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Low-Pressure Study of the Reactions of Br Atoms with Alkenes. 1. Reaction with Propene

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The reaction of Br atoms with propene was studied by the mass spectrometry discharge-flow method at low pressure (0.5−2.0 Torr of He) between 233 and 320 K. Under these experimental conditions, both the hydrogen atom abstraction $Br + C_3H_6 \rightarrow C_3H_5 + HBr$ (1a) and the addition $Br + C_3H_6 + M \rightarrow C_3H_6Br + M$ (1b) channels were observed. The Arrhenius expressions $k_{1a} = (8.15 \pm 4.5) \times 10^{-13}\exp\{-(1250 \pm 160/T)\}$ cm^3 molecule^{-1} s^{-1} and $k_{1b} = (3.8 \pm 0.8) \times 10^{-33} \exp\{(1200 \pm 50)/T\}$ cm^6 molecule^{-2} s^{-1} were obtained for these channels, respectively. The expression $k_{1b}k_{10}/k_{-1b} = (8.9 \pm 3.1) \times 10^{-36} \exp\{(4140 \pm 200)/T\}$ cm^6 molecule^{-2} s^{-1} was obtained for the combination of the rate constants for the adduct formation (k_{1b}) and adduct decomposition (k_{-1b}) reactions and for the reaction $C_3H_6Br + Br_2 \rightarrow C_3H_6Br_2 + Br$ (10). From these kinetic data, the enthalpy of reaction 1b and the heat of formation of the C_3H_6Br radical were calculated: $\Delta H^\circ_{1b} = -(7.7 \pm 1.4)$ kcal mol^{-1} and $\Delta H^\circ_f(C_3H_6Br) = 23.8 \pm 1.4$ kcal mol^{-1}. In addition, the rate constant of the reaction $Br + C_3H_5 \rightarrow C_3H_5Br$ (6) was measured: $k_6 = (2.0 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, at $T = 298$ K and 1 Torr total pressure.

Introduction

The present increasing interest in studying the reactions of Br atoms with hydrocarbons is due to several factors. First, there is a lot of evidence that bromine compounds play a significant role in the ozone chemistry both in the troposphere and in the stratosphere. For example, the episodic ozone losses observed in the Arctic troposphere during springtime (e.g., refs 1, 2) have been attributed, at least partly, to bromine chemistry. The occurrence of bromine reactions was inferred from field measurements of unsaturated hydrocarbon concentrations. Bromine atoms react quite rapidly with such compounds, in contrast with their reactions with saturated hydrocarbons.

Another interest in measuring kinetic parameters for the reactions of Br with hydrocarbons is the possible derivation of thermochemical data for the species which are formed in these reactions. The major channel which is expected for the reactions of Br atoms with alkene is the addition of the atom to the double bond. The adduct thus formed is unstable. A second channel, consisting of the direct abstraction of hydrogen atom, is also possible. The occurrence of this channel is more likely than for the reactions of Br atoms with alkanes. This is explained by the lower value of the C−H bond dissociation energy for allylic hydrogen compared with that in alkanes, and also by the possibility of indirect addition−elimination process in this H atom abstraction.

Presently, the kinetic data for Br reactions with alkenes are rather scarce.[3] Most previous studies used the relative kinetic method to determine the rate constant of the addition channel at a total pressure of 760 Torr of synthetic air at room temperature. The present study is the first one of a series of absolute kinetic investigations of the reactions of Br atoms with alkenes to be carried out in this laboratory. The studies include the determination of the temperature dependence of the rate constant for the two observed channels (addition and H atom abstraction).

The reaction of Br with C_3H_6 (1) has been studied previously.[4−6] This reaction possesses two possible channels:

$$Br + C_3H_6 \rightarrow HBr + CH_2{=}CHCH_2 \qquad \Delta H = 0.7 \text{ kcal mol}^{-1} \quad (1a)$$

$$Br + C_3H_6\ (+M) \rightarrow C_3H_6Br\ (+M) \qquad \Delta H = -(7.7 \pm 1.4) \text{ kcal mol}^{-1} \quad (1b)$$

(the structure of the adduct could not be specified in the present work).

The heats of formation used are from ref 7, except for $\Delta H_{f,298}(C_3H_5)$,[8] whereas the enthalpy of reaction 1b is derived from this work (see below). Kondo et al.[4] have carried out a very low pressure study of the H atom transfer channel (1a). In the two other studies,[5,6] the relative rate method was used to measure the rate constant of the addition channel (1b) at atmospheric pressure.

Experimental Section

A discharge-flow system coupled to a modulated molecular beam mass spectrometer was used and has been described earlier (e.g. ref 9). The main reactor consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) with a jacket for the circulation of the thermostated liquid (Figure 1). In order to reduce the heterogeneous loss of active species, the walls of the main reactor and of the double central injector were coated with halocarbon wax.

Two methods for the generation of Br atoms were used: either the dissociation of Br_2 in a microwave discharge of Br_2/He mixtures or the fast reaction 2:

$$Cl + C_2H_3Br \rightarrow Br + C_2H_3Cl \qquad (2)$$

$$k_2 = 1.43 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ [ref 10]}$$

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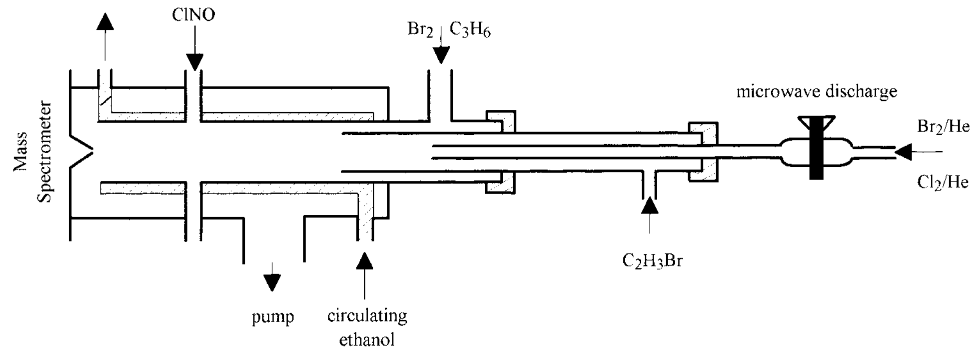

Figure 1. Schematic diagram of the flow reactor.

Cl atoms were produced from the microwave discharge of Cl_2/He mixtures. In all experiments, Br atoms were introduced into the reactor through the movable double injector. When reaction 2 was used, the reaction of an excess of C_2H_3Br with Cl atoms took place in the outer tube of the injector (downstream of the end of the inner tube) and was completed before the entrance in the main reactor. This could be verified by measuring both Cl consumption and Br production by mass spectrometry.

