J. Phys. Chem. A **1999,** *103,* 4026−4033

Low-Pressure Study of the Reactions of Br Atoms with Alkenes. 2. Reactions with Ethene and *trans*-2-Butene

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Received: January 25, 1999; In Final Form: March 18, 1999

The reactions of Br atoms with ethene and *trans*-2-butene have been studied by the mass spectrometry discharge-flow method, at a total pressure of helium 0.5−2.0 Torr in the temperature range 233−320 K. The expression $k_1^\circ = (3.0 \pm 1.2) \times 10^{-33} \exp\{(730 \pm 220)/T\}$ cm^6 molecule^{-2} s^{-1} has been obtained for the low-pressure limit of the rate constant for the addition reaction $Br + C_2H_4 + M \leftrightarrow C_2H_4Br + M$ (1,−1). The expressions $k_1k_5/k_{-1} = (3.1 \pm 0.6) \times 10^{-36} \exp\{(3540 \pm 280)/T\}$ cm^6 molecule^{-2} s^{-1} and $k_1k_{6a}/k_{-1} = (1.8 \pm 0.9) \times 10^{-35} \exp\{(3390 \pm 270)/T\}$ cm^6 molecule^{-2} s^{-1} have been obtained for the combinations of the rate constants of reactions (1,−1) and reactions $Br_2 + C_2H_4Br \rightarrow Br + C_2H_4Br_2$ (5) and $Br + C_2H_4Br \rightarrow C_2H_4Br_2$ (6a). For the reaction of Br atoms with *trans*-2-butene, both the addition channel, $Br + C_4H_8 \leftrightarrow C_4H_8Br$ (2a,−2a), and the H atom abstraction channel, $Br + C_4H_8 \rightarrow C_4H_7 + HBr$ (2b) have been observed and the following kinetic data were obtained: $k_{2a}^\circ = (2.1 \pm 0.8) \times 10^{-32} \exp\{(1300 \pm 90)/T\}$ cm^6 molecule^{-2} s^{-1}, $k_{2a}k_9/k_{-2a} = (3.8 \pm 1.7) \times 10^{-36} \exp\{(4630 \pm 230)/T\}$ cm^6 molecule^{-2} s^{-1} (where k_9 is the rate constant of the reaction $C_4H_8Br + Br_2 \rightarrow C_4H_8Br_2 + Br$) and $k_{2b} = (5.8 \pm 1.7) \times 10^{-12} \exp\{-(960 \pm 160)/T\}$ cm^3 molecule^{-1} s^{-1}. Thermochemical data around room temperature could be derived from these kinetic measurements; the enthalpies of reactions 1 and 2a are $\Delta H_1^\circ = -(6.8 \pm 1.6)$ kcal mol^{-1} and $\Delta H_{2a}^\circ = -(8.8 \pm 1.5)$ kcal mol^{-1}, and the heats of formation of the adducts C_2H_4Br and C_4H_8Br are $\Delta H_f^\circ(C_2H_4Br) = 32.4 \pm 1.6$ kcal mol^{-1} and $\Delta H_f^\circ(C_4H_8Br) = 20.5 \pm 1.8$ kcal mol^{-1}.

Introduction

The reactions of Br atoms with unsaturated hydrocarbons are possible important steps in the chemistry of the atmosphere and particularly in the marine boundary layer. To assess this role, kinetic investigations of these reactions are necessary. In a previous study from this laboratory,[1] the kinetic parameters for the reaction of Br atoms with propene have been measured. The present paper reports the kinetic investigation of the reactions of Br atoms with two other alkenes, ethene (C_2H_4) and *trans*-2-butene (C_4H_8). There is very little published kinetic data for these reactions. Using the relative rate technique, the overall rate constants for $Br + C_2H_4$[2−4] and for $Br + C_4H_8$[2,3,5] have been determined at room temperature and at a total pressure of 1 atm of synthetic air. In one study,[2] the reaction $Br + C_2H_4$ has been also investigated at $T = 293-355$ K and in the pressure range 25−760 Torr (in a $N_2 + O_2$ mixture, with the O_2 pressure being varied from 5 to 100 Torr). Finally, in the most recent work,[6] laser flash photolysis combined with Br atom detection by atomic resonance fluorescence was applied to study reactions 1 and −1 between 160 and 185 K and at 25−100 Torr total pressure.

$$Br + C_2H_4\ (+M) \leftrightarrow C_2H_4Br\ (+M) \qquad (1,-1)$$

In the present work, which has been performed at low pressure (0.5−2.0 Torr), the mechanism of reactions 1 and 2 has been also investigated, since these reactions may proceed via different and competing channels.

$$\begin{aligned} Br + C_4H_8\ (+M) &\leftrightarrow C_4H_8Br\ (+M)(2a,-2a) \\ &\rightarrow HBr + C_4H_7 \qquad (2b) \end{aligned}$$

The low-pressure limits of the rate constants for the addition channels 1 and 2a and the rate constant for the H atom abstraction channel 2b have been determined as a function of temperature. Besides, some thermochemical parameters could be derived for some species or reactions involved in this kinetic study.

Experimental Section

The discharge-flow mass spectrometric method has been employed to study the kinetics of reactions 1 and 2. The modulated molecular beam mass spectrometer has been described in detail earlier.[7] The reactor consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) with a jacket for the thermostated liquid circulation (ethanol). The configuration of the movable double injector, used for the introduction of reactants, is shown in Figure 1. To reduce the wall loss of Br atoms, the inner surfaces of the reactor and of the two tubes of the injector were coated with halocarbon wax. Br atoms, produced from the microwave dissociation of Br_2 (diluted in helium), were introduced into the reactor through the internal tube of the movable injector. For the mass spectrometric detection of Br atoms, a scavenger (nitrosyl chloride, ClNO) was introduced in excess at the end of the reactor (at around 5 cm upstream from the sampling cone) and converted Br into BrCl in the fast reaction

$$Br + ClNO \rightarrow BrCl + NO \qquad (3)$$

$$k_3 = 1.5 \times 10^{-11} \exp(-52/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad \text{(ref 8)}$$

Thus, Br atoms were detected as $BrCl^+$, at $m/e = 116$. This detection method was preferred to the direct detection of Br at $m/e = 79/81$, due to the contribution of Br_2 molecules at this

