# Laser Flash Photolysis Study of the Br + $I-C_4H_{10} \rightleftharpoons HBr + t-C_4H_9$ Reaction. Heat of Formation of $t-C_AH_9$

Paul W. Seakins<sup>†</sup> and Michael J. Pilling<sup>\*</sup>

School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K., and Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, U.K. (Received: May 8, 1991; In Final Form: July 15, 1991)

The heat of formation of the tert-butyl radical has been determined in two independent ways using laser flash photolysis coupled with detection of Br by resonance fluorescence. The  $t-C_4H_9$  + HBr reaction was studied by monitoring the rise of the Br product at room temperature following photolysis of  $(t-C_4H_9)_2N_2$  at 351 nm. Combination of the rate constant with  $k(Br+i-C_4H_{10})$  gives  $\Delta H^{\Theta}_{1,298}(t-C_4H_9) = 50.9 \pm 3.5 \text{ kJ mol}^{-1}$ . The measured value of  $k(t-C_4H_9+HBr)$  ((3.2 ± 1.0)  $\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) is in reasonable agreement with the measurements of Russell et al. and of Richards et al. Equilibration in the reaction system  $Br + i - C_4 H_{10} = HBr + t - C_4 H_9$  was studied by generating Br by photolysis of  $CF_2 Br_2$  at 248 nm in the presence of  $i - C_4 H_{10}$  and HBr and observing the relaxation of [Br]. These experiments were conducted at 573 and 641 K. The measurements yield data for both forward and reverse rate constants, for the equilibrium constant, and hence for  $\Delta H^{\Theta}_{1,298}(t-C_4H_9)$ , giving values of 44.2 ± 4.0 and 48.1 ± 4.0 kJ mol<sup>-1</sup> at the respective temperatures. Combination of the three independent estimates gives  $\Delta H^{\Theta}_{1,298}(t-C_4H_9) = 47.3 \pm 3.5 \text{ kJ mol}^{-1}$ . The values for  $k(t-C_4H_9+HBr)$  at these elevated temperatures agree with the data of Russell et al. and demonstrate a negative temperature dependence in the rate constant.

#### Introduction

Heats of formation of saturated alkyl radicals have stimulated much experimental interest in recent years and no little controversy.<sup>1,2</sup> Of central concern has been the tert-butyl radical, where discrepancies have been greatest with values for  $\Delta H^{\Theta}_{f,298}$  ranging from 31.8<sup>3</sup> to 51.7 kJ mol<sup>-1.1</sup> Most measurements have been based on the halogenation reactions

$$Br + i - C_4 H_{10} \rightleftharpoons HBr + t - C_4 H_9 \qquad (R1, R-1)$$

$$I + i - C_4 H_{10} \rightleftharpoons HI + t - C_4 H_9 \qquad (R2, R-2)$$

Rate coefficients for the forward reactions,  $k_1$  and  $k_2$ , are reasonably well-defined, and we report elsewhere determination of k(T) by laser flash photolysis/resonance fluorescence for Br plus a series of alkanes.<sup>4</sup> The origin of the controversy relates to the temperature dependence of the reverse reactions and is illustrated by two recent determinations of  $k_{-1}$ . Muller-Markgraf et al.<sup>5</sup> studied the reaction

$$DBr + t - C_4H_9 \rightarrow Br + i - C_4H_9D$$

in a very low pressure photolysis (VLP $\phi$ ) apparatus. After correction for the primary isotope effect, they calculated rate coefficients of 2.1  $\times$  10<sup>-13</sup> and 5.4  $\times$  10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for reaction R-1 at 295 and 384 K. Russell et al.<sup>6</sup> utilized a photoionization mass spectrometer (PIMS) to detect the tert-butyl radical in time-resolved experiments. Measurements of reaction R-1 over the temperature range 298-533 K gave

$$k_{-1} = (9.86 \pm 1.30) \times$$

 $exp((5.8 \pm 0.9) \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 

In contrast to the VLP $\phi$  study, Russell et al. measured a *negative* activation energy and a room-temperature rate coefficient a factor of 50 times greater than that determined in the VLP $\phi$  study. Using identical values (at 298 K) for  $k_1$ , third law calculations gave values of 38.5 and 48.5 kJ mol<sup>-1</sup> for  $\Delta H^{\Theta}_{f,298}(t-C_4H_9)$  from the VLP $\phi$  and PIMS studies, respectively.

