

OH Reactivity and UV Spectra of Propane, *n*-Propyl Bromide, and Isopropyl BromideSergey N. Kozlov,[†] Vladimir L. Orkin,^{*‡} Robert E. Huie, and Michael J. Kurylo

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The rate constants for the reactions of OH radicals with the 1-bromopropane, 2-bromopropane, and propane were measured using the flash photolysis resonance fluorescence technique over the temperature range between 210 and 480 K. Arrhenius plots exhibit a noticeable curvature, and the rate constants can be represented using a three-parameter modified Arrhenius expression over the temperature range of the experiments with ca. 2% precision. Such a fit also describes the available high-temperature data for propane quite well. The best three-parameter fits to the data are: $k_{\text{C}_3\text{H}_8}(T) = 1.96 \times 10^{-12} \times (T/298)^{1.83} \times \exp\{-167/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_{\text{nPB}}(T) = 2.99 \times 10^{-13} \times (T/298)^{2.79} \times \exp\{+369/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; and $k_{\text{iPB}}(T) = 1.66 \times 10^{-13} \times (T/298)^{2.95} \times \exp\{+461/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For the low temperature range of atmospheric interest, the reaction rate constants can be accurately presented by standard Arrhenius expressions. Based on the available low-temperature data the following rate constants can be recommended for the purpose of atmospheric modeling: $k_{\text{C}_3\text{H}_8}(T < 300 \text{ K}) = 8.66 \times 10^{-12} \times \exp\{-615/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_{\text{nPB}}(T < 300 \text{ K}) = 3.03 \times 10^{-12} \times \exp\{-330/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_{\text{iPB}}(T < 300 \text{ K}) = 1.77 \times 10^{-12} \times \exp\{-260/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Atmospheric lifetimes were estimated to be ca. 14, 14, and 19 days for $\text{CH}_3\text{CH}_2\text{CH}_3$, $\text{CH}_2\text{BrCH}_2\text{CH}_3$, and $\text{CH}_3\text{CHBrCH}_3$, respectively. The ultraviolet absorption spectra of these bromopropanes were measured between 164 and 270 nm.

Introduction

Brominated alkanes are the primary source gases for bromine in the stratosphere where bromine participates in the catalytic destruction of ozone. The production of industrial bromine containing halocarbons is consequently being phased out under the provisions of the Montreal Protocol and its Amendments. Nevertheless, a few Br-containing compounds are still in use or are under consideration for use in industrial applications due to their possible environmental acceptability as a result of their extremely short residence times in the atmosphere. One of them, $\text{CH}_2\text{Br}-\text{CH}_2-\text{CH}_3$ (1-bromopropane, *n*-propyl bromide, nPB) is an industrial cleaning solvent. Previous kinetic studies^{1–4} of the reaction of nPB with hydroxyl radicals and atmospheric model calculations^{5–7} indicated its atmospheric lifetime to be as short as 8–34 days. However, the spread among the available kinetic data at room temperature and above was ca. 30%, and the temperature dependence was not well determined. While the present work was in progress, new rate constant measurements and a reaction mechanism study⁸ was conducted that decreased these uncertainties. Taking into account the practical importance of this reaction and the possibility of curvature of the Arrhenius temperature dependence due to different reaction sites available for OH attack, we investigated the reaction of OH + *n*-propyl bromide over a wide temperature range (210–480 K) in order to better assess the temperature dependence of the rate constant.

The rate constants for reactions of OH with $\text{CH}_3-\text{CHBr}-\text{CH}_3$, (2-bromopropane, isopropyl bromide, iPB) and propane ($\text{CH}_3-\text{CH}_2-\text{CH}_3$) were also investigated over the same tem-

perature interval. The isopropyl bromide reaction has been investigated in some of the earlier mentioned studies.^{1,2,4}

The reaction of OH with propane has been intensively studied over the past 35 years⁹ and its value at room temperature is well established. There are also four fairly recent studies at temperatures below 300 K by different research groups using different experimental methods including pulse techniques,^{10,11} a flow technique (high-pressure turbulent flow),¹² and a relative technique.¹³ Thus, this reaction presents a good opportunity to examine measurement accuracy in the determination of OH reaction rate constants for very reactive hydrohalocarbons. Thus, we report the results of our measurements of the OH + propane reaction obtained over a temperature interval that includes low temperatures of atmospheric interest and extends far enough above the room temperature to be compared with the results of higher temperature measurements.