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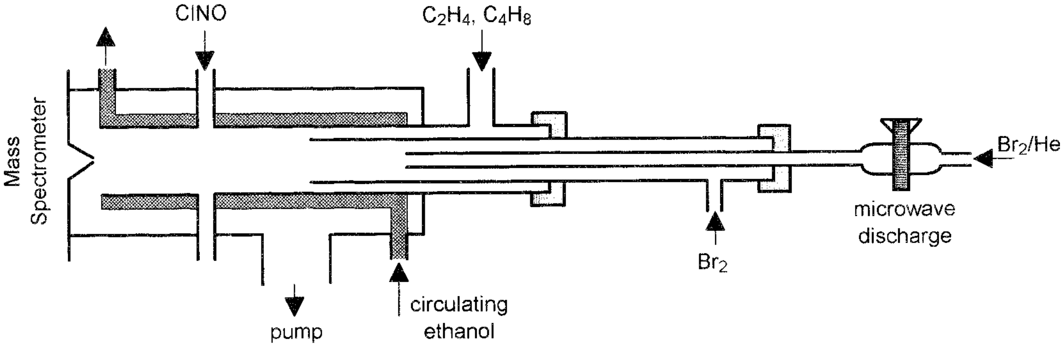

Figure 1. Diagram of the apparatus used.

mass (Br_2 was added at relatively high concentrations; see below) since the Br_2 fragmentation in the ion source of the mass spectrometer could not be avoided, with this source being operated at 25−30 eV electron energy. It was verified that the addition of ClNO had no influence on the kinetics of the products detected during the study of reactions 1 and 2, $C_2H_4Br_2$, $C_4H_8Br_2$, HBr, C_4H_7Br. The 1,2-dibromoethane molecule ($C_2H_4Br_2$) was detected at the mass of the fragment $C_2H_4Br^+$ ($m/e = 107/109$), for which the intensity was around 30 times higher than that of the parent peak (at $m/e = 188$). Similarly, $C_4H_8Br_2$ was detected at $m/e = 137/139$ (mass of the fragment $C_4H_8Br^+$). All other relevant species were detected at their parent peaks.

The procedure for the determination of the absolute concentration of Br atoms was the same as that detailed in the previous study[1] and was based on the calibration of BrCl using reaction 3 or/and reaction 4:

$$\mathrm{Cl} + \mathrm{Br_2} \rightarrow \mathrm{ClBr} + \mathrm{Br} \qquad (4)$$

$$k_4 = 2.3 \times 10^{-10} \exp(-135/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \qquad \text{(ref 9)}$$

For the absolute calibration of HBr as a possible reaction product, both the reaction of hydrogen atoms with an excess of Br_2 molecules and the direct introduction of HBr into the reactor were used (see also ref 1). The molecular reactants, ethene and *trans*-2-butene, were introduced into the reactor through a sidearm tube (Figure 1). The concentration of these reactants, as well as that of all the molecular species of this study (Br_2, ClNO, $C_2H_4Br_2$, $C_4H_8Br_2$, C_4H_7Br), was calculated from the pressure drop of known mixtures in calibrated volumes.

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); ClNO, >99.2% (Matheson); 1,2-dibromoethane, >99% (Aldrich); *trans*-2-butene, >99% (Fluka); meso-2,3-dibromobutane, 98% (Aldrich); *trans*-crotylbromide, $CH_3CH{=}CHCH_2Br$, 85% (with 15% of 3-bromo-1-butene, Aldrich). C_2H_4 of different purities (99.5 and 99.95%) was used, and no difference was observed on the kinetic results.

Results

Reaction Br + C_2H_4 (1). As already mentioned in our previous paper,[1] the major experimental complications in the kinetic study of Br reactions with alkenes arise from the instability of the adduct formed (leading to its rapid decomposition back to the reactants).

$$\mathrm{Br} + \mathrm{C_2H_4}\ (+\mathrm{M}) \leftrightarrow \mathrm{C_2H_4Br}\ (+\mathrm{M}) \qquad (1,-1)$$

To avoid such a complication in the study of reaction 1, the unstable adduct-radical C_2H_4Br was partly scavenged by reaction 5, after addition of Br_2 into the reactor.

$$\mathrm{C_2H_4Br} + \mathrm{Br_2} \rightarrow \mathrm{C_2H_4Br_2} + \mathrm{Br} \qquad (5)$$

Thus, the rate of formation of the stable molecule $C_2H_4Br_2$ was measured as a function of Br and Br_2 concentrations.

In the case of ethylene, another experimental complication resulted from the low rate of reaction 1, which implied the use of relatively high initial concentrations of Br atoms in order to produce detectable amounts of the product, $C_2H_4Br_2$. Under these conditions, reaction 1 was also followed by reaction 6, with several possible channels:

$$\mathrm{C_2H_4Br} + \mathrm{Br}\ (+\mathrm{M}) \rightarrow \mathrm{C_2H_4Br_2}\ (+\mathrm{M}) \qquad (6a)$$

$$\rightarrow \mathrm{C_2H_4} + \mathrm{Br_2} \qquad (6b)$$

$$\rightarrow \mathrm{C_2H_3Br} + \mathrm{HBr} \qquad (6c)$$

Another experimental observation of a nearly constant Br concentration was due to the Br atom regeneration in reaction 5. Thus, the Br concentration was considered as constant in the following kinetic analysis (except in a few kinetic runs, where a decrease up to 25% was observed and a mean value of [Br] was considered). Assuming a steady state for the adduct C_2H_4Br resulting from the reaction sequence (1,−1,5,6), the following formation rate of $C_2H_4Br_2$ can be obtained:

$$\frac{d[\mathrm{C_2H_4Br_2}]}{dt} = k_1[\mathrm{Br}][\mathrm{C_2H_4}]\frac{k_{6a}[\mathrm{Br}] + k_5[\mathrm{Br_2}]}{k_{-1} + k_6[\mathrm{Br}] + k_5[\mathrm{Br_2}]} \qquad (7)$$

where $k_6 = k_{6a} + k_{6b} + k_{6c}$.

