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Kinetics and Thermochemistry of the $t\text{-}C_4H_9$ Radical. Study of the Equilibrium $t\text{-}C_4H_9 + HBr \rightleftharpoons i\text{-}C_4H_{10} + Br$

John J. Russell,[†] Jorma A. Seetula,[†‡] Raimo S. Timonen,[†‡] David Gutman,*[†] and David F. Nava*[§]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616, and Laboratory for Extraterrestrial Physics, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771. *Received October 5, 1987*

Abstract: The kinetics of both the forward (4) and the reverse (−4) reactions involved in the equilibrium $t\text{-}C_4H_9 + HBr \rightleftharpoons i\text{-}C_4H_{10} + Br$ were studied as a function of temperature and pressure. Reactions 4 (296–532 K) and −4 (533–710 K) were isolated for direct investigation in a tubular reactor coupled to a photoionization mass spectrometer. Reaction −4 was also investigated (298–478 K) by using a temperature-controlled flash photolysis apparatus equipped for time-resolved detection of Br using atomic resonance fluorescence. The temperature dependencies of the rate constants measured below 532 K were used to determine $\Delta H^\circ_f(298)$ and $S^\circ(298)$ for the $t\text{-}C_4H_9$ radical. The Arrhenius expressions obtained from these measured rate constants are as follows (units are cm^3 molecule^{-1} s^{-1}): $k_4(296\text{–}532\ K) = 9.86\ (\pm 1.3) \times 10^{-13} \exp\{5.8\ (\pm 0.9)\ \text{kJ mol}^{-1}/RT\}$; $k_{-4}(298\text{–}478\ K) = 1.83\ (\pm 0.18) \times 10^{-10} \exp\{-28.7\ (\pm 0.8)\ \text{kJ mol}^{-1}/RT\}$. The values of two thermodynamic variables for $t\text{-}C_4H_9$ obtained directly from these results are $\Delta H^\circ_f(298) = 48.6 \pm 1.7$ kJ mol^{-1} and $S^\circ(298) = 316 \pm 7$ J mol^{-1} K^{-1}. The tertiary C–H bond energy (298 K) in $i\text{-}C_4H_{10}$ is $DH(t\text{-}C_4H_9\text{–}H) = 401.2 \pm 1.7$ kJ mol^{-1}. The difference between the observed negative activation energy for the $t\text{-}C_4H_9 + HBr$ reaction and its presumed value accounts for the disparity between heats of formation of the $t\text{-}C_4H_9$ radical obtained in prior studies of this bromination equilibrium and from kinetic studies of dissociation–recombination equilibria. A mechanism is proposed to account for the kinetic behavior of the $t\text{-}C_4H_9 + HBr$ reaction which includes the formation of a bound adduct that may either dissociate to re-form the original reactants or rearrange to produce the final products.

Knowledge of the heats of formation of the smaller alkyl radicals (R) is of wide-ranging importance. In particular, this information establishes the magnitudes of the primary, secondary, and tertiary C–H bond energies that have come to be associated with the enthalpy changes of the following reactions:[1-3]

$$C_2H_6 \rightarrow C_2H_5 + H \qquad (1)$$

$$C_3H_8 \rightarrow i\text{-}C_3H_7 + H \qquad (2)$$

$$i\text{-}C_4H_{10} \rightarrow t\text{-}C_4H_9 + H \qquad (3)$$

These and other bond energies are of immense value for estimating the heats of formation of stable molecules as well as those of labile intermediates.[4] Access to accurate thermochemical information of this type has made it possible to establish plausible reaction routes, identify likely reaction intermediates, and in favorable instances, differentiate between competing explanations of chemical behavior where this behavior is determined, at least in part, by the potential energy along the reaction coordinate.[4,5]

Surprisingly, the C–H bond energies still have significant uncertainties associated with them, 10–15 kJ mol^{-1}, a situation caused by persisting disparities in the measured heats of formation of the alkyl radicals. Such an uncertainty in a free-radical heat of formation results in quite significant uncertainties in related parameters, e.g., a factor of 100 uncertainty in reaction equilibrium constants at ambient temperature and hence a comparable uncertainty in the predicted rate constant of a reverse reaction based on the measured rate constant of the forward reaction.