While the reactions with hydroxyl radicals dictate the residence time of bromoalkanes in the atmosphere, their photolysis in the stratosphere also releases Br atoms that trigger the destruction of stratospheric ozone. To complete the photochemical information related to the atmospheric fate of bromopropanes, we have measured their ultraviolet absorption spectra between 164 and 270 nm.

Experimental Section

Detailed descriptions of the apparatus and the experimental methods used to measure the rate constants for the reactions with OH and absorption spectra of the bromopropanes are given in previous papers.^{14–17} Therefore, only brief descriptions are given here.

OH Reaction Rate Constant Measurements. The principal component of the flash photolysis–resonance fluorescence (FPRF) apparatus is a Pyrex reactor (of approximately 50 cm³ internal volume) thermostated with methanol, water, or mineral

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TABLE 1: Molar Concentration of the Main Detected Impurities in Bromopropane Samples^a

compound					
<i>n</i> -propyl bromide			isopropyl bromide		
main impurities	original sample (99%)	after GC purification	main impurities	99.2% sample	99.8+% sample
propene	0.007%		propene	0.16% ^b	
acetone	0.02%		acetone		0.05%
chloropropane	0.02%		<i>i</i> -propanol	0.20%	0.09%
propanol	0.09%		bromoethane	0.01%	
isopropyl bromide	0.17%	0.01%	di- <i>i</i> -propyl ether	0.021%	0.017%
di- <i>n</i> -propyl ether	0.34%	0.005%	<i>n</i> -propyl bromide	0.04%	0.05%
toluene	0.02%		1,2-dibromopropane	0.1%	0.09%
1-bromopentane	0.04%				
1,2-dibromopropane	0.03%				

^a The italicized values were obtained without direct calibration of GC with the sample of the compound by accepting the sensitivity to closest analogues. ^b The result of analysis of liquid phase. Approximately 5% of propene was detected in the vapor phase of this sample.

oil circulated through its outer jacket. Reactions were studied in argon carrier gas (99.9995% purity) at a total pressure of 4.00 kPa (30.0 Torr). Flows of dry argon, argon bubbled through water thermostated at 276 K, and (bromo)propane mixtures (containing 0.05% or 0.1% of the reactant diluted with argon) were premixed and flowed through the reactor at a total flow rate between 0.3 and 0.6 cm³ s⁻¹, STP. Flow rates of argon, the H₂O/argon mixture, and reactant/inert gas mixtures were measured by Tylan mass flow meters calibrated for each gas mixture. The concentrations of the gases in the reactor were calculated from the flow rates and the total pressure measured with a MKS Baratron manometer.

Uncertainties due to systematic effects in our measurements can be associated with such procedures as the absolute calibration of the MKS Baratron manometer (which measures the pressure in the reaction cell), the calibrations of the three Tylan mass flow meters (argon, argon/water, and reactant mixture flows), and the temperature stability and measurements in the reaction cell. The stated accuracy of the reaction cell manometer (ca. 0.1%) was verified by its absolute calibration. The manometers used to prepare the reactant mixtures were intercalibrated and their linearity was found to be accurate to within ca. 0.2%. All mass flow meters were calibrated by measuring the rate of pressure change in the reaction cell (an additional volume was connected for larger flow rates) isolated from the vacuum pump. These calibrations were usually reproducible within 0.5–1%. The determination of the reactant concentration in the cell only requires relative gas flow rates and one absolute pressure measurement. In addition, we verified the composition of the bromopropane mixtures in the storage bulbs by comparing the measured UV absorption between 166 and 171 nm for the mixture with that for a corresponding amount of pure bromopropane. For example, the absorption of 25 Torr of 0.100% mixture of *n*BP in argon was compared with the absorption of 0.0250 Torr of pure *n*BP. Such comparison revealed no difference within the precision of these absorption measurements (estimated as ca. 0.5%). The uncertainty of the temperature in the reaction cell was around 0.3 K between 250 and 370 K. This increased to about 1 K at the low temperature end and to about 2 K at the high temperature end of the temperature range used in this study due primarily to temperature fluctuations. The relative error that can be introduced by the gas temperature fluctuations is decreased essentially by the opposite temperature dependencies of the reactant concentration and the measured rate constant. To quantify the combined uncertainty associated with our experimental procedure, we added the square root of the sum-of-the-squares of the flow meter calibration uncertainties to the other uncertainties mentioned above. Thus we estimate the expanded uncertainty due to possible instrumental effects to be ca. 4% (95% confidence interval).

