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Reactions of C_2H_5 Radicals with HBr and Br at 298 K and Millitorr Pressures

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Abstract: The rates of the reactions of ethyl radicals with HBr (k_7) and with Br atoms (k_8) have been measured at 298 K and millitorr pressures using the Very Low Pressure Reactor (VLPR) technique. The rate constants at 298 K are the following: $k_7 = (6.67 \pm 0.14) \times 10^{-13}$ cm^3/(molecule•s) and $k_8 = (1.19 \pm 0.04) \times 10^{-11}$ cm^3/(molecule•s). Reaction 7 is a factor of about 14 times slower than had been reported in the only other two direct measurements made (Nicovich, J. M. *et al. J. Phys.Chem.* **1991**, *95*, 9890. Seakins, P. W. *et al. J. Phys Chem.* **1992**, *98*, 9847) which also reported a negative activation energy for k_7 of from −0.8 to −1.1 kcal/mol. Using broadly accepted thermochemistry for reaction 7 and reported values for the reverse reaction, it is shown that all reported data give a positive activation energy for k_7.

Introduction

The reactions of alkyl radicals with hydrogen halides (HX), particularly HI and HBr, have been a subject of lively interest for over three decades. These reactions and their reverse reactions have provided the basis for the measurements of bond dissociation energies[1] in simple molecules since the early part of this century. If the equilibrium constant K_a of the general reaction

$$X + RH \overset{a}{\rightleftharpoons} HX + R$$

is measured as a function of temperature then a Van't Hoff plot of K_a against $1/T$ will yield the average heat of reaction ΔH_a and the average entropy change ΔS_a over the temperature range measured. If the entropy change is known then a measurement at a single convenient temperature T_i will yield ΔH_a at T_i with good precision.[2] This has been possible in only a few cases, Cl + CH_4,[2a] Cl + c-C_3H_6,[2b] and Br + $C_4H_9O_2H$.[2c] In early studies of the reaction of Br_2 or I_2 with alkanes and/or substituted hydrocarbons, it was usually only possible to extract the rate constant k_a and its Arrhenius parameters from the data. Since

$$\Delta H_a = E_a - E_{-a} \qquad \text{(a)}$$

and E_a was measured, it was necessary to provide or estimate the value of E_{-a} in order to obtain ΔH_a. This can also be written in thermodynamic language as

$$\Delta H_a = \Delta_f H^\circ(R) + \Delta_f H^\circ(HX) - \Delta_f H^\circ(X) - \Delta_f H^\circ(RH) \quad \text{(a')}$$

where generally all values of the heats of formation are known except that for R. Thus, a knowledge of ΔH_a will yield $\Delta_f H^\circ(R)$.

In most early studies of bromination reactions, it was found that E_{-a} was very small,[3] in the range of 0−3 kcal/mol. Iodination studies[1] found even smaller values, 0−1 kcal/mol, and it was then assumed that this would be a general result which until a decade ago provided many of our accepted values for bond dissociation energies and their associated values of $\Delta_f H^\circ$ for the radical R. These would perhaps be only of academic interest except that such information has been incorporated in the data bases used to model and interpret complex chemical processes. Of great importance among the latter, both societally and industrially, are photochemical smog, combustion, stratospheric chemistry of the ozone layer, and many large scale processes such as hydrocarbon cracking and petroleum refining.

In the past decade, however, a number of laboratories have reported "direct" studies of the reverse reaction R + HX whose temperature behavior showed small negative activation energies in the range 0.5−2.0 kcal/mol.[4,5] The net effect of these has been to raise the values of ΔH_a by 0.5 to 2.0 kcal/mol (eq a) and, consequently, to increase the related bond dissociation energies DH°(R−X) and also $\Delta_f H^\circ$(R) (eq a′). We therefore felt that it was of some interest to use alternative methods to measure these reactions.

Experimental Section

In the past few years we have developed the Very Low Pressure Reactor (VLPR) system to the point where it is capable of measuring individual rates of rapid reactions occurring in complex atom/radical/molecule systems with precisions of 1−3%.[6] Since we have also used it to produce relatively high concentrations of C_2H_5 radicals, it was directly suited to a study of the C_2H_5 + HBr reaction.

Our three-stage, all turbo-pumped VLPR system used in earlier kinetic studies has been well described[2,6−8] so we shall not repeat the detailed description. However, the system parameters, experimental sequence, and data handling are briefly summarized in the following.

A thin Teflon coated Knudsen reactor cell (V_r = 217.5 cm^3) is sealed to the top entrance of the main vacuum chamber. The reactor bottom is seated on a rapidly adjustable slide[2] having three interchangeable escape orifices of 0.193-, 0.277-, and 0.485-cm diameters. These orifices enable us to change the residence time in the reactor in three

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Table 1. Initial and Steady-State Concentrations

(a) Initial and Steady-State Concentrations[a] of Reactants and Ethyl Radical Formed before Introducing HBr into the System

No./ϕ_x	$\frac{I^\circ_{Cl}}{I^\circ_{Cl} + I^\circ_{HCl}} \times 10^2$	$[Cl]_0$	$[C_2H_6]_0$	$\frac{I_{Cl}}{I_{Cl} + I_{HCl}} \times 10^2$	[Cl]	$[C_2H_6]$	$[C_2H_5]$	ΣP_i[b]
1/ϕ_5	58.12	4.381	6.609	7.71	0.581	3.698	2.257	0.27
2/ϕ_5	58.12	4.381	6.609	7.71	0.581	3.698	2.257	0.27
3/ϕ_5	51.55	3.797	5.923	7.27	0.536	3.430	1.959	0.26
4/ϕ_5	51.46	3.791	5.755	7.08	0.534	3.503	1.561	0.25
5/ϕ_5	51.46	3.791	5.755	7.08	0.534	3.503	1.561	0.25
6/ϕ_3	39.01	8.294	10.470	1.67	0.354	5.175	3.240	0.56
7/ϕ_3	39.01	8.294	10.470	1.67	0.354	5.175	3.240	0.56
8/ϕ_3	38.11	8.060	10.470	1.64	0.374	5.041	3.276	0.56
9/ϕ_3	38.11	8.060	10.470	1.64	0.374	5.041	3.276	0.56
10/ϕ_3	39.37	7.173	8.384	2.02	0.368	4.030	2.714	0.46
11/ϕ_3	52.10	9.492	6.780	5.49	1.001	1.658	2.548	0.42
12/ϕ_3	52.10	9.492	6.780	5.49	1.001	1.660	2.539	0.42
13/ϕ_2	30.25	12.353	14.223	0.77	0.217	6.859	3.532	0.91
14/ϕ_2	52.09	21.272	12.727	2.54	1.038	1.925	3.332	0.87
15/ϕ_2	44.97	21.144	14.840	1.38	0.650	3.425	4.076	2.21
16/ϕ_2	44.97	21.144	14.840	1.38	0.650	3.425	4.076	2.21

(b) Steady-State Concentrations[c] of Reactants after Introducing the Initial Concentration of $[HBr]_o$ into the Cl + C_2H_6 Reaction System

