of O_2, were not explicitly included in their steady-state analysis. Their observation of a distinct pressure dependence of their measured rate constants supports reaction 4 as an important step in the mechanism. We found a significant dependence on O_2 for the rate constants of the reactions of Br with ethene measured relative to diethyl ether, which is consistent with the measurements of Barnes et al. relative to TMP and of Yarwood et al. relative to formaldehyde. On the other hand, our measurements made with mixtures of dimethyl ether and diethyl ether, discussed in more detail later, suggest that the rate constant for the reaction of Br with diethyl ether may also have some dependence on the O_2 concentration. This would mean that some of the O_2 dependence of the rate constant ratio measured in mixtures of ethene and diethyl ether could be attributable to a dependence on O_2 of the rate constant for the reaction of Br with diethyl ether. The explicit inclusion of the reaction of the C_2H_4Br radical with Br_2 requires the reaction

$$C_2H_4Br + Br_2 \rightarrow C_2H_4Br_2 + Br \tag{7}$$

By analogy with existing kinetic data[9] for the reactions of aliphatic free radicals with Br_2, reaction 7 is expected to be rapid and will be in direct competition with reaction 5. In the presence of a large excess of Br_2, the combination of reactions 7 and 4 provides a catalytic process for consuming ethene through its reaction with Br and is expected to result in a larger steady-state concentration of Br than would be the case if reaction 7 were unimportant. Reaction 5 reduces the effectiveness of the catalysis by removing C_2H_4Br in a way that does not regenerate atomic bromine. The efficiency with which this takes place is governed by the ratio $k_5[O_2]/k_7[Br_2]$. Typical values[9] of k_5 are roughly 10^9 L mol^{-1} s^{-1} while typical values of k_7 vary from roughly 10^8 to 10^{11} L mol^{-1} s^{-1} so values of this ratio are likely to fall in the range $10[O_2]/[Br_2]$ to $0.01[O_2]/[Br_2]$. This suggests that $[O_2]/[Br_2]$ ratios of as much as 1000 might be required to produce effective attenuation of the catalytic effect of Br_2 for regenerating Br. Other removal processes for Br such as heterogeneous recombination will alter this value. While this variation in the concentration of Br as a result of the presence of O_2 will affect the rate at which organic reactants are consumed, it should not affect the relative rate constant measurements since the concentration of Br cancels in these calculations.

The formation of the $C_2H_4BrO_2$ free radical in reaction 5 requires that we consider possible reactions for its subsequent removal. Examination of kinetic databases such as ref 9 provides no indication of a reaction between organic peroxy radicals and halogens. We conclude that the $C_2H_4BrO_2$ radical is not likely to react significantly with Br_2 and will be more likely to react with itself or with other free radicals in the system or to simply decompose. If formation of the adduct C_2H_4Br is reversible, consideration should also be given to the possibility of reversal of reaction 5 in which the $C_2H_4BrO_2$ free radical is formed. Available kinetic data, such as that of ref 9, suggests that the reverse of reaction 5 is very slow relative to other potential loss routes. While formation of an activated peroxy radical might alter this situation, we consider such a situation to be unlikely under our experimental conditions and will assume that the reverse of reaction 5 is unimportant in our experiments.

Finally, the observation of significant production of HBr in the reactions of many organic compounds with Br, in both the presence and absence of O_2, requires us to consider a direct decomposition channel for C_2H_4Br such as reaction 8.

$$C_2H_4Br \rightarrow \text{products} \tag{8}$$

The addition of O_2 will clearly compete with this channel as well. The infrared spectra of Figures 2 and 3 indicate that decomposition of C_2H_4Br to HBr is negligible compared to the production of HBr in the other reactions we examined. This is consistent with the endothermicity of abstraction of a hydrogen atom from ethene by Br and with other experimental results[22] on the reaction of Br with ethene in the absence of O_2. We therefore conclude that reaction 8 will be unimportant in the reaction of ethene with Br. However, the infrared spectra clearly indicate that production of HBr is an important process in the reactions of Br with the ethers and with 2-methylpropane. We will retain reaction 8 in our analysis in anticipation of subsequent adaptation of this mechanism to reactions such as those of Br with the ethers in which formation of HBr is important.