Hydroxyl radicals were produced by the pulsed photolysis (1–4 Hz repetition rate) of H₂O (introduced via the 276 K argon/H₂O bubbler) by a xenon flash lamp focused into the reactor. Earlier studies with this apparatus indicated that the initial OH concentration was of the order of 10¹¹ molecule/cm³. The initial concentration was increased by up to a factor of between 4 and 20 by variation in the flash intensity and/or H₂O concentration. The variation in flash intensity and H₂O concentration serves as a diagnostic for kinetic errors associated with the reactions of OH with either primary reaction products or with products from the possible photolysis of the reactant.¹⁶ No statistically significant difference was observed in the rate constants obtained over most of the range of this variation. Differences of up to 5% could be obtained only at the highest concentration of H₂O coupled with the highest flash intensity. Nevertheless, all kinetic experiments were conducted at lowest values of both the flash energy and H₂O concentration.

The OH radicals were monitored by their resonance fluorescence near 308 nm, excited by a microwave-discharge resonance lamp (330 Pa or 2.5 Torr of a ca. 2% mixture of H₂O in UHP helium) focused into the reactor center. The resonance fluorescence signal was recorded on a computer-based multichannel scanner (channel width 100 μs) as a summation of 500 to 5000 consecutive flashes. The resonance fluorescence decay at each reactant concentration was analyzed as described by Orkin et al.¹⁵ to obtain the first-order decay rate coefficient (10 to 350 s⁻¹) due to the reaction under study. At each temperature the rate constant was determined from the slope of a plot of the decay rate versus (bromo) propane concentration. The concentration ranges and number of determinations used at each temperature are given in Table 2.

UV Absorption Cross Section Measurements. The absorption spectra of undiluted bromopropanes and methyl bromide (measured for comparison) were obtained over the wavelength range of 164 nm to 270 nm using a single-beam apparatus consisting of a 1-m vacuum monochromator equipped with a 600 lines/mm grating. The radiation source was a Hamamatsu L1385 deuterium lamp, and the detector was a Hamamatsu R166 photomultiplier. Spectra were recorded at increments of 0.5 nm at a spectral slit width of 0.5 nm. The pressure inside the 16.9 ± 0.05 cm absorption cell was measured by a MKS Baratron manometer at *T* = 295 ± 1 K. Absorption spectra of the evacuated cell and of the cell filled with a gas sample were alternately recorded several times, and the absorption cross sections at the wavelength λ were calculated as

$$\sigma(\lambda) = \frac{\ln\{I_0(\lambda)/I_{[\text{BP}]}(\lambda)\}}{[\text{BP}] \times L}$$

where [BP] is the concentration of bromopropane in the

TABLE 2: Rate Constants Measured in the Present Work for the Reactions of OH with *n*- and *i*-Bromopropane and Propane^a

temp, K	$k(T),^b 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		
	$\text{CH}_2\text{Br}-\text{CH}_2-\text{CH}_3$	$\text{CH}_3-\text{CHBr}-\text{CH}_3$	$\text{CH}_3-\text{CH}_2-\text{CH}_3$
210	6.40 ± 0.24 <i>0.33–1.5 (13)</i>	5.1 ± 0.3 <i>0.33–1.8 (10)</i>	4.6 ± 0.2 <i>0.66–2.3 (11)</i>
220	6.78 ± 0.40 <i>0.62–2.2 (4)</i>	5.45 ± 0.10 <i>0.32–2.2 (14)</i>	5.39 ± 0.07 <i>0.33–2.2 (8)</i>
230	7.33 ± 0.18 <i>0.32–2.1 (12)</i>	6.00 ± 0.10 <i>0.16–2.8 (35)</i>	5.79 ± 0.09 <i>0.32–2.1 (17)</i>
250	8.08 ± 0.08 <i>0.56–2.6 (12)</i>	6.37 ± 0.10 <i>0.29–2.5 (25)</i>	7.32 ± 0.12 <i>0.29–2.0 (17)</i>
272	9.15 ± 0.09 <i>0.51–2.4 (12)</i>	6.87 ± 0.10 <i>0.26–2.4 (30)</i>	8.84 ± 0.16 <i>0.26–1.8 (15)</i>
298	10.1 ± 0.15 <i>0.26–1.8 (28)</i>	7.58 ± 0.12 <i>0.24–1.6 (17)</i>	11.3 ± 0.2 <i>0.12–0.82 (22)</i>
330	11.8 ± 0.2 <i>0.42–1.5 (8)</i>	8.85 ± 0.20 <i>0.13–1.5 (21)</i>	14.3 ± 0.3 <i>0.24–0.84 (8)</i>
370	14.8 ± 0.5 <i>0.19–1.3 (7)</i>	10.9 ± 0.2 <i>0.11–1.2 (27)</i>	18.6 ± 0.5 <i>0.22–7.5 (9)</i>
420	19.0 ± 0.3 <i>0.12–0.83 (18)</i>	13.5 ± 0.3 <i>0.13–1.6 (24)</i>	24.3 ± 0.4 <i>0.20–1.0 (20)</i>
480	24.2 ± 0.5 <i>0.081–0.68 (28)</i>	17.7 ± 0.3 <i>0.16–1.6 (41)</i>	33.4 ± 0.7 <i>0.16–1.1 (16)</i>