The most accurate source of heats of formation of polyatomic free radicals is kinetic studies of equilibria that involve these labile intermediates. Unfortunately, studies involving different classes of reactions have yielded different results, particularly for the alkyl radicals. Studies of bromination and iodination processes, which have provided information on the kinetics of reactions A–C, have

$$RI + I \rightleftharpoons I_2 + R \qquad (A)$$

$$R\text{–}H + I \rightleftharpoons R + HI \qquad (B)$$

$$R\text{–}H + Br \rightleftharpoons R + HBr \qquad (C)$$

yielded heats of formation for these radicals that are generally 10–15 kJ mol^{-1} lower than those that are derived from studies of other equilibria such as reactions D and E. These differences

$$R\text{–}R' \rightleftharpoons R + R' \qquad (D)^{6}$$

$$R \rightleftharpoons \text{olefin} + H(CH_3) \qquad (E)$$

have been discussed in detail in recent reviews of free-radical thermochemistry by McMillen and Golden[3] and by Tsang.[7,8] Still, the origin of these disparities has not been established. It is this inability to identify the source of these differences that is the cause of the lingering uncertainties in the heats of formation of C_2H_5, $i\text{-}C_3H_7$, and $t\text{-}C_4H_9$ (and hence of the primary, secondary, and tertiary C–H bond energies).

Studies of the kinetics of reactions A–C and reactions D and E have required different assumptions to obtain the heats of formation of free radicals.[2,3,7-9] It is therefore possible that the origin of the disparities in their results is connected with one or more of these assumptions. In the halogenation studies (reactions A–C), heats of formation of R have been calculated from determinations of the enthalpy change of the reaction under investigation using the known heats of formation of the reactants and second product.[2,9] The enthalpy change was obtained directly from the difference in activation energies between that of the forward and reverse reactions. In essentially every study to date, the activation energy was measured in only one direction. That for the reverse reaction has had to be assumed ($E_{R+I_2} = 0 \pm 4$ kJ mol^{-1} for all radicals[2,9]) or inferred from measured activation energy differences and the assumed value for $R + I_2$ activation energies. (The inferred activation energies are $E_{R+HBr} = 8 \pm 4$ kJ mol^{-1} and $E_{R+HI} = 4 \pm 4$ kJ mol^{-1}.[2,3,9]) The evidence supporting

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[†] Illinois Institute of Technology.

[‡] Permanent address: Department of Physical Chemistry, University of Helsinki, Helsinki, Finland.

[§] NASA Goodard Space Flight Center.

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the basic assumption and the values of the inferred activation energies have been discussed in detail by Golden and Benson[9] as well as by O'Neal and Benson.[2]

To obtain heats of formation from studies of reactions D and E has required combining results from more than one study. In the case of reaction D, this has generally involved combining measurements of thermal decomposition rate constants obtained at high temperatures with those of the recombination process obtained at much lower temperatures.[7,8] Equilibrium constants are calculated at some intermediate or reference temperature using assumed or calculated extrapolations of rate constants. These studies have all involved third-law determinations of reaction enthalpy changes, i.e., determinations of a free energy change from an equilibrium constant at some temperature combined with a calculated entropy change based on current knowledge of the entropies of reactants and products. Any errors in either the rate constant extrapolations or the calculated free-radical entropies (which have some uncertainties associated with them) result in an error in the calculated heat of formation. Additional uncertainties arise if the pressure dependencies of these unimolecular reactions are not fully characterized.

We have conducted a new investigation of one of the halogenation reactions

$$t\text{-}C_4H_9 + HBr \rightleftharpoons i\text{-}C_4H_{10} + Br \qquad (4)$$

over a wide range of experimental conditions. The purpose of this study was twofold: first to obtain accurate determinations of the heat of formation and entropy of t-C_4H_9 without using any of the assumptions discussed above that were used in prior studies of reactions A–C or reactions D and E, and second to use the kinetic information obtained on reaction 4 to begin to test the accuracy of the basic assumptions associated with the determination of free-radical heats of formation from studies of the kinetics of halogenation processes. In separate groups of experiments, both the forward and reverse reactions were isolated for direct study and rate constants determined over a significant temperature range (296–532 K for reaction 4 and 298–710 K for reaction –4). The heat of formation and entropy of t-C_4H_9 were obtained essentially directly from these measurements.

