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Low-Pressure Study of the Reactions of Br Atoms with Alkenes. 3. Reactions with 2-Methyl-2-butene, 2,3-Dimethyl-2-butene, and 1-Hexene

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The kinetics of the reactions of Br atoms with 2-methyl-2-butene (C_5H_{10}), 2,3-dimethyl-2-butene (C_6H_{12}), and 1-hexene have been studied by the mass spectrometry discharge-flow method at 0.5−2.0 Torr of He over the temperature range $T = 233-320$ K. The occurrence of both hydrogen atom abstraction and addition channels has been observed for all the reactions. The Arrhenius expressions $k_{1a} = (5.2 \pm 2.5) \times 10^{-16}$ $\exp\{(1910 \pm 250)/T\}$ and $k_{2a} = (8.4 \pm 6.3) \times 10^{-16} \exp\{(1950 \pm 290)/T\}$ cm^3 molecule^{-1} s^{-1} have been obtained (at 1 Torr total pressure of He) for the addition reactions $\mathrm{Br} + C_5H_{10} \leftrightarrow C_5H_{10}\mathrm{Br}$ (1a,−1a) and $\mathrm{Br} + C_6H_{12} \leftrightarrow C_6H_{12}\mathrm{Br}$ (2a,−2a), respectively. Considering k_7 and k_8 as the rate constants for the reactions of Br_2 with $C_5H_{10}\mathrm{Br}$ and $C_6H_{12}\mathrm{Br}$, respectively, the following expressions have been determined: $k_{1a}k_7/k_{-1a} = (1.4 \pm 0.8) \times 10^{-35} \exp\{(5250 \pm 300)/T\}$ and $k_{2a}k_8/k_{-2a} = (6.2 \pm 6.8) \times 10^{-35} \exp\{(5190 \pm 510)/T\}$ cm^6 molecule^{-2} s^{-1}. Kinetic data have been also obtained for the H atom abstraction channels: $k_{1b} = (2.1 \pm 0.2) \times 10^{-11} \exp\{-(655 \pm 40)/T\}$, $k_{2b} = (2.4 \pm 0.6) \times 10^{-11} \exp\{-(75 \pm 130)/T\}$, and $k_{3b} = (3.25 \pm 0.4) \times 10^{-12} \exp\{-(425 \pm 70)/T\}$ cm^3 molecule^{-1} s^{-1}, for the reactions of Br with 2-methyl-2-butene, 2,3-dimethyl-2-butene, and 1-hexene, respectively. From this kinetic study, the enthalpies of reactions 1a and 2a and the heats of formation of the adduct radicals $C_5H_{10}\mathrm{Br}$ and $C_6H_{12}\mathrm{Br}$ have been estimated: $\Delta H^\circ_{1a} = -(10.0 \pm 1.6)$, $\Delta H^\circ_{2a} = -(9.8 \pm 2.1)$, $\Delta H^\circ_f(C_5H_{10}\mathrm{Br}) = 6.8 \pm 1.6$, and $\Delta H^\circ_f(C_6H_{12}\mathrm{Br}) = 0.1 \pm 2.5$ (in kcal mol^{-1}).

Introduction

Results of experimental studies of the reactions of Br atoms with ethene, propene, and *trans*-2-butene have been reported in two recent papers.[1,2] It was shown that successive replacement of an H atom in ethene by a methyl group led to an increase of the rate constant of both the H atom abstraction and the addition channels of the reaction of Br with the alkene by about 1 order of magnitude. The present paper deals with the reactions of Br atoms with two alkenes possessing an increased degree of methylation: 2-methyl-2-butene, $CH_3CH{=}C(CH_3)_2$, and 2,3-dimethyl-2-butene, $(CH_3)_2C{=}C(CH_3)_2$:

$$\mathrm{Br} + \text{2-methyl-2-butene} \leftrightarrow C_5H_{10}\mathrm{Br} \qquad (1a,-1a)$$

$$\rightarrow C_5H_9 + \mathrm{HBr} \qquad (1b)$$

$$\mathrm{Br} + \text{2,3-dimethyl-2-butene} \leftrightarrow C_6H_{12}\mathrm{Br} \qquad (2a,-2a)$$

$$\rightarrow C_6H_{11} + \mathrm{HBr} \qquad (2b)$$

(the structure of the adduct $C_5H_{10}\mathrm{Br}$ is not specified in the present work). Reactions 1 and 2 have already been investigated,[3] using the relative kinetic method to determine their rate coefficients in 1000 mbar of synthetic air at 298 K.

In the present study, the measurements of the temperature-dependent rate constants for both H atom abstraction and adduct formation channels of reactions 1 and 2 (over the temperature range $T = 233-320$ K) are reported. From the kinetic measurements, the C−Br bond dissociation energy in the adduct radicals as well as the enthalpy of formation of these radicals has been estimated. In addition, the temperature dependence (at $T = 248-320$ K) of the rate constant for the H atom abstraction channel of the reaction of Br atoms with 1-hexene (3b), $CH_3(CH_2)_3CH{=}CH_2$, is reported:

$$\mathrm{Br} + \text{1-hexene} \leftrightarrow C_6H_{12}\mathrm{Br} \qquad (3a,-3a)$$

$$\rightarrow C_6H_{11} + \mathrm{HBr} \qquad (3b)$$

Experimental Section

The experimental equipment used in the present study, a discharge flow system combined with modulated molecular beam mass spectrometer, is the same as that described in previous papers.[1,2]