When a steady-state analysis is applied to this expanded mechanism composed of reactions 4 through 8, we obtain the following relation for the second-order rate constant for consumption of ethene by atomic bromine in which k is the empirical second-order rate constant for loss of ethene as it appears in eq 3 for the relative rate calculation and M is any suitable third body capable of stabilizing the free radical formed in reaction 4.

$$\frac{1}{k} = \frac{1}{k_4[M]} + \frac{k_{-4}}{k_4(k_5[O_2] + k_7[Br_2] + k_s)} \tag{9}$$

Equation 9 differs from the function used by Barnes et al.[13] to fit their data only in replacement of $k_c[O_2]$ in their relation by $(k_5[O_2] + k_7[Br_2] + k_8)$. If reactions 7 and 8 are removed from the mechanism, this term reduces to $k_5[O_2]$ and eq 9 becomes identical with the function deduced by Barnes et al. The denominator in eq 9 is no longer directly proportional to $[O_2]$ and the increase in $k_7[Br_2]$ with increasing bromine concentration degrades the linearity of plots of $1/k$ against $1/[O_2]$ at small concentrations of oxygen. This effect was also noted by Barnes et al. where it was also attributed to competition between O_2 and Br_2 for the adduct. However, they found this to be unimportant at O_2 pressures greater than 2 Torr and did not include the reaction of C_2H_4Br with Br_2 in their steady-state analysis. This competition is more important at the much larger Br_2 concentrations used in our experiments. While eq 9 contains too many rate constants for fitting and only concentration ranges of bromine are available for the work in the literature rather than the precise concentrations of bromine, it is at least possible to obtain information from the trends that are evident in Figure 9 and from the parameters fitted to the curves in that figure.

TABLE 5: Summary of Reaction Conditions and Fitting Parameters for the Reaction of Br with C_2H_4

parameter	ref 13	ref 14	this work
temp (K)	293	296	300
$[Br_2]$ (mol L^{-1})	2×10^{-7} to 2×10^{-6}	5×10^{-7} to 1×10^{-6}	1×10^{-5} to 1.6×10^{-5}
pressure (Torr)	760	700	720
ref reactant	2,2,4-trimethylpentane	formaldehyde	diethyl ether
limiting rate constant at large $[O_2]$ (L mol^{-1} s^{-1})	$3.2 \times 10^{8} \pm 15\%$	$2.9 \times 10^{8} \pm 16\%$	$9.0 \times 10^{7} \pm 25\%$
A (eq 10)	$3.6 \times 10^{-11} \pm 3 \times 10^{-12}$	$7.1 \times 10^{-11} \pm 3.5 \times 10^{-11}$	$2.4 \times 1^{-10} \pm 2 \times 10^{-11}$
B (eq 10)	completely uncertain	completely uncertain	$7.2 \times 10^{-4} \pm 1.6 \times 10^{-4}$
C (eq 10)	approximately 4×10^{-10}	approximately 3×10^{-9}	$1.0 \times 10^{-8} \pm 3 \times 10^{-9}$
k_4[M] (L mol^{-1} s^{-1})	approximately 3×10^{9}	approximately 3×10^{8}	$1.0 \times 10^{8} \pm 30\%$

For convenience in comparing with the plots already used to obtain the limiting rate constants at high concentrations of O_2, eq 9 can be converted to a function in which the independent variable is $1/[O_2]$. For a series of experiments in which $[O_2]$ is varied while $[Br_2]$ and [M] remain constant, this function takes the form

$$\frac{1}{k} = \frac{A/[O_2] + C}{B/[O_2] + 1} \qquad (10)$$

in which $A = (1/k_4k_5)[(k_7[Br_2]/[M]) + k_{-4}]$, $B = k_7[Br_2]/k_5$, and $C = 1/k_4[M]$ and we have recognized that reaction 8 is negligible in the reaction of Br with ethene. The results of fitting our data and that from refs 13 and 14 to eq 10 are indicated by the dotted lines in Figure 9 and the results of this fit are summarized in Table 5, together with the Br_2 concentrations used in these experiments. Presentation of the experimental rate constant ratios, k_{ether}/k_{ethene}, in Figure 9 amounts to multiplying each side of eq 10 by k_{ether}. The parameters A, B, and C in Table 5 were then calculated by assuming a value of 1.34×10^{7} L mol^{-1} s^{-1} for k_{ether}.