In most experiments, nitrosyl chloride (ClNO) was added at the downstream end of the reactor, in order to convert Br atoms into BrCl via the fast reaction 3:

$$\mathrm{Br + ClNO \rightarrow BrCl + NO} \tag{3}$$

$$k_3 = 1.5 \times 10^{-11} \exp(-52/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{[ref 11]}$$

Thus, Br could be detected as $BrCl^+$ (at $m/e = 116$). The advantage of this procedure was to avoid any complication in the direct detection of Br (at its parent peaks, $m/e = 79$ and 81) arising from the possible contribution of either the Br precursors or Br-containing products of reaction 1. The dissociation of these species was possible in the ion source, which was operated at 25−30 eV. The concentrations used for ClNO ($\sim 10^{14}$ molecules cm^{-3}) were high enough for reaction 3 to be completed before sampling into the mass spectrometer. Besides, it was verified that the addition of ClNO had no influence on the kinetics of the detected products of reaction 1 such as HBr, C_3H_5Br, and $C_3H_6Br_2$. The absolute concentrations of Br atoms were determined from the calibration of BrCl (at $m/e = 116$) using two methods. The first one used the titration reaction 3, with an excess of ClNO over a known concentration of Br which was derived from the measurement of the dissociated fraction of a known Br_2 concentration. The second method was based on the rapid conversion of Cl into BrCl using an excess of molecular bromine in reaction 4:

$$\mathrm{Cl + Br_2 \rightarrow BrCl + Br} \tag{4}$$

$$k_4 = 2.3 \times 10^{-10} \exp(-135/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{[ref 12]}$$

The measured Br_2 consumed yielded the BrCl concentration. Both methods agreed within experimental uncertainties.

Propene was introduced into the reactor through a sidearm tube, and its concentration was calculated from its flow rate. HBr, C_3H_5Br, and $C_3H_6Br_2$ were detected as products of this Br + C_3H_6 reaction system, at $m/e = 80$, 82 (HBr^+); 120,122 ($C_3H_5Br^+$); and 121,123 ($C_3H_6Br^+$), respectively. HBr was calibrated from the titration of hydrogen atoms by an excess of Br_2 in reaction 5:

$$\mathrm{H + Br_2 \rightarrow Br + HBr} \tag{5}$$

$$k_5 = 6.7 \times 10^{-10} \exp(-673/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{[ref 13]}$$

This calibration method was preferred to that using the direct flow rate of known amounts of HBr into the reactor, since it was very convenient for the relative measurement of HBr and BrCl, described in the next section. Besides, this method avoided any complication arising from the HBr decomposition during its storage. It was verified that the flow of preliminary purified by distillation HBr into the reactor gave the same results (within 10% uncertainty) as the other calibration method. The signals measured for the other stable products C_3H_5Br and $C_3H_6Br_2$ were calibrated directly by flowing known concentrations of these compounds.

The purities of the gases were as follows: He, >99.9995% (Alphagaz), was passed through a liquid nitrogen trap before entering the reactor; Br_2 >99.99% (Aldrich); HBr 99.8% (Praxair); Cl_2 >99.0% (UCAR); ClNO >99.2% (Matheson); C_2H_3Br >99.5% (UCAR); C_3H_6 >99.99% (Philips); CH_2CHCH_2Br 99% (Aldrich); $CHBrCHCH_3$ 98% (Aldrich); CH_2CBrCH_3 99% (Aldrich); $CH_3CH(Br)CH_2Br$ 97% (Aldrich).

Results

Determination of k_{1a}. *Br Kinetics.* The kinetics of reaction 1 was first studied from the consumption of Br atoms at three temperatures (T = 318, 298, and 273 K). As will be shown below, in this temperature range, channel −1b toward the adduct decomposition was favored relative to its formation:

$$\mathrm{Br + C_3H_6 + M \leftrightarrow C_3H_6Br + M} \tag{1b,−1b}$$

Therefore, the kinetics of Br decay were defined by the abstraction channel (1a):

$$\mathrm{Br + C_3H_6 \rightarrow HBr + C_3H_5} \tag{1a}$$

In preliminary experiments, it has been observed that the rate of Br consumption in the presence of an excess of propene was dependent on the Br initial concentration. The formation of a reaction product at $m/e = 120$, 122 (assigned to C_3H_5Br) was also observed. This was attributed to the existence of the secondary reaction 6, which was likely very fast since this reaction was observed even at low Br concentrations ($[Br]_0 = (2{-}5) \times 10^{11}$ molecules cm^{-3}):

$$\mathrm{Br + C_3H_5\ (+M) \rightarrow C_3H_5Br\ (+M)} \tag{6}$$

The occurrence of a fast secondary reaction was discussed in a

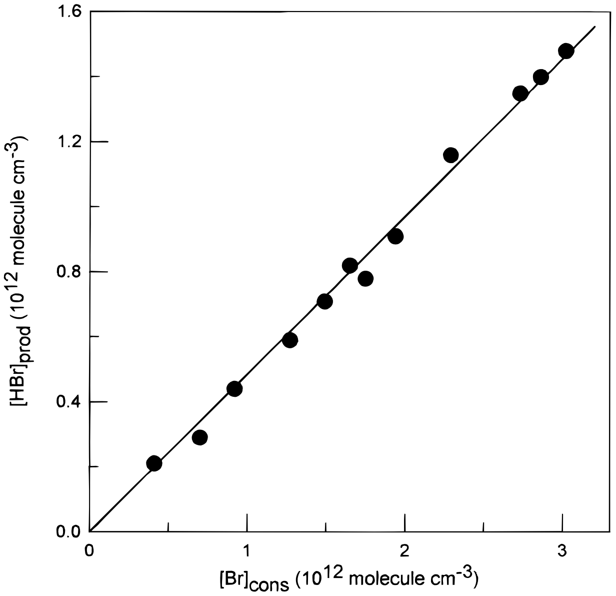

Figure 2. Concentration of HBr produced in reaction 1a as a function of the concentration of Br consumed.

previous study,[4] where the abstraction reaction (6′) was considered, with an estimated rate constant $k_{6'} > 10^{-12}$ cm^3 molecule^{-1} s^{-1}:

$$Br + C_3H_5 \rightarrow HBr + C_3H_4 \qquad (6')$$

A series of experiments were performed (at $T = 298$ K, in 1 Torr of He) to establish the mechanism of the reaction of Br atoms with allyl radicals. Reaction 2 was used as the source of Br atoms, since this Br_2-free system precluded the occurrence of the fast reaction 7:

$$C_3H_5 + Br_2 \rightarrow Br + C_3H_5Br \qquad (7)$$

$$k_7 = 4.8 \times 10^{-12} \exp(192/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ [ref 14]}$$

The concentrations of consumed Br atoms and produced HBr molecules were measured for a fixed reaction time ($t \approx 30$ms), with initial concentrations of Br around 5×10^{12} molecules cm^{-3} and of C_3H_6 in the range (1.3−13.9) $\times 10^{14}$ molecules cm^{-3}. The dependence of [HBr]$_{produced}$ as a function of [Br]$_{consumed}$ is shown in Figure 2. The observed linear dependence yields the ratio Δ[HBr]/Δ[Br] = 0.50 ± 0.02, where the uncertainty represents twice the standard deviation. In these experiments the "relative" procedure for the calibration of both HBr and Br (detected as BrCl) was used. As described before, the HBr and BrCl signals were calibrated simultaneously from the consumed fraction of the known concentration of Br_2 resulting from the reactions of Br_2 with H (reaction 5) and Cl (reaction 4), respectively. Thus, the ratio of the sensitivity for both HBr and BrCl could be related to the Br_2 concentration by considering the relative intensities of mass spectral signals. This procedure significantly reduced the final experimental uncertainty given for the ratio Δ[HBr]/Δ[Br]. The result obtained for this ratio indicates that only one molecule of HBr is formed for two consumed Br atoms in the reaction sequence (1) + (6). This demonstrates that reaction 6′ is negligible under the present experimental conditions. Furthermore, the detection of C_3H_5Br as a reaction product clearly indicates that the reaction between Br and C_3H_5 proceeds via an addition mechanism (reaction 6).