Br atoms, generated in a microwave discharge of $\mathrm{Br_2/He}$ mixtures, were introduced into the reactor through the movable double injector. They were scavenged by ClNO at the end of the reactor (around 5 cm upstream of the sampling cone) and were detected as BrCl^+ ($m/e = 116$):

$$\mathrm{Br} + \mathrm{ClNO} \rightarrow \mathrm{BrCl} + \mathrm{NO} \qquad (4)$$

$$k_4 = 1.5 \times 10^{-11} \exp(-52/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \qquad \text{(ref 4)}$$

The advantage of detecting Br as BrCl^+, rather than directly detecting Br^+, is that it avoids interfering signals from the dissociative ionization of the precursors of Br atoms and/or Br-containing products (ion source was operated at 25−30 eV energy).

The absolute concentrations of Br atoms were determined using the titration reaction (4) (with $[\mathrm{Br}] = \Delta[\mathrm{ClNO}] = [\mathrm{BrCl}]$) and (5) (with $[\mathrm{Br}] = [\mathrm{BrCl}] = \Delta[\mathrm{Br_2}]$):

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$$\mathrm{Cl} + \mathrm{Br_2} \rightarrow \mathrm{BrCl} + \mathrm{Br} \qquad (5)$$

$$k_5 = 2.3 \times 10^{-10} \exp(-135/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad \text{(ref 5)}$$

The reacting alkene molecules were introduced into the reactor through its sidearm. The concentrations of the alkenes as well as the concentrations of the other stable species were determined from the pressure drop rate in the calibrated volumes containing species/He mixtures of known dilution.

The formation of HBr, $C_5H_{10}Br_2$, $C_6H_{12}Br_2$ was observed in reactions 1−3 under the experimental conditions used. $C_5H_{10}Br_2$ and $C_6H_{12}Br_2$ were detected at $m/e = 149/151$ (corresponding to the fragment $C_5H_{10}Br^+$) and $m/e = 163/165$ ($C_6H_{12}Br^+$), respectively, since the intensity of the parent peaks was much lower. The absolute calibration of the mass spectrometric signals was achieved by flowing known concentrations of 1,2-dibromohexane and 2,3-dibromopentane, respectively, into the reactor (see discussion below). The signal of HBr molecules, which were formed in reactions (1b), (2b), (3b), was also calibrated from a known concentration of HBr flowing into the reactor and from the H atom titration by an excess of Br_2 ($[HBr] = \Delta[Br_2]$):

$$\mathrm{H} + \mathrm{Br_2} \rightarrow \mathrm{Br} + \mathrm{HBr} \qquad (6)$$

$$k_6 = 6.7 \times 10^{-10} \exp(-673/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad \text{(ref 6)}$$

The results obtained by these two methods were consistent within 10%.

The purities of the gases used were as follows: He >99.9995% (Alphagaz) was passed through liquid nitrogen traps; Cl_2 >99% (Ucar); Br_2 >99.99% (Aldrich); HBr, 99.8% (Praxair), was degassed at $T = 77$ K; ClNO >99.2% (Matheson); 2-methyl-2-butene >99% (Aldrich); 2,3-dimethyl-2-butene >99% (Aldrich); 1-hexene >99% (Aldrich); 1,2-dibromopentane, 98% (Aldrich); 1,2-dibromohexane, 98% (Aldrich).

Results

Reactions of Br Atoms with 2-Methyl-2-butene and 2,3-Dimethyl-2-butene: Addition Channels 1a and 2a. The same experimental approach described in previous papers[1,2] was used in the present work for the determination of the rate constants of the adduct forming channels of reactions 1 and 2. Briefly, it consisted in the addition of Br_2 molecules to the reaction system in order to partly scavenge the unstable adduct-radicals formed in reactions 1a and 2a:

$$\mathrm{C_5H_{10}Br} + \mathrm{Br_2} \rightarrow \mathrm{C_5H_{10}Br_2} + \mathrm{Br} \qquad (7)$$

$$\mathrm{C_6H_{12}Br} + \mathrm{Br_2} \rightarrow \mathrm{C_6H_{12}Br_2} + \mathrm{Br} \qquad (8)$$

Experimentally, the rate of formation of the stable molecules $C_5H_{10}Br_2$ and $C_6H_{12}Br_2$ was measured as a function of the added Br_2 concentration. The treatment of the experimental data was based on the expressions 9 and 10 (for 2-methyl-2-butene and 2,3-dimethyl-2-butene, respectively):

$$\frac{1}{k_{1\mathrm{aobs}}} = \frac{1}{k_{1\mathrm{a}}} + \frac{1}{K_1 k_7 [Br_2]} \qquad (9)$$

$$\frac{1}{k_{2\mathrm{aobs}}} = \frac{1}{k_{2\mathrm{a}}} + \frac{1}{K_2 k_8 [\mathrm{Br_2}]} \qquad (10)$$