Both experiments have been criticised on the basis of potential interferences from surface effects.<sup>7</sup> A simple model calculation of the complex through which reaction R-1 is presumed to proceed if the negative temperature dependence is to be understood predicts a negative kinetic isotope effect  $(k_{\rm H} < k_{\rm D})$ , which is the opposite of the behavior expected for a metathesis reaction.<sup>8</sup>

This paper reports two experimental measurements designed to provide additional, independent information in an attempt to

resolve this disagreement. In the first, reaction R-1 is studied at room temperature by laser flash photolysis using resonance fluorescence to monitor the rate of formation of Br. The second involves measurements of the approach to equilibrium following production of  $t-C_4H_9$  by laser flash photolysis in the presence of HBr and  $i-C_4H_{10}$ . This relaxation experiment enables both  $k_1$  and  $k_{-1}$  and hence  $K_1$  to be determined,<sup>9</sup> and since it was conducted at elevated temperatures (573 and 641 K), it provides an additional check on the temperature dependence of  $k_{-1}$ .

#### **Experimental Section**

tert-Butyl or Br radicals were produced by pulsed excimer laser (Lumonics TE861S) photolysis in a heated Pyrex flow reactor. The photolysis of azoisobutane at 351 nm was used to generate tert-butyl radicals

$$(t-C_4H_9)_2N_2 \xrightarrow{351 \text{ nm}} 2t-C_4H_9 + N_2$$

CF<sub>2</sub>Br<sub>2</sub> photolysis at either 193 or 248 nm was the source of Br atoms6,10-12

$$CF_2Br_2 \xrightarrow{248 \text{ nm}} CF_2Br + Br$$

Mixtures of the radical precursor, substrate, and helium diluent (>99%) were flowed through the uncoated Pyrex reactor at total pressures of between 50 and 300 Torr. Flow rates were metered by flow controllers (Tylan FM360/MKS 260 flow ratio controllers). The cell was heated by flat element heating tape wrapped around the flow cell. The tape and cell were surrounded by

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<sup>\*</sup> To whom correspondence should be addressed at the University of Leeds. \* Present address: Joint Institute Laboratory Astrophysics, University of Colorado, Boulder, CO 80309-0440.

 $Br + i - C_4 H_{10} \rightleftharpoons HBr + t - C_4 H_9$ 

thermal cladding to produce a more uniform temperature profile across the observation zone. Temperatures above and below the observation/photolysis zone were monitored by two thermocouples, which acted as sensors for the temperature controller.

The time-dependent bromine atom concentration in both experiments was monitored by resonance fluorescence. Exciting radiation was generated from a microwave discharge lamp of conventional design.<sup>13</sup> A mixture of 0.2% Br in a helium diluent was flowed through the lamp at a pressure of approximately 1 Torr. Resonance radiation passed into the cell through MgF<sub>2</sub> or CaF<sub>2</sub> windows. Fluorescence radiation was detected, perpendicular to a plane defined by the resonance lamp and photolysis beam, by a solar blind photomultiplier (Thorn EMI 9413 CsI). The analogue voltage output from the photomultiplier was amplified and then digitized by a Biomation 8100 waveform recorder. Recorder sweeps were triggered by a pulse synchronized to the laser discharge. The Biomation was set to record 20% of the sweep as pretrigger baseline. The final decay, averaged typically over 200-1500 laser pulses, was transferred to a microcomputer for storage.

Br<sub>2</sub> (BDH, Aristar grade), CF<sub>2</sub>Br<sub>2</sub> (Aldrich), and azoisobutane (Fairfield Chemicals) were degassed by several freeze-pump-thaw cycles. HBr (BDH, >99%) was degassed and distilled from -80 to -196 °C. Mixtures of HBr in helium (BIOC, CP grade) were made up in blackened Pyrex bulbs. During experimental runs a cold finger in the bulb was kept at 20 °C to trap any Br<sub>2</sub>. Isobutane (BDH, CP grade) and helium diluent (BOC, CP grade) were used directly.