Experimentally, apparent zeroth order kinetics of $C_2H_4Br_2$ formation (linear dependence of $[C_2H_4Br_2]$ on reaction time) were observed (as a consequence of the constant concentrations of the reactants, Br and C_2H_4) and the so-called observed rate constant was measured.

$$k_{1\mathrm{obs}} = \frac{1}{[\mathrm{Br}][\mathrm{C_2H_4}]}\frac{d[\mathrm{C_2H_4Br_2}]}{dt}$$

From eq 7, one can derive

$$\frac{1}{k_{1\mathrm{obs}}} = \frac{1}{k_1}\left(1 + \frac{k_{6b} + k_{6c}}{k_{6a} + k_5[\mathrm{Br_2}]/[\mathrm{Br}]}\right) + \frac{1}{[\mathrm{Br}]}\frac{1}{K_1k_{6a} + K_1k_5[\mathrm{Br_2}]/[\mathrm{Br}]} \qquad (8)$$

where $K_1 = k_1/k_{-1}$ is the equilibrium constant for reactions 1 and −1. Equation 8 was used for analytical treatment of the

TABLE 1: Reaction Br + $C_2H_4 \rightarrow C_2H_4Br$ (1): Experimental Conditions and Results

No./exptl[a]	T (K)	P (Torr)	$[C_2H_4] \times 10^{-15}$ [b]	$[Br] \times 10^{-13}$ [b]	$[Br_2]/[Br]$	k_1[c]	K_1k_{6a}[d]	K_1k_5[d]
20	298	1.0	2.1−3.7	0.4−13.7	1.4; 2.7; 27; 69	1.2 ± 0.3[e]	1.45 ± 0.25[e]	0.40 ± 0.07[e]
14	287	2.0	3.7−5.2	0.3−7.6	1.9; 16; 74	3.0 ± 0.6	2.7 ± 0.7	0.70 ± 0.12
15	278	1.0	2.5−4.7	0.3−11.0	1.3; 7.7; 68	1.5 ± 0.3	3.6 ± 0.6	1.1 ± 0.2
15	263	1.0	3.2−5.1	0.2−7.2	1.6; 16; 73	1.6 ± 0.3	6.5 ± 1.3	2.5 ± 0.4
19	261	1.0	1.8−2.8	0.2−8.4	1.7; 3.2; 32; 75	1.8 ± 0.3	9.0 ± 1.2	2.5 ± 0.4
16	248	1.0	2.8−4.4	0.2−4.1	1.5; 15; 80	2.3 ± 0.3	13.0 ± 2.7	5.8 ± 0.9
15	240	0.5	1.7−3.0	0.2−11.3	1.6; 15; 70	1.5 ± 0.2	25.0 ± 6.0	6.8 ± 1.0
20	233	1.0	1.9−3.2	0.2−3.0	1.6; 3.2; 32; 75	3.0 ± 0.4	40.0 ± 6.5	11.7 ± 1.6

[a] Number of kinetic runs. [b] Units for the concentrations are molecule cm^{-3}. [c] Units are 10^{-15} cm^3 $molecule^{-1}$ s^{-1}. [d] Units are 10^{-30} cm^6 $molecule^{-2}$ s^{-1}. [e] Quoted errors represent $1\sigma + 10\%$.

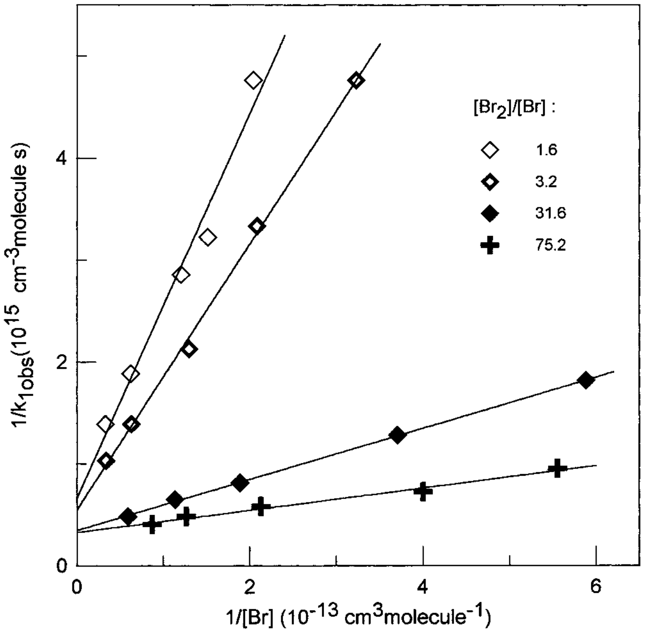

Figure 2. Reaction Br + C_2H_4 (1). Examples of the dependence of $1/k_{1obs}$ (see expression 8 of the text) on the reciprocal of the concentration of Br atoms for different ratios $[Br_2]/[Br]$, obtained at P = 1 Torr total pressure and T = 233 K.

experimental data and for the derivation of the subsequent kinetic parameters.

Experiments were carried out in the pressure range 0.5−2.0 Torr, over the temperature range 233−298 K. The linear flow velocity in the reactor was in the range 500−750 cm s^{-1}. As already mentioned, zeroth order kinetics of $C_2H_4Br_2$ were observed, and the values of k_{1obs} were measured as a function of Br concentration for different constant $[Br_2]/[Br]$ ratios at various temperatures. All experimental conditions of these kinetic experiments are detailed in Table 1.

An example of the dependence of $1/k_{1obs}$ as a function of $1/[Br]$, measured at T = 233 K and at a total pressure of 1 Torr, and measured for four different $[Br_2]/[Br]$ ratios is shown in Figure 2. As expected from eq 8, the intercept of the linear plots of Figure 2 depended on the $[Br_2]/[Br]$ ratio. It decreased with increasing $[Br_2]/[Br]$, down to a constant value for the highest values of the $[Br_2]/[Br]$ ratio. This lowest value of the intercept was used to determine the rate constant of the reaction 1, as given in Table 1.

Other kinetic information could be extracted from the plots shown in Figure 2; from eq 8, the reciprocal of the slopes of the straight lines of Figure 2, $K_1k_{6a} + K_1k_5[Br_2]/[Br]$, has been plotted as a function of the $[Br_2]/[Br]$ ratio. An example (corresponding to the data of Figure 2) is shown in Figure 3. From the zero intercept and the slope of the straight line obtained, the values can be derived for K_1k_{6a} and K_1k_5, respectively.

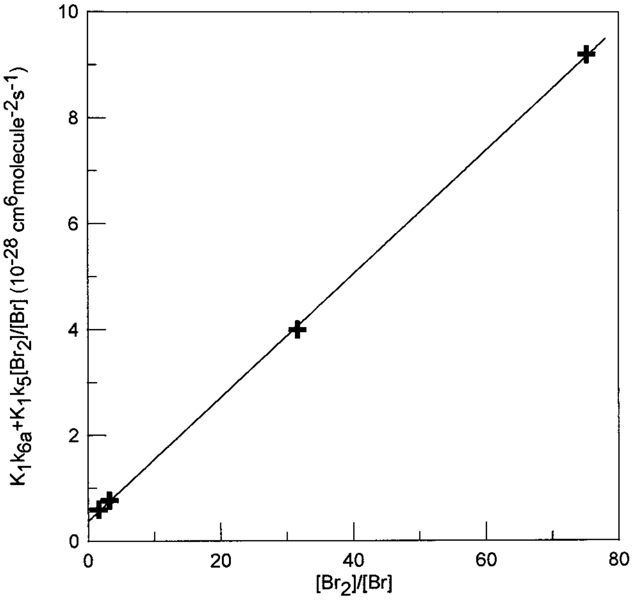

Figure 3. Reaction Br + C_2H_4 (1). Dependence of the value $K_1k_{6a} + K_1k_5[Br_2]/[Br]$ on the $[Br_2]/[Br]$ ratio. Points correspond to the experimental results presented in Figure 2.