These expressions were obtained from the reaction mechanisms 1a, −1a, and 7 and 2a, −2a, and 8, respectively, assuming a steady state concentration for the adduct radicals (see refs 1 and 2). $K_1 = k_{1a}/k_{-1a}$ and $K_2 = k_{2a}/k_{-2a}$ are the equilibrium constants for the reactions 1a,−1a and 2a,−2a and the so-called "observed rate constants" $k_{1a\ obs}$ and $k_{2a\ obs}$ are defined as

$$k_{1\mathrm{aobs}} = \frac{1}{[\mathrm{Br}][\mathrm{C_5H_{10}}]} \frac{d[\mathrm{C_5H_{10}Br_2}]}{dt} \qquad (11)$$

$$k_{2\mathrm{aobs}} = \frac{1}{[\mathrm{Br}][\mathrm{C_6H_{12}}]} \frac{d[\mathrm{C_6H_{12}Br_2}]}{dt} \qquad (12)$$

According to expressions 9 and 10, the dependencies of the reciprocal of the observed rate constant on the reciprocal of the concentration of Br_2 led to the values of $1/k_{1a}$ and $1/k_{2a}$ (as the zero intercepts) and $1/K_1k_7$ and $1/K_2k_8$ (as the slopes).

Under the present experimental conditions, Br atoms consumed in the primary reactions 1 and 2 were rapidly regenerated through reactions −1a, −2a, 7, and 8, and 13 and 14:

$$\mathrm{C_5H_9} + \mathrm{Br_2} \rightarrow \mathrm{C_5H_9Br} + \mathrm{Br} \qquad (13)$$

$$\mathrm{C_6H_{11}} + \mathrm{Br_2} \rightarrow \mathrm{C_6H_{11}Br} + \mathrm{Br} \qquad (14)$$

Thus, the consumption of Br atoms as well as that of alkenes, which were used in excess over Br, was negligible and the concentrations of both reactants could be considered as constant. For some kinetic runs where the consumption of reactants was significant (up to 25%) the mean concentrations were used in the calculations of the observed rate constant. A linear temporal increase of the concentration of the products, $C_5H_{10}Br_2$ and $C_6H_{12}Br_2$, was observed, as one could expect, from the unchanged concentrations of reactants. This allowed for the simple analytical treatment of the experimental kinetics as described above.

Experiments were carried out at 0.5−2.0 Torr total pressure of helium at $T = 298{-}233$ K. The linear flow velocity in the reactor was in the range 500−800 cm s^{-1}. Figure 1 shows typical examples of the dependencies of $1/k_{1a\ obs}$ on the reciprocal of Br_2 concentration for reaction 1a. Similar dependencies were also observed for reaction 2a. The detailed experimental conditions and all the results obtained from the studies of reactions 1a and 2a are summarized in Tables 1 and 2. The temperature dependencies for k_{1a},k_{2a} and K_1k_7,K_2k_8 are also shown in Figures 2 and 3, respectively. The data shown in Figure 2 correspond to 1 Torr total pressure. The values of k_{1a} and k_{2a} obtained at $P = 0.5$ and 2 Torr have been multiplied and divided by two, respectively, in the corresponding plots. The Arrhenius expressions derived for the kinetic parameters are:

$$k_{1a} = (5.2 \pm 2.5) \times 10^{-16} \exp\{(1910 \pm 250)/T\}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_{2a} = (8.4 \pm 6.3) \times 10^{-16} \exp\{(1950 \pm 290)/T\}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$K_1k_7 = (1.4 \pm 0.8) \times 10^{-35} \exp\{(5250 \pm 300)/T\}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}}$$

$$K_2k_8 = (6.2 \pm 6.8) \times 10^{-35} \exp\{(5190 \pm 510)/T\}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}}$$

TABLE 1: Reaction Br + 2-Methyl-2-butene → $C_5H_{10}Br$ (1a): Experimental Conditions and Results

no. of expts	T (K)	P (Torr)	$[C_5H_{10}] \times 10^{-13\,a}$	$[Br] \times 10^{-12\,a}$	$[Br_2] \times 10^{-14\,a}$	$k_{1a}{}^{b}$	$K_1k_7{}^{c}$
5	298	1.0	1.7−2.0	1.4−1.6	1.45−5.5	3.5 ± 1.1^{d}	0.6 ± 0.1^{d}
10	280	1.0	1.9−2.2	0.7−1.7	0.4−4.0	4.6 ± 0.8	2.1 ± 0.3
8	271	2.0	0.77−0.85	0.8−0.9	0.3−3.8	10.7 ± 1.7	3.8 ± 0.6
9	263	1.0	1.3−1.6	0.6−2.0	0.4−4.9	7.2 ± 1.1	5.8 ± 0.8
9	248	1.0	1.3−1.5	0.2−1.1	0.3−3.6	10.0 ± 1.3	20.8 ± 3.2
8	241	0.5	2.2−2.7	0.35−1.2	0.4−3.6	7.7 ± 1.0	34.0 ± 6.0
8	233	1.0	1.3−1.4	0.3−0.45	0.3−2.6	20.0 ± 2.4	98.7 ± 16.0

[a] Units for the concentrations are molecules cm^{-3}. [b] Units are 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. [c] Units are 10^{-27} cm^6 $molecule^{-2}$ s^{-1}. [d] Quoted errors represent $1\sigma + 10\%$.