The results obtained in this study clearly identify the source of the disparity between the heat of formation of t-C_4H_9 obtained in prior bromination studies and values obtained in recent investigations of reactions D and E. The measured t-C_4H_9 + HBr activation energy (–5.8 kJ mol^{-1}) is 14 kJ mol^{-1} below the presumed value. This significant difference suggests a broader explanation for the above-mentioned disparities in heats of formation, namely, that the assumed R + I_2 activation energies and those inferred for R + HBr (HI) reactions are less accurate than had been presumed. The accuracy of these assumptions is tested further and discussed in more detail in the following paper[10] (part 2), in which the results of additional studies of the kinetics of R + HBr reactions are presented.

There have been prior studies of reaction 4 used to determine the heat of formation of t-C_4H_9.[11-13] Recently, Islam and Benson[12] studied this equilibrium in a very low pressure reactor. Equilibrium constants were directly measured in this study, which abrogated the need to use assumptions regarding any activation energy to determine the t-C_4H_9 heat of formation. Unfortunately there were experimental complexities associated with this study that were undetected.[13] Benson, Kondo, and Marshall reinvestigated the kinetics of reaction 4.[13] In the new study, only measurements of k_{-4} were possible, which, when combined with the usual presumed R + HBr activation energy, yielded a calculated value of the t-C_4H_9 heat of formation (40 ± 2 kJ mol^{-1}) in agreement with those from other halogenation studies.

The significant negative activation energy observed for the t-C_4H_9 + HBr reaction is not consistent with what is currently known about energy barriers and activation energies for direct H-atom metathesis processes. To account for the observed kinetic behavior of this reaction, an alternate mechanism is proposed and discussed.

Experimental Section

The study of reaction 4 was conducted with two experimental facilities in order to cover a wide range of experimental conditions. The first, which is at the Illinois Institute of Technology (IIT), consists of a heatable tubular reactor coupled directly to a photoionization mass spectrometer with which it is possible to monitor reactants and products in time-resolved experiments. (This equipment was used for determinations of both k_4 and k_{-4}.) The second facility, which is at NASA Goddard Space Flight Center (NASA–GSFC), was used to measure k_{-4}. It consists of a temperature-controlled flash photolysis apparatus equipped for monitoring atom decay profiles using resonance fluorescence methods. Only new features of the equipment required for these studies and new experimental procedures are presented here in detail. The descriptions of the facilities and the results obtained at each are described separately in this section.

I. Kinetic Studies Using Photoionization Mass Spectrometry. Details of the IIT facility and its use for kinetic studies of this type have been reported.[14] Briefly, pulsed unfocused 193-nm radiation from a Lambda Physik EMG 101E excimer laser is collimated by two irises and then directed along the axis of a heatable 1.05-cm-i.d. tubular reactor (Pyrex for the t-C_4H_9 + HBr investigation and quartz for the Br + i-C_4H_{10} study). Gas flowing through the tube at 5 m s^{-1} was completely replaced between laser pulses. The flowing gas contained the t-C_4H_9 source (4,4-dimethyl-1-pentene or 2,2,4,4-tetramethyl-3-pentanone) or the Br-atom source (CF_2Br_2) in very low concentrations (<0.1%), the second reactant (HBr or i-C_4H_{10}) in varying amounts, and the carrier gas (He or N_2 in large excess (>98%)). Gas was sampled through a 0.4-mm-diameter hole (located at the end of a nozzle in the wall of the reactor) and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and then mass selected. Temporal ion signal profiles were recorded from a short time before each laser pulse to as long as 25 ms following the pulse using a multichannel scalar. Data from 1000–30 000 repetitions of the experiment were accumulated before the data were analyzed.

Experiments were conducted under conditions where there were only two significant reactions consuming the labile reactant (R′ = t-C_4H_9 or Br):

$$R' + (HBr \text{ or } i\text{-}C_4H_{10}) \rightarrow R'H + (Br \text{ or } t\text{-}C_4H_9) \qquad (F)$$

$$R' \rightarrow \text{heterogeneous loss} \qquad (G)$$

In both sets of experiments tests were conducted to ensure that radical–radical or radical–atom reactions had negligible rates compared to either reaction F or G. Initial concentrations of Br or t-C_4H_9 were reduced until the measured atom or radical decay constants in the absence of the stable reactant no longer depended on the initial radical concentration (which could be lowered by reducing either the radical precursor concentration or the laser fluence). Some secondary photolysis of t-C_4H_9 during the laser pulse is possible at 193 nm. Its occurrence, if present, simply lowers the initial t-C_4H_9 concentration slightly but has no effect on the decay constant of the radical.