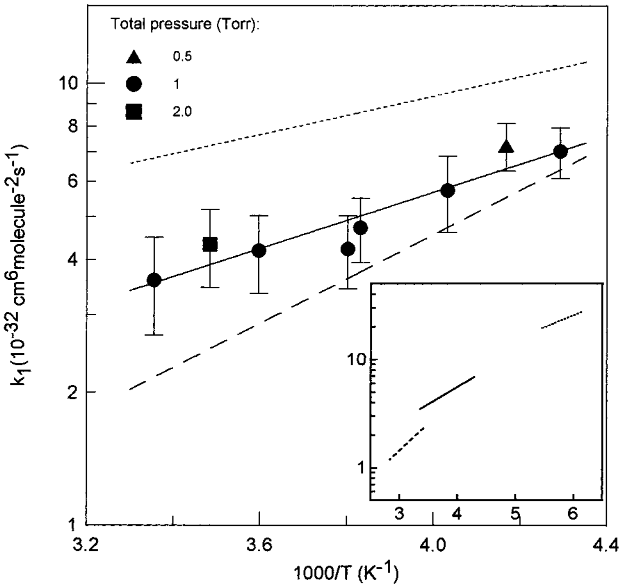

Figure 4. Temperature dependence of the rate constant of the reaction Br + C_2H_4 + M → C_2H_4Br + M (1): (dash line) extrapolation from ref 2; (dotted line) extrapolation from ref 6; (solid line) this study. Insertion represents original results from refs 2 and 6 and this work.

All the kinetic results obtained using this procedure are summarized in Table 1. These data are also shown in Figure 4, where low-pressure regime for k_1 was assumed and 0.5 and 2 Torr values of k_1 were adjusted to 1 Torr total pressure. The negligible deviation of these values from those obtained at 1

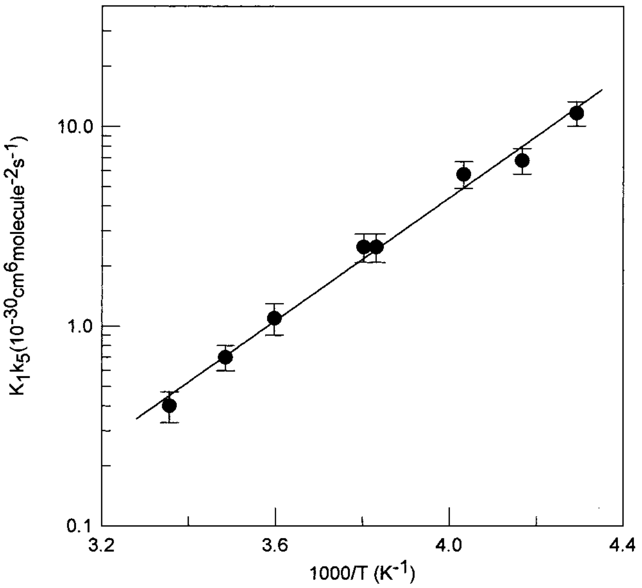

Figure 5. Reaction Br + C_2H_4 (1). Temperature dependence of K_1k_5 (see text).

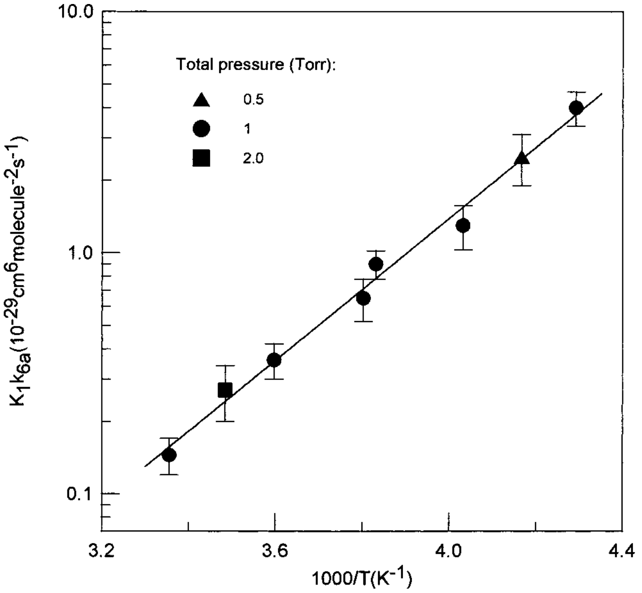

Figure 6. Reaction Br + C_2H_4 (1). Temperature dependence of K_1k_{6a} (see text).

Torr seems to support the above assumption of a termolecular behavior of reaction 1 under the present experimental conditions. Finally, the least-squares fit to the experimental data gives the following Arrhenius expression:

$$k_1 = (3.0 \pm 1.2) \times 10^{-33} \exp\{(730 \pm 220)/T\}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}\ (\text{for M} = \text{He})$$

The temperature dependencies for K_1k_5 and K_1k_{6a} are presented in Figures 5 and 6, respectively, and lead to the following Arrhenius expressions:

$$K_1k_5 = (3.1 \pm 0.6) \times 10^{-36} \exp\{(3540 \pm 280)/T\}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}$$

$$K_1k_{6a} = (1.8 \pm 0.9) \times 10^{-35} \exp\{(3390 \pm 270)/T\}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}$$

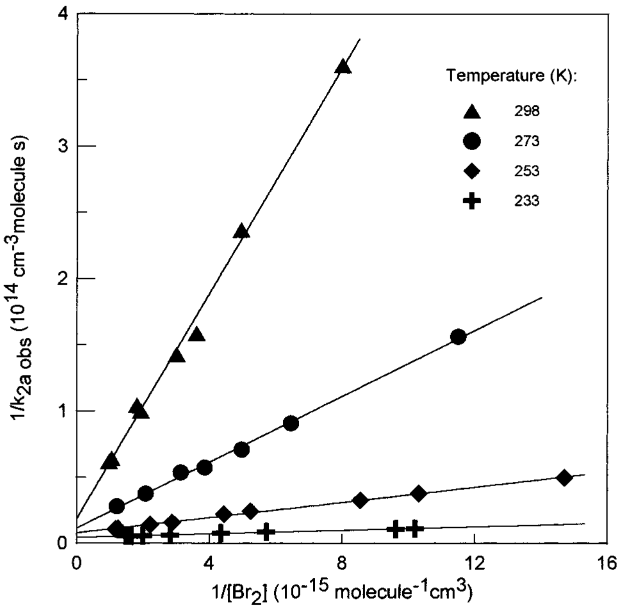

Figure 7. Reaction Br + C_4H_8 → C_4H_8Br (2a). Examples of the dependence of $1/k_{2aobs}$ on the reciprocal of the concentration of Br_2 at different temperatures.