Unfortunately, eq 10 has a form that does not lend itself readily to accurate fitting of all the coefficients. When the concentration of bromine is small, the fit is quite insensitive to the numerical values of B and C leading to a large uncertainty in the fitted parameters. While the coefficient A can be fitted with reasonable accuracy, its functional form is too complex a function of elementary rate constants to have significant quantitative utility. However, we can estimate the magnitudes of the various terms in eq 10 in the following way. The average of k_4[M] measured in our work and calculated in our analysis of the O_2 dependence of refs 13 and 14 is approximately 2×10^{8} L mol^{-1} s^{-1}. The equilibrium constant for reaction 4 has been estimated[22] on the basis of thermodynamic arguments to be approximately 4×10^{4} at 298 K. Numerical values for k_5 and k_7 are not available to our knowledge, but the corresponding values at 298 K for the C_2H_5 radical are 4.82×10^{9} L mol^{-1} s^{-1} for the reaction of C_2H_5 with O_2[23] and 6.24×10^{10} L mol^{-1} s^{-1} for the reaction of C_2H_5 with Br_2.[24] This leads to the estimates $A \approx (6 \times 10^{-8}[Br_2] + 4 \times 10^{-14})$ mol^2 L^{-2} s, $B \approx 15[Br_2]$ mol L^{-1}, and $C \approx 5 \times 10^{-9}$ mol L^{-1} s. Typical bromine concentrations used in our experiments are of the order of 1×10^{-5} mol L^{-1} and in much of the work in the literature the bromine concentrations were 1 to 2 orders of magnitude smaller than this. Consequently, the numerical value of A in our work is likely to be roughly 6×10^{-13} mol^2 L^{-2} s with smaller values for the other data presented in Figure 9. The term $B/[O_2]$ will be approximately 0.004 for pure O_2 and will increase as the O_2 concentration decreases. However, over most of the O_2 concentration range covered in our work its value will be somewhat less than 1 and it will be even smaller for the other work presented in Figure 9. These rough estimates of A, B, and C are generally consistent with the values of these parameters presented in Table 5. The effect of bromine concentration will decrease as the concentration of O_2 increases and the terms $A/[O_2]$ and $B/[O_2]$ become progressively less important relative to the constant terms in the numerator and denominator of eq 10.

We now turn our attention to the measurements of the rate constants of the reactions of atomic bromine with dimethyl ether and diethyl ether. These would normally be represented as simple hydrogen abstraction reactions. In that case, the relevant reactions for both the ethers and the reference compound, 2-methylpropane, would be

$$RH + Br \rightarrow HBr + R \qquad (11)$$

$$R + O_2 \rightarrow RO_2 \qquad (12)$$

$$R + Br_2 \rightarrow RBr + Br \qquad (13)$$

$$RO_2 \rightarrow \text{products} \qquad (14)$$

In this case, no dependence of the rate constant ratio on O_2 is expected in relative rate experiments because the rate of loss of the organic reactant is given for both the test and reference reactant as $-d[RH]/dt = k_{11}[Br][RH]$. The effect of O_2 is reflected only in the concentration of Br and this cancels in the relative rate calculation. On the other hand, in the mechanism for the reaction of ethene with Br the regeneration of reactants in reaction −4 leads to the following expression for the loss of ethene.

$$\frac{d[C_2H_4]}{dt} = k_4[Br][C_2H_4][M] \times \left\{1 - \frac{k_{-4}[M]}{(k_{-4}[M] + k_5[O_2] + k_7[Br_2])}\right\} \qquad (15)$$

While the concentration of Br still cancels in the relative rate calculation, the effective second-order rate constant is now a composite quantity depending on the concentrations of O_2 and Br_2. The observation of a small but definite dependence on O_2 concentration in our experiments on the reaction of Br with mixtures of dimethyl ether and diethyl ether leads us to consider the possibility of a mechanism for the reactions of Br with the ethers that is similar to that for its reaction with ethene.

Atomic bromine is an electrophilic reagent as reflected in its comparatively rapid reaction with olefins and the good correlation of its rate constants with those for reactions of other electrophilic reagents such as OH and $O(^3P)$.[16] In examining these correlations, it is evident that the rate constants for the reactions of atomic bromine span a significantly wider range of numerical values than those of these other electrophiles, reflecting a greater selectivity of the Br atom reactions which may be a result of the greater polarizability of the bromine atom as well as the comparatively small exothermicity of a number

TABLE 6: Comparison of Measured Rate Constants[a] for the Reactions of Br with Diethyl Ether and Dimethyl Ether with Those Predicted by Correlations Based on Linear Free Energy Relations[16]

organic reactant	measured (L mol^{-1} s^{-1})	calcd for addition			calcd for abstraction		
		RH + OH	RH + NO_3	RH + O(^{3}P)	RH + OH	RH + NO_3	RH + O(^{3}P)
$(CH_3)_2O$	9.43×10^5	5.2×10^7	4.1×10^8	4.7×10^7	3.6×10^5	4.0×10^7	1.5×10^6
$(C_2H_5)_2O$[b]	1.41×10^7	5.9×10^8	1.3×10^9	1.2×10^8	2.5×10^8	4.6×10^{10}	1.6×10^7
$(C_2H_5)_2O$[c]	4.7×10^7	5.9×10^8	1.3×10^9	1.2×10^8	2.5×10^8	4.6×10^{10}	1.6×10^7