^a The italicized values represent reactant concentration range, 10^{14} molecule/cm³ (number of points in parentheses). ^b Uncertainties represent statistical levels of confidence of 95% and do not include an estimated uncertainty of 4% associated with possible systematic errors.

absorption cell with the optical path length L . $I_0(\lambda)$ and $I_{[\text{BP}]}(\lambda)$ are the radiation intensities measured after the absorption cell when the bromopropane concentration was zero and [BP], respectively. The complete spectrum of each compound was constructed from data taken over several overlapping wavelength ranges. Data over each spectral range were obtained at 5 to 6 pressures of each bromoalkane to verify adherence to the Beer–Lambert absorption law. The total range of reactant pressures used for these measurements was 6.7 Pa to 20 kPa (0.05 Torr to 150 Torr). The coincidence of the contiguous parts of spectra taken over overlapping wavelength ranges was usually better than ca. 1%. The overall instrumental error associated with uncertainties in the path length, pressure, temperature stability, and the measured absorbance was estimated to be less than 2% over most of the wavelength range (up to 250 nm), increasing to ca. 10–20% above 250 nm due to increased uncertainty in measuring low absorbance values.

Reactants. The sample of *n*-propyl bromide (99% stated purity) and two samples of isopropyl bromide (99.2% and 99.8% stated purity) were obtained from Sigma-Aldrich Co. The sample of propane was obtained from MG Scientific gases. Our GC-MS and GC-FID analysis of the propane sample revealed ca. 0.04% of isobutane, the only reactive impurity presented in noticeable amount. The presence of isobutane at such a low level can result in an overestimation of the measured rate constant by only 0.2% at the lowest temperature in this study.⁹ Propene and ethene are the most undesirable reactive impurities that can be present in propane, since their OH reaction rate constants are approximately $3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively at 210 K.⁹ Fortunately, their presence can be easily detected by their extremely strong absorption near 170 nm.¹⁸ Therefore, in addition to GC analysis, we also measured the absorption spectrum of the propane sample between 165 and 175 nm in order to check for the possible presence of alkenes. Based on the results of UV absorption measurements, we conclude that the concentration of neither ethene nor propene exceeds 0.003% in the sample of propane. This level of alkene impurities cannot

cause any noticeable overestimation of the measured rate constant. Therefore, we used this sample without further purification after several freeze/pump/thaw cycles.

We analyzed the samples of *n*PB and *i*PB using GC-MS and GC coupled with a thermoconductivity detector. Results of these analyses are presented in Table 1. The GCs were calibrated by direct injections of the chemicals whose impurity levels could cause the greatest kinetic concern: propene, acetone, propanol, 2-propanol, toluene, and di-*n*-propyl ether. Other impurities should have an OH reactivity comparable with that of the bromopropanes under study and, therefore, cannot result in any noticeable overestimation of the measured rate constants. Another possible complication in the study of brominated compounds is contamination with molecular bromine, which is very reactive toward OH radicals.⁹ Fortunately, because Br₂ absorbs visible light, even a contamination level as low as ca. 0.01% is readily visible with the naked eye in transparent liquid samples. Analysis of the liquid samples of bromopropanes using a spectrophotometer revealed no absorption near 400 nm, thereby allowing us to estimate the bromine concentration to be less than ca. 0.002%. All experiments were performed with mixtures prepared from the liquid phase of the samples to ensure the absence of errors due to any impurities.

To eliminate errors associated with the presence of the reactive impurities we purified the *n*PB sample using a preparative scale gas chromatograph. Results of GC analyses of the purified sample are presented in Table 1. The residual impurities cannot result in any overestimation of the measured rate constant, and this purified sample was used for both kinetic and spectral measurements. In the case of *i*PB, we performed diagnostic measurements with both samples of different purity. At 220 K where the kinetic effect of impurities would be the greatest, the rate constant obtained using the 99.2% purity sample was about 10% larger than that obtained using the 99.8+% purity sample. This difference could be quantitatively assigned to OH reactions with the impurities at the abundances listed in Table 1 (with propene contributing approximately 80% of this difference and *i*-propanol the remainder). Consequently, all of the kinetic (and spectral) data reported here for *i*PB were obtained using mixtures prepared from the liquid phase of the 99.8+% purity sample. For both the kinetic and spectral measurements all bromopropane samples were used after outgassing by several freeze/pump/thaw cycles.