(the quoted uncertainties represent two standard deviations for the temperature coefficient and one for the preexponential factor).

Reaction Br + C_4H_8 → C_4H_8Br: Addition Channel (2a). The same experimental procedure as for reaction 1 was used to measure the rate constant for the addition channel of reaction 2. Br_2 was added into the reactor to convert the adduct-radical C_4H_8Br into the stable molecule $C_4H_8Br_2$ in reaction 9.

$$C_4H_8Br + Br_2 \rightarrow C_4H_8Br_2 + Br \qquad (9)$$

Since reaction 2a is much faster than reaction 1, lower initial concentrations (if compared with the above experiments) could be used for Br atoms (i.e., higher $[Br_2]/[Br]$ ratios) so that the secondary reaction of Br atoms with the adduct could be neglected. Therefore, expression 8 could be simplified and reduced to

$$\frac{1}{k_{2aobs}} = \frac{1}{k_{2a}} + \frac{1}{K_2k_9[Br_2]}$$

where $K_2 = k_{2a}/k_{-2a}$ is the equilibrium constant for reactions 2a and −2a.

Experiments were carried out at a total pressure of helium of 0.5−2.0 Torr and in the temperature range 233−298 K. As in the previous series of measurements, apparent zeroth order kinetics of the product formation ($C_4H_8Br_2$) were observed and its rate as a function of Br_2 concentration was measured. Figure 7 gives examples of the dependence of $1/k_{2aobs}$ as a function of $1/[Br_2]$. The values of $1/k_{2a}$ and $1/K_2k_9$ were obtained from the zero intercepts and slopes of such linear plots, respectively. All the experimental conditions and results are presented in Table 2. The temperature dependence of k_{2a} (obtained at 1Torr total pressure of He), shown in Figure 8, leads to the following Arrhenius expression:

$$k_{2a} = (2.8 \pm 1.1) \times 10^{-16} \exp\{(1560 \pm 105)/T\}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

TABLE 2: Reaction Br + C_4H_8 → C_4H_8Br (2a): Experimental Conditions and Results

No./exptl[a]	T (K)	P (Torr)	$[C_4H_8] \times 10^{-13}$ [b]	$[Br] \times 10^{-11}$ [b]	$[Br_2] \times 10^{-14}$ [b]	k_{2a}[c]	K_2k_9[d]
8	298	1.0	2.1−3.7	23.1−57.1	1.2−10.3	0.54 ± 0.19[e]	0.23 ± 0.03[e]
8	280	1.0	3.7−5.2	10.1−30.3	0.9−9.2	0.79 ± 0.25	0.51 ± 0.06
7	273	1.0	2.5−4.7	6.6−12.2	0.9−8.2	0.87 ± 0.20	0.80 ± 0.10
7	263	1.0	3.2−5.1	12.1−15.1	0.9−9.3	0.94 ± 0.15	1.75 ± 0.21
6	261	2.0	1.8−2.8	8.7−10.1	0.6−6.8	2.15 ± 0.46	2.08 ± 0.24
9	253	1.0	2.8−4.4	7.6−9.7	0.7−8.5	1.27 ± 0.20	3.48 ± 0.42
7	243	0.5	1.7−3.0	5.9−9.5	0.7−6.5	0.98 ± 0.12	7.67 ± 1.12
8	233	1.0	1.9−3.2	7.2−8.6	1.0−6.7	2.26 ± 0.30	15.1 ± 2.1

[a] Number of kinetic runs. [b] Units for the concentrations are molecule cm^{-3}. [c] Units are 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. [d] Units are 10^{-28} cm^6 $molecule^{-2}$ s^{-1}. [e] Quoted errors represent 1σ + 10%.

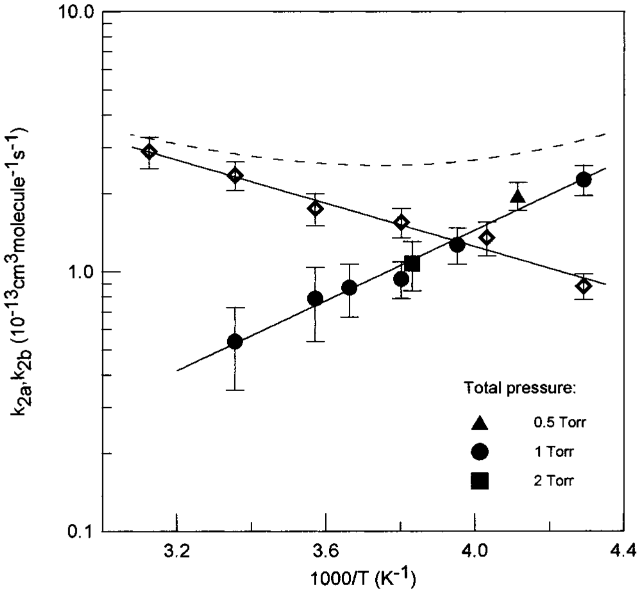

Figure 8. Reaction Br + C_4H_8 (2). temperature dependence of the rate constant for addition (filled symbols) and H atom abstraction (open symbols) channels. Dashed line represents the overall rate constant.