No./ϕ_x	$[HBr]_o \times 10^{-12}$	$\frac{I_{Cl}}{I_{Cl} + I_{HCl}} \times 10^2$	$[Cl] \times 10^{-11}$	$[C_2H_6] \times 10^{-11}$	$[C_2H_5] \times 10^{-11}$	$\frac{I_{Br}}{I_{Br} + I_{HBr}} \times 10^2$	$[HBr] \times 10^{-12}$	$[Br] \times 10^{-11}$	ΣP_i[b]
1/ϕ_5	8.347	4.43	0.334	4.971	0.566	6.95 ± 0.14	7.767	5.765	0.53
2/ϕ_5	6.596	5.19	0.391	4.643	0.683	7.70 ± 0.05	6.088	5.047	0 .46
3/ϕ_5	4.345	5.56	0.402	4.155	0.818	8.20 ± 0.62	3.989	3.541	0.39
4/ϕ_5	1.828	6.11	0.461	3.674	1.255	7.88 ± 0.27	1.684	1.432	0.31
5/ϕ_5	0.599	5.87	0.442	3.646	1.547	7.73 ± .047	0.553	0.460	0.27
6/ϕ_3	9.703	1.30	0.277	6.156	0.491	11.03 ± 0.41	8.633	10.634	0.86
7/ϕ_3	14.959	0.95	0.203	6.887	0.334	9.14 ± 0.55	13.592	13.586	1.02
8/ϕ_3	6.167	1.13	0.259	6.092	0.845	9.22 ± 0.58	5.598	5.650	0.77
9/ϕ_3	10.502	0.99	0.226	6.764	0.454	9.68 ± 0.48	9.486	10.102	0.90
10/ϕ_3	13.085	1.10	0.200	5.622	0.255	9.01 ± .059	11.906	11.715	0.87
11/ϕ_3	4.970	4.28	0.779	1.995	0.447	23.79 ± 0.38	3.788	11.749	0.57
12/ϕ_3	2.737	5.48	0.999	1.672	0.790	25.61 ± 0.41	2.0346	6.965	0.50
13/ϕ_2	13.205	0.32	0.129	8.859	0.297	10.17 ± 0.43	11.862	13.345	1.32
14/ϕ_2	3.087	1.84	0.725	2.336	0.846	23.909 ± 0.86	2.346	7.323	0.97
15/ϕ_2	5.257	1.35	0.636	3.724	0.461	25.65 ± 0.33	3.909	13.399	2.37
16/ϕ_2	8.486	0.98	0.460	4.033	0.371	23.83 ± 0.26	6.464	20.094	2.47

[a] All concentrations are in units of 10^{11} particles/cm^3. [b] ΣP_i is the total pressure in mTorr unit of the system calculated from steady-state concentrations of all species including HCl and He. [c] All concentrations are in units of particles/cm^3.

steps over a 5-fold range without breaking the vacuum. The use of these orifices in different runs is indicated as ϕ_2, ϕ_3, and ϕ_5, respectively, in Tables 1a and 1b, and are marked with different symbols in the figures. With the reactor volume V_r, the unimolecular gas dynamic escape rate constant for any gas component of mass M is given by $k_{eM} = a_\phi(T/M)^{1/2}$ s^{-1}, where T is the absolute temperature and $a_\phi = 0.258$ for ϕ_2, 0.546 for ϕ_3, and 1.321 for ϕ_5 orifices.[2a]

Three gas inlets are located at the top of the reactor cell for separate Cl_2, C_2H_6, and HBr inlet flows. They are preceded by separate capillary flow subsystems calibrated for regulating the fluxes of initial gas components with the use of Validyne transducers. The Cl_2 flow traverses a H_3PO_4 coated quartz discharge tube centered in the Opthos microwave generator cavity of a McCarrol antenna before arriving at the inlet of the reactor cell.

The VLPR technique delivers a molecular beam through the exit orifice which is chopped and further collimated by two orifices at the entrances of two consecutive differentially pumped chambers to reduce the background mass signals. This beam is sampled with the off-axis mass analyser of a BALZERS QMG 511 quadrupole mass spectrometer, whose signal is fed to a phase-sensitive, lock-in amplifier tuned to the chopping frequency. The mass range of interest is repeatedly scanned, usually 20–25 times, and the mass intensities are recorded for data acquisition. Each mass signal is corrected for its background value recorded prior to the start up of mass flow.

In the operation of the present three-component reaction system, the Cl_2 flow is started up first using a 4.5% Cl_2/He gas mixture (both are Matheson research-grade gases). Mass range *m*/*e* 70 −74 is repeatedly scanned using 20 V electron energy and the intensities of Cl_2 mass isotopes 70, 72, and 74 are recorded. The Cl_2 signal intensity of *m*/*e* 70 is also used for checking the constancy in time of the mass spectral efficiency α_{Cl_2}.

Next, the microwave generator is turned on and its power is adjusted to 100% dissociation of Cl_2 controlled by observing the disappearance of Cl_2 mass signals. Then, mass range 35−38 is scanned using 20 eV energy to record the mass signal intensities of Cl atom isotopes at *m*/*e* 35 and 37 and those of HCl at *m*/*e* 36 and 38. Cl atom production is always accompanied with some HCl formation arising presumably from Cl atom reaction with H_3PO_4 on the wall of the microwave discharge tube. Depending on the excessive wear of the discharge tube, this HCl formation may constitute 40−60% of the overall Cl content (see column 2 of Table 1a), but it is constant during a given run.

After the Cl and HCl mass signals have reached steady values, the ethane flow is started into the reactor using 5% of a C_2H_6/He gas mixture (both are Matheson research-grade gases) and increased gradually until the mass 35 Cl signal drops to 1/10 to 1/30 of its original value. Mass range 35−38 is scanned again to record the new signal intensities of Cl and HCl with 20 eV mass spectrometry. Mass range *m*/*e* 25−30 is also scanned to record the C_2H_6 and C_2H_5 signals, as well as the distribution of their fragments. The scanning of this latter mass range is then repeated using the more sensitive 40 eV mass spectrometry.

Finally, the flow of pure HBr (Matheson 99.8% purity, further purified by trap-to-trap vacuum distillation) is started and increased until some increase of mass signal 30 (and some decrease in mass signal 29) is observed. Mass ranges of 34−38, 25−30, and 79−82 are scanned to record the signal intensities for Cl/HCl, C_2H_6/C_2H_5, and Br/HBr distributions, respectively, using 20 eV mass spectrometry. Then the latter two mass ranges are also scanned with the more sensitive 40

V electron energy. For the measurement of Br/HBr distribution, mass signals of both ^{79}Br and ^{81}Br isotopes were used.

Mass ranges of 114−118 and 158−162 were also checked regularly for possible traces of BrCl and Br_2 recombination products which might be formed in the runs with HBr reactions. No detectable signal increase of these masses over their background values was ever observed.

The purified HBr was stored in a completely darkened glass bulb at somewhat below 1 atm of pressure and fed to the buffer volume of the capillary flow subsystem through greaseless stopcocks. We have not found any HBr decomposition even at long storage times. Such observations are in contrast with the latest reports of HBr handling[9] where HBr had to be freshly purified for each run to avoid ~50% decomposition during storage.[4] Earlier runs using metal tank held HBr[4] had apparently undergone up to 50% decomposition to H_2.

Analytical Methods

Before starting kinetic studies, mass spectral calibration for each individual gas component is made by measuring the given mass signal intensity (I_M) as a function of the specific flux F(M) according to the relationship $I_M = \alpha_M F(M)$, where α_M is the mass spectral efficiency for ion peak of mass M and $F(M) = (\text{flux})/V_r$ in molecule/(cm^3·s). The steady state concentration of the gas component M then can be calculated from the relation $[M] = F(M)/k_{eM}$, molecule/cm^3. In the range of use, the plot of I_M vs F(M) invariably gives straight lines passing through the origin. This procedure works well for stable molecules such as Cl_2, HCl, O_2, HBr, C_2H_6, C_2H_4, etc.,[6−8,10] but needs to be changed for reactive atoms and radicals such as Cl, Br, C_2H_5, C_2H_3, etc. by correcting for the fragment contribution from the parent molecule. For the latter, use is made of mass balances. Thus on introducing a gas mixture of Cl_2/He into the system we can measure the intensities of Cl_2 signals (at 70, 72, and 74 AMU) and calibrate the spectrometer for Cl_2 specific flow $F(Cl_2)$. Turning on the microwave to high enough power levels to dissociate all Cl_2 we see the Cl_2 peaks disappear. In their place we find peaks due to Cl atoms (35 and 37 amu) and HCl (36 and 38 amu). At 20 V ionizing electron energy, fragmentation of HCl into Cl^+ is 0.24% and usually negligible but corrections can be made for this if necessary. Since we can generally measure concentrations to about 2−3%, this permits us to calibrate the Cl signal.[7]