Results and Discussion

The rate constants obtained for the title reactions are presented in Table 2. Figure 1a shows the data obtained for propane along with the results of previous studies that were conducted below room temperature. The data obtained for *n*-propyl bromide and isopropyl bromide are presented graphically in Figures 2 and 3, respectively, along with those available from the literature. All three figures clearly illustrate that the Arrhenius plots for these reactions exhibit noticeable curvature over the temperature range of our study.

OH + CH₃–CH₂–CH₃. Arrhenius curvature has been reported by all groups who studied this reaction below room temperature using absolute techniques. A three-parameter fit to our data yields the following expression:

$$k_{\text{C}_3\text{H}_8}(T) = 1.96 \times 10^{-12} \times (T/298)^{1.83} \times \exp\{-167/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (1)$$

This expression gives the rate constants that are within 1.7% of the values measured in the present work and reported in Table

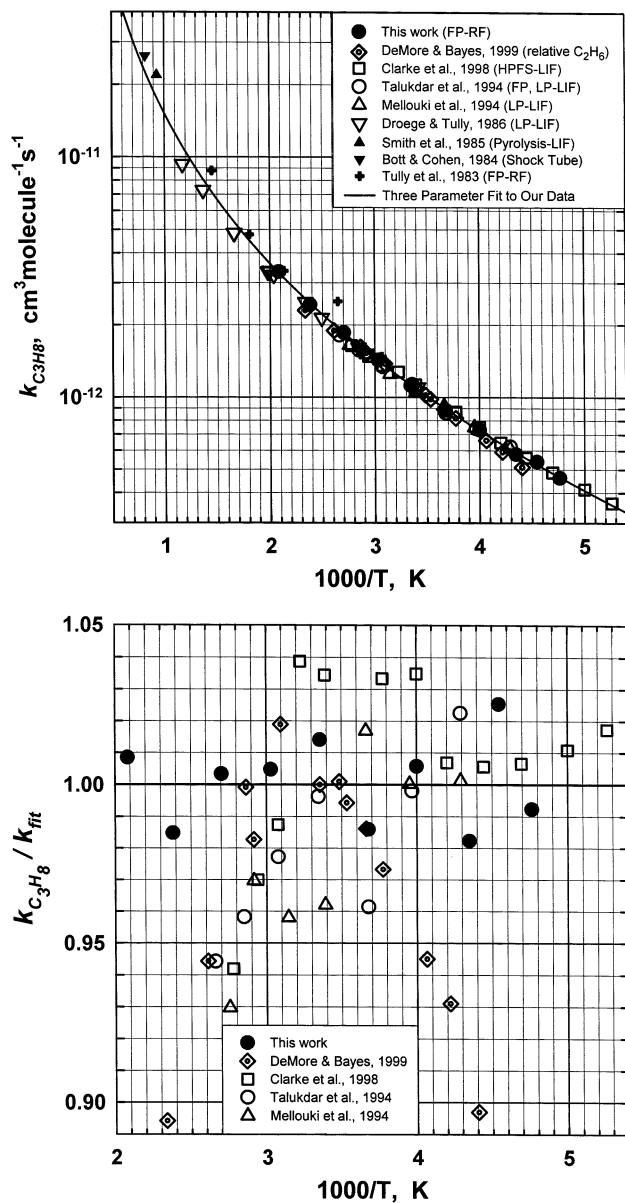


Figure 1. (a) Arrhenius plot for the reaction of OH with propane. (b) Rate constants for the reaction of OH with propane normalized to a three-parameter fit to the data from the present work.

2 (except for $k_{C_3H_8}$ (220 K), which is 2.5% higher). These deviations are smaller than the 95% statistical confidence intervals of individual determinations (again, except for $k_{C_3H_8}$ (220 K), which has the 95% confidence interval of 1.2%). Although derived from data below 480 K one can see from Figure 1a that this three-parameter fit reasonably describes the results of the higher-temperature measurements including the latest and most comprehensive study,¹⁹ which was performed over the temperature interval between 293 and 854 K and probably supersedes the earlier results from the same laboratory²⁰ (less than 4% deviation below 430 K, which increases up to 16% at 854 K). This extrapolation agrees even with the available results of measurements at highest temperatures $T = 1075$ K²¹ and $T = 1220$ K²² (deviations are 25% and 16% respectively, well within the uncertainty of measurements).