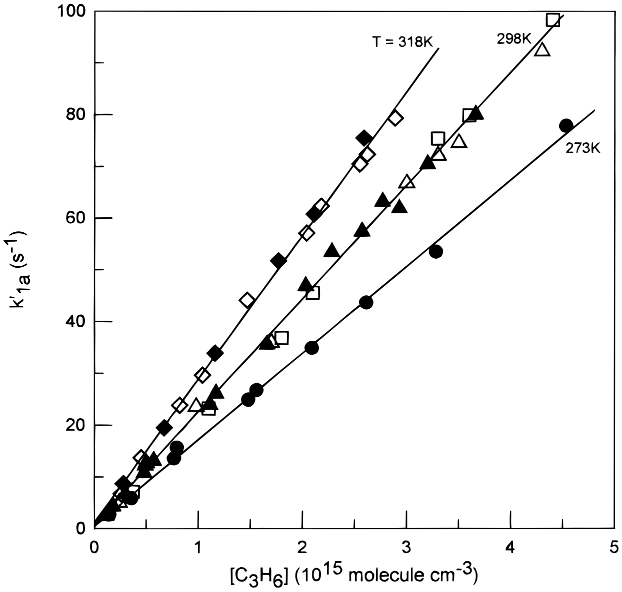

Figure 3. Pseudo-first-order plots of Br decays. Sources for Br atoms: open symbols, reaction Cl + C_2H_3Br (2); filled symbols, dissociation of Br_2. Total pressure in all experiments $P = 1$ Torr, except at $T = 298$ K: $P = 2$ Torr (□).

TABLE 1: Experimental Conditions and Results for the Measurements of k_{1a} (Abstraction Channel)

no. of expts	T (K)	[C_3H_6] × 10^{-14} (molecules cm^{-3})	[Br]$_0$ × 10^{-12} (molecules cm^{-3})	k_{1a} × 10^{14} (cm^3 molecule^{-1} s^{-1})	method
10	320	1.2−30	2.5−26.4	1.7 ± 0.2	*a*
7	320	1.8	6.5−47.0	1.90 ± 0.25	*b*
16	318	2.5−29	4.0−22	1.40 ± 0.15	*c*
11	298	2.2−24	0.5−13.4	1.1 ± 0.1	*a*
9	298	1.1−2.7	6.5−73	1.3 ± 0.2	*b*
30	298	1.0−44	4.0−45	1.10 ± 0.15	*c*
9	278	1.0−24	3.8−24.2	1.00 ± 0.25	*a*
10	273	1.5−45	8−10	0.82 ± 0.10	*c*
5	270	2.1	10.2−59	0.83 ± 0.10	*b*
10	263	2.4−30	2.0−22.4	0.65 ± 0.10	*a*
10	248	2.0−25	37−37.7	0.49 ± 0.08	*a*
10	233	2.0−48	2.1−29.4	0.4 ± 0.1	*a*

[a] From HBr formation kinetics. [b] From C_3H_5Br formation kinetics. [c] From Br decay kinetics (see text). Quoted errors represent 2 standard deviations.

The measurements of the rate constant k_{1a} from the Br decay kinetics were conducted with relatively high initial concentrations of Br atoms to ensure that the overall stoichiometry was 2. The two sources of Br atoms, dissociation of Br_2 and reaction 2, were used. The initial concentrations of Br were in the range (4−45) × 10^{12} molecules cm^{-3}, whereas those of C_3H_6 were in the range (0.1−4.5) $\times 10^{15}$ molecules cm^{-3}. The mean flow velocity in the reactor ranged between 900 and 1100 cm s^{-1}. Exponential decays of Br atom concentrations were observed, and the rate appeared to be independent of the initial concentration of Br. The pseudo-first-order rate constants, $k'_{1a} = 2k_{1a}[C_3H_6] + k_w$ (where k_w is the heterogeneous loss rate of Br), as a function of the propene concentration are shown in Figure 3 at three temperatures (273, 298 and 318 K). The linear least-squares fit to the experimental data provides the values of k_{1a}, which are summarized in Table 1. From the data at $T = 298$ K (Figure 3) no change in k_{1a} was observed in the pressure range 1−2 Torr of He. The rate of the heterogeneous loss of Br atoms, obtained from the intercepts in Figure 3, and also from the direct measurements in the absence of C_3H_6, was very low: $k_w = 1.0 \pm 0.5$ s^{-1}.

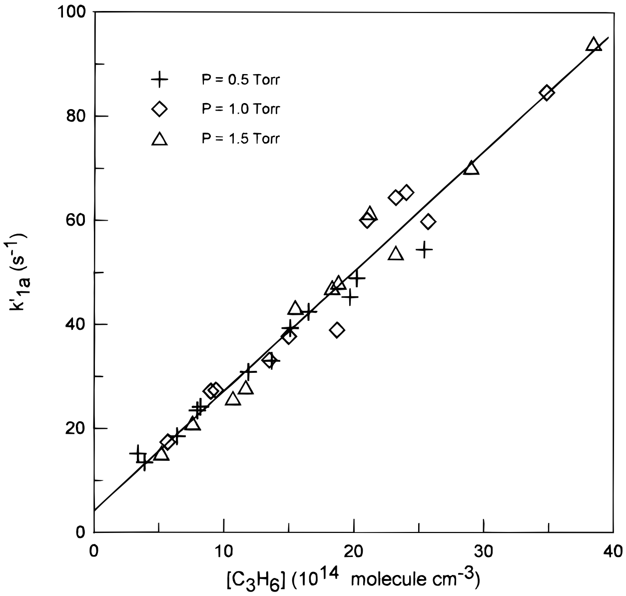

Figure 4. Pseudo-first-order plots of Br decays with direct detection of Br atoms (EPR) at three pressures.

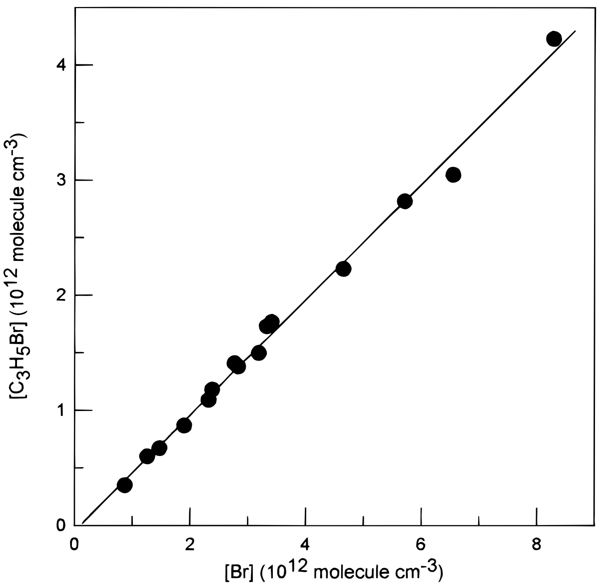

Figure 5. Concentration of C_3H_5Br produced in reaction 1a as a function of the concentration of consumed Br atoms.