With the Cl/HCl distributions listed in column 2 of Table 1a and the initial $F(Cl_2)$ flow rate , the initial steady state concentration of Cl can be calculated as $[Cl]_0 = 2F(Cl_2)I^\circ_{Cl}/(I^\circ_{Cl} + I^\circ_{HCl})k_{eCl}$ (see column 3 of Table 1a). Now introducing C_2H_6 at flow rates corresponding to the $[C_2H_6]_0$ concentrations given in column 4 of Table 1a, the Cl peaks are reduced to 1/10 to 1/30 of the original I°_{Cl} values due to reaction with C_2H_6 and this produces HCl manifested by the increase of HCl signal intensities, so that $I_{Cl} + I_{HCl} = I^\circ_{Cl} + I^\circ_{HCl}$ within our 2−3% precision. These new Cl/HCl distributions and the calculated Cl concentrations for different experimental runs are given in columns 5 and 6 of Table 1a, respectively. Similarly, when HBr is introduced as a third component into the system at flow rates corresponding to $[HBr]_0$ concentrations given in column 2 of Table 1b, the Cl signal drops further along with a stoichiometric increase in the HCl signal intensity, and these Cl/HCl distributions, as well as the calculated Cl concentrations, are given in columns 3 and 4 of Table 1b, respectively.

Depending on the ionizing electron energies, C_2H_6 undergoes a complex mass fragmentation.[11] The distribution of mass fragments measured with varying $F(C_2H_6)_0$ between 4.61 × 10^{-11} and 23.2 × 10^{-11} molecule/(cm^3·s) is as follows:

$$I^\circ_{26}:I^\circ_{27}:I^\circ_{28}:I^\circ_{29}:I^\circ_{30} = 0.12:0.52:58.3:8.05:33.0$$

with 20 eV mass spectrometry, and

$$I_{25}:I^\circ_{26}:I^\circ_{27}:I^\circ_{28}:I^\circ_{29}:I^\circ_{30} = 0.36:7.72:15.4:48.7:11.8:16.1$$

with 40 eV mass spectrometry, where the subscripts of I°_M denote the mass numbers of fragment signals. The I_{30} ratio is taken as proportional to $F(C_2H_6)_0$ directly ($\alpha_{30} = \alpha_{RH}$) according to the relationship: $0.161\,\Sigma_{25}^{30}I^\circ_M = \alpha_{RH}F(RH)_0$ with 40 eV and $0.330\Sigma_{26}^{30}I^\circ_M = \alpha'_{RH}F(RH)_0$ with 20 eV mass spectrometry, where RH stands for C_2H_6. These relationships provide α_{RH} and α'_{RH} values. Using the above distribution ratios, mass spectral efficiencies of α_{29}, α_{28}, α_{27}, etc. can also be calculated for mass fragments with the same relationships.

When the reaction Cl + C_2H_6 takes place, the above signal intensity distributions change. I°_{30} decreases to I_{30} while the others, especially I_{29} and I_{28}, increase. With the recorded I_{30}, the steady state concentration of ethane can now be calculated as $[C_2H_6] = I_{30}/\alpha_{RH}k_{eRH}$ using both 20 and 40 eV mass spectrometries. Since the concentrations from the two electron voltage measurements differ very slightly, the two data were averaged and the results are given in column 7 of Table 1a. The same procedure is employed when C_2H_6 is also produced by the reaction of C_2H_5 + HBr in the three-component reaction system. These C_2H_6 concentrations, also averaged for the two electron energy measurements, are given in column 5 of Table 1b.

With the Cl + C_2H_6 reaction, the steady state concentration of ethyl radicals formed can be calculated[7] as

$$[R] = \frac{2\Delta[RH]k_{eRH} - k_1[RH][Cl]}{k_2[Cl] + k_{eR}} \tag{1}$$

where R stands for the C_2H_5 radical and $\Delta[RH] = [RH]_0 - [RH]$. With the use of $k_1 = 6.1 \times 10^{-11}$ cm^3/(molecule·s) and $k_2 = 1.2 \times 10^{-11}$ cm^3/molecule-s taken from our earlier study,[7] the calculated C_2H_5 radical concentrations in each run, averaged for 20 and 40 eV mass spectrometries, are given in column 8 of Table 1a.

Three different investigations[12] have reported values of k_2 which are about 24 to 30 times larger than the values we have measured.[7,8] This would have the effect of reducing the [R] concentration (eq 1) by a factor of from 8 to 30 depending on the orifice used. It would also require the production of a 2- to 3-fold increase in HCl which would destroy the Δ[HCl]/Δ[Cl] mass balance we observed. It would also require a huge increase in C_2H_4 production which was not observed in our earlier work[6,7] and finally a much smaller Cl signal than the one we measure. We shall return to this later.

Alternatively, and more directly, the excess intensity at 29 calculated as $\Delta I_{29} = I_{29} - \alpha_{RH}I_{30}/\alpha_{29}$ can be taken for the mass intensity of the chemically generated F(R) flow and the mass spectral efficiency (α_R) for the C_2H_5 radical can be recovered from the relationship $\Delta I_{29} = \alpha_R[R]k_{eR}$. α_R values calculated for each run of Table 1a are constant, giving (1.300 ± 0.066) × 10^{-11} for 40 eV and (0.882 ± 0.067) × 10^{-11} for 20 eV mass spectrometries on the average of 16 runs. These α_R values are used for converting the measured ΔI_{29} values from the C_2H_5 + HBr reactions into C_2H_5 concentrations given in column 6 of Table 1b.

Mass fragmentation of HBr was investigated in our preceding work[10] where the ratios of $10^2I_{Br}/(I_{Br} + I_{HBr})$ were found to be 0.30 ± 0.08 with 20 eV and 25.64 ± 0.19 with 40 eV mass spectrometries measured by varying the HBr flow rate in the range of (1.07 to 15.78) × 10^{12} molecule/(cm^3·s) and analyzing the measured intensities of both stable Br isotopes.

Mass signal intensities of *m/e* 79 and 80, as well as 81 and 82, were recorded in the three-component reaction system with both 20 and 40 V electron energies and corrected for the above mass fragmentation ratios, respectively. Corrections for fragmentation with 20 eV measurements are small but still significant due to the high concentrations of HBr used. These Br/HBr distributions averaged for the above four mass spectral measurements for each run are given in column 7 of Table 1b. Due to multiple reconversions of HBr in this complex reaction system, the scatter of Br/HBr distribution is somewhat larger than was found for the simple Cl + HBr reaction system,[10] but still accurate to ±3.8% on average. Combining these Br/HBr distributions

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with $[HBr]_0$, the concentrations of HBr and Br are given in columns 8 and 9 of Table 1b, respectively.

The above data analysis is slightly different from those used in our earlier works with C_2H_5 radical reactions.[6-8] It was developed to meet the special requirements for this three-component reaction system, namely that we must start up the HBr reaction with relatively high C_2H_5 and low Cl concentrations to maintain the relatively slow rate of the C_2H_5 + HBr reaction competitive with the faster rate of the Cl + HBr conversion.

Treatment of Data and Results

The mechanism of the Cl + C_2H_6 reaction system consists of the following consecutive elementary steps in the millitorr pressure range given in the last column of Table 1a:

$$Cl + C_2H_6 \xrightarrow{1} HCl + C_2H_5$$

$$Cl + C_2H_5 \xrightarrow{2} HCl + C_2H_4$$

$$2C_2H_5 \xrightarrow{3} C_2H_6 + C_2H_4$$

$$Cl + C_2H_4 \xrightarrow{4} HCl + C_2H_3$$

$$Cl + C_2H_3 \xrightarrow{5} HCl + C_2H_2$$

This is a well-explored system where all five rate constants and their temperature dependencies are known from earlier VLPR measurements.[7,11] The surface of the reactor cell covered with a very thin Teflon film shows no evidence of surface reactions with any of the atoms or radicals[7] we have introduced or generated. The average mass 30 amu species make about 10^4 wall collisions (ϕ_3 orifice) before escaping. With the initial Cl and C_2H_6 concentrations given in Table 1a, it produces C_2H_5 radicals in the concentration range of (1.5 to 4.0) × 10^{11} radicals/cm^3 which can be used as reactant with a third component such as HBr.