Figure 1b shows all of the low-temperature data available in the literature normalized to the rate constants calculated from eq 1. One can see that the results of all absolute measurements below ca. 350 K agree with the above presentation to better than ca. 4% and their spread in Figure 1b is essentially random.

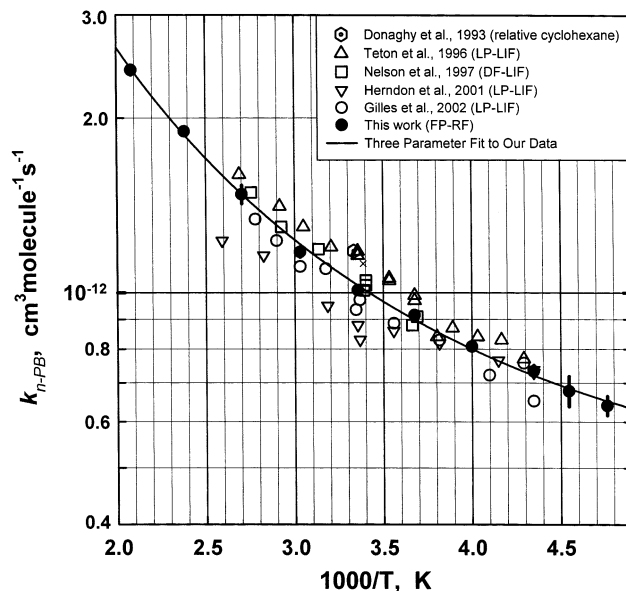


Figure 2. Arrhenius plot for the reaction of OH with *n*-propyl bromide.

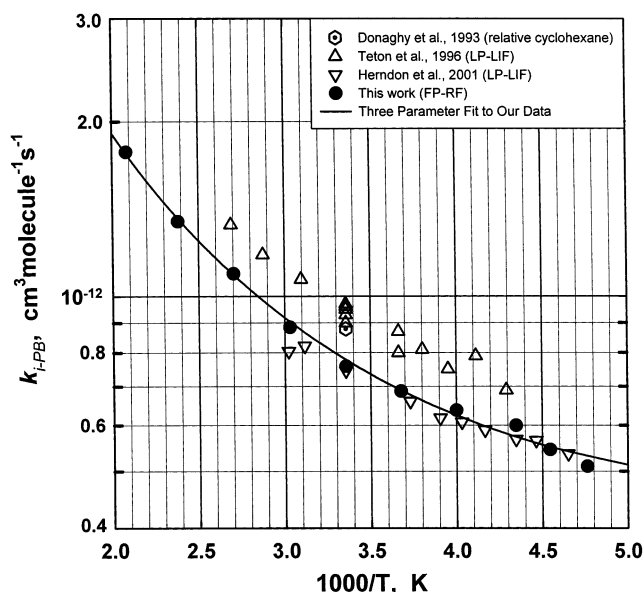


Figure 3. Arrhenius plot for the reaction of OH with isopropyl bromide.

The results of the relative rate measurements¹³ show no Arrhenius curvature and agree with the absolute data near room temperature with differences increasing to 10–11% at both lower and higher temperatures. This is seen from a parabolic shape of these data as presented in Figure 1b, which is suggestive of possible systematic errors in the measurements. For example, while the results of relative measurements accumulate the uncertainty of the reference reaction (OH + C₂H₆ in this particular case) along with their own possible instrumental error, no simple renormalization of the relative rate data will bring them into coincidence with the absolute studies. Recalculating the ratios reported in ref 13 using the rate constant for the reference reaction from the latest OH + C₂H₆ study performed over a temperature interval mainly below room temperature¹² decreases the low-temperature deviation to less than 7% while increasing the discrepancy above room temperatures. This is because all studies of the OH + C₂H₆ rate constant show essentially linear behavior of the Arrhenius plots as do the rate constant ratios ($k_{C_3H_8}/k_{C_2H_6}$) obtained in ref 13. We, thus, conclude that the rate constant for the reaction between

OH and propane has been well established by absolute measurement techniques over the temperature range of atmospheric interest and that the relative rate data from ref 13 underestimate the Arrhenius curvature.

Our data on the OH reaction with propane between 298 and 210 K can be represented by the standard Arrhenius expression with $k(298 \text{ K}) = 1.10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E/R = 624 \text{ K}$.