TABLE 2: Reaction Br + 2,3-Dimethyl-2-butene → $C_6H_{12}Br$ (2a): Experimental Conditions and Results

no. of expts	T (K)	P (Torr)	$[C_6H_{12}] \times 10^{-13a}$	$[Br] \times 10^{-11a}$	$[Br_2] \times 10^{-14a}$	$k_{2a}{}^{b}$	$K_2k_8{}^{c}$
5	298	1.0	1.5−1.8	2.8−3.8	2.4−9.1	0.67 ± 0.13^{d}	0.3 ± 0.08^{d}
6	288	2.0	1.3−1.5	2.3−2.5	1.3−8.4	1.25 ± 0.20	0.39 ± 0.06
6	280	1.0	0.6−1.2	3.3−3.5	0.55−3.7	0.8 ± 0.15	0.66 ± 0.10
8	271	0.5	4.4−5.8	5.3−5.8	0.45−4.7	0.7 ± 0.09	1.3 ± 0.2
6	263	1.0	3.8−4.1	5.5−6.0	0.4−3.4	1.25 ± 0.2	2.35 ± 0.35
7	255	0.5	0.7−0.9	2.9−3.7	0.35−4.7	0.95 ± 0.11	3.45 ± 0.45
9	248	1.0	0.6−0.75	1.3−3.9	0.4−4.1	2.0 ± 0.25	6.7 ± 1.2
7	241	1.0	2.9−3.5	2.4−2.7	0.3−6.6	3.5 ± 0.4	10.7 ± 1.3
8	233	1.0	0.4−0.5	1.4−2.0	0.2−4.1	3.15 ± 0.35	48.0 ± 9.5

[a] Units for the concentrations are molecules cm^{-3}. [b] Units are 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. [c] Units are 10^{-26} cm^6 $molecule^{-2}$ s^{-1}. [d] Quoted errors represent $1\sigma + 10\%$.

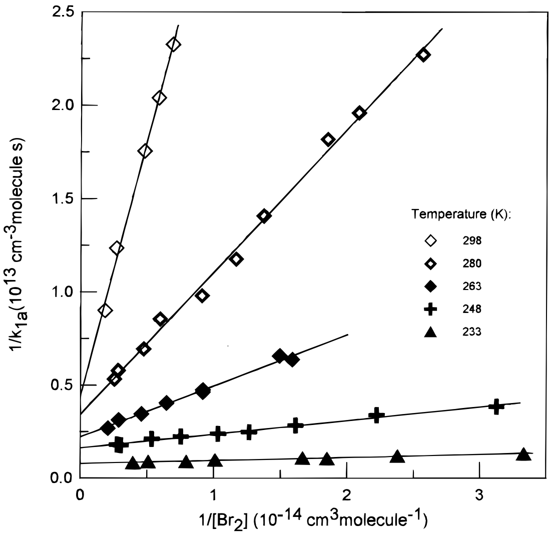

Figure 1. Reaction Br + 2-methyl-2-butene (1a): examples of the dependence of $1/k_{1a\ obs}$ on the reciprocal of the concentration of Br_2 at different temperatures and 1 Torr total pressure of He.

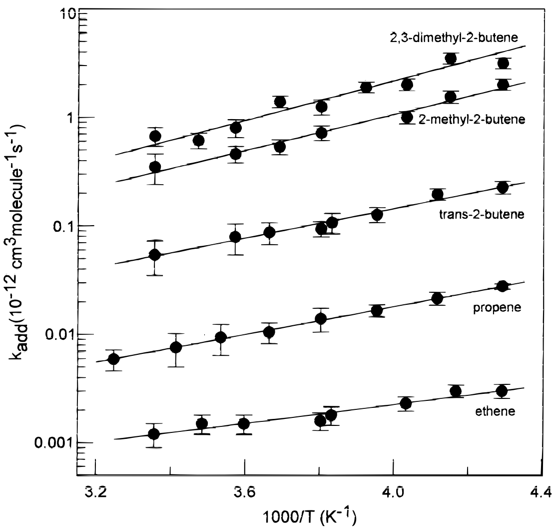

Figure 2. Temperature dependence of the rate constants of the adduct-forming channels of Br atoms reactions with alkenes (for 1 Torr total pressure of He): ethene,[2] propene,[1] *trans*-2-butene,[2] and 2-methyl-2-butene and 2,3-dimethyl-2-butene (this study).

Quoted uncertainties represent one standard deviation for the preexponential factor and 2σ for the activation energy.

As already mentioned, the absolute concentrations of the products $C_5H_{10}Br_2$ ($(CH_3)_2CBrCBrHCH_3$) and $C_6H_{12}Br_2$ ($(CH_3)_2CBrCBr(CH_3)_2$) were determined from the calibration of their signals (at $m/e = 151$ and 165, respectively) using known flow rates of 2,3-dibromopentane and 1,2-dibromohexane. In fact, these species do not possess the structure of the detected products and their use in these calibration experiments could lead to systematic errors in k_{1a} and k_{2a}. However, it seems to be acceptable to consider that the sensitivity of the mass spectrometer (operated at electron energy in the range 25−30 eV) to the above molecules at their fragment peaks ($C_5H_{10}Br^+$ and $C_6H_{12}Br^+$) does not strongly depend on their structure. The mass spectrometer sensitivity to different isomers is defined mainly by their ionization cross sections, which in our case, are functions of the appearance energy (AE) of the daughter ions. The difference in AE values is expected to be <0.1 eV, which supports the above assumption. The resulting error in the measurements is likely overlapped by the rather high uncertainty on the preexponential factor given above for k_{1a} and k_{2a}. One may also note that a possible systematic error can only affect the preexponential factor but not the values of the activation energy.