At lower temperatures ($T = 233-243$ K), pure exponential kinetics of Br decays was not observed. The rates of Br decays were strongly dependent on $[Br]_0$, especially at high initial Br concentrations. Such an effect was likely due to the possible reaction of Br with the C_3H_6Br adduct:

$$\mathrm{Br} + \mathrm{C_3H_6Br} \rightarrow \text{products} \qquad (8)$$

At these low temperatures, reaction 8 could compete with the adduct decomposition reaction (−1b). Consequently, the measurements of k_{1a} in this set of experiments were limited to $T = 273$ K.

The kinetic results given in Figure 3 were obtained with Br detected as BrCl (see above). In experiments using the direct detection of Br atoms (at their parent peaks $m/e = 79, 81$) the values obtained for k_{1a} were underestimated, since a decrease of Br decay rate with reaction time was observed, which could be attributed to the decomposition of brominated products of reaction 1 in the ion source of the mass spectrometer. In order to validate the procedure used for the detection of Br, an independent measurement of k_{1a} was conducted using an EPR spectrometer (Varian) combined with a discharge-flow reactor. Under the following experimental conditions: $T = 298$ K, $P = 0.5-1.5$ Torr, $[Br]_0 = (3-6) \times 10^{12}$ and $[C_3H_6] = (3.4-38.4) \times 10^{14}$ molecules cm^{-3}, flow velocity = 1100−1650 cm s^{-1}, the direct EPR detection of Br led to the pseudo-first-order plot shown in Figure 4. A pressure-independent value was obtained for $k_{1a} = (1.1 \pm 0.1) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. This value is in excellent agreement with that obtained using the mass spectrometric detection of Br as BrCl (see Table 1).

HBr Kinetics. In another series of experiments, k_{1a} was derived from the kinetics of HBr formation, under the same experimental conditions as for the Br decay kinetics. The conditions and the results of these experiments are also presented in Table 1. No dependence of the measured values for k_{1a} on the initial concentration of either Br or propene was observed within the experimental uncertainty, although wide ranges of concentrations were used. This indicates that no secondary chemistry leading to additional production of HBr occurred under the experimental conditions used.

C_3H_5Br Kinetics. As mentioned above, C_3H_5Br was detected as a reaction product and was assumed to be formed in the secondary reaction 6. Although, the formation of allyl radical is the only thermochemically feasible channel of reaction 1a, experimental runs were attempted in order to identify the structure of C_3H_5Br. To identify structure of the C_3H_5Br molecule produced in reaction 6, the mass spectrum obtained was compared with the mass spectra of allyl bromide (CH_2CHCH_2Br), 1-bromo-1-propene ($CHBrCHCH_3$) and 2-bromopropene (CH_2CBrCH_3). It was first observed that the mass spectrometer sensitivity (at 25−30 eV electron energy) at the parent peaks of these three species ($m/e = 120, 122$) was equal (within 5%) for 1-bromo-1-propene and allyl bromide and about 2 times higher for 2-bromopropene. Considering the measured yield of C_3H_5Br formed in reactions 1a and 6, it could be concluded that 2-bromopropene was not a reaction product. This was demonstrated by measuring the dependence of C_3H_5Br produced ($\Delta[C_3H_5Br]$) as a function of Br consumed ($\Delta[Br]$) (similarly as for the HBr formation experiments). Again, the Br_2-free system was used (i.e., with reaction 2 for Br production). The experimental conditions were $T = 298$ K, $P = 1$ Torr, and $[Br]_0 = (3-15) \times 10^{12}$ and $[C_3H_6] = (3.5-20) \times 10^{14}$ molecules cm^{-3}. Allyl bromide was used for the absolute calibration of the signal at $m/e = 122$. From the results shown in Figure 5, the value of $\Delta[C_3H_5Br]/\Delta[Br] = 0.50 \pm 0.02$ was derived. This value was expected if the formation of one molecule of C_3H_5Br was considered for two consumed atoms of Br in reactions 1a and 6. It can be noted that the production of 2-bromopropene would have led to a value about 2 times lower than the above experimental value of $\Delta[C_3H_5Br]/\Delta[Br]$ (considering, as mentioned above, the dependence of the mass spectrometer sensitivity on the structure of C_3H_5Br). The data presented in Figure 5 were obtained using different initial concentrations of Br ($[Br]_0$ was varied over a factor 5). No dependence of the C_3H_5Br yield on $[Br]_0$ was observed. In additional experiments with low Br concentrations ($<5 \times 10^{11}$ molecules cm^{-3}) and with $[C_3H_6] = 2 \times 10^{15}$ molecules cm^{-3}, the decrease of C_3H_5Br yield was observed simultaneously with the decrease of the Br decay rate. This confirms that C_3H_5Br originates in reaction 6.

To distinguish between allyl bromide and 1-bromo-1-propene, the ratio of the peak intensities at $m/e = 120, 122$ ($C_3H_5Br^+$) and $m/e = 105{,}107$ ($C_2H_2Br^+$) was measured for the product of reaction 6 and for each of these compounds. These ratios,

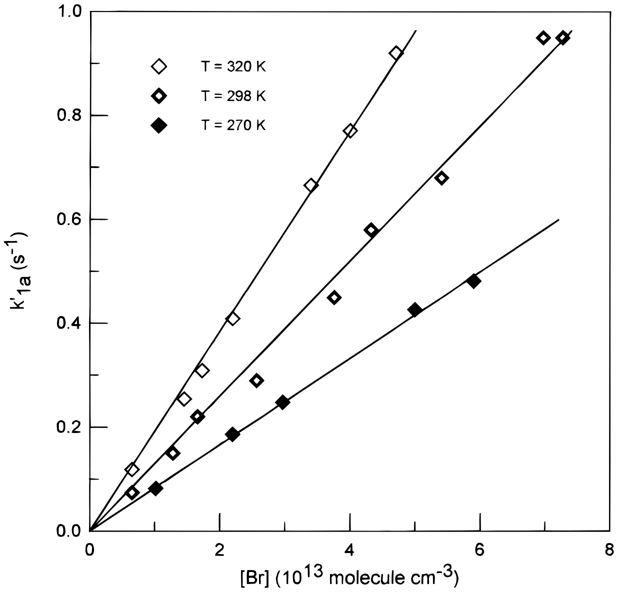

Figure 6. Pseudo-first-order plots of C_3H_5Br formation in the reaction sequence (1a) and (6) at three temperatures.