#### **Results and Discussion**

1. Photolysis of Azoisobutane. Azoisobutane forms a convenient photolytic source of tert-butyl radicals at 351 nm, which is close to the absorption maximum. The photolysis of azoisobutane has been studied by Thomas and Calvert<sup>14</sup> and has been used in a number of kinetic studies.<sup>5,15-17</sup> There is no evidence for generation of alkyl radicals other than  $t-C_4H_9$  at these wavelengths. As the primary quantum yield for N<sub>2</sub> production decreases with pressure,<sup>17,18</sup> it is thought that the initial absorption of a photon produces an electronically excited state which either dissociates or is collisionally stabilized; alternatively, the reaction may proceed partly via a direct dissociation. There is no evidence to suggest that the  $t-C_4H_9N_2$  radical has a significant lifetime. However, it is not known whether the dissociation is direct or proceeds via the  $t-C_4H_9N_2$  radical intermediate, in an analogous way to acetone dissociation at 193 nm.<sup>19</sup> The kinetic data recorded by Osborne and Waddington<sup>17</sup> for t-C<sub>4</sub>H<sub>9</sub> radicals produced by photolytic and pyrolytic methods were identical, indicating that the  $t-C_4H_9$  radicals formed in the photolysis are not vibrationally excited on the time scale of the chemical reaction. Some vibrational excitation of the nascent radical photoproduct is to be expected because of the change in geometry and is indeed observed for CH<sub>3</sub> formed in the photolysis of CH<sub>3</sub>N<sub>2</sub>CH<sub>3</sub><sup>20</sup> or CH<sub>3</sub>COC- $H_3^{19}$  at 193 nm. Observations of collisional relaxation to the ground vibrational state of CH<sub>3</sub> demonstrate that the process is quite rapid, being complete in 5  $\mu$ s at  $\approx 10$  Torr of argon.<sup>20</sup> Vibrational relaxation of  $t-C_4H_9$  is unlikely to be slower, since the rate-determining step is usually the V-T transfer process from the lowest excited vibrational level and the collisional efficiency increases as the vibration frequency decreases.<sup>21</sup> The appropriate

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TABLE I

no.	reaction	$k(298 \text{ K})/\text{cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>
<b>R</b> -1	$t-C_4H_9 + HBr \rightarrow Br + i-C_4H_{10}$	floated
R3	$t-C_4H_9 + t-C_4H_9 \rightarrow \text{products}$	$1.52 \times 10^{-11}$
R4	$t-C_4H_9 + Br \rightarrow products$	$5.0 \times 10^{-11}$
R5	Br→	25ª
R6	$t-C_4H_9 \rightarrow$	20ª

<sup>a</sup> First-order diffusive loss. Units of s<sup>-1</sup>.

<b>CABLE II:</b> Experimental	Values of <i>l</i>	k_1 at 298 k	ζ
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10 <sup>13</sup> [HBr]/ molecules cm <sup>-3</sup>	$10^{12}[t-C_4H_9]_0/molecules cm^{-3}$	$\frac{10^{-11}k_{-1}}{\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}}$
3.65	1.5	3.46 ± 0.13
6.39	1.5	$3.03 \pm 0.20$
8.74	3.0	$3.21 \pm 0.30$
8.94	1.5	$3.22 \pm 0.30$
13.0	1.5	$3.20 \pm 0.30$

TABLE III:	Experimental	Measurements	of k_1	at	298	K
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reference	method	$10^{11}k_{-1}(298 \text{ K})/cm^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Russell et al.6	laser flash photolysis/PIMS	1.0 ± 0.2
Muller-Markgraf et al. <sup>5</sup>	$VLP\phi(DBr+t-C_4H_9)$ corrected to HBr	$(2.1 \pm 0.6) \times 10^{-2}$
Richards et al. <sup>26</sup>	laser flash photolysis/IR diode laser absorption	$1.0 \pm 0.2$
this work	laser flash photolysis/ resonance fluorescence	3.2 ± 1.0
Nicovich et al. <sup>27</sup>	laser flash photolysis/ resonance fluorescence	2.7 ± 1.0

vibrational frequencies are 606 cm<sup>-1</sup> for CH<sub>3</sub> and 200 cm<sup>-1</sup> for  $t-C_4H_9$ ,<sup>8</sup> neglecting the hindered CH<sub>3</sub> internal rotors. The present experiments were conducted at a typical pressure of 200 Torr (He) and on a time scale of 1-10 ms.

2. Determination of  $k_{-1}$  at 298 K. Figure 1 shows a typical bromine atom profile following photolysis of azoisobutane in the presence of HBr. The zero signal observed at zero time confirms that, as expected, there is no photolysis of HBr at 351 nm. No signal was observed in the absence of the tert-butyl precursor.