When HBr is added to the system at a high enough flow rate, the Cl, C_2H_5, and HBr mass spectrometric signals decrease, while C_2H_6, HCl, and C_2H_4 signals increase, and the Br signal appears in excess of that from the HBr fragmentation. These chemical changes point to the existance of the following additional reactions:

$$Cl + HBr \xrightarrow{6} HCl + Br$$

$$C_2H_5 + HBr \xrightarrow{7} C_2H_6 + Br$$

$$Br + C_2H_5 \xrightarrow{8} HBr + C_2H_4$$

At low overall pressures, such as those given in the last column of Table 1b, the Knudsen reactor of the VLPR system behaves like a well-stirred reactor, and at fixed flows, the system reaches a true steady state in which algebraic equations replace differential equations. If concentrations of all species are known, the resulting equations are first order in rate constants and the latter can be uniquely determined. The steady state equations needed to solve the kinetics of the present system can be derived from the above reactions as follows:

for C_2H_6 (designated as RH)

$$\Delta[RH]k_{eRH} - k_1[RH][Cl] + k_3[R]^2 + k_7[HBr][R] = 0 \quad (2)$$

for C_2H_5 (designated as R)

$$k_1[RH][Cl] - \{k_2[Cl] + k_7[HBr] + k_8[Br] + k_{eR}\}[R] - 2k_3[R]^2 = 0 \quad (3)$$

for HBr

$$\Delta[HBr]k_{eHBr} - \{k_6[Cl] + k_7[R]\}[HBr] + k_8[Br][R] = 0 \quad (4)$$

for Br

$$\{k_6[Cl] + k_7[R]\}[HBr] - \{k_8[R] + k_{eBr}\}[Br] = 0 \quad (5)$$

where $\Delta[HBr] = [HBr]_0 - [HBr]$.

Combination of eqs 2 × (2) + (3) gives the steady state ethyl radical concentration as:

$$[R] = \frac{2\Delta[RH]k_{eRH} - k_1[RH][Cl]}{k_2[Cl] - k_7[HBr] + k_8[Br] + k_{eR}} \quad (6)$$

where [R] is measured directly in the three component system (see column 6 of Table 1b).

Summing eqs 2, 3, and 4, we obtain an exact kinetic equation for HBr consumption in reaction (7):

$$k_7[HBr] = \frac{\Delta[RH]k_{eRH} + \Delta[HBr]k_{eHBr} - k_6[HBr][Cl]}{[R]} - \{k_2[Cl] + k_3[R] + k_{eR}\} \quad (7)$$

Combination of eqs 3 × (2) + 2 × (3) + (4) gives the exact rate equation for Br atom concentration:

$$k_8[Br] = \frac{3\Delta[RH]k_{eRH} + \Delta[HBr]k_{eHBr} - \{k_1[RH] + k_6[HBr]\}[Cl]}{[R]} - \{2k_2[Cl] + k_3[R] + 2k_{eR}\} \quad (8)$$

The sum of eqs 4 and 5 provides the mass balance for HBr conversion in our three-component reaction system:

$$\Delta[HBr]k_{eHBr} = [Br]k_{eBr} \quad (9)$$

the experimental verification of which is given in our preceding work.[10]

Equations 7 and 8 are of special interest for obtaining rate constants k_7 and k_8. $k_3 = 2.0 \times 10^{-12}$ cm^3/(molecule·s) is taken from our earlier work[7] and all concentrations involved are measured (see Table 1b), but the solutions require the knowledge of k_6.

In a prior study[10] we remeasured reaction 6 after having discovered some errors in the earlier work.[13] It is a simple and well-behaved system with only a single reaction, Cl + HBr, taking place which leads to a simple rate equation of

$$\frac{\Delta[Cl]}{[Cl]}k_{eCl} = \frac{[Br]}{[Cl]}k_{eBr} = k_6[HBr] \quad (10)$$

However, the use of 30 V electron energy[13] to ionize HBr in our mass spectrometer produces 17.5% fragmentation[10] to Br^+. This introduced an error in our earlier study which accounts for the low rate constant reported there.[13] In Figure 1 we show the results from our new study[10] which gives the rate constant value for reaction (6) at 298 K:

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[13] Lamb, J. J.; Kondo, O.; Benson, S. W. *J. Phys.Chem.* **1986**, *90*, 914.

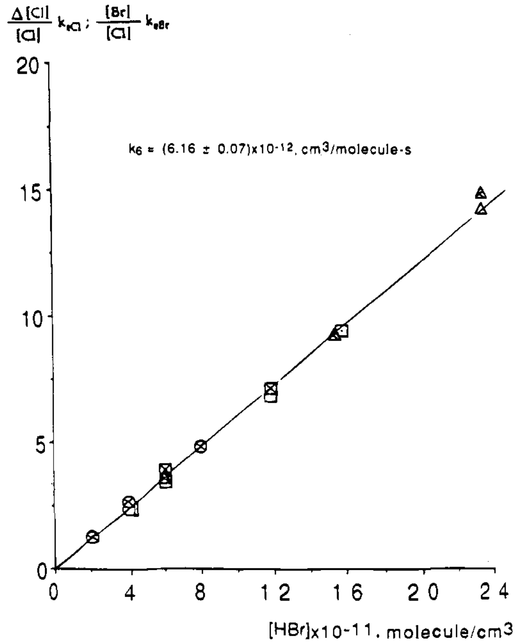

Figure 1. Dependence of relative Cl atom consumption (open symbols) and Br atom formation (crossed symbols) according to eq 10 at 298 K. The slope gives k_6 directly. Symbols indicating the orifices used for given data pairs are as follows: ○, ϕ_2; △, ϕ_3; □, ϕ_5

$$k_6 = (6.16 \pm 0.07) \times 10^{-12}\ \mathrm{cm^3/(molecule{\cdot}s)}$$

This value is now in excellent agreement with that obtained by time-resolved Cl fluorescence measurements[14] and tentatively agrees with the results of laser initiated chemiluminescence studies[15] of the Cl_2/HBr system.

Of special note in Figure 1 is the zero intercept and the fact that reactions at different residence times fit on the same straight line through the origin. Equally noteworthy is the fact that measurements made by observing the disappearance of Cl atoms (open symbols) fall on the same line as those made from the appearance of Br atom product (crossed symbols), again confirming our mass balances.

With the above value of k_6, rate constant k_7 can now be computed using the measured concentration data of Table 1b. A plot of the left side of eq 7 vs [HBr] is presented in Figure 2, where the rate constant k_7 is obtained directly from the slope as

$$k_7 = (6.67 \pm 0.14) \times 10^{-13}\ \mathrm{cm^3/(molecule{\cdot}s)}$$

Recent studies[9,16] of rate constant k_7 had yielded values about 1.5 times larger than the value of k_6 so that it appeared that on the introduction of small amounts of HBr, with [Cl] low, reaction 6 would be almost negligible. It was, therefore, of great surprise when we discovered that large amounts of HBr (see column 2 of Table 1b) had to be added in order to observe any reaction with C_2H_5! At these large concentrations of HBr, reaction 6, even at low [Cl], was comparable to reaction 7 in producing Br atoms and reaction 8 became of importance. It can be evaluated by solving eq 8 for k_8 with the use of measured concentrations given in Table 1b.