$I_{120,122}/I_{105,107}$, were 75 ± 10, 75 ± 10, and >200 for 1-bromo-1-propene ($CHBrCHCH_3$), 2-bromopropene ($CH_2C(Br)CH_3$), and allyl bromide (CH_2CHCH_2Br), respectively. This could be expected if the following ionization processes are considered:

$$CHBrCHCH_3 + e^- \rightarrow CHBrCH^+ + CH_3 + 2e^-$$

$$CH_2C(Br)CH_3 + e^- \rightarrow CH_2CBr^+ + CH_3 + 2e^-$$

$$CH_2BrCHCH_2 + e^- \rightarrow R^+ + CH_3 + 2e^-$$

The third reaction is very unlikely. In the experiments where the product was detected, the above ratio ($I_{120,122}/I_{105,107}$) was found to be >200. Therefore, it can be concluded that the C_3H_5Br molecule formed in the sequence of reactions 1a and 6 most likely corresponded to allyl bromide, as one could expect from thermochemistry.

Another set of experiments was performed in order to derive the rate constant k_{1a} from the kinetics of C_3H_5Br formation. Experiments were carried out at a pressure of about 1 Torr and at $T = 320$, 298, and 270 K. Br was produced in the microwave discharge of a Br_2/He mixture. Relatively high variable Br and relatively low fixed C_3H_6 concentrations (given in Table 1) were used. Under these conditions, the concentration of Br atoms versus reaction time was almost constant (the consumption of Br did not exceed 15% for a reaction time ≈ 0.03 s) and linear kinetics of C_3H_5Br formation were observed. The corresponding pseudo-first-order rate constants were determined as

$$k'_{1a} = k_{1a}[Br] = \frac{1}{[C_3H_6]}\frac{\Delta[C_3H_5Br]}{\Delta t}$$

The pseudo-first-order plots are shown in Figure 6. Straight lines were obtained from a linear fit to the experimental data and the values of the rate constant, derived from the slope, are shown in Table 1.

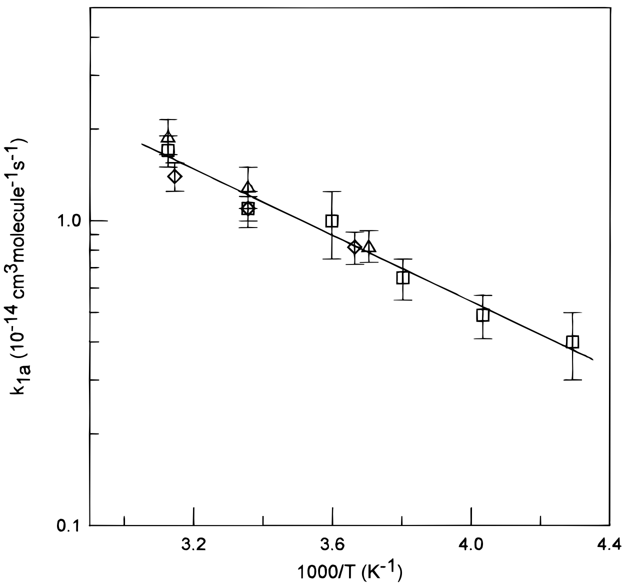

Figure 7. Arrhenius plot of the rate constant for the reaction Br + $C_3H_6 \rightarrow HBr + C_3H_5$ (1a): data from kinetics of HBr (□), Br (◇), and C_3H_5Br (△).

All the experimental determinations of k_{1a}, summarized in Table 1, have been plotted as a function of $1/T$ in Figure 7. The kinetic results obtained by the three different methods are in good agreement within the uncertainty range. The best fit to all data, presented in Figure 7, gives the following Arrhenius expression for the rate constant of the hydrogen atom abstraction channel of reaction 1:

$$k_{1a} = (8.15 \pm 4.5) \times 10^{-13} \times \exp\{-(1250 \pm 160)/T\}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

(quoted errors are 2σ and represent precision only).

Determination of k_6. The abstraction channel (1a) leads to the formation of C_3H_5 radicals. As was shown above, experimental evidence of the fast secondary reaction of these radicals with Br atoms was observed:

$$Br + C_3H_5\ (+M) \rightarrow C_3H_5Br\ (+M) \qquad (6)$$

The rate constant of this reaction has been determined in two series of experiments. In the first one, the Br decay kinetics were measured for different initial Br concentrations. The experiments were carried out at $T = 298$ K, $P \approx 1$ Torr, and $[C_3H_6] = (3.5-4.2) \times 10^{15}$ molecules cm^{-3}. The Br initial concentration was varied in the range $(0.09-7.9) \times 10^{12}$ molecules cm^{-3}. As would be expected, the change in k'_{1a} (by a factor of 2) was observed in this range of $[Br]_0$. The value of k_6 was determined from the simulation of the temporal profiles of Br using a simple chemical scheme including reaction 1a with the rate constant $k_{1a} = 1.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, reaction 6 with k_6 as variable, the heterogeneous loss of Br atoms with $k_w = 1.0$ s^{-1} and reaction 9:

$$C_3H_5 + C_3H_5\ (+M) \rightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2\ (+M) \qquad (9)$$

using the high-pressure limit of the rate constant $k_9 = 1.7 \times 10^{-11} \exp(-132/T)$ cm^3 molecule^{-1} s^{-1}.[15] The heterogeneous loss of C_3H_5 was assumed to be low compared to the consumption rate of C_3H_5 by Br atoms in reaction 6. The results obtained for k_6 were found to be insensitive to reaction 9 or to the Br heterogeneous loss rate. The mean value of k_6 thus obtained from the simulation of 13 independent kinetics was $k_6 = (2.0 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (quoted uncertainty represents precision only).

In the second series of experiments, Br_2 molecules were added to the reactor, leading to the simultaneous occurrence of reactions 6 and 7. The regeneration of Br atoms in reaction 7 induced an apparent decrease of the Br decay rate in reactions 1a and 6. Thirteen Br decay kinetic runs were performed at $P \approx 1$ Torr, $T = 298$ K, $[C_3H_6]_0 \approx 1.4 \times 10^{15}$ molecules cm^{-3}, $[Br]_0 \approx 2.8 \times 10^{12}$ molecules cm^{-3} and $[Br_2]$ varied in the range $(4.5 \times 10^{11}) - (3.1 \times 10^{14})$ molecules cm^{-3}. The Br decays were simulated using the same mechanism as above with the addition of reaction 7. Again, k_6 was entered as variable in order to obtain the best fit to the experimental data. The resulting value obtained for k_6 was $k_6 = (2.1 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The values of k_6 obtained by the two different approaches are in good agreement. The final and mean result for k_6 is, at $T = 298$ K:

$$k_6 = (2.0 \pm 0.5) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

Determination of k_{1b}. The addition channel (1b) was then investigated:

$$Br + C_3H_6\ (+M) \rightarrow C_3H_6Br\ (+M) \qquad (1b)$$

A major experimental complication associated with the determination of the rate constant for this channel is the instability of the C_3H_6Br adduct, since a rapid decomposition back to the reactants was observed, even at the lowest temperatures of the present study ($T = 233$ K):

$$C_3H_6Br + M \rightarrow C_3H_6 + Br + M(-1b)$$

However, C_3H_6Br was long-lived enough to be partly scavenged by Br_2 molecules (added to the reactor) by reaction 10:

$$C_3H_6Br + Br_2 \rightarrow C_3H_6Br_2 + Br \qquad (10)$$

The stable product formed (1,2-dibromopropane) was detected directly by mass spectrometry and its absolute concentrations were measured after calibration of the mass spectrometer from known concentration of $C_3H_6Br_2$. The addition of Br_2 led to the production of Br atoms via reactions 7 and 10, making Br consumption negligible (lower than 5% under the experimental conditions described below). Therefore, a linear dependence of the concentration of $C_3H_6Br_2$ formed on reaction time was observed, which allowed for a simple analytical treatment of the experimental data. Assuming steady-state conditions for the C_3H_6Br adduct the rate of $C_3H_6Br_2$ formation is:

$$d[C_3H_6Br_2]/dt = k_{1b}[Br][C_3H_6]\{k_{10}[Br_2]/(k_{-1b} + k_{10}[Br_2])\}$$