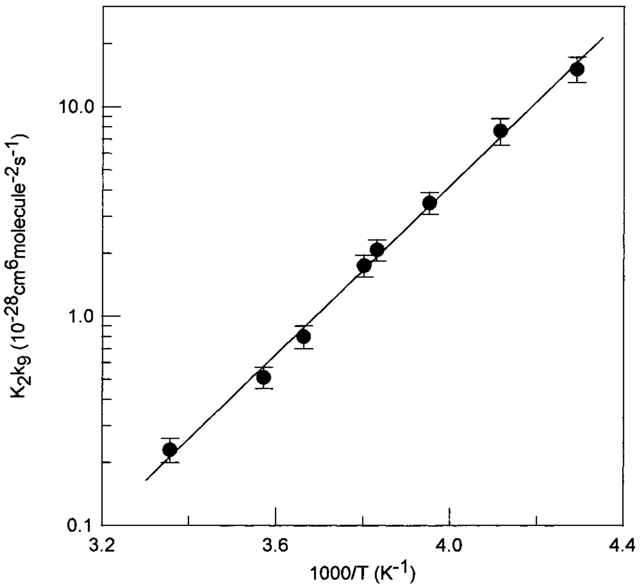

Figure 9. Reaction Br + C_4H_8 → C_4H_8Br (2a). Temperature dependence of K_2k_9 (see text).

Similarly to reaction 1, the data obtained at 0.5 and 2 Torr total pressure were adjusted to 1 Torr, assuming linear dependence of k_{2a} on pressure. If a termolecular regime is considered for reaction 2a in the pressure range of the present study, the low-pressure limit of k_{2a} can be expressed as

$$k^{\circ}_{2a} = (2.1 \pm 0.8) \times 10^{-32} \exp\{(1300 \pm 90)/T\}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}}$$

Besides, the temperature dependence for the product K_2k_9, illustrated in Figure 9, leads to the following expression:

$$K_2k_9 = (3.8 \pm 1.7) \times 10^{-36} \exp\{(4630 \pm 230)/T\}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}}$$

(the quoted uncertainties in the above expressions represent 1σ for the preexponential factor and 2σ for the activation energy).

Reaction Br+C_4H_8 → HBr + C_4H_7: Abstraction Channel (2b). In another series of experiments, HBr molecules were detected as the product of the reaction of Br atoms with *trans*-2-butene, indicating the existence of an H atom abstraction channel for reaction 2. The rate constant k_{2b} was obtained from the measured HBr formation rate. To simplify the procedure for such a measurement, Br_2 molecules (at a concentration of (2−3) × 10^{14} molecule cm^{-3}) were added into the reactor. This led to the regeneration, via reaction 10, of Br atoms consumed in the primary reaction 2b.

$$C_4H_7 + Br_2 \rightarrow C_4H_7Br + Br \qquad (10)$$

The addition channel of reaction 2 did not lead to Br decay, as a consequence of the fast decomposition of the adduct, in reaction −2a and/or Br regeneration in reaction 9. The detected consumption of Br atoms was generally lower than 10%, and was therefore considered as negligible in the following kinetic calculations. Under these conditions (constant concentrations of both reactants, Br and C_4H_8, with C_4H_8 in high excess over Br atoms), zeroth order kinetics of HBr formation were observed, according to the equation

$$d[HBr]/dt = k_{2b}[Br][C_4H_8]$$

Experimentally, the HBr formation rate was measured as a function of the concentration of reactants, [Br] (basically constant) and $[C_4H_8]$ (varied). Examples of the pseudo-first-order plots obtained for the HBr formation channel of reaction 2 are shown in Figure 10. From the slopes of the straight lines, the values of k_{2b} at different temperatures were calculated. All the experimental conditions and results are presented in Table 3. At T = 298 K, the initial concentration of Br atoms was varied over a factor of 7 and no influence was observed on the calculated values of k_{2b}. This precludes any contribution of secondary reactions, leading to HBr formation or consumption at a comparable rate with that of reaction 2b.

Another product has been detected, under the same experimental conditions as above, C_4H_7Br molecules, which could be formed in reaction 10 and also possibly in reaction 11.

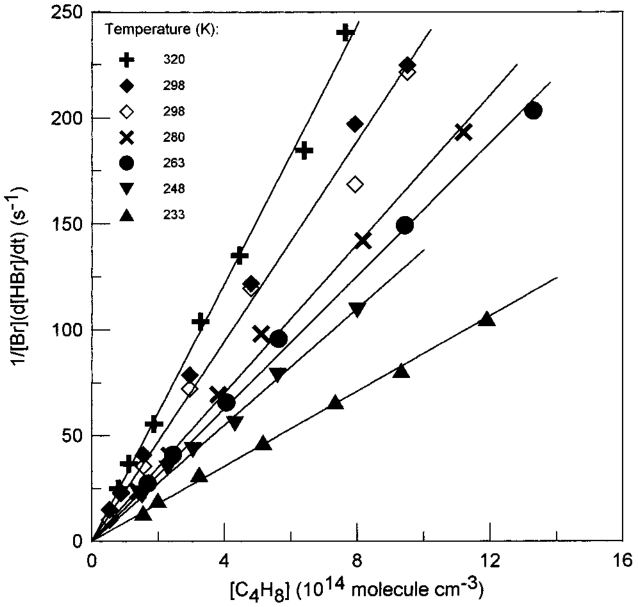

Figure 10. Reaction Br + $C_4H_8 \rightarrow C_4H_7$ + HBr (2b). Pseudo-first-order plots for HBr formation in reaction 2b and C_4H_7Br (open symbols) formation in the sequence of reactions 2b and 10.

TABLE 3: Reaction Br + $C_4H_8 \rightarrow C_4H_7$ + HBr (2b): Experimental Conditions and Results

No./exptl[a]	T(K)	[Br] × 10^{-12} [b]	[C_4H_8] × 10^{-14} [b]	k_{2b}[c]
7	320	0.57−0.8	0.8−7.7	2.9 ± 0.4[d]
7	298	0.15−1.0	0.5−8.0	2.35 ± 0.30
6	280	0.5−0.7	1.4−8.2	1.75 ± 0.25
6	263	0.54−0.7	1.70−9.45	1.55 ± 0.20
7	248	0.6−0.8	1.4−8.0	1.35 ± 0.20
7	233	0.6−1.0	1.55−11.9	0.88 ± 0.10

[a] Number of kinetic runs. [b] Units for the concentrations are molecule cm^{-3}. [c] Units are 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. [d] Quoted errors represent 1σ + 10%.

$$\mathrm{Br} + \mathrm{C_4H_7}\ (+\mathrm{M}) \rightarrow \mathrm{C_4H_7Br}\ (+\mathrm{M}) \qquad (11)$$

If the Br_2 concentration is high enough to make C_4H_7 loss through reaction 10 predominant over C_4H_7 wall loss and its self-reaction and if no C_4H_7-forming reaction other than reaction 2b is assumed, in such a case the rate of C_4H_7Br formation is the following:

$$\mathrm{d[C_4H_7Br]}/\mathrm{d}t = k_{2b}[\mathrm{Br}][\mathrm{C_4H_8}]$$

In a series of experiments performed at 298 K, k_{2b} was determined from the kinetics of C_4H_7Br formation. The experimental conditions for the determination of k_{2b} were exactly the same as for the detection of HBr. The mass spectrometric signal of C_4H_7Br was calibrated from a known flow of *trans*-crotylbromide, $CH_3CH{=}CHCH_2Br$. The results thus obtained are also presented in Figure 10, together with the data obtained from the HBr kinetics. It is seen that the results obtained by these two different methods are in excellent agreement.