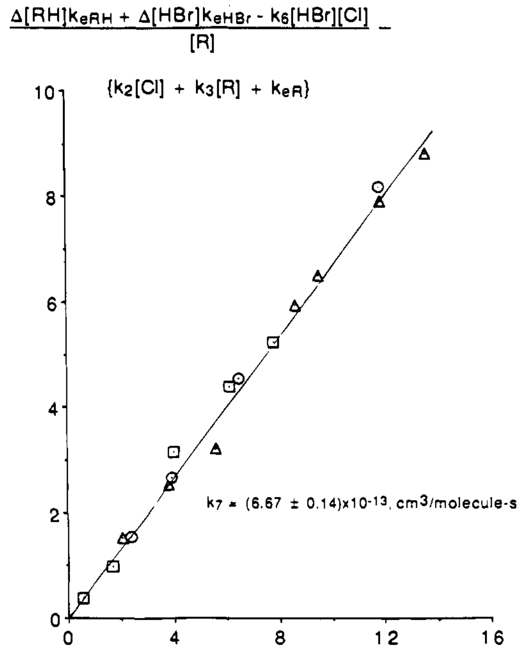

Figure 2. Dependence of HBr consumption and formation rates on the steady-state concentration of HBr according to eq 7. The slope gives k_7 directly. Symbols of orifices are the same as in Figure 1.

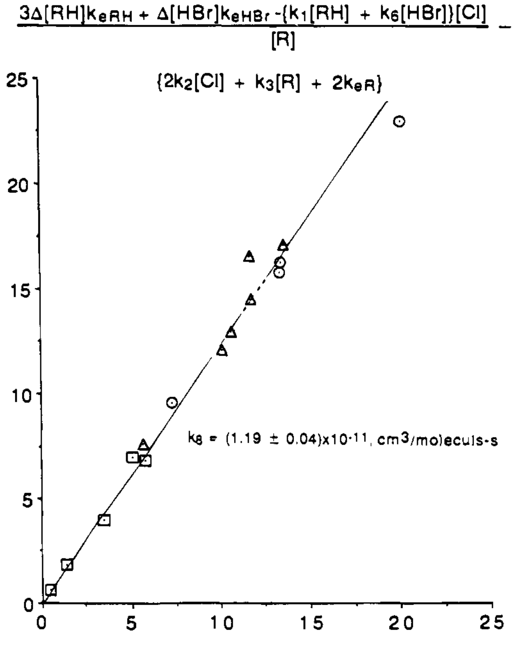

Figure 3. Dependence of Br atom formation and consumption rates on the steady-state concentration of Br according to eq 8. The slope gives k_8 directly. Symbols of orifices are the same as in Figure 1.

A plot of the left side of eq 8 vs [Br] is presented in Figure 3, where rate constant k_8 is given by the slope as

$$k_8 = (1.19 \pm 0.04) \times 10^{-11}\ \mathrm{cm^3/(molecule{\cdot}s)}$$

In connection with eqs 7 and 8 we note that the ethyl radical consumption in reactions 2 and 3 is of minor importance and radical escape is the major process contributing to the bracketed terms on the right-hand side so that $\{k_2[Cl] + k_3[R] + k_{eR}\} \sim k_{eR}$. Also, due to low [Cl], $\{k_7[HBr]$ or $k_8[Br]\} \gg k_2[Cl]$. However, taking reactions 2 and 3 into account, reduces the

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(14) Nicovich, J. M.; Wine, P. H. *Int. J. Chem. Kinet.* **1990**, *22*, 379.

(15) Wodarczyk, F. J.; Moore, C. B. *Chem. Phys. Lett.* **1974**, *26*, 484. Bergman, K.; Moore, C. B. *J. Chem.Phys.* **1975**, *63*, 643. Mei, C. C.; Moore, C. B. *J. Chem. Phys.* **1977**, *67*, 3936. Nesbitt, D. J.; Leone, S. R. *J. Chem. Phys.* **1981**, *75*, 4949.

(16) Nicovich, J. M.; van Dijk, C. A.; Kreutter, K. D.; Wine, P. H. *J. Phys. Chem.* **1991**, *95*, 9890.

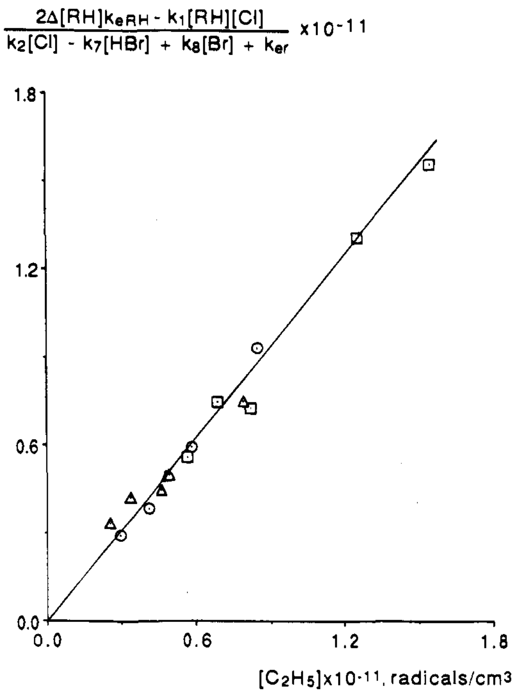

Figure 4. Comparison of ethyl radical concentrations calculated accordind to eq 6 with measured C_2H_5 concentrations given in column 6 of Table 1b (abscissa). Symbols of orifices are the same as in Figure 1.

scatter of the measured k_7 and k_8 values. Use of any of the high values of k_2 reported lately[12] would have reduced both k_7[HBr] and k_8[Br] to disconcerting negative values.

With the above rate constants k_7 and k_8, the ethyl radical concentration can now be calculated according to eq 6 and checked against the radical concentrations measured for each run given in column 6 of Table 1b. This comparison is presented in Figure 4, where the abscissa is taken for the measured [C_2H_5] of column 6 of Table 1b. The slope of 0.988 ± 0.011 indicates that the overall ethyl radical concentrations in this multicomponent reaction system can be measured to within 98.8 ± 1.1% accuracy by the kinetic scheme and rate constants presented here.

Discussion

No values have been reported for k_8, but the value found above is almost identical with that found for the similar reaction of Cl atoms with C_2H_5, $(1.20 \pm 0.08) \times 10^{-11}$ cm^3/(molecule·s).[7] This latter reaction has been studied over the temperature range 203−343 K and shows no variation with temperature. Both reactions are expected to proceed via a recombination to form $(C_2H_5X)^*$, where X = Br or Cl, followed by a very rapid 4-center elimination to give C_2H_4 + HX. The activation energy observed for C_2H_5Br thermal decomposition is 53 kcal/mol[17] while the bond strength of the C−Br bond is 70 kcal/mol, so about 17 kcal/mol excess energy is available for the 4-center elimination. A crude estimate of the lifetime of the excited $(C_2H_5Br)^*$ gives about 10^{-7} s which is very short compared to the time of about $10^{-4.5}$ s between collisions in VLPR.

There have been only three values reported at 298 K of the direct reaction of HBr with C_2H_5. These are listed in Table 2 along with our own value of k_7. As can be seen there is a gross discrepancy between our result and the other three values, the differences ranging from a factor of 6 to a factor of 14.

Table 2. Experimental Values of the Rate Constant k_7 for the Reaction of C_2H_5 + HBr at 298

$10^{13}k_7$(298K), cm^3/(molecules·s)	ref
6.67 ± 0.14	current work (1994)
91 ± 5	9 (1992)
83 ± 3	16 (1991)
42 ± 1[a]	4 (1988)

[a] This value has been discounted by the authors after discovering that their HBr source may have been impure.