Consequently, the rate constant k_{1b} can be expressed as

$$k_{1b} = \frac{1}{[Br][C_3H_6]}\frac{d[C_3H_6Br_2]}{dt}\frac{k_{-1} + k_{10}[Br_2]}{k_{10}[Br_2]} = k_{obs}\frac{k_{-1} + k_{10}[Br_2]}{k_{10}[Br_2]}$$

where k_{obs} is the observed rate constant:

$$k_{obs} = \frac{1}{[Br][C_3H_6]}\frac{d[C_3H_6Br_2]}{dt}$$

The values of k_{obs} were determined for different Br_2 concentrations. Thus, by plotting $(1/k_{obs})$ as a function of $(1/[Br_2])$ according to

$$\frac{1}{k_{obs}} = \frac{1}{k_{1b}} + \frac{1}{K_{1b}k_{10}[Br_2]}$$

the values of k_{1b} and $K_{1b} \times k_{10}$ (where K_{1b} is the equilibrium constant $= k_{1b}/k_{-1b}$) could be derived. Under the experimental conditions used, reaction 8 between the adduct and Br atoms could be considered as negligible compared to reaction 10, as a consequence of the high ratios $[Br_2]/[Br]$. This was verified experimentally, since the results obtained for k_{obs} were independent of the initial concentration of Br atoms (which was varied over a wide range, see Table 2).

Experiments were carried out at a total pressure between 0.5 and 2.0 Torr, over the temperature range (233−308) K. All experimental conditions and results obtained for k_{1b} and $K_{1b}k_{10}$ are summarized in Table 2. Figure 8 shows typical examples of the dependence of $1/k_{obs}$ on $1/[Br_2]$. The $1/k_{1b}$ values were obtained from the intercepts and $1/(K_{1b}k_{10})$ from the slopes of the straight lines. Figure 9 shows the results obtained at $T = 253$ K at three pressures, 0.5, 1.0, and 2.0 Torr. As expected, the three slopes obtained were approximately equal, whereas the k_{1b} values obtained from the intercepts showed a linear pressure dependence, within the limits of experimental uncertainty (see Table 2). This result indicates that reaction 1b is in the termolecular regime in the pressure range used in this work.

The temperature dependence of k_{1b} is shown in Figure 10. The linear least-squares fit to experimental data provides the following Arrhenius expression for the addition channel (with He as a third body):

$$k_{1b} = (3.8 \pm 0.8) \times 10^{-33} \exp\{(1200 \pm 50)/T\}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}$$

(quoted errors are 2σ). k_{1b} can be also expressed as

$$k_{1b} = (2.15 \pm 0.10) \times 10^{-31}(T/298)^{-4.5 \pm 0.3}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}$$

The temperature dependence of the product $K_{1b}k_{10}$, shown in Figure 11, can be expressed as

$$K_{1b}k_{10} = (8.9 \pm 3.1) \times 10^{-36} \exp\{(4140 \pm 200)/T\}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}$$

These results are discussed in the next section.

Discussion

The value of k_{1a} obtained in the present work can be compared with the results of ref 4, where reaction 1a was studied at very low pressure (about 0.001 Torr) over the temperature range 263−363 K, using the very low pressure reactor technique with mass spectrometric detection of Br atoms. In these experiments, an inverse dependence of the apparent rate constant on initial Br concentration was observed, which was attributed to the production of excited metastable $Br(^2P_{1/2})$ in the microwave discharge. The actual values of the rate constant were extracted from the intercepts of the plots of the measured rate constants versus $1/[Br]_0$ at each temperature. Finally, the recommended Arrhenius expression was obtained: $k_{1a} = 8.35 \times 10^{-12} \exp(-2214/T)$ cm^3 molecule^{-1} s^{-1} (using a calculated preexponential factor and the best value of k_{1a} measured at $T = 363$ K). As one can see, the temperature dependence disagrees

TABLE 2: Experimental Conditions and Results for the k_{1b} and $K_{1b}k_{10}$ Measurements (Addition Channel)

no. of expts	T (K)	P (Torr)	$[C_3H_6]^a$	$[Br]^b$	$[Br_2]^c$	$k_{1b}{}^d$	$K_{1b}k_{10}{}^e$
10	308	1.0	1.8−4.6	4.8−10.5	0.76−5.02	1.9 ± 0.4	0.66 ± 0.08
10	293	1.0	2.2−3.3	5.2−11.1	0.57−4.9	2.3 ± 0.8	1.30 ± 0.19
14	283	1.0	2.2−2.8	1.7−7.5	0.46−6.4	2.75 ± 0.9	1.78 ± 0.25
9	273	1.0	2.5−4.4	3.0−4.6	0.56−5.7	3.0 ± 0.6	3.10 ± 0.42
11	263	1.0	1.6−2.0	2.5−8.1	0.25−6.3	3.8 ± 0.9	6.87 ± 0.94
9	253	0.5	1.4−2.0	7.2−7.7	0.26−7.7	4.65 ± 0.9	11.31 ± 1.75
12	253	1.0	2.1−2.7	2.0−6.5	0.36−9.7	4.35 ± 0.5	11.81 ± 3.19
10	253	2.0	2.4−3.0	1.9−2.4	0.22−6.2	4.0 ± 1.1	11.67 ± 1.55
12	243	1.0	1.8−2.3	1.7−2.9	0.24−7.55	5.4 ± 0.7	21.88 ± 2.54
13	233	1.0	1.9−2.4	1.7−7.6	0.19−6.0	6.7 ± 1.0	47.62 ± 6.8

[a] 10^{15} molecules cm^{-3}. [b] 10^{11} molecules cm^{-3}. [c] 10^{14} molecules cm^{-3}. [d] 10^{-31} cm^6 molecule^{-2} s^{-1}. [e] 10^{-29} cm^6 molecule^{-2} s^{-1}. Uncertainties are 1σ plus 10% systematic error.