All of the literature data below room-temperature yield about the same E/R factors (613 K,¹⁰ 613 K,¹¹ and 608 K¹²), except those obtained by a relative rate technique¹³ that yields $E/R = 745 \text{ K}$. Based on a combined fit to the data obtained at and below room temperature using absolute techniques, we recommend the following Arrhenius expression for use in atmospheric modeling:

$$k_{\text{C}_3\text{H}_8}(T < 300 \text{ K}) = 8.66 \times 10^{-12} \exp\{-615/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (2)$$

OH + CH₂Br-CH₂-CH₃. The results obtained in the present work for the reaction between OH and *n*-propyl bromide are shown in Figure 2 together with existing literature data. A three-parameter fit to our data results in the following expression:

$$k_{\text{nPB}}(T) = 2.99 \times 10^{-13} \exp\{+369/T\} \times (T/298)^{2.79} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (3)$$

which gives the rate constants that are within 2% of the measured values reported in Table 2. Our results lie in the middle of the complete database for this reaction. Despite their higher scatter, most of the previously reported data are within 10% of the best fit to our results. In particular, our results are in very good agreement with the results of the discharge flow-LIF study reported in ref 3. A very recent paper by Gilles et al.⁸ reports new results obtained between 230 and 360 K that probably supersede the previously reported data from the same laboratory⁴ and are in better agreement with our data. As with propane, the data at and below room temperature are reasonably represented by a standard Arrhenius expression. A fit to the complete data set over this temperature region yields the expression

$$k_{\text{nPB}}(T < 300 \text{ K}) = 3.03 \times 10^{-12} \exp\{-330/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

This expression provides values for $k_{\text{nPB}}(298 \text{ K})$ and E/R identical with those obtained in this work and can be recommended for atmospheric modeling purposes. Using the parameterization of the NASA Panel for Data Evaluation, we recommend $k_{\text{nPB}}(298 \text{ K}) = 1.00 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E/R = 330 \text{ K}$ with an uncertainty factor (1σ) of

$$f_{\text{nPB}}(T) = 1.1 \times \exp\left\{50 \times \left[\frac{1}{T} - \frac{1}{298}\right]\right\} \quad (5)$$

OH + CH₃-CHBr-CH₃. An Arrhenius plot for this reaction also exhibits noticeable curvature and a three-parameter fit to our data results in the following expression:

$$k_{\text{iPB}}(T) = 1.66 \times 10^{-13} \exp\{+461/T\} \times (T/298)^{2.95} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

which gives rate constants that are within 4% of the values measured in the present work and reported in Table 2. The result

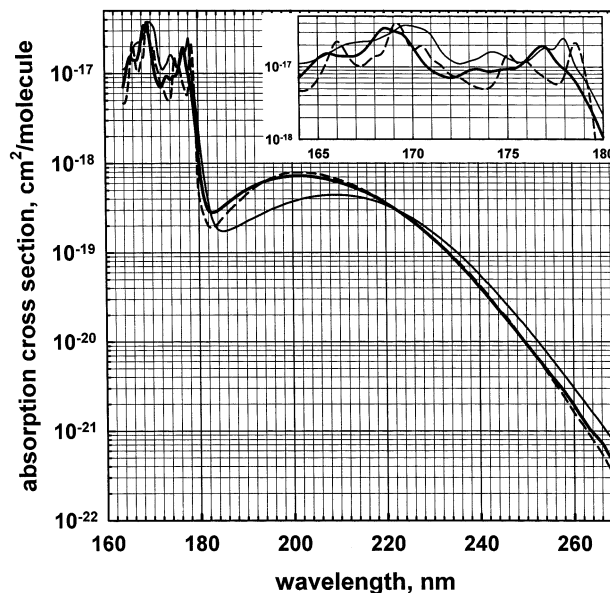


Figure 4. Ultraviolet absorption spectra for *n*-propyl bromide (solid thick line), isopropyl bromide (solid thin line), and methyl bromide (dashed line).

of this fit is shown in Figure 3 along with our data and data from the literature.

Our results for this reaction are in very good agreement with those reported in ref 4, the agreement being better than 4.5%, except at the highest temperature reported in ref 4 where it is 11%. The results of two other studies^{1,3} are systematically higher and the discrepancy with our data is greater than in the case of the CH₂Br-CH₂-CH₃ reaction.