Table 3. Thermochemistry[a] of the Reaction Br + C_2H_6 ⇌ HBr + C_2H_5

	species				
	Br[b]	C_2H_6[c]	HBr[b]	C_2H_5[d]	Δ(property)
$\Delta_fH^\circ_{298}$	26.7	−20.0	−8.7	28.4 ± 0.5[e]	13.0 ± 0.5
S°_{298}	41.8	54.9	47.5	59.6	10.4 ± 0.5
C°_{P300}	5.0	12.7	7.0	11.1	0.4
C°_{P500}	5.0	18.7	7.0	16.3	−0.4
C°_{P600}	5.0	21.1	7.4	18.3	−0.4
		$\langle\Delta C^\circ\rangle^{300}_{PT600} = -0.1 \pm 0.5$			

[a] Enthalpies are in units of kcal/mol. Entropies and C°_P are in units of (cal/mol·K). [b] Data from JANAF tables. [c] S° and C°_P from JANAF; Δ_fH° from ref 18. [d] Δ_fH° from ref 19. S° and C°_P are based on a coplanar geometry $H_3C{-}\dot{C}{<}^{H}_{H}$ in C_2H_5 and a 0 barrier to rotation. [e] Reference 9 recommends a value of 28.9 kcal/mol while ref 16 recommends 29.1 ± 0.6 kcal mol. A 1990 assessment[5] by the authors of ref 4 gives a "best" value of 28.3 ± 0.4 kcal/mol. This was based on the kinetics of the C_2H_5 + HI reaction as well as a C_2H_5 ⇌ C_2H_4 + H equilibrium study.

Table 4. Kinetic Values for k_{-7} [cm^3/(molecules·s)] from 300 to 600 K[a]

temp range, K	$k_{-7} \times 10^{15}$ 600 K	$k_{-7} \times 10^{16}$ 500 K	$k_{-7} \times 10^{17}$ 400 K	$k_{-7} \times 10^{20}$ 300 K	ref
473−621	5.7	6.8	2.8 ex	12.4 ex	9 (1992)
259−427	11[b] (7.2)	16[b] ex (9.7)	8.2[b] (4.4)	53[b] (23)	16 (1991)
336−472	16.9 ex	20	8.0	17	4 (1988)
494−592	5.4	5.1	1.48 ex	4.2 ex	21 (1970)
350−500	2.4 ex	2.4	0.75	2.4 ex	22 (1966)
332−472	1.7 ex	1.8	0.62	2.3	20 (1960)
295				4.2[b] (1.8)	current work

[a] Note: Values followed by "ex" have been extrapolated beyond the experimental temperature range given using the author's Arrhenius paramenters. Values in parentheses have been estimated using the increase in $-\Delta H_7$ to 13.5 kcal/mol suggested by refs 16 and 20. This makes k_7 larger by a factor of 2.3 and 1.5 at 300 and 600 K, respectively. [b] Values have been calculated from directly measured values of k_7 (Table 2) and K_7 (Table 3); $k_{-7} = k_7/K_7$.

A somewhat less direct comparison can be made by using values measured for the reverse rate constant k_{-7} and the equilibrium constant K_7. They are related by $k_7 = K_7k_{-7}$. In Table 3 are listed the thermochemical data on the species involved in reaction 7 from which K_7 can be calculated. Of particular interest in Table 3 is the very small change in ΔC_p for the reaction over the temperature range 300−600 K. It is so small that it can be neglected compared to the errors of measurement. It implies that ΔH_7 and ΔS_7 do not change with temperature over this range. We also note that the value of 28.4 ± 0.5 kcal/mol selected for $\Delta_fH_{298}(C_2H_5)$ is in good agreement with the small proposed increases (footnote *d* of Table 3) suggested by recent authors.

Before considering the consistency of the directly measured k_7 it is necessary to examine the values reported for k_{-7} from direct measurements. These are listed in Table 4 at selected temperatures over the range 300−600 K. Of particular interest is the relatively good agreement at 500 and 600 K of the flash

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(17) Benson, S. W.; O'Neal, E. H. *Kinetic Data on Gas Phase Unimolecular Reactions;* NSRDS-NSB 21; National Bureau of Standards: Washington, DC, 1970; p 128.

(18) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds;* 2nd ed.; Chapman and Hall: New York, 1986.

(19) Pilling, M. J. *Int. J. Chem. Kinet.* **1989**, *21*, 267.

(20) Fettis, G. C.; Knox, J. H.; Trotman-Dickenson, A. T. *J. Chem. Soc.* **1960**, 4177. See also ref 3.

Table 5. Experimental Values[a] of k_7 [10^{-12} cm^3/(molecules·s)][a]

300 K	400 K	500 K	600 K	ref
9.1	6.0	4.7	3.9 ex	9 (1992)
0.88 ex (2.1)	1.8 (3.3)	1.75 (2.9)	1.72 (2.6)	9 (1992)[b]
8.3	5.3	4.0 ex	3.3 ex	16 (1991)
0.69 ex	0.96 ex	1.31	1.63	21 (1970)[b]
0.40 ex	0.48 ex	0.62	0.73 ex	22 (1966)[b]
0.38 ex	0.40	0.46	0.5 ex	20 (1960)[b]
0.66				current work

[a] Note: Values accompanied by "ex" have been extrapolated outside the range of measured temperatures (see Table 4) using the Arrhenius paramenters reported by the authors. Values in parentheses have been calculated using the value of $\Delta H_7 = -13.5$ kcal/mol proposed by refs 9 and 16. [b] These values were calculated from measured values of k_{-7} (see Table 2) and the values of the equilibrium constant K_7 (Table 3); $k_7 = k_{-7}/K_7$.

photolysis measurements[9] and the thermal reaction.[21] Extrapolating both to 400 K leads to a difference of almost a factor of 2 and a factor of 3 at 300 K. Two direct studies, refs 9 and 4, show disagreement with each other by a factor of about 3 at 400, 500, and 600 K. They curiously disagree by a factor of $^1/_2$ at 300 K. Two thermal studies of the reaction[21,22] are within a factor of 2 of each other while the third[20] is close to ref 22 but about 4% to 26% lower over the range.

Most striking is the fact that the three thermal studies[20–22] report markedly lower values of k_{-7} than the flash photolysis studies.[4,9,16] From our current work we have a single value at 298 K which agrees remarkably well with the data from the thermal study.[21] This agreement is even more striking when it is considered that the thermal study had to be extrapolated by 250 K from the middle of its range and divided by an equilibrium constant obtained from totally independent studies. We note in passing that there is not a great deal of consistency among the flash photolysis results while the thermal studies show much more.

In Table 5 are tabulated the directly measured values of k_7 together with the indirectly measured values obtained from the product of k_{-7} and K_7. Of immediate interest is the observation that the directly measured values[9] are in poor agreement with those estimated from the product $k_{-7}K_7$. If we use a value of $\Delta H_7 = -13.5$ kcal/mol[9,16] instead of -13.0 kcal/mol used in Table 3 then K_7 will be larger at 300 K by a factor of 2.3 and a factor of 1.5 at 600 K. This will reduce the discrepancy between the direct and indirect values but the remaining gap at 300 K is still a factor of 5.

Of particular interest is the observation that values of k_7 obtained from $k_{-7}K_7$ of ref 9 show no evidence of the negative activation energy found in the direct measurements. These indirect values are also in better agreement with the thermal values of ref 21.

Once again the data from the studies of k_{-7} from the thermal reaction are in better agreement with each other and with our own measurement. The value of ref 21 is in remarkable agreement with our own value while perhaps of great interest is the observation that the indirect k_7 value of ref 9 at 300 K is in excellent agreement with our own value.