Radical-radical reactions and diffusive loss make the differential equations, controlling the bromine atom concentrations with time, insoluble by analytic methods. Experimental atom profiles were transferred to a VAX computer for numerical analysis. The numerical fitting was performed using the FACSIMILE package,<sup>22</sup> a numerical integrator based on the Gear algorithm. The mechanism used to fit the data is given in Table I. The rate coefficient for diffusive loss of bromine atoms  $(k_5)$  was measured in separate experiments where Br was generated from the photolysis of CF<sub>2</sub>Br<sub>2</sub> at 193 nm in a helium diluent. Calculations based on estimates for the collision cross sections of Br and t- $C_4H_9^{23}$  were used to estimate a value of  $k_6$ , the rate constant for diffusive loss of the *tert*-butyl radical.  $k_3$  is the combined disproportionation/recombination rate coefficient for the mutual removal of the *tert*-butyl radical, and the value obtained by Parks and Quinn<sup>15</sup> using molecular modulation spectroscopy was employed. There have been no studies of reaction R4. However, Washida and Bayes<sup>24</sup> have measured a value of  $(8.6 \pm 1.3) \times 10^{-10}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the overall reaction of oxygen atoms with tert-butyl radicals at 298 K:

$$t-C_4H_9 + O(^{3}P) \rightarrow OH + C_4H_8$$
 (77%) (R7a)

$$\rightarrow$$
 CH<sub>3</sub>COCH<sub>3</sub> + H (23%) (R7b)

Considering the low reactivity of bromine atoms and the absence

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Figure 1. Bromine atom profile following generation of  $t-C_4H_9$  by photolysis of  $(t-C_4H_9)_2N_2$  at 351 nm in the presence of HBr. The full line shows the numerical fit based on the model shown in Table I. [HBr] =  $3.65 \times 10^{13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

of an available reaction channel analogous to (R7b), a significantly lower value of  $5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was estimated for  $k_4$ . A possible contribution from the reaction of Br with 2-methylpropene, formed in the disproportionation reaction of  $t-C_4H_9$ 

$$Br + (CH_3)_2CCH_2 \rightarrow products$$
 (R8)

was checked by incorporating reaction R8 in the mechanism, with  $k_8$  set to 7.5 × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, based on the rate coefficient measured by Barnes et al.<sup>25</sup> for Br + *trans*-but-2-ene. No significant change was observed in the value returned for  $k_{-1}$ .

Table II lists the best-fit values for  $k_{-1}$  as a function of [HBr] and  $[t-C_4H_9]_0$ , which was estimated from the incident laser energy and the absorption cross section of  $(C_4H_9)_2N_2$ ; these latter estimates may be too high because a quantum yield of unity was assumed.

The numerical integration program returned 95% confidence limits for  $k_{-1}$  of  $\pm 5-10\%$ . Larger contributions to the error limits derive from the uncertainties in  $k_4$  and  $[t-C_4H_9]_0$ . Increasing  $k_4$ to  $3 \times 10^{-10}$  cm<sup>-3</sup> molecule<sup>-1</sup> s<sup>-1</sup> decreased the value of  $k_{-1}$  returned by the analysis program by ~35%, while decreasing  $k_4$  to  $10^{-11}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> increased  $k_{-1}$  by ~7%. Similar variations were observed on changing  $[t-C_4H_9]_0$ . Finally, a contribution of ~ ±10% derives from errors in determining [HBr]. Combining these uncertainties with the mean value for  $k_{-1}$  from Table II gives  $k_{-1}$  $= (3.2 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 

Table III presents a comparison of room-temperature determinations of  $k_{-1}$ . The present value is somewhat higher than those of Russell et al.<sup>6</sup> and of Richards et al.<sup>26</sup> but is in excellent agreement with the value recently reported by Nicovich et al.<sup>27</sup> By contrast, all four of these determinations give rate coefficients a factor of  $\approx 100$  higher than that obtained by Muller-Markgraf et al.5 using very low pressure photolysis. The measurement of Russell et al.<sup>6</sup> has been criticised because of possible contributions

from wall reactions or from vibrationally excited radicals.<sup>28</sup> Wall reactions are of no significance in the present study, and as discussed above, vibrational relaxation is complete on the experimental time scale.

Contributions from reactions of other species can similarly be rejected; the tert-butyl radical precursor, azoisobutane, was carefully chosen to minimize such effects. The other potential products from the photolysis of azoisobutane, H and CH<sub>3</sub> (although not observed in previous studies<sup>17,18</sup>), that could generate bromine atoms from HBr have been shown to react at slower rates than  $t-C_4H_9$ :

$$CH_3 + HBr \rightarrow CH_4 + Br$$
 (R9)

$$H + HBr \rightarrow H_2 + Br$$
 (R10)