In the study of the Br reaction with 2,3-dimethyl-2-butene (2a), a slight deviation from linearity is observed at the lowest Br_2 concentrations, especially at the highest temperatures of the study (where very low concentrations of the product, $C_6H_{12}Br_2$, were detected). The reason for this can be various: formation of $C_6H_{12}Br_2$ in a secondary reaction of Br atoms with adduct,[2] relatively higher stability of the adduct and its own contribution to the signal at $m/e = 165$, heterogeneous product formation, etc. This question has not been fully investigated and the initial linear part of the experimental plots was used for the kinetic calculations. However, the above effect was more pronounced in the case of the Br reaction with 1-hexene, for

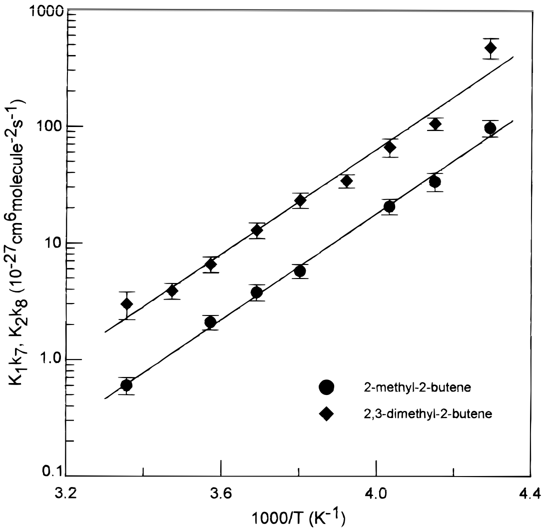

Figure 3. Temperature dependence of the combinations of the rate constants K_1k_7 and K_2k_8.

which only the rate constant of the H atom abstraction channel has been measured in this study.

Reactions of Br Atoms with 2-Methyl-2-butene, 2,3-Dimethyl-2-butene and 1-Hexene: H Atom Abstraction Channels 1b, 2b, and 3b. The procedure for the determination of the rate constants for the abstraction channels of reactions 1−3 was exactly the same as that used in the study of Br reaction with *trans*-2-butene.[2] The rate of formation of the reaction product, HBr, was measured as a function of the concentrations of the reactants, Br atoms and alkenes. As in the previous experiments, the concentrations of the reactants under the experimental conditions used (Br_2 concentrations in the range (2−4) × 10^{14} molecules cm^{-3} were added into the reactor) were almost constant with reaction time and linear kinetics of HBr formation were observed according to

$$\Delta[\mathrm{HBr}]/\Delta t = k_\mathrm{b}[\mathrm{Br}][\mathrm{alkene}]$$

The experiments were conducted at 1 Torr total pressure of helium, at temperatures between 233 and 320 K. The flow velocity in the reactor was in the range 500−850 cm s^{-1}. Examples of the dependencies of (1/[Br]) d[HBr]/dt on the alkene concentration are presented in Figure 4 for reaction 3b. The experimental conditions and all the results obtained are given in Table 3. As one can see, the variation of the Br concentration by a factor 3−4 had no influence on the experimental results, showing that no secondary chemistry occurred, leading to either HBr formation or consumption with a rate comparable with that of the primary reactions. The temperature dependencies of k_{1b}, k_{2b}, and k_{3b} are shown in Figure 5, with the corresponding Arrhenius expressions

$$k_{1b} = (2.1 \pm 0.2) \times 10^{-11} \exp\{-(655 \pm 40)/T\}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_{2b} = (2.4 \pm 0.6) \times 10^{-11} \exp\{-(75 \pm 130)/T\}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_{3b} = (3.25 \pm 0.4) \times 10^{-12} \exp\{-(425 \pm 70)/T\}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

(uncertainties are one standard deviation for the preexponential factor and 2σ for the activation energy).

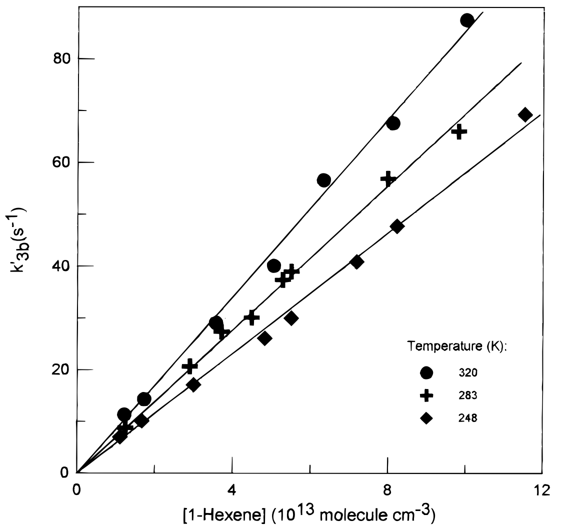

Figure 4. Reaction Br + 1-hexene (3a): dependence of the pseudo-first-order rate constant of HBr formation, k'_{3b} = 1/[Br](d[HBr]/dt), on the concentration of 1-hexene.