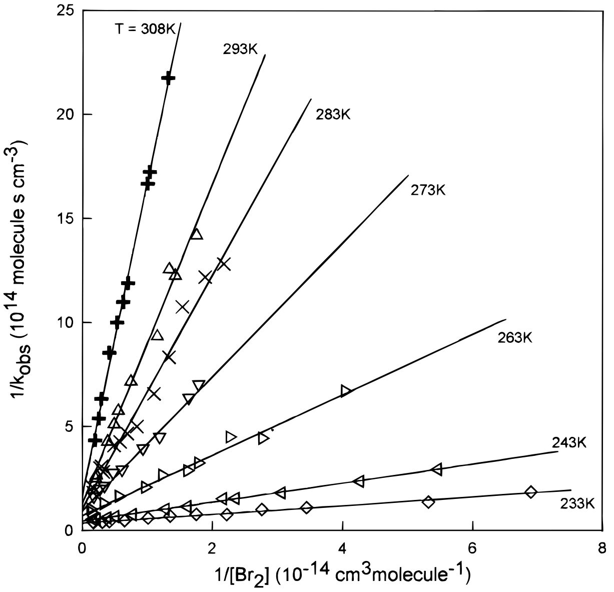

Figure 8. Reaction Br + C_3H_6 + M → C_3H_6Br + M (1b): $1/k_{obs}$ as a function of $1/[Br_2]$ at different temperatures (see text).

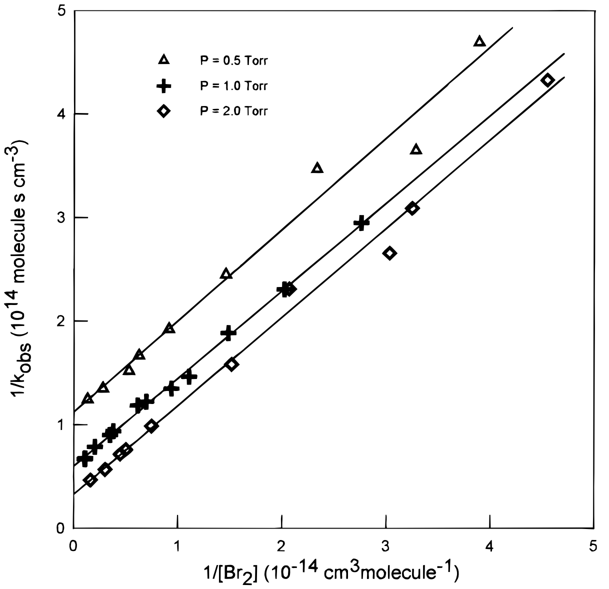

Figure 9. Reaction Br + C_3H_6 + M → C_3H_6Br + M (1b): $1/k_{obs}$ as a function of $1/[Br_2]$, observed at T = 253 K for different pressures (see text).

significantly with that obtained in the present study using a direct method. However, it can be noted that the difference in the absolute determinations of k_{1a} measured in both studies does not exceed a factor of 2 over the same temperature range.

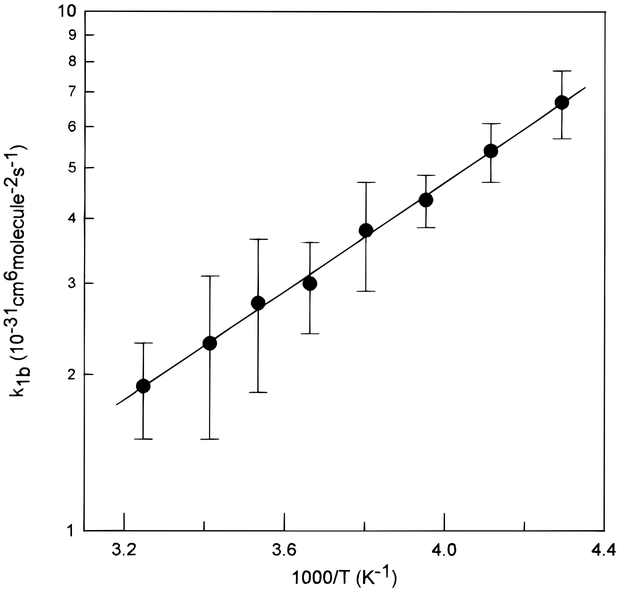

Figure 10. Arrhenius plot of the rate constant for the reaction Br + C_3H_6 + M → C_3H_6Br + M (1b).

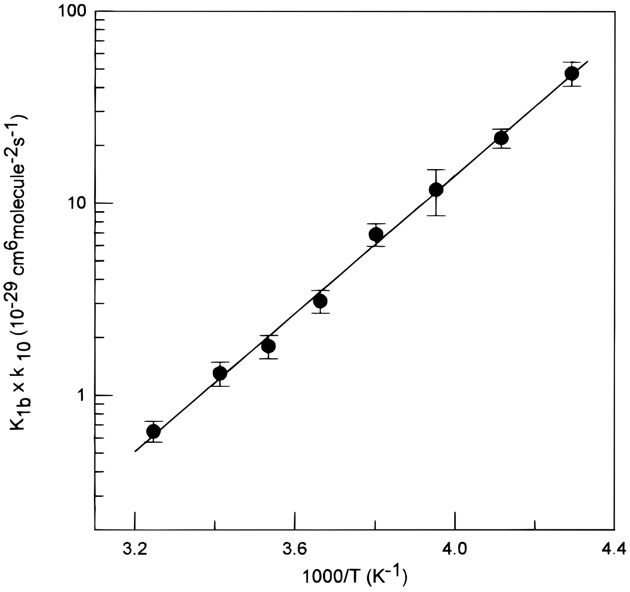

Figure 11. Temperature dependence of $K_{1b}k_{10}$ (see text).

In the present study of reaction 1a, it has been shown that the radical formed in the net hydrogen atom abstraction from propene by Br atom is $H_2C{=}CHCH_2$, showing that the transfer of the allylic H atom from the methyl group occurs preferentially. Therefore, it is of interest to compare the results obtained for k_{1a} with the literature data obtained for the reactions of Br atoms with CH_3 containing alkane molecules:

$$Br + C_2H_6 \rightarrow HBr + C_2H_5 \qquad \Delta H = 13.6 \pm 0.4 \text{ kcal mol}^{-1} \quad (11)$$

$$Br + C_3H_8 \rightarrow HBr + C_3H_7 \qquad \Delta H = 11.0 \pm 0.4 \text{ kcal mol}^{-1} \quad (12)$$

Several studies[16−20] exist for these two reactions. The values of k_{11} and k_{12} obtained in the most recent work[20] are $k_{11} = (2.35 \pm 1.12) \times 10^{-10} \exp\{-(6410 \pm 250)/T\}$ ($T = 473-621$ K) and $k_{12} = (8.78 \pm 3.00) \times 10^{-11} \exp\{-(4330 \pm 240)/T\}$ cm^3 molecule^{-1} s^{-1} ($T = 476-667$ K). In the same work, it was also estimated that the rate constant for the primary hydrogen atom abstraction was only 3% of k_{12} at $T = 473$ K and 12% at $T = 671$ K. These values of k_{11} and k_{12} ($k_{11} = 1.1 \times 10^{-19}$ and $k_{12} = 4.3 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at $T = 298$ K) are several orders of magnitude lower than the value of k_{1a} measured here ($k_{1a} = 1.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}). Such a large difference can be explained by thermochemistry since reactions 11 and 12 are highly endothermic (by 13.6 and 11.0 kcal mol^{-1}, respectively) whereas reaction 1a is thermoneutral ($\Delta H = 0.7$ kcal mol^{-1}). Another mechanism for the net H-abstraction reaction 1a may be addition−elimination:

$$Br + H_2C{=}CHCH_3 \rightarrow [CH_2BrCHCH_3]^* \rightarrow HBr + CH_2CHCH_2$$

(Br also may add to central carbon atom). Such mechanism can be possible only if the activation barrier to form products from the adduct is not too high. A similar mechanism, simultaneous with the direct H atom abstraction from the methyl group of the propene molecule, has been suggested in a recent investigation of the Cl + C_3H_6 reaction,[21] where a pressure dependence of the H atom abstraction rate constant was observed.