A deuterated analogue  $(CD_3 + HBr)$  of reaction 3.12 has been studied by Donaldson and Leone<sup>29</sup> using time-resolved chemiluminescence from vibrationally excited CD<sub>3</sub>H to follow the reaction. After correction for the secondary isotope effect, a value of (3.8  $\pm$  0.4)  $\times$  10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was determined for k<sub>9</sub>. Russell et al.<sup>30</sup> determined a value of  $(1.5 \pm 0.2) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> m using the PIMS technique. Finally, Gac et al.<sup>31</sup> studied CH<sub>3</sub> + DBr between 600 and 1000 K using a very low pressure pyrolysis reactor. Correction for the primary isotope effect, estimated by the authors as 1.5, yields a temperature-independent value of 4.8  $\times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Reaction R10 has been studied by several investigators; 32-35 the mean room-temperature value for  $k_{10}$  is (6.3 ± 0.2) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

Bromine atoms could be generated via reaction of  $t-C_4H_9$  with Br<sub>2</sub>:

$$t-C_4H_9 + Br_2 \rightarrow i-C_4H_9Br + Br$$
 (R11)

Although the reaction vessel and the vacuum system were constructed almost entirely of Pyrex, there were short metal bellows sections leading to the vessel that might have catalyzed the decomposition of HBr to form Br<sub>2</sub>. Timonen et al.<sup>36</sup> have measured  $k_{11}(298) = 9.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ so that high concen-}$ trations of  $Br_2$  ([ $Br_2$ ] > 0.2[HBr]) would be needed if reaction R11 were to make an appreciable contribution. Spectrophotometric measurements of the HBr following passage through the reaction vessel showed negligible decomposition and no detectable levels of Br<sub>2</sub>.

The origin of the disagreement in the determination of  $k_{-1}$  by Muller-Markgraf et al.<sup>5</sup> and the other studies entered in Table III remains obscure. Gutman<sup>7</sup> has proposed a rationalization based on radical wall loss in the VLP $\phi$  experiment based on his own measurements of radical wall loss rates in the flow reactor using PIMS. This explanation has been questioned by Golden,<sup>28</sup> but direct measurements of wall loss rates of alkyl radicals in the VLP $\phi$  reactor are needed to support his argument. Overall, the weight of experimental evidence favors the higher value of  $k_{-1}$ .

3. Direct Study of Equilibration. The approach to equilibrium in reactions R1 and R-1 was observed by generating Br from the photolysis of  $CF_2Br_2$  in the presence of both HBr and  $i-C_4H_{10}$  at elevated temperatures (573 and 641 K). Substrate concentrations were adjusted so that the forward and reverse pseudo-first-order rate coefficients were comparable. Assuming that reactions R1, R-1, R5, and R6 contribute to the kinetics, then the time-de-

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 $Br + i - C_4 H_{10} \rightleftharpoons HBr + t - C_4 H_9$ 

pendent bromine atom concentration is given by

$$[\mathbf{Br}]_t = A \exp(-\lambda_1 t) + B \exp(-\lambda_2 t)$$

where

$$\mathcal{A} = \frac{[\mathbf{Br}]_0(\alpha - \lambda_2)}{(\lambda_1 - \lambda_2)} \qquad \mathcal{B} = \frac{[\mathbf{Br}]_0(\alpha - \lambda_1)}{(\lambda_2 - \lambda_1)}$$
$$\lambda_1 - \lambda_2 = [(\alpha + \delta)^2 + 4(\beta\gamma + \alpha\delta)]^{0.5} \qquad \lambda_1 + \lambda_2 = \alpha + \delta$$
$$\lambda_1 \lambda_2 = \alpha \delta - \beta \gamma$$

and

$$\alpha = k_1[i - C_4 H_{10}] + k_5 \qquad \beta = k_{-1}[HBr]$$
  
$$\gamma = k_1[i - C_4 H_{10}] \qquad \delta = k_{-1}[HBr] + k_6$$

As previously,  $k_5$  was measured independently from the photolysis of CF<sub>2</sub>Br<sub>2</sub> in He and  $k_6$  was calculated from  $k_5$ . Interference from the reaction

$$CF_2Br + HBr \rightarrow CF_2BrH + Br$$

in the equilibration experiments was shown to be negligible through control experiments in  $CF_2Br_2/HBr/He$  mixtures. Finally, experiments were conducted over a range of radical and substrate concentrations to check for the presence of other interferences e.g. from radical/radical reactions.