The stable reactant concentration was always in great excess over the initial concentration of the labile species. Rate constants for reactions 4 and –4 were obtained from slopes of plots of the exponential radical decay constant (k', from $[R']_t = [R']_0 \exp(-k't)$) vs [HBr] (or [$i$-$C_4H_{10}$]). A representative ion signal decay profile and decay constant plot from one set of experiments to measure k_4 are shown in Figure 1. The results obtained from all experiments are given in Table I.

Study of the Br + i-C_4H_{10} Reaction. Reaction –4 was studied between 533 and 710 K using an uncoated quartz reactor. The reaction was too slow to study by using this experimental method below 533 K. Initial Br-atom concentrations were below 1 × 10^{11} atoms cm^{-3}. They could not actually be determined because the extent of CF_2Br_2 depletion due to laser photolysis was too low to measure (<0.25%). The major photolysis route of CF_2Br_2 is the process

$$CF_2Br_2 \xrightarrow{193\text{ nm}} CF_2Br + Br \qquad (5)$$

Minor amounts of CF_2 were also produced by the 193-nm photolysis.

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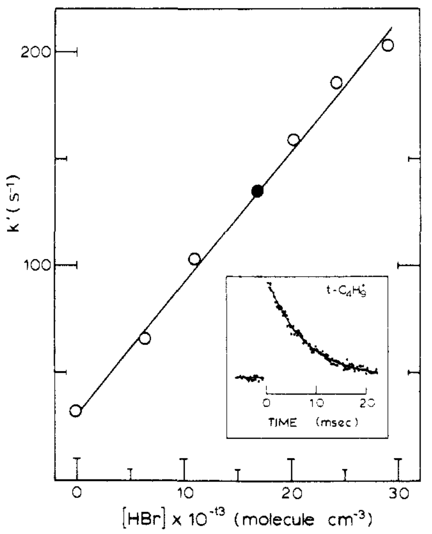

Figure 1. Plot of first-order decay constants k' for t-C_4H_9 vs [HBr] for one set of experiments conducted at 385 K. (For additional information, see Table I.) Insert is actual ion signal profile of t-$C_4H_9^+$ recorded during one of the plotted experiments ([HBr] = 1.7×10^{13} molecule cm^{-3}). The line through the data is an exponential function fitted by a nonlinear least-squares procedure. The first-order decay constant (k') for t-$C_4H_9^+$ in the displayed ion signal profile is 134 s^{-1}.

Table I. Conditions and Results of Experiments Using Photoionization Mass Spectrometry To Measure Rate Constants of the Reaction t-C_4H_9 + HBr $\rightleftharpoons$ i-C_4H_{10} + Br

T,[a] K	P, Torr	10^{-12}[X],[b] molecule cm^{-3}	k_G, s^{-1}	wall coating material[c]	$10^{12}k$,[b] cm^3 molecule^{-1} s^{-1}
		Br + i-C_4H_{10} Reaction (k_{-4})			
533	1.99	56.7–234	42	N	0.38
571	2.07	29.0–195	13	N	0.59
623	2.27	12.9–157	8.2	N	0.93
664	2.42	44.6–169	11	N	1.4
704	2.60	28.1–112	11	N	1.7
710	2.62	20.8–92.1	7.2	N	1.7
		t-C_4H_9 + HBr Reaction (k_4)			
296	1.06	6.0–21.3	97	HW	10.1
	1.06	4.3–19.2	85	HW	12.1
	1.16	6.7–32.4	94	HW	8.91[d]
	3.01	6.4–31.9	102	HW	8.90[d]
319	1.14	6.1–23.8	74	HW	8.63
	1.15	5.2–23.6	71	HW	8.98
348	1.24	6.9–28.0	67	HW	7.43
	1.25	6.9–31.3	67	HW	7.01
	2.56	6.2–27.7	88	HW	6.87
	0.592	5.4–26.7	65	HW	8.20
	1.24	6.6–28.3	43	FHW	7.95
	1.24	8.7–26.5	61	PTFE	7.40
385	1.37	6.2–24.4	32	FHW	6.10
427	1.51	8.5–36.1	37	PTFE	4.75
478	1.67	9.5–40.3	17	PTFE	4.23[e]
532	1.86	9.7–51.3	8.6	PTFE	3.65[e]