The value we find for $k_7(300\text{K}) = 6.6 \times 10^{-13}$ cm^3/(molecule·s) is low enough to suggest a small activation energy for k_7. If we could have a value of A_7 we could estimate E_7. A quick approach using experimental data is to adopt the value measured for the reaction of Cl atoms with ethane[7] at 300 K (k'_{-7}).

$$\mathrm{HCl} + \mathrm{C_2H_5} \underset{}{\overset{7'}{\rightleftharpoons}} \mathrm{C_2H_6} + \mathrm{Cl} \qquad S_{7'}(300\text{K}) = 9.8\ \text{cal/(mol·K)}$$

As a first approximation, the A factor for (-7), the reaction of Br atoms with C_2H_6, should have about the same value. A quick review of the entropies of organic molecules containing Br or Cl atoms shows about 2.5 ± 0.3 cal/(mol·K) difference in entropies[23] favoring Br over Cl. $S°_{\mathrm{Br}}(300\text{K}) - S°_{\mathrm{Cl}}(300\text{K}) = 2.3$ cal/(mol·K) and $S°_{\mathrm{HBr}}(300\text{K}) - S°_{\mathrm{HCl}}(300\text{K}) = 2.9$ cal/(mol·K). For reaction ($-7'$) it is reported[7]

$$\log(A_{-7'}\ \text{cm}^3/(\text{molecule·s})) = -10.10 \pm 0.01$$

If we assume that the TS for Br + C_2H_6 has 2.5 cal/(mol·K) more entropy than that for Cl + C_2H_6 while $S°_{\mathrm{Br}} - S°_{\mathrm{Cl}} = 2.3$ cal/(mol·K), we can estimate

$$\log(A_{-7}\ \text{cm}^3/(\text{molecule·s})) = -10.05 \pm 0.1$$

Now using the value of $\Delta S°_7(300\text{K}) = 10.4 \pm 0.5$ cal/(mol·K) (Table 3) we can calculate

$$\log(A_7\ \text{cm}^3/(\text{molecule·s})) = -12.3$$

or

$$A_7 = 5 \times 10^{-13}\ \text{cm}^3/(\text{molecule·s})$$

This has an estimated uncertainty of about a factor of 2. Taken literally it would imply a negative activation energy $E_7 = -0.17 \pm 0.6$ kcal/mol. It is close enough to k_7 to confirm that $|E_7|$ is very small, less than 1 kcal/mol in absolute value.

An alternative method for estimating A_7 is to use the value reported in the direct study of the thermal reaction[21] Br + C_2H_6, namely $A_{-7} = 6.7 \times 10^{-10}$ cm^3/(molecule·s). This was measured at a mean temperature of 550 K. Since ΔS_7 has negligible temperature dependence we can calculate from Table 3 that $A_7(550\text{K}) = 3.6 \times 10^{-12}$cm^3/(molecule·s). A tight model for the transition state[23] yields an average value of $\langle C_p \rangle = 3.0$ cal/(mol·K). From this value we deduce that a modified Arrhenius A factor would be written as

$$A_7 = A'_7\left(\frac{T}{300}\right)^{1.5} \tag{11}$$

Equating this to $A_7(550\text{K})$ we estimate $A'_7 = 1.45 \times 10^{-12}$ cm^3/(molecule·s) which also is the value of the Arrhenius A factor at 300 K. Comparing this to our measured value of $k_7(300) = 6.6 \times 10^{-13}$cm^3/(molecule·s) we can calculate an activation energy E_7 of 0.46 kcal/mol at 300 K.

The modified Arrhenius equation also implies a temperature-dependent activation energy:

$$E_{-7} = \Delta H^{\ddagger}_{-7} + nRT \tag{12}$$

Using the estimated value of $n = 1.5$ and the Arrhenius parameters from ref 21, $E_{-7} = 14.0 \pm 0.3$ kcal/mol, we estimate $\Delta H^{\ddagger}_{-7} = 12.35$ kcal/mol at 550 K, the midpoint of the experimental range. At 300 K $E_{-7} = 13.25 \pm 0.6$ kcal/mol, which fits very well all the values reported which range from 12.7 ± 0.5 kcal/mol[4,9] to 13.7 ± 0.1 kcal/mol[20] at mean temperatures of 400, 550, and 425 K.[20] Using the thermochemistry of Table 3 it yields $E_7(300\text{K}) = 0.25 \pm 0.75$ kcal/mol.

The Modified Arrhenius equation for the value of k_{-7} reported in ref 21 is

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(21) King, K. D.; Golden, D. M.; Benson, S. W. *Trans. Faraday Soc.* **1970**, *66*, 2794.

(22) Coomber, J. W.; Whittle, E. *Trans. Faraday Soc.* **1966**, *62*, 1553, 2188.

(23) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley: New York, 1976.

$$k_{-7\mathrm{M}} = 6.0 \times 10^{-11}(T/300)^{1.5-12.35/\theta}\ \mathrm{cm^3/(molecule{\cdot}s)}$$

where $\theta = 2.303RT$ in kcal/mol. This has been obtained by fitting to the original data at 530 K. It gives values at 600 and 500 K within 2% of the original data. It takes on the values 1.65×10^{-17} at 400 K compared to the extrapolated value of 1.48×10^{-17} cm^3/(molecule•s) in Table 4 and 6.0×10^{-20} at 300 K compared to the extrapolated value of 4.2×10^{-20} cm^3/(molecule•s).

The Modified Arrhenius equation for k_{-7} also improves the agreement between ref 9 and ref 21, putting them within the combined experimental errors of both studies.

Treating the transition state of reaction 7 by the usual technique[23] for a nonlinear tight transition state yields a value for A_7 of 2.3×10^{-13} cm^3/(molecule•s), about a factor of from 1.5 to 5.0 lower than the values estimated above from experimental values. While a factor of 2 would be typical of maximum deviations these values suggest that the transition state is looser than the standard tight model. A similar deviation of a factor of 2 was reported[8] in the calculation of the A factor for Cl + C_2H_6 again suggesting a looser transition state.

Is there any way in which we can reconcile our low value of k_7 with the higher values reported over the past 6 years?[9,16] Unfortunately no. The factor of 14 is too large to bridge. In simplest terms, in our system it would require that [C_2H_5] be 14 times smaller than our measured value. Our mass balances will not permit errors larger than about 3%, certainly not factors of 14. As we have noted two independently calculated values of [R] agree to within 1.5% for all of our experiments. A glaring difference between our study and those of refs 4 and 9 is that we find no evidence of a surface reaction while with similar surfaces they report a very irregular one which can vary from 5 to 24 s^{-1}.

Our study differs from the other flow studies such as ref 4 or ref 9 in that we do mass balances on *all* species. In this regard it is unique among current kinetic methods which observe appearance or disappearance of a single species.

A particular problem with the flow method used in refs 4 and 9 is that radicals are produced by flash photolysis using 193- or 248-nm radiation. The energy of these photons is far in excess of the energy needed to break bonds in precursor molecules such as C_2H_5Br or diethyl ketone.

At 193 nm, 148 kcal[4,9] are used to rupture a 79-kcal/mol bond[23] in $(C_2H_5)_2CO$, and 69 kcal/mol of excess energy are deposited in the molecule and shared between the C_2H_5CO and C_2H_5 fragments. This is more than sufficient to further decompose C_2H_5CO into C_2H_5 + CO which requires 13.4 kcal/mol. In either case it is assumed the excess energy is quenched by the bath gas, He or N_2 at 1 or 2 Torr. In 1 ms these gases will make about 10^4 collisions with the radicals. It is far from demonstrated that this is sufficient to thermalize this excess energy. The chief evidence for thermalization is indirect in that the results seem to be independent of precursor light energy, background gas (He or N_2), or pressure (1−2 Torr). While this seems a plausible conclusion there is still an unanswered problem, namely the effect of excess energy on the mass spectral signal. The use of photoionization at wave lengths close to the ionization potential limit requires working on an ionization yield−energy curve which is very steep and strongly energy dependent. Even small changes in energy can produce large changes in ion yield.