Table IV lists the mean values for  $k_1$  and  $k_{-1}$  obtained from the analysis of the biexponential decays.  $k_1$  is compared with recent measurements in this laboratory over the temperature range 423-621 K under single-exponential (i.e., irreversible  $[HBr]_0 =$ 0) conditions. The agreement is excellent.  $k_{-1}$  is compared with the measurements of Russell et al. using PIMS.<sup>6</sup> Once again the agreement is satisfactory, and although  $k_{-1}(641 \text{ K})$  measured in the present experiments is greater than  $k_{-1}(573 \text{ K})$ , both values are significantly less than  $k_{-1}(298 \text{ K})$ , confirming the negative temperature dependence observed by Russell et al.<sup>6</sup> Figure 2 shows an Arrhenius plot for the data and demonstrates the satisfactory agreement. This confirmation of the negative activation energy for  $t-C_4H_9$  + HBr first observed by Russell et al.<sup>6</sup> deserves further comment. Gutman and workers have found negative activation energies for a series of alkyl radicals, R, in the reaction R + HX (X = Br, I) with the magnitude of the activation energy increasing with the size of R.<sup>6,37,38</sup> McEwen and Golden<sup>8</sup> tested a simple two-channel RRKM model for such a reaction, in which the reactants first form a bound complex R-X-H which can dissociate to regenerate the reactants or generate products via a cyclic transition state. Their model predicts a negative kinetic isotope effect  $(k_{\rm H}/k_{\rm D} < 1)$ . The experimental observations of negative activation energies for a wide class of related reactions, and the present confirmation for one member of that class, are of considerable significance within the field of chemical kinetics because they are contrary to prior expectation. The calculations of McEwan and Golden<sup>8</sup> demonstrate that the observations can be rationalized, albeit via a simplified model. Further work, both experimental and theoretical, is clearly needed in order to assess the prevalence of complex mechanisms of this type and to afford a framework of understanding.

4.  $\Delta H^{\Theta}_{1,298}(t-C_4H_9)$ . The experimental data reported in subsections 2 and 3 can be used to calculate the heat of formation of the *tert*-butyl radical. A third law technique was employed using  $S^{\Theta}_{298}(t-C_4H_9) = 314 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$  calculated by Pacansky et al.<sup>39,40</sup>

The value for  $k_{-1}$  of  $(3.2 \pm 1.0) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> at 298 K was combined with the measurement of  $k_1$  by Russell et al., who reported  $k_1 = (1.7 \pm 0.1) \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

TABLE IV: Rate Coefficients Determined in the Equilibrium Experiments

	10 <sup>13</sup> k molecu	1/cm <sup>3</sup> 1le <sup>-1</sup> s <sup>-1</sup>	10 <sup>12</sup> k molect	$\frac{1}{1}$ cm <sup>3</sup> 1 le <sup>-1</sup> s <sup>-1</sup>
T/K	this work	ref 4	this work	ref 6
573	3.7 ± 1.0	$3.8 \pm 0.4$	$2.9 \pm 1.0$	3.3 • 0.5
641	$6.5 \pm 1.5$	$8.4 \pm 0.8$	4.7 🌨 1.5	$2.9 \pm 0.5$

TABLE V: Dependence of $\Delta H^{\circ}_{(298)}(t-C_4H_9)$ on $ CF_2 $	Br,	B	,	2	2	2	5	l,	1	ì	F	F	l	l		2	2	2	2	2	2	2	2	2	2	2	2	2	2	C	C	(	(	ſ			ł	đ	I	)	D	(		)	)	Ľ	•	l	I	Ì	H	ł	J	4	2	2	C	C	(	-	•	t	1	ĺ	ł	8		•	9	H	2	1	•	r	1	1	•	9	e	Ę	Ę	ę	ę	e	ę	ę	ę	e	e	Ę	Ę	Ę	e	Ð	Э	Э	•	•	•	•	1	1	1	•	f	f	f	r	r	r	r	r	•	•	•						•	1	1	1	1	2	2	2	2	2	2	2	2	2	X			•	9	9	•					8
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[CF <sub>2</sub> Br <sub>2</sub> ]/ molecules cm <sup>-3</sup>	$\begin{array}{c} \Delta H^{\Theta}_{\mathrm{f},298}(t\text{-}\mathrm{C_4H_9})/\\ \mathrm{kJ\ mol^{-1}} \end{array}$
$5 \times 10^{13} \\ 8 \times 10^{13} \\ 12 \times 10^{13} \\ 16 \times 10^{13} \\ 10 \times 1$	$49.5 \pm 2.0 47.3 \oplus 2.0 48.0 \pm 2.0 47.3 + 2.0 + 2.0 + 2.0 + 2.0 + 2.0 + 2.0$
16 × 10.5	$47.3 \pm 2.0$

 $^{a}$  [HBr] = 3.95 × 10<sup>13</sup>, [*i*-C<sub>4</sub>H<sub>10</sub>] = 6.06 × 10<sup>14</sup> cm<sup>-3</sup>.