Similarly, the temperature dependence of k_{2b} is also shown in Figure 8, together with the temperature dependence of the rate constant for the addition channel (2a). The resulting Arrhenius expression is

$$k_{2b} = (5.8 \pm 1.7) \times 10^{-12} \exp\{-(960 \pm 160)/T\}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

(uncertainties are 1σ for the preexponential factor and 2σ for the activation energy).

Discussion

In the Experimental Section, only the addition channel has been considered for the reaction between bromine atoms and ethene.

$$\mathrm{Br} + \mathrm{C_2H_4}\ (+\mathrm{M}) \rightarrow \mathrm{C_2H_4Br}\ (+\mathrm{M}) \qquad (1)$$

The alternative H atom abstraction channel (1′) is too endothermic to possess a measurable rate in the temperature range of this study.

$$\mathrm{Br} + \mathrm{C_2H_4} \leftrightarrow \mathrm{C_2H_3} + \mathrm{HBr} \qquad \Delta H = 23.2 \pm 1\ \mathrm{kcal\ mol^{-1}} \quad (1')$$

(the thermochemical data used for the calculation of the reaction enthalpy are from ref 10).

The temperature dependence obtained for k_1, $k_1 = (3.0 \pm 1.2) \times 10^{-33} \exp\{(730 \pm 220)/T\}$ cm^6 $molecule^{-2}$ s^{-1}, using He as a third body, can be compared with the data from a previous study,[2] where k_1 was measured in the pressure range 25−760 Torr at T = 293−353 K, in a N_2 + O_2 mixture. A relative kinetic method was used (with addition of O_2 to scavenge the adduct-radical) and the C_2H_4 kinetics were measured relative to 2,2,4-trimethylpentane. The value obtained was $k_1 = (4.49 \pm 4.04) \times 10^{-34} \exp\{(1155 \pm 280)/T\}$ cm^6 $molecule^{-2}$ s^{-1}. In another study,[6] reactions 1,−1 were studied between 160 and 185 K from laser flash photolysis of C_2H_4/CF_2Br_2/N_2 mixtures with monitoring of Br kinetics by atomic resonance fluorescence. Analysis of the Br kinetics yielded both k_1 and k_{-1} as a function of temperature. The expression $k_1 = 3.42 \times 10^{-15} \exp(763/T)$ cm^3 $molecule^{-1}$ s^{-1} was derived for the rate constant of reaction 1 at 20 Torr total pressure. To facilitate the comparison of this result with the present data and those from ref 2 and assuming low-pressure regime for reaction 1 at P = 20 Torr, the last expression can be represented as a third-order rate constant, $k_1 = 1.26 \times 10^{-32} \exp(501/T)$ cm^6 $molecule^{-2}$ s^{-1}. This result as well as that from ref 2 can be compared with the present data by extrapolating corresponding expressions for k_1 to the temperature range of this study, as shown in Figure 4. As one can see, the difference between absolute values of k_1 from the three studies is rather large, although present data seem to be in reasonable agreement with two other studies if the experimental uncertainties are considered. The reason for the rather large discrepancy between Arrhenius parameters obtained for k_1 in the three studies can be to some extent due to relatively narrow temperature ranges used, as illustrated in insertion of Figure 4. Besides, it should be noted that the results under discussion were obtained with different molecules as a third body, M = N_2 + O_2[2], N_2,[6] and He in this work, although it cannot be excluded that, in the present study, C_2H_4 and Br_2 which were used at rather high concentrations (up to 5.0×10^{15} and 1.0×10^{15} molecule cm^{-3}, respectively) could contribute to the stabilization of the adduct. Taking into account that the third body efficiency of nitrogen is generally 2−3 times larger than that of helium, the agreement between the present result and that from ref 6 can be considered as reasonable.

Finally, the linear extrapolation of the low-pressure limit of k_1 obtained in this work (at 1 Torr) to 760 Torr gives the value $k_1 \approx 9 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, which is not inconsistent with the lower values 1.3×10^{-13},[2] $\leq 2.3 \times 10^{-13}$,[3] and 1.6 ×

10^{-13} cm^3 molecule^{-1} s^{-1},[4] measured at $P = 760$ Torr, taking into account that the latter values are in the fall-off or high-pressure limit regime.

The data obtained for the reaction between C_2H_4Br and Br, which are summarized in Table 1 and in Figure 6, can give kinetic information on the addition channel 6a.

$$C_2H_4Br + Br\ (+M) \rightarrow C_2H_4Br_2\ (+M) \qquad (6a)$$

First, it is observed that the product K_1k_{6a} does not depend on the total pressure, and one may conclude that this addition reaction 6a is in its second-order regime in the pressure range of this study. Besides, the value of the rate constant k_{6a} can be estimated from the k_{6a}/k_5 ratio, which can be calculated from the data obtained here for K_1k_5 and K_1k_{6a}, leading to

$$k_{6a}/k_5 = (5.8 \pm 5.9)\exp\{-(150 \pm 550)/T\}$$

Considering for k_5 the same value as that of the rate constant for the reaction of C_2H_5 radicals with Br_2,[11]

$$C_2H_4Br + Br_2 \rightarrow C_2H_4Br_2 + Br \qquad (5)$$

$$C_2H_5 + Br_2 \rightarrow C_2H_5Br + Br \qquad (12)$$

$$k_{12} = (2.6 \pm 0.8) \times 10^{-11} \exp\{(410 \pm 205)/T\}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (\text{ref } 11)$$

Thus, it becomes $k_{6a} \approx 1.5 \times 10^{-10}\exp(260/T)$ cm^3 molecule^{-1} s^{-1}, which gives $k_{6a} \approx 3.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at room temperature. Of course, these simple calculations are speculative, since the H atom substitution by a halogen atom in the alkyl radical reduces the reactivity with Br_2.[12] Nevertheless, it can be concluded that the addition reaction 6a proceeds with a rate close to the gas kinetic limit, even at the low pressure of this study (ca. 1 Torr). This conclusion also confirms the observation made in the study of the analogous reaction of the allyl radical $C_3H_5 + Br \rightarrow C_3H_5Br$,[1] for which the value measured for the rate constant was 2×10^{-10} cm^3 molecule^{-1} s^{-1}, at a total pressure of 1 Torr.