In the Experimental Section (determination of k_{1a} from Br decay kinetics), it was considered that the addition channel did not contribute to Br consumption due to the rapid decomposition of the adduct back to the reactants. In order to estimate the adduct decomposition rate under the present experimental conditions, a simple calculation can be made. Using the expressions given above for k_{1b} and $K_{1b}k_{10}$ and taking for k_{10} the value $2.4 \times 10^{-11}\exp\{(540 \pm 230)/T\}$ cm^3 molecule^{-1} s^{-1} (measured in ref 22 for the reaction of i-C_3H_7 with Br_2), we get $k_{-1b} = 1.0 \times 10^{-8}\exp\{-(2400 \pm 480)/T\}$ cm^3 molecule^{-1} s^{-1}, i.e., 10^4-10^5 s^{-1} for the adduct decomposition rate in the pressure and temperature range of this study. Although the adduct decomposition rate thus obtained is overestimated (H atom substitution by halogen reduces the reactivity of the alkyl radicals toward Br_2[14,23]), such a calculation shows that the adduct decomposition proceeds very rapidly.

Reaction 1b has been studied previously[5,6] at atmospheric pressure of $N_2 + O_2$ mixtures, using the relative rate method with the Br + CH_3CHO reaction as a reference. The measured rate constant was found to be dependent on O_2 concentration.[5] At $T = 298$ K and 760 Torr pressure of synthetic air, the rate constant values 2.7×10^{-12} (ref 5) and 3.85×10^{-12} cm^3 molecule^{-1} s^{-1} (ref 6) were obtained. There is no experimental data for the low-pressure limit of k_{1b} for comparison to the results of the present study: $k_{1b} = (3.8 \pm 0.8) \times 10^{-33} \exp\{(1200 \pm 50)/T\}$ cm^6 molecule^{-2} s^{-1}.

TABLE 3: Arrhenius Rate Constant Parameters of the Reactions of Free Radicals with Molecular Bromine (from Ref 14)

radical	log A (cm^3 molecule^{-1} s^{-1})	E_a (kcal mol^{-1})	ref
t-C_4H_9	-10.71 ± 0.11	-0.98 ± 0.45	22
i-C_3H_7	-10.62 ± 0.11	-1.08 ± 0.45	22
C_2H_5	-10.58 ± 0.12	-0.81 ± 0.41	22
CH_3	-10.70 ± 0.08	-0.38 ± 0.26	22
CH_2I	-11.11 ± 0.08	-0.76 ± 0.19	23
CH_2Br	-11.29 ± 0.08	-0.76 ± 0.22	23
CH_2Cl	-11.32 ± 0.08	-0.67 ± 0.19	23
$CHCl_2$	-12.01 ± 0.08	-0.38 ± 0.14	23
CF_2Cl	-11.88 ± 0.09	-0.12 ± 0.31	23
CF_3	$-11.69 \pm$	$+0.36$	23
$CFCl_2$	-12.19 ± 0.08	-0.10 ± 0.19	23
CCl_3	-12.52 ± 0.08	$+1.43 \pm 0.29$	23

Thermochemical information can be extracted from the temperature dependence of the product $K_{1b}k_{10}$ measured in this work. Although the absolute value of the rate constant k_{10} is not known, its temperature dependence can be assessed. For a series of R + Br_2 reactions (where R are carbon-centered radicals), kinetic data have been obtained by Gutman and coworkers.[14,22,23] It has been shown[14] that the rate constants of all the studied reactions of hydrocarbon radicals with Br_2 are very high (see Table 3). It has been also demonstrated[23] that halogen substitution reduced the reactivity. Table 3 contains some of these experimental data (discussed in ref 14) which show that substitution of hydrogen atom of the CH_3 radical by halogen atom does not change significantly the activation energy E_a (slightly negative) of the reaction of the substituted CH_3 radical with Br_2. Therefore, it is realistic to assume that the same picture will hold for the C_3H_7 radical and its halogen-substituted analogues, particularly for C_3H_6Br. Then, if the same value is considered for the activation energy of reaction 10 as for the corresponding reaction of C_3H_7 radical, the activation energy of this reaction is $E_a = -(1.1 \pm 1.0)$ kcal mol^{-1}(1 kcal mol^{-1} uncertainty has been added). Using this value and the present Arrhenius expression for $K_{1b}k_{10}$ ($K_{1b}k_{10} = (8.9 \pm 3.1) \times 10^{-36} \exp\{(4140 \pm 200)/T\}$ cm^6 molecule^{-2} s^{-1}), we obtain

$$K_{1b} = k_{1b}/k_{-1b} \sim \exp\{(7180 \pm 1400)/RT\}$$

Considering the expression $K_{1b} = \exp(\Delta S_{1b}/R) \exp(-\Delta H_{1b}/RT)$, the enthalpy of reaction 1b can be calculated $\Delta H_{1b} = -(7.2 \pm 1.4)$ kcal mol^{-1}, which gives for the standard state

$$\Delta H^\circ_{1b} = -(7.2 \pm 1.4) \text{ kcal mol}^{-1} - RT \approx -(7.7 \pm 1.4) \text{ kcal mol}^{-1}$$

(calculated at $T = 265$ K, mean value of the temperature range used). Consequently, the enthalpy of formation of C_3H_6Br radical can be derived:

$$\Delta H^\circ_f(C_3H_6Br) = 23.8 \pm 1.4 \text{ kcal mol}^{-1}$$

These thermochemical data can be compared with recently reported results for the analogous reaction of Br with ethene:[24] $\Delta H_{f,298}(CH_2CH_2Br) = 32.1 \pm 0.5$ kcal mol^{-1} and $D_0^{298}(Br-CH_2CH_2) = 7.1 \pm 0.5$ kcal mol^{-1}. This latter value is, as can be expected, close to the present determination: $D_0(Br-C_3H_6) = -\Delta H^\circ_{1b} = 7.7 \pm 1.4$ kcal mol^{-1}. Let us note that the thermochemical parameters obtained in ref 24 are in excellent agreement with our data recently obtained for Br + C_2H_4 reaction.[25]

In conclusion, new kinetic data have been obtained for the addition and abstraction channels of the reaction of Br with propene. The temperature dependence of the rate parameters has allowed for the determination of new thermochemical data. This study is the first of a series which aim at establishing the kinetics and mechanism of the reactions of Br with other alkenes. Some of these alkenes are of atmospheric relevance, and these Br + alkene reactions may be important in the chemistry taking place in the marine boundary layer at high and mid latitudes. More specially, it has been suggested that, in the arctic atmosphere, active bromine could be released from ice (or snow) or sea salt aerosol, thus initiating ozone-destroying cycles. The reactions of Br atoms with alkene molecules could act as bromine sinks. Therefore, it is important to know the rate of such reactions as well as their mechanisms in order to assess the stability of the bromine reservoirs formed in these reactions.

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