The data at and below room temperature can be represented by a standard Arrhenius expression. A combined fit to our data and those from ref 4 yield the following expression, which is recommended for atmospheric modeling purposes:

$$k_{\text{iPB}}(T < 300 \text{ K}) = 1.77 \times 10^{-12} \exp\{-260/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

Using the parameterization of the NASA Panel for Data Evaluation, this corresponds to $k_{\text{iPB}}(298 \text{ K}) = 7.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E/R = 260 \text{ K}$, with an uncertainty factor (1σ) of

$$f_{\text{iPB}}(T) = 1.15 \times \exp\left\{50 \times \left[\frac{1}{T} - \frac{1}{298}\right]\right\} \quad (8)$$

Ultraviolet Spectra. The ultraviolet absorption spectra of bromopropanes obtained in this work are presented in Figure 4 along with the spectrum of CH₃Br for comparison. We measured the CH₃Br spectrum between 164 and 180 nm and accepted the latest recommendation²³ between 180 and 270 nm. All three spectra look alike and have the same features at the shortest wavelengths characterizing the C-Br band absorption in alkanes. Table 3 lists the measured absorption cross sections with a step of 2 nm over the stratospheric transparency window near 200 nm. The detailed absorption cross sections over entire wavelength range are available in the Supporting Information and at www.nist.gov/kinetics/spectra/index.htm.

Atmospheric Implications. The atmospheric lifetimes of singly brominated propanes can be estimated based on the photochemical properties obtained in the present work. These compounds are very reactive toward OH while their absorption cross sections for tropospheric UV radiation (above 290 nm)

TABLE 3: Absorption Cross Sections of Bromopropanes between 180 and 230 nm at $T = 295$ K

wavelength, nm	absorption cross section, 10^{-19} , cm ² /molecule	
	CH ₂ Br-CH ₂ -CH ₃	CH ₃ -CHBr-CH ₃
180	10.85	22.02
182	2.99	3.65
184	2.95	1.82
186	3.56	1.76
188	4.27	1.94
190	4.98	2.21
192	5.65	2.48
194	6.25	2.80
196	6.70	3.13
198	7.02	3.43
200	7.18	3.73
202	7.26	3.99
204	7.12	4.20
206	6.88	4.35
208	6.52	4.42
210	6.10	4.42
212	5.65	4.36
214	5.15	4.22
216	4.66	4.01
218	4.14	3.74
220	3.58	3.41
222	3.08	3.07
224	2.60	2.71
226	2.18	2.36
228	1.78	2.02
230	1.44	1.68

are negligible (i.e., they are $< 10^{-22}$ cm²/molecule and the chemicals are not photolyzed in the troposphere). However, accurate values of the shorter wavelength UV cross sections are required for calculating bromine release from nPB and iPB in the stratosphere and the ozone depletion potentials of such compounds.

The reactions with hydroxyl radicals in the troposphere thus dictate the atmospheric lifetimes of propane, *n*-propyl bromide, and isopropyl bromide. A simple scaling procedure has been proved to be valid for relatively long-lived compounds that are well mixed throughout the troposphere. For such chemicals, lifetimes can be estimated using the equation²⁴

$$\tau_i^{\text{OH}} = \frac{k_{\text{MC}}(272)}{k_i(272)} \cdot \tau_{\text{MC}}^{\text{OH}} \quad (9)$$

where τ_i^{OH} and $\tau_{\text{MC}}^{\text{OH}} = 5.9$ years are the atmospheric lifetimes of the compound of interest and methyl chloroform (MC), respectively, due to reactions with hydroxyl radicals in the troposphere only, and $k_i(272)$ and $k_{\text{MC}}(272) = 6.0 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ (ref 23) are the rate constants for the reactions of OH with these substances at $T = 272$ K. The value of $\tau_{\text{MC}}^{\text{OH}} = 5.9$ years was obtained following the procedure used by Prinn et al.²⁵ from the measured lifetime of MC, $\tau_{\text{MC}} = 4.8$ years, when an ocean loss of 85 years and a stratospheric loss of 37 years are taken into account. Applying this method to the title compounds of this study yields the estimated atmospheric lifetimes of 14 days, 14 days, and 19 days for propane, *n*-propyl bromide, and isopropyl bromide, respectively. As can be seen, the lifetimes derived here are very short, much shorter than the characteristic time of mixing processes in the troposphere and hence are only crude estimates. The correct residence time of the compounds in the atmosphere will depend on the geographical location and season of the emissions as well as local atmospheric conditions. Some results of detailed atmospheric modeling can be found in the recent publications.^{6,7} Neverthe-

less, the presented estimations demonstrate that these chemicals are very short-lived ones, give reasonable average values of their lifetimes and a useful scaling among such compounds.

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Supporting Information Available: The ultraviolet absorption cross sections of nBP and iBP are presented in Table 4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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