For the reaction of Br atoms with *trans*-2-butene, only relative kinetic studies have been performed so far.[2,3,5]

$$Br + C_4H_8\ (+M) \leftrightarrow C_4H_8Br\ (+M) \qquad (2a,-2a)$$

$$\rightarrow HBr + C_4H_7 \qquad (2b)$$

In these previous studies, using 1 atm of synthetic air, the following values of the overall rate constant were obtained: $(7.5 \pm 3.0) \times 10^{-12}$,[2] $(9.5 \pm 0.76) \times 10^{-12}$,[3] and $(9.26 \pm 1.85) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[5] No data are available in the literature for the low-pressure limit of k_{2a} and for the rate constant of the H atom abstraction channel 2b. As one can see from Figure 8, the absolute values obtained in this study for the rate constants of the addition (2a) and abstraction (2b) channels have the same magnitude and possess a negative and positive activation energy, respectively. The temperature dependence of the overall rate constant, shown as the dotted line of Figure 8, has been calculated from the Arrhenius expressions obtained for k_{2a} and k_{2b}. However, it was not possible under the present conditions to measure the total rate constant of reaction 2, due to the rapid decomposition of the adduct formed in channel 2a.

From the comparison of the results obtained here for ethene and *trans*-2-butene and in our previous study[1] for propene, it can be seen that the substitution of an H atom by a CH_3 group leads to an increase of the rate constant for the addition channel by about 1 order of magnitude. A similar trend was already observed[5] for the high-pressure rate constants of Br reactions with alkenes, and it was explained by a positive inductive effect of the methyl group, leading to an increase of the electronic density on the double bond. The major factor influencing the low-pressure limit rate constant is the density of states of the adduct, which increases with the number of degrees of freedom, when adding CH_3 groups to the system.

Finally, using the same approach as applied previously,[1] thermochemical information on reactions 1 and 2a can be extracted from the kinetic data obtained for the temperature dependence of K_1k_5 and K_2k_9, respectively. Taking for the value of the activation energy of reaction 5 that of the reaction of C_2H_5 radical with Br_2 (as discussed in ref 1 and based on the results of refs 11−13), including an additional uncertainty of 1 kcal mol^{-1}, i.e., $E = -(0.8 \pm 1.0)$ kcal mol^{-1}, and considering the Arrhenius expression for K_1k_5 obtained in this work, it can be derived for the equilibrium constant of the reactions 1 and −1:

$$K_1 = k_1/k_{-1} \sim \exp\{(6300 \pm 1600)/RT\}$$

Comparing further this result with the expression

$$K_1 = k_1/k_{-1} = \exp(\Delta S_1/R)\exp(-\Delta H_1/RT)$$

the enthalpy of reaction 1 can be calculated; $\Delta H_1 = -(6.3 \pm 1.6)$ kcal mol^{-1}, which leads to

$$\Delta H_1^\circ = -(6.3 \pm 1.6) - RT \approx -(6.8 \pm 1.6)\ \text{kcal mol}^{-1}$$

(considering $T = 260$ K, which is the midvalue of the temperature range used). Consequently, using this value together with those known[10] for the enthalpies of formation of Br atoms (26.7 kcal mol^{-1}) and of C_2H_4 (12.45 kcal mol^{-1}), the enthalpy of formation of the C_2H_4Br radical can be calculated.

$$\Delta H_f^\circ(C_2H_4Br) = (32.4 \pm 1.6)\ \text{kcal mol}^{-1}$$

One may note that, for this calculation, the value of the activation energy taken for reaction 5 is consistent with the upper limit which can be also estimated from the data obtained for the k_{6a}/k_5 ratio. Indeed, using for this ratio $k_{6a}/k_5 = (5.8 \pm 5.9)\exp\{-(150 \pm 550)/T\}$, it becomes $E_5 = E_{6a} - (0.3 \pm 1.1)$ kcal mol^{-1}, that is, since reaction 6a is an association reaction with a negative activation energy, $E_5 < -(0.3 \pm 1.1)$ kcal mol^{-1}. Such a rough calculation shows that the range considered above for $E_5 = -(0.8 \pm 1.0)$ kcal mol^{-1} is realistic.

Repeating the same calculation as above with the value of the activation energy for reaction 9, $E_9 = (1.0 \pm 1.0)$ kcal mol^{-1} (i.e., that of the reaction $Br_2 + t\text{-}C_4H_9$[11] with addition of 1 kcal mol^{-1} uncertainty), and with the expression for K_2k_9 obtained above, it can be obtained for the enthalpy of reaction 2a and for the enthalpy of formation of the C_4H_8Br radical

$$\Delta H_{2a}^\circ = -(8.8 \pm 1.5)\ \text{kcal mol}^{-1}$$

$$\Delta H_f^\circ(C_4H_8Br) = (20.5 \pm 1.8)\ \text{kcal mol}^{-1}$$

(In the latter calculation, the value of the enthalpy of formation of *trans*-2-butene =2.58 ± 0.24 kcal mol^{-1} (ref 14) has been used).

In all these thermochemical calculations, no correction was taken into account for the temperature dependence of the thermochemical parameters, since it is negligible compared with the uncertainty of the present estimations.

The thermochemical data obtained here for the reaction of Br atoms with ethene can be compared with those reported in ref 6, $\Delta H_{f,298}(CH_2CH_2Br) = 32.1 \pm 0.5$ kcal mol^{-1} and $D_0^{298}(Br-CH_2CH_2) = 7.1 \pm 0.5$ kcal mol^{-1}. These values are in excellent agreement with the present determinations, 32.4 ± 1.6 and 6.8 ± 1.6 kcal mol^{-1}, respectively.

Finally, a last comparison can be made for the C−Br bond dissociation energy from the series of values derived from the present study for C_2H_4Br (6.8 ± 1.6) and C_4H_8Br (8.8 ± 1.5), and from ref 1 for C_3H_6Br (7.7 ± 1.4 kcal mol^{-1}). A trend is clearly observed, showing an increase of the C−Br bond strength with the number of CH_3 substituents in the brominated alkyl radical.

Acknowledgment. This work has been performed within the Environment Program of the European Commission (HALOTROP project).

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