[a] Reference rate constants were obtained from ref 9. [b] Measured relative to 2-methylpropane and dimethyl ether. [c] Measured relative to ethene.

of its reactions, including hydrogen abstraction. Two linear relations are clearly present in these correlations, one attributable to addition reactions with dienes, chloroethenes, alkenes, and alkynes and the other involving reactions with alkanes and aldehydes which, unlike the addition reactions, produce large yields of HBr and are usually characterized as hydrogen abstractions. The slope of the correlation with the abstraction reactions is much steeper than that for the correlation with addition reactions and seems to reflect the endothermicity of many hydrogen abstraction reactions of atomic bromine. The overlap region of the addition and abstraction reactions spans atomic bromine rate constants of approximately 10^7 to 10^9 L mol^{-1} s^{-1}. While our rate constant for the reaction of Br with dimethyl ether falls distinctly in the region characterized as hydrogen abstraction, the rate constants for both diethyl ether and ethene fall in the region where both mechanisms are found. Our measured rate constants for the reactions of atomic bromine with the ethers are compared in Table 6 with the values calculated with use of the correlations of ref 16 and rate constants for the required reactions of OH, NO_3, and O(^{3}P) taken from ref 9. Although the rate constants calculated for the reaction of Br with diethyl ether seem on the whole to be more consistent with the abstraction channel, the results for the addition channel also fall close to the authors' suggested uncertainty of about 1 order of magnitude for their correlations. The presence of an oxygen atom in the ethers provides a region of much higher electron density than is present in saturated hydrocarbons and raises the possibility of formation of a moderately stable addition complex between Br and the oxygen atom in the ether. The possibility of formation of such an adduct has also been suggested for reactions of O(^{3}P) with organic compounds containing an oxygen atom[25] and has been suggested as a possible explanation for the negative activation energy in the reactions of O(^{3}P) with dimethyl sulfide and ethylene sulfide.[26]

The reactions of atomic bromine with organic reactants can be formally represented as an addition step followed by decomposition to products. When saturated organic reactants are involved, the situation differs from that in the reaction of Br with ethene in several important ways. Since HBr is the dominant reaction product in these reactions, it is clear that reaction 8, which was unimportant in the reaction with ethene, is now very significant. In addition, the adduct will be much less stable than that formed between Br and ethene. Equation 15 is now modified for saturated hydrocarbons RH to include reaction 8. Also, the adduct no longer has an obvious structural resemblance to an aliphatic free radical and it is not clear that it would be able to react with Br_2. This would result in the term $k_7[Br_2]$ being negligible. With these changes, the relation for the measured second-order rate constant becomes

$$k = k_4[M]\left\{\frac{(k_5[O_2] + k_8)}{(k_{-4}[M] + k_5[O_2] + k_8)}\right\} \tag{16}$$

Provided $k_{-4}[M]$ is much smaller than $k_5[O_2] + k_8$, the situation is identical to the simple abstraction mechanism and no dependence of the measured rate constant on O_2 is expected. Observation of a significant dependence of the measured rate constant on O_2 would require a significant numerical value for both $k_5[O_2]$ and $k_{-4}[M]$ relative to k_8. The numerical value of the measured rate constant, k, would then be predicted to increase with increasing concentration of O_2 giving a limiting value at high O_2 concentrations that is equal to $k_4[M]$.