**Figure 2.** Arrhenius plot for  $k_{-1}$ : O, this work;  $\bullet$ , Richards et al.;<sup>26</sup>  $\Box$ , Muller-Markgraff et al.;<sup>5</sup>  $\blacksquare$ , Nicovich et al.;<sup>27</sup> —, Russell et al.<sup>6</sup>

Combining the equilibrium constant,  $K_1 (=k_1/k_{-1})$ , with  $\Delta S^{\Theta}_{1,298}$ gives  $\Delta H^{\Theta}_{1,298} = 37.5 \pm 3.5$  kJ mol<sup>-1</sup> and  $\Delta H^{\Theta}_{t,298}(t-C_4H_9) = 50.9 \pm 3.5$  kJ mol<sup>-1</sup>. The uncertainties in the kinetic measurements (mainly in  $k_{-1}$ ) and in  $S^{\Theta}(t-C_4H_9,298$  K) both make significant contributions to the uncertainty limits.

The forward and reverse rate coefficients determined in the equilibration experiments may be used directly to calculate the equilibrium constant and hence  $\Delta H^{\Theta}_{1,298}$  via calculations of  $\Delta S^{\Theta}_{1,298}$  and  $\Delta C_p(T)$  based on the data of Pacansky et al.<sup>39,40</sup> and of Burcat.<sup>41</sup>

In order to check the validity of the approach, experiments were conducted over a range of precursor concentration, which resulted in a variation in the initial bromine atom concentration and hence in the contribution from radical-radical reactions to the atom/time profile. The resulting values for  $\Delta H^{\odot}_{f,298}(t-C_4H_9)$  are shown in Table V; the absence of any systematic variation with  $[CF_2Br_2]$ justifies the neglect of radical-radical reactions implicit in the above analysis. Average values for the heat of formation of  $t-C_4H_9$ resulting from the equilibration studies at the two elevated temperatures are

 $T = 573 \text{ K}, \quad \Delta H^{\Theta}_{f,298}(t-C_4H_9) = 44.2 \pm 4.0 \text{ kJ mol}^{-1}$ 

 $T = 641 \text{ K}, \quad \Delta H^{\Theta}_{f,298}(t-C_4H_9) = 48.1 \pm 4.0 \text{ kJ mol}^{-1}$ 

Combining these three independent estimates gives

<sup>(37)</sup> Russell, J. J.; Seetula, J. A.; Gutman, D. J. Am. Chem. Soc. 1988, 110, 3092.

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$$\Delta H^{\Theta}_{f,298}(t-C_4H_9) = 47.3 \pm 3.5 \text{ kJ mol}^{-1}$$

### Conclusions

Reaction R-1 has been studied at room temperature by monitoring the rate of formation of Br following initial photolytic generation of  $t-C_4H_9$  in HBr/He. A rate coefficient of  $(3.2 \pm$ 1.0)  $\times$  10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was obtained, confirming the high value determined by Russell et al.6

The approach to equilibrium was monitored following photolytic generation of Br in the presence of HBr and i-C<sub>4</sub>H<sub>10</sub>, enabling  $k_1, k_{-1}$ , and hence  $K_1$  to be determined at elevated temperatures (~600 K). Values of  $k_1$  are in good agreement with independent measurements made, using the same technique, under irreversible conditions. The  $k_{-1}$  values are in satisfactory agreement with the measurements of Russell et al.6 and confirm the negative temperature dependence in  $k_{-1}$ .

The  $k_{-1}$  value at 298 K can be combined with the measurements of  $k_1$  by Russell et al.<sup>6</sup> to give  $\Delta H^{\Theta}_{1,298}(t-C_4H_9)$ ; estimates of this quantity can also be made from the  $k_1$  and  $k_{-1}$  determinations in the equilibration experiments. Combining these several estimates gives  $\Delta H_{1,298}^{\Theta}(t-C_4H_9) = 47.3 \pm 3.5 \text{ kJ mol}^{-1}$ .

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Registry No. Br, 10097-32-2; i-C4H10, 75-28-5; HBr, 10035-10-6; CF<sub>2</sub>Br<sub>2</sub>, 75-61-6; t-C<sub>4</sub>H<sub>9</sub>, 1605-73-8; azoisobutane, 3896-19-3.