TABLE 3: H Atom Abstraction Reactions 1b, 2b, and 3b: Experimental Conditions and Results (for 1 Torr Total Pressure)

no. of expts	T (K)	[Br] × 10^{-12a}	[alkene] × 10^{-13a}	k^b
		Br + 2-Methyl-2-butene → C_5H_9 + HBr		
8	320	0.55−1.35	0.8−10.7	2.65 ± 0.35[c]
9	298	0.4−11.7	1.1−11.8	2.3 ± 0.3
7	280	1.1−1.4	0.35−5.45	2.05 ± 0.25
9	263	0.5−12.3	0.9−14.3	1.75 ± 0.25
9	248	0.65−1.65	0.9−9.3	1.45 ± 0.20
9	233	0.8−1.8	0.5−3.3	1.25 ± 0.20
		Br + 2,3-Dimethyl-2-butene → C_6H_{11} + HBr		
8	320	0.2−0.22	0.2−1.65	18.5 ± 2.5[c]
8	298	0.26−0.96	0.2−1.3	20.5 ± 2.5
8	280	0.21−0.24	0.25−2.3	18.5 ± 2.5
8	263	0.25−0.3	0.3−2.1	17.5 ± 2.5
9	248	0.25−0.9	0.2−1.5	17.0 ± 2.5
8	233	0.22−0.3	0.25−1.9	18.5 ± 2.5
		Br + 1-Hexene → C_6H_{11} + HBr		
7	320	0.7−1.0	1.2−10.0	0.86 ± 0.12[c]
6	298	0.8−1.2	1.5−9.6	0.79 ± 0.10
8	283	0.4−1.9	1.2−9.8	0.70 ± 0.11
7	263	0.8−1.1	1.4−10.4	0.66 ± 0.08
8	248	0.5−1.3	1.1−11.5	0.58 ± 0.08

[a] Units for the concentrations are molecules cm^{-3}. [b] Units are 10^{-12} cm^3 molecule^{-1} s^{-1}. [c] Quoted errors represent 1σ + 10%.

Discussion

Reactions 1 and 2 have been studied previously,[3] in 1 atm of synthetic air at T = 298 K and the rate constants were measured from the kinetics of 2-methyl-2-butene and 2,3-dimethyl-2-butene relative to *trans*-2-butene with the resulting values (1.91 ± 0.38) × 10^{-11} and (2.82 ± 0.56) × 10^{-11} cm^3 molecule^{-1} s^{-1}, respectively. The total rate constants for the two channels (addition and abstraction) measured in the present work for these reactions (at T = 298 K and 1 Torr total pressure of helium) are (2.65 ± 0.4) × 10^{-12} and (2.1 ± 0.3) × 10^{-11} cm^3 molecule^{-1} s^{-1}, respectively. In fact, a comparison of the results of the two studies made at different pressures is not very easy. For example, the rate constant of the H atom abstraction channel, measured in the present low-pressure study, cannot be considered as the same at atmospheric pressure if this abstraction proceeds (even partly) through an addition−elimination mechanism, which is very likely.

TABLE 4: Summary of Kinetic Results Obtained for Br Reactions with Alkenes

	H atom abstraction channel[a]			addition channel[a]			
alkene	*A* factor[b]	E_a/R (K)	k_{298}[b]	*A* factor[c]	E_a/R (K)	k_{298}[d]	ref
ethene				0.42 ± 0.17	−995 ± 210	0.012 ± 0.003	2
propene	0.082 ± 0.045	1250 ± 160	0.0012 ± 0.0002	0.5 ± 0.06	−1475 ± 60	0.076 ± 0.026	1
trans-2-butene	0.58 ± 0.17	960 ± 160	0.024 ± 0.003	2.8 ± 1.1	−1560 ± 205	0.54 ± 0.19	2
2-methyl-2-butene	2.1 ± 0.2	655 ± 40	0.23 ± 0.03	5.2 ± 2.5	−1910 ± 250	3.5 ± 1.1	*e*
2,3-dimethyl-2-butene	2.4 ± 0.6	75 ± 130	2.0 ± 0.25	8.4 ± 6.3	−1950 ± 290	6.7 ± 1.3	*e*
1-hexene	0.33 ± 0.04	425 ± 70	0.079 ± 0.010				*e*

[a] Data for 1 Torr total pressure of He. [b] Units are 10^{-11} cm^3 molecule^{-1} s^{-1}. [c] Units are 10^{-16} cm^3 molecule^{-1} s^{-1}. [d] Units are 10^{-13} cm^3 molecule^{-1} s^{-1}. [e] This work.

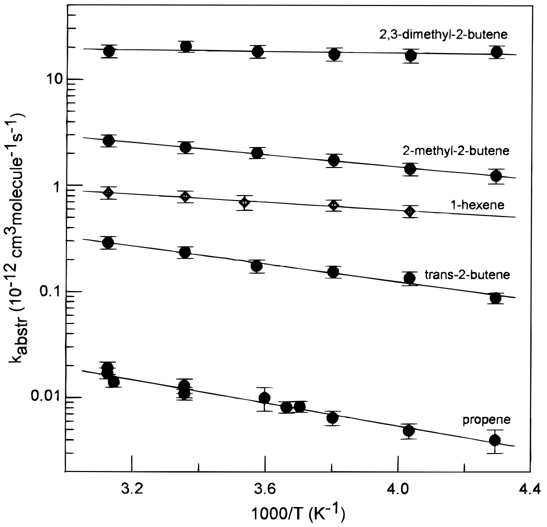

Figure 5. Temperature dependence of the rate constants of the H atom abstraction channels of Br atoms reactions with alkenes (at 1 Torr total pressure of He): propene,[1] *trans*-2-butene,[2] and 2-methyl-2-butene, 2,3-dimethyl-2-butene, and 1-hexene (this study).