The dependence on O_2 concentration found with the mixtures of dimethyl ether and diethyl ether and indicated in Figure 4c would be consistent with adduct formation if the adduct with dimethyl ether were to be more stable than that with diethyl ether. In that case, eq 16 suggests that the rate constant for the reaction of Br with dimethyl ether would be more sensitive to O_2 than that for the reaction with diethyl ether, causing the rate constant ratio in Figure 4c to decrease with increasing concentration of O_2. However, if that were to be the case one would expect to see a variation with O_2 concentration for the rate constant ratios measured with mixtures of dimethyl ether and 2-methylpropane since 2-methylpropane does not have a source of comparatively large electron density that might lead to formation of an adduct with atomic bromine. The results in Figure 5a show no indication of a dependence on O_2 over a wide range of O_2 concentrations. If formation of a stable adduct were to be important, we should also have been able to observe a dependence of the measured rate constants on pressure. However, we were not able to detect a pressure dependence of the rate constant ratios in our experiments with mixtures of dimethyl ether and diethyl ether or with mixtures of dimethyl ether or diethyl ether with 2-methylpropane. The pressure range in these experiments was limited by the presence of O_2 to a minimum of about 200 Torr and by the construction of the apparatus to a maximum of 1 atm. The lack of a measurable dependence of the rate constants on total pressure suggests that if an adduct does form it is much less stable than that formed between Br and ethene. The conclusion to be reached from this analysis is that adduct formation in the reactions of Br with diethyl ether, dimethyl ether, and 2-methylpropane is not kinetically important.

The origin of these apparently contradictory results is not clear. A significant difficulty in the relative rate measurements for the mixtures of diethyl ether with both dimethyl ether and 2-methylpropane arises from the large difference in reactivity of the two organic reactants in the mixtures. This makes it difficult to make accurate measurements of the small extent of reaction of the less reactive component of the mixture under conditions for which the extent of reaction of the more reactive component is sufficiently small to prevent secondary reactions from having an effect. When the extent of consumption of the organic reactants was large, the relative rate plots exhibited strong curvature which we attribute to secondary reactions involving the oxidation products. As noted earlier, our kinetic measurements were always restricted to extents of reaction that were much smaller than those at which this curvature became apparent. The maximum effect of O_2 on the measured rate constant ratios for the reactions of Br with the ether mixtures was nearly a factor of 10 smaller than that obtained for the mixtures of diethyl ether with ethene and this contributed to the difficulty in making precise measurements of the effect of O_2. Despite the apparently contradictory results obtained in the measurements of oxygen dependence, the rate constant for the reaction of Br with diethyl ether calculated from the limiting value of the rate constant ratio obtained with the ether mixtures at high O_2 concentrations is in good agreement with the value obtained from the more direct measurement based on the mixtures of diethyl ether with the primary reference reactant 2-methylpropane. This provides some confidence that the value obtained for the rate constant of the reaction of Br with diethyl ether is reasonably accurate. An understanding of the mechanism for the intervention of O_2 in our measurements with the ether mixtures will require additional experiments with other reference reactants whose rate constants for their reactions with Br are closer to that for diethyl ether.

Conclusions

The effect on rate constants for reactions of atomic bromine with organic compounds of varying O_2 concentration can be significant even for measurements made in synthetic air. The limiting value of the rate constant for which the effects of secondary reactions have been eliminated can, however, be obtained by extrapolating plots of rate constant ratios against $1/[O_2]$ to obtain a limiting value at large $[O_2]$. This procedure requires measurements over a substantial range of values of $1/[O_2]$, extending to oxygen concentrations much larger than those in synthetic air, so that the distance of extrapolation is short and represents only a small proportion of the span of values of $1/[O_2]$. The sensitivity of the variation with O_2 concentration of the rate constant for the reaction of Br with ethene depends on the concentration of Br_2 and it is likely that this is a general effect for the reactions of Br with olefins. The use of comparatively small concentrations of Br_2 in such experiments provides a less severe dependence of the rate constant on $[O_2]$ and a correspondingly more reliable extrapolation to the limiting value at large concentrations of O_2 provided the measurements include values at very large concentrations of O_2. It is evident that the results of relative rate measurements in synthetic air, particularly those using photolysis of Br_2 as the atomic Br source, must be treated with caution and may not represent limiting values of the rate constants being measured. It would be prudent to experimentally demonstrate whether such measurements are appreciably affected by the concentration of O_2.

The results of our experiments and of those in the literature for the reaction of Br with ethene can be interpreted in terms of a mechanism that is a simple extension of one provided earlier to describe the reaction of Br with ethene. Steady-state analysis of this mechanism indicates that the limiting rate constant extrapolated to large $[O_2]$ can be reliably interpreted as the effective second-order rate constant for the reaction of Br with the organic reactant. Reactions of free radicals with Br_2 lead to regeneration of atomic bromine, thereby providing a catalytic route for consumption of the organic reactant and increasing the steady-state concentration of atomic bromine. The effect of O_2 is to compete with these reactions, providing a route to oxidation products and reducing the steady state atomic bromine concentration. However, the reactions responsible for regeneration of atomic bromine only affect the measured rate constants to the extent that they play a role in determining the concentration of the adduct formed between Br and the organic reactant.

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