[a] Temperature uncertainty: ±3 K (296–385 K), ±4 K (427–478 K), ±5 K (532–571 K), ±6 K (>600 K). [b] [X] designates the concentration of the stable reactant (i-C_4H_{10} or HBr). [c] Wall coating materials used: none (N), halocarbon wax (HW), fluorinated halocarbon wax (FHW), and poly(tetrafluoroethylene) (PTFE). [d] N_2 used as carrier gas (helium used when not otherwise designated). Accuracy of k_4 reduced to ±20% when N_2 is the carrier gas. [e] t-C_4H_9 precursor used: 4,4-dimethyl-1-pentene ((3.0–10) × 10^{12} molecule cm^{-3}). In experiments conducted to measure k_4 below 478 K, the t-C_4H_9 precursor was 2,2,4,4-tetramethyl-3-pentanone ((3.0–10) × 10^{12} molecule cm^{-3}).

Study of the t-C_4H_9 + HBr Reaction. Reaction 4 was studied between 296 and 532 K using a Pyrex reactor coated to reduce heterogeneous loss of t-C_4H_9, which can be significant in an uncoated reactor. Three different coating materials were used in this investigation: halocarbon wax,[15] fluorinated halocarbon wax,[16] and poly(tetrafluoroethylene) (PTFE).[17] Rate constants for reaction 4 were measured by using all three coating materials. The results obtained were independent of the coating used. These results are interpreted as indicating that there is no detectable heterogeneous bimolecular reaction occurring between t-C_4H_9 and HBr under our experimental conditions. All three coating materials were used at T = 348 K. Above 400 K only PTFE remains a solid and was the only wall coating employed. The upper temperature limit of these experiments was determined by the loss of stability of PTFE above 550 K.

Suppression of extraneous photolysis processes was necessary in this study. Unusually low laser fluences had to be used in these experiments (below ≈7 mJ cm^{-2}) to eliminate a minor dependence of the radical decay constant on this parameter. (The unfocused laser light was attenuated by using either screens or quartz plates.) HBr does photodecompose to a minor extent (≈1%) when unattenuated laser radiation (≈ 50 mJ cm^{-2}) is used in these experiments. Effective elimination of this and possibly other unidentified extraneous photolysis processes was possible with the use of these lower laser fluences.

An attempt was made to monitor the growth of bromine atoms during the course of reaction 4. It was not successful due to interference from the ion signal of HBr (which is in great excess) at the adjacent mass number and the presence of a small amount of Br atoms produced by the minor photolysis of HBr discussed above.

The experimental determinations of k_4 were made not only as a function of temperature but also as a function of gas density, carrier gas identity, and t-C_4H_9 precursor. The measured rate constants were independent of these latter three parameters as expected. A fourfold density range was covered for helium carrier gas at 348 K and a threefold change at 296 K when N_2 was the carrier. The compound 2,2,4,4-tetramethyl-3-pentanone was used as a second t-C_4H_9 source (instead of 4,4-dimethyl-1-pentene). This second t-C_4H_9 precursor was required to conduct experiments at $T \geq 450$ K because heated 4,4-dimethyl-1-pentene fragments in the photoionization mass spectrometer at the t-C_4H_9 mass number. This fragmentation interferes with the detection of t-C_4H_9 and hence reduces the accuracy of the measurement of the t-C_4H_9 decay constants. Tests were conducted that verified that the t-C_4H_9 decay constants were independent of the radical precursor used.

Reagent Sources and Purification Procedures. The gases and liquids used were obtained from Matheson (i-C_4H_{10}, ≥99.5%; HBr, ≥99.8%), Aldrich (CF_2Br_2, ≥99%; 2,2,4,4-tetramethyl-3-pentanone, ≥99%), Fluka (4,4-dimethyl-1-pentene, ≥99%), and Linde (He, ≥99.995%; N_2, 99.998%). The carrier gases, He and N_2, were used as provided. All other gases and liquids (with the exception of HBr) were purified and degassed by using freeze–pump–thaw cycles. The HBr was not purified but was analyzed and found to be free of Br_2.

Photoionization Energies Used To Detect Reactants. Two photoionization energies were used in this investigation. An argon resonance lamp (11.62, 11.83 eV) was used to detect Br and HBr, and a chlorine lamp (8.9–9.1 eV) was used to detect t-C_4H_9.