It is presently accepted that at atmospheric pressure reactions of Br atoms with unsaturated organic compounds proceed mainly via an addition mechanism [e.g. ref 3]. The results of this study show that the H atom abstraction pathway can be comparable or even dominate the addition channel, at least at low pressures (∼1 Torr).

All the data obtained for the rate constants of the H atom abstraction channels of the reactions of Br atoms with alkenes (from this study and[1,2]) are summarized in Table 4 and Figure 5. One may note a significant increase (about 1 order of magnitude) in the value of the rate constant for each replacement of H by CH_3 from propene to 2,3-dimethyl-2-butene. A simultaneous increase in the preexponential factor and a decrease in the activation energy are also observed. In the study of the Br atoms reaction with propene,[1] it has been shown that as one could expect the H atom abstraction channel proceeds through an allylic H atom abstraction from the methyl group. The observed increase of the rate constant for the abstraction channels with the increase of the number of methyl groups on the alkenic C atoms seems to indicate that the reactions of Br with the higher alkenes also proceed mainly (if not exclusively) through this H atom transfer from the CH_3 group. Besides, the comparison of the results obtained for the rate constants of the H atom abstraction channel in the reactions of Br with 2,3-dimethyl-2-butene and with 1-hexene seems to support this conclusion. Another interesting observation is that the value of the preexponential factor for the rate constant of the Br reaction with 1-hexene lies between the values for the Br + propene and Br + *trans*-2-butene reactions. This again shows that an increasing of the number of CH_3 groups increases the steric factor, that is, the probability that the reactants possess the orientation required for the chemical reaction to occur. The thermochemistry is another important factor determining the reactivity of Br atoms toward alkenes. In the example given above, the *A* factor for the reaction of 1-hexene with Br is lower than that for the *trans*-2-butene reaction. Nevertheless, the absolute value for the rate constant of reaction 3b is higher than that of the Br + *trans*-2-butene reaction due to the difference in the activation energies. Compared with propene, the rate constant for the abstraction channel of the Br reaction with 1-hexene is much higher (about 2 orders of magnitude under the present experimental conditions), again mainly due to the lower value of the activation energy: the H atom abstraction by Br from propene is slightly endothermic ($\Delta H \approx 0.7$ kcal mol^{-1}), whereas the enthalpy for the reaction with 1-hexene (unfortunately unknown) is expected to be much lower.

The selectivity of Br atoms in the H atom abstraction from alkenes seems to be very important and may lead to interesting applications. One of them is the selective generation of allyl and allylperoxy radicals in laboratory studies, especially for the higher alkenes, for which the abstraction channel is important. This can be especially useful for the kinetic studies relevant to combustion processes, since at elevated temperatures the formation of the adduct radical can be ignored due to its very rapid decomposition back to reactants.

As one can see from Table 4, the rate constant increases with the complexity of the alkene molecule for the addition channels of the Br reactions with alkenes as observed for the abstraction channels. Such a trend has been also observed for the high-pressure rate constants of the Br reactions with alkenes.[3] This was explained by a positive inductive effect of the methyl group, leading to an increase of the electronic density on the double bond, favoring the electrophilic addition. However, the major factor influencing the low-pressure limit rate constant for the addition reactions is the density of states of the adduct, which increases with the number of degrees of freedom, i.e., with the complexity of the alkene molecule, allowing for an efficient distribution of excess energy within the adduct, favoring its stabilization process and, therefore, increasing the rate constant. In this context, the kinetic data for the adduct forming channel of the Br reaction with 1-hexene (possessing only one CH_3 group “far” from the double bond) could be very useful. Although this channel has not been studied in detail in the present work (due to the experimental difficulties mentioned above), the value of its rate constant was experimentally estimated to be higher than that for the Br addition reaction to *trans*-2-butene (with two CH_3 groups “close” to the double bond).

Although for all the investigated reactions an apparently linear dependence was observed for the measured values of the addition rate constant with pressure (which was changed from 0.5 to 2.0 Torr), a trend of slight deviation from this linearity was also observed. Considering the rather narrow pressure range of this study, it seems to be speculative to postulate, especially

TABLE 5: Summary of the Thermochemical Data Obtained for Br Addition Reaction to Alkenes

alkene	C−Br bond energy in adduct (kcal mol^{-1})	$\Delta H°_f$(adduct-radical) (kcal mol^{-1})	ref	$\Delta H°_f$(alkyl radical) (kcal mol^{-1})[b]
ethene	6.8 ± 1.6	32.4 ± 1.6	2	28.4 ± 0.5 (ethyl)
propene	7.7 ± 1.4	23.8 ± 1.4	1	23.9 ± 0.5 (*n*-propyl) 22.0 ± 0.5 (isopropyl)
trans-2-butene	8.8 ± 1.5	20.5 ± 1.8	2	16.0 ± 0.5 (2-butyl)
2-methyl-2-butene	10.0 ± 1.6	6.8 ± 1.8	*a*	6.7 ± 0.7 (2-methylbut-2-yl)
2,3-dimethyl-2-butene	9.8 ± 2.4	0.1 ± 2.5	*a*	

[a] This work. [b] Data from ref 12.

for the higher alkenes, that the studied reactions are in the termolecular regime.