# Time-Resolved Study of H + HBr $\rightarrow$ Br + H<sub>2</sub> and Reanalysis of Rate Data for the H<sub>2</sub> + Br, Reaction over the Temperature Range 214–1700 K

Paul W. Seakins<sup>†</sup> and Michael J. Pilling<sup>\*</sup>

School of Chemistry, University of Leeds, Leeds LS29JT, U.K., and Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, U.K. (Received: May 29, 1991; In Final Form: July 22, 1991)

The rate coefficient,  $k_1$ , for the reaction H + HBr  $\rightarrow$  H<sub>2</sub> + Br has been measured by laser flash photolysis of HBr at 193 nm, observing both the rate of disappearance of H and the rate of appearance of Br by resonance fluorescence, over the temperature range 298-546 K, giving  $k_1 = 1.87 \times 10^{-11} \exp(-310 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Combining the data with other measurements of  $k_1$  and of estimates of  $k_{-1}$  from higher temperature photolysis and pyrolysis studies of the H<sub>2</sub> + Br<sub>2</sub> chain reaction, coupled with the equilibrium constant,  $K_1$ , gives  $k_1 = 2.1 \times 10^{-14} (T/K)^{1.05} \exp(-82 K/T) \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> over the temperature range 214–1700 K and  $k_{-1} = 6.9 \times 10^{-12} (T/K)^{0.43} \exp(-8970 K/T) \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. Finally, combination of the expression for  $k_1$  with the inhibition term for the H<sub>2</sub> + Br<sub>2</sub> chain reaction results in  $k_2 = (1.6 \pm 0.6) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the reaction H + Br<sub>2</sub>  $\rightarrow$  HBr + H over the temperature range 300-500 K, rising to (5<sup>+5</sup>-3) × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 1700 K.

## Introduction

High-precision measurements of rate coefficients for metathesis reactions over a wide range of temperatures have revealed distinct curvature in Arrhenius plots.<sup>1-3</sup> This curvature is most evident for reactions with low activation energies as evidenced by the extreme behavior for the CO + OH reaction.<sup>4</sup> Non-Arrhenius behavior can lead to difficulties in the comparison of rate coefficient quotients with equilibrium constants if the forward and reverse reactions have been studied in different temperature ranges. This problem may be illustrated by reference to the reactions

$$H + HBr \rightleftharpoons Br + H_2 \qquad (1, -1)$$

At high temperatures, the available rate data are based on classical thermal and photochemical studies of the  $H_2/Br_2$  chain reaction.<sup>5</sup> In the thermal reaction the rate of production of HBr depends on the rate coefficient for the slow propagation step

$$Br + H_2 \rightarrow HBr + H$$
 (-1)

on the ratio of the rate coefficients for the inhibition reaction

$$H + HBr \rightarrow Br + H_2 \tag{1}$$

and for the fast propagation step

$$H + Br_2 \rightarrow HBr + Br$$
 (2)

and on the equilibrium constant  $K_c$ , for  $Br_2$  dissociation. The evaluation of the rate coefficients for these elementary reactions by Baulch et al.<sup>5</sup> is derived from the steady-state expression for the rate of HBr production

$$d[HBr]/dt = k[H_2][Br_2]^{1/2}/(1 + k_1[HBr]/k_2[Br_2])$$

where  $k = 2k_{-1}K_c^{1/2}$ .  $k_{-1}$  was obtained by combining k and the equilibrium constant for bromine dissociation.  $k_1$  was then calculated from  $k_{-1}K_1$  and  $k_2$  from the inhibition ratio. The recommended rate coefficient expression for  $k_1$ , shown in Table I, was limited to the experimental temperature range, 500-1700 K, and quite large uncertainties (up to a factor of 2) were proposed.

There is poor agreement between the extrapolation of  $k_1$  to 300 K and recent direct studies of  $k_1$  by Husain and Slater<sup>6</sup> (flash photolysis, Lyman  $\alpha$  resonance fluorescence), Jourdain et al.<sup>7</sup> (discharge flow/EPR), and Umemoto et al.<sup>8</sup> (pulse radiolysis, resonance absorption), the values differing by a factor of  $\approx 3.5$ (Table I). Better agreement is found with the earlier discharge flow/EPR study of Endo and Glass,9 who obtained an activation energy of 10.7 kJ mol<sup>-1</sup>, close to that proposed Baulch et al. (10.1

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<sup>&</sup>lt;sup>†</sup>Present address: Joint Institute for Laboratory Astrophysics, Boulder, CO 80309.