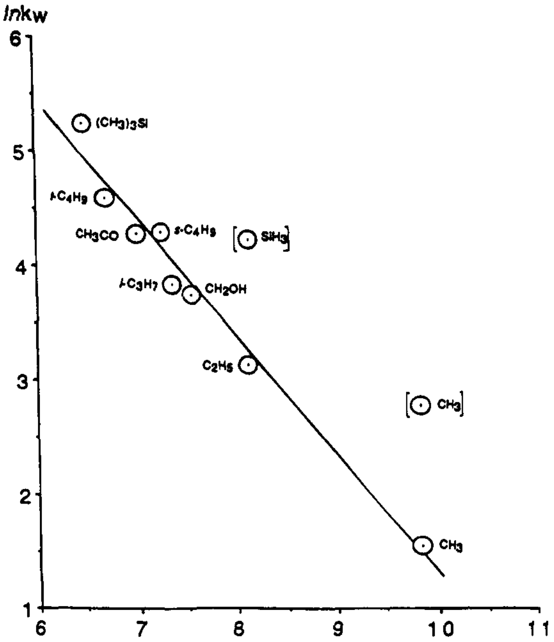

Figure 5. The apparent free energy change of radical removal by the "wall" reported for R + HBr reactions[9,24−28,30−32] using 193-nm (or 248-nm) laser flash generation of R as a function of the ionization potential of radicals.

One would expect that as collisions occur there is a decrease in internal energy of the C_2H_5 fragments. In the absence of HBr, collisional thermalization of the radicals leads to a decrease in the photoionization cross section with decreasing energy (electron + internal energy) which appears as a loss in C_2H_5 radicals. The authors[4,9] have interpreted this as a loss of C_2H_5 radicals to the wall and they report k_w values in the range 5−15 s^{-1} for this first order "wall loss"[4] and 21−24 s^{-1} in a second identical study.[9] Similar wall losses in our system would preclude our ability to study any of the ethyl radical reactions we have measured. With similar wall coatings we can set an upper limit of 0.01 s^{-1} for heterogeneous reactions in our system where we only produce thermalized C_2H_5 radicals. No products of this wall reaction has ever been reported or suggested.

In further support of this hypothesis we note that wall loss rates increase[9] with radical complexity, k_w for $CH_3 < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$. With increasing number of atoms and hence increasing degrees of freedom we could expect faster thermalization (interpreted by ref 9 as faster wall reaction). We note further that k_w tends to decrease with increasing temperature.

Since observed radical signal decay rates are "corrected" by substracting these values of k_w, the resulting bimolecular rates k_b are very sensitive to k_w since k_w can be a very large fraction of k_b[HBr]. It is quite possible that all the negative activation energies simply reflect this rate of thermalization interpreted as a negative activation energy for k_w. The pronounced variability of k_w from run to run makes it very difficult to try to analyze it very meaningfully.

The 193-nm and occassionally 248-nm photolysis of radical precursors was used in a systematic investigation of R + HBr reactions using the photoionization mass spectrometry of radicals so that it allows some insight into the kinetics of the assumed wall reaction. In Figure 5 we have plotted k_w values averaged near 300 K reported for $(CH_3)_3Si$,[24] $t\text{-}C_4H_9$,[9] CH_3O,[25] $s\text{-}C_4H_9$,[26] SiH_3,[27] $i\text{-}C_3H_7$,[9] CH_2OH,[28] C_2H_5,[9] and CH_3[9] radicals as a

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function of their ionization potential IP(R).[29] The bracketed k_w for CH_3 of this series is higher than that found in other reactions, such as with HCl,[30] HI,[31] and $2CH_3$ recombination[32] which are shown without brackets. Apart from the two bracketed data, Figure 5 suggests that the free energy change of radical removal by the "wall" is a linear, negative function of IP(R). It is so distinct that it overrides any effect of different wall coatings (halo-carbon wax, Teflon, poly(dimethylsiloxane), or B_2O_3) used and of flow tube diameter variations[25] investigated. Such a relation is uncharacteristic of surface reactions, but it supports our suggestions on the photoionization cross section of vibrationally excited radicals. We also note that no H atom removal by wall interaction was observed[33] in the H + HBr reaction using also 193-nm laser pulses for H atom generation, but time-resolved resonance fluorescence of H and Br atoms for analysis. This reaction has a positive activation energy of 1.0 kcal/mol.

In contrast to the results of refs 4 and 9, the results of ref 16 were obtained by following the appearance of Br atoms (atom resonance fluorescence) produced by reaction of C_2H_5 + HBr. They obtained C_2H_5 radicals from flash photolysis of C_2H_5I (266 nm) or from the flash photolysis of Cl_2/C_2H_6 mixtures (355 nm). The former uses 108 kcal to break a 56-kcal/mol bond leaving 52 kcal of excess energy in $(C_2H_5I)^*$. While 23 kcal might be used in producing the $I(^2P_{1/2})$ excited state, a 29-kcal excess will still be left in the C_2H_5 fragment. The Cl_2/C_2H_6 system will produce thermal C_2H_5 radicals and both precursors appear to give the same results. These seem to be very carefully conducted experiments and the authors have considered all the possible systematic errors except for one, the effect of the monitoring radiation (Br_2/He microwave discharge) which appears to have emission lines of Br radiation from 140 to 160 nm. It would be of importance to know the effect of this radiation on C_2H_5 and HBr. Their major correction is for diffusion of species from the light beam. Some of these comments have been made in our earlier discussion[7] of reaction 4.

An unresolved problem in their system is a very large loss of alkyl radicals by processes which produce no Br. This can account for from 80% to 20% of $[C_2H_5]_0$. They attribute this to the presence of 10 mTorr of O_2 but cannot otherwise explain it. With "O_2 contamination" of 3×10^{14} molecule/cm^3, as supposed,[16] the absorption, dissociation, and resonance fluorescence of atomic and molecular oxygen in the 140−160 nm spectroscopic wavelength range should also have been considered. It also shows a marked decrease with increasing temperature which could be responsible for the apparent negative activation energy of −1.1 kcal/mol.

A final problem with the photolytic generation of radicals from precursors arises from the presence of HBr. At 193 nm the cross section[34] of HBr is 8×10^{-19} cm^2. This is about six times larger than the cross section of the precursor ketones used which were present at about the same concentration. We should thus expect more H atoms and Br atoms from HBr photolysis than R radicals from the RCOR′ precursor. While initial radical concentrations are kept to below 5×10^{10} molecules/cm^3 to avoid significant R/R reactions at the lowest HBr concentrations used, $\sim 1 \times 10^{12}$ molecules/cm^3, H and Br concentration can be near 10^{12} molecules/cm^3 at the highest concentrations used and significantly affect the concentrations of R. This would tend to make for apparently higher values of R + HBr at the larger HBr concentrations.

Conclusion

VLPR is today a unique kinetic tool. It is the only technique which can routinely measure *all* reactants and products in a bimolecular reaction. It currently does this and measures mass balances to ±3%. If for no other reason it must be given considerable weight when compared to alternative techniques which measure loss of a single reactant or follow production of a single product. Rate constants reported in the last 6 years with VLPR have shown excellent agreement with well-established rate constants. This includes such reactions as Cl + CH_4,[2a] Cl + C_2H_6, and Cl + C_2H_4,[7] Cl + C_2D_6,[8] Cl + HBr,[10] H + HBr,[35] C_2H_5 (and C_2D_5) disproportionation,[7,8] HO_2 + Cl, $2HO_2$, and C_2H_5 + HO_2.[6]

The values reported here for k_7 are consistent with currently accepted thermochemistry and the reported data on the reverse reaction. The much larger values of k_7 in the photolysis systems are not consistent with current thermochemistry and the data on the reverse reaction. We hope to measure E_7 in the future and will reserve further discussion until then.

Values of k_8(Br + C_2H_5) reported here are very similar, as expected, to the values of k_2(Cl + C_2H_5) found earlier for the analogous reaction. Both are smaller by factors of about 25 than values obtained from much less direct studies.[12] The latter require collision cross sections for these reactions with diameters from 8 to 11 Å, far in excess of what can be explained by any known forces between neutral species.

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