Using the same procedure as that employed previously,[1,2] thermochemical data for the enthalpies of reactions 1 and 2, as well as for the enthalpies of formation of the adduct radicals $C_5H_{10}Br$ and $C_6H_{12}Br$, can be extracted from the kinetic expressions obtained above for K_1k_7 and K_2k_8. Considering for the activation energy of reaction 7 the value $E_7 = -(1000 \pm 1000)$ cal mol^{-1} (by analogy with similar reactions of alkyl radicals, as already discussed[1] and based on the results of previous studies[7−9]) and using the Arrhenius expression obtained here for K_1k_7, the equilibrium constant for the reactions 1a,−1a can be derived:

$$K_1 = k_{1a}/k_{-1a} \sim \exp\{(9430 \pm 1600)/RT)$$

Expressing K_1 as $K_1 = \exp(\Delta S_1/R)\exp(-\Delta H_1/RT)$, one obtains the enthalpy of reaction 1: $\Delta H_1 = -(9.43 \pm 1.6)$ kcal mol^{-1}, which (expressed in pressure units) leads to the standard state value:

$$\Delta H°_1 = -(10.0 \pm 1.6) \text{ kcal mol}^{-1}$$

Using this value and the enthalpies of formation of Br atoms (26.7 kcal mol^{-1} [10]) and 2-methyl-2-butene (−(9.9 ± 0.2) kcal mol^{-1} [11]), the heat of formation of the adduct radical $C_5H_{10}Br$ can be calculated:

$$\Delta H°_f(C_5H_{10}Br) = (6.8 \pm 1.8) \text{ kcal mol}^{-1}$$

A similar calculation for the 2,3-dimethyl-2-butene (with $E_8 = -(1000 \pm 1000)$ cal mol^{-1} and $\Delta H°_f(C_6H_{12}) = -(16.8 \pm 0.36)$ kcal mol^{-1} [11]) gives

$$\Delta H°_2 = -(9.8 \pm 2.1) \text{ kcal mol}^{-1}$$

$$\Delta H°_f(C_6H_{12}Br) = (0.1 \pm 2.5) \text{ kcal mol}^{-1}$$

As previously,[1,2] no correction is made for the temperature dependence of the thermochemical parameters because of the rather large uncertainty of the above estimations.

All the thermochemical data obtained in the present and previous[1,2] studies are collected in Table 5. It can be seen that the C−Br bond dissociation energy in the alkene−Br adduct tends to increase with the complexity of the alkene molecule. A slight departure of this trend for the 2,3-dimethyl-2-butene seems to originate from the uncertainties of both the experiments and the estimations. The data obtained for the heats of formation of adduct radicals seem to be realistic, especially if compared with the available analogous data for the corresponding alkyl radicals given in Table 5.

The *atmospheric application* of the present data can be briefly discussed. New information arising from the present kinetic and mechanistic measurements is that Br + alkene reactions do produce HBr and can, potentially, be a significant source of HBr in the marine atmosphere. The reaction of Br atoms with formaldehyde is currently considered as the main source of HBr in the troposphere. Considering a typical concentration of 0.2 ppbv of formaldehyde in remote marine air and the values of the rate constants for the reactions of Br + formaldehyde ($k = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [10]) and Br + alkenes (Table 4, assuming that measured kinetic data are applicable at atmospheric pressure), one can expect that the contribution of the Br + alkenes reactions to HBr production could be comparable with that from the reaction with formaldehyde, even at concentrations of a few tens pptv for the alkenes higher than C_3. Such concentrations can be found, at least in some locations; for example, 1-C_4H_8, iso-C_4H_8, 1-C_5H_{10}, and 1-C_6H_{12} concentrations up to 1 ppb have been measured in the intertropical South Pacific marine boundary layer (Hao atoll).[13]

HBr would be a reservoir for bromine, with a lifetime toward OH reaction of about 1 day, considering that the uptake by sea salt aerosol and further release of photolabile species (BrCl, Br_2) is not too fast. In such a case, HBr is expected to be more stable that the other bromine reservoirs, the brominated carbonyl compounds produced by the Br + alkene addition reaction,[3] and HOBr produced from the reaction of BrO with HO_2 and possibly CH_3O_2.[14] Therefore, the formation of HBr by Br + alkene reactions could significantly influence the bromine partitioning in the marine atmosphere by reducing the active bromine concentrations. However, this effect could be less if a fast uptake of HBr by sea salt aerosols and subsequent release of Br_2 or BrCl is significant.

It should be mentioned again that the above discussion on the possible role of Br + alkene reactions as a source of tropospheric HBr remains speculative. In order to better assess this role, the knowledge of the chemical mechanism of H atom abstraction from alkene by Br atom and/or information on pressure dependence of the corresponding rate constants are needed. If H atom transfer proceeds mainly by Br addition to the double bond with subsequent elimination of HBr, the branching ratio for HBr forming channel is expected to decrease with increasing pressure because of increased stabilization of the adduct, so that HBr production could become negligible at atmospheric pressure. On the other hand, if the rate constants measured in the present work correspond to direct H atom abstraction, in this case, as shown above, HBr formation in reactions of Br atoms with some alkenes can be an important source of HBr under atmospheric conditions.

The results of the present work do not allow to conclude about the mechanism of the H atom transfer. Both direct H atom abstraction and Br addition to the double bond, with subsequent elimination of HBr, may occur. To clarify the actual mechanism of HBr formation in the Br + alkene reactions, additional kinetic and mechanistic studies of these reactions at higher pressures (up to pressures corresponding to the high-pressure regime of the relevant addition reactions) would be very useful.

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