II. Kinetic Study Using Flash Photolysis–Atomic Resonance Fluorescence. The NASA-GSFC flash photolysis–resonance fluorescence apparatus[18] and details of its use for determinations of the absolute rate coefficient for reactions of bromine atoms[19,20] have been described in previous publications. Briefly, experiments to measure k_{-4} were carried out in a heatable, Teflon-coated brass reaction cell housed within an evacuated brass outer chamber that allows temperature control to ±2 K. Flash photolysis of $CHBr_3$ at $\lambda > 190$ nm (Ultrasil window) was the source of bromine atoms. Bromine atom resonance radiation was generated by flowing a premixed Br_2–He mixture at 0.5 Torr ($X_{Br_2} = 2 \times 10^{-4}$) through a microwave discharge lamp, fitted with a sapphire window ($\lambda > 145$ nm). The resonantly scattered light was filtered with a flow of dry N_2 and a BaF_2 flat ($\lambda \geq 135$ nm) and detected with a photomultiplier placed at right angles to both the photolysis and resonance light sources. In each experiment, bromine atom decay signals were recorded from repetitive photolytic flashes (typically 100–500) by a multichannel analyzer operating in a multiscaling mode. Experiments were performed at eight temperatures from 298 to 478 K over a substantial range of [i-C_4H_{10}] and total pressure and also covering a moderate range of flash intensity (20–68 J), the latter to vary the initial concentration of Br. The slow rate of this reaction prevented its study below 298 K. The measured values of k_{-4} were independent of total pressure and also independent of

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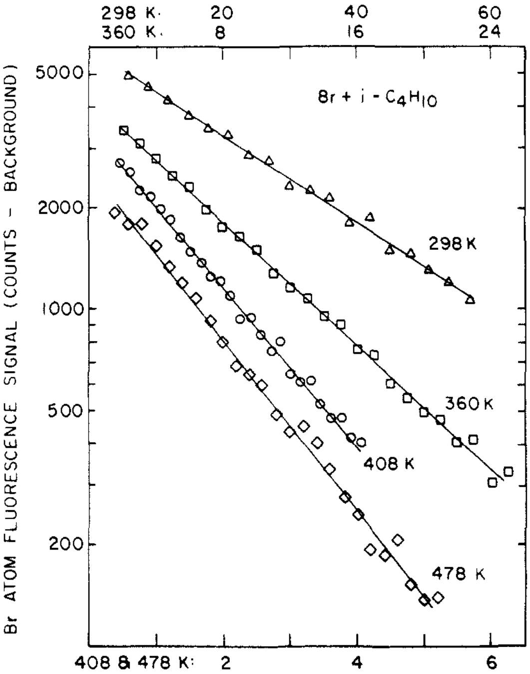

Figure 2. First-order decay plots of the logarithm of Br atom fluorescence counts vs time from typical experiments to measure the rate constant k_{-4}. Conditions of these four individual experiments are listed in the following order based on the temperature of the experiment: 298, 360, 408, and 478 K. $[CHBr_3] = 6.48 \times 10^{14}$, 10.1×10^{14}, 19.5×10^{14}, and 11.8×10^{14} molecule cm^{-3}; $[i\text{-}C_4H_{10}] = 1.63 \times 10^{16}$, 8.09×10^{15}, 1.32×10^{16}, and 3.94×10^{15} molecule cm^{-3}; pressure (Ar) = 30, 60, 100, and 75 Torr; flash energy = 36, 46, 36, and 46 J; $k_{obsd} = 30 \pm 1$, 105 ± 3, 542 ± 5, and 595 ± 4 s^{-1}; $k_d = 3.0 \pm 0.1$, 4.3 ± 0.1, 7.1 ± 0.4, and 97 ± 1 s^{-1}. The lines are from linear least-squares analyses of the data from each experiment.

flash intensity in the range used (the latter independence indicating true isolation of the reaction under study). At significantly higher intensities, the measured fluorescence decay constants did depend to some degree on flash intensity, indicating interference from other reactions. Pseudo-first-order conditions were always maintained, $[i\text{-}C_4H_{10}] \gg [Br]_0$. The concentrations of $i\text{-}C_4H_{10}$ used were always greater than or equal to 1.3×10^{15} molecule cm^{-3}, while $[Br]_0 \approx 5 \times 10^{11}$ atom cm^{-3}.

Reaction mixtures ($i\text{-}C_4H_{10}$, $CHBr_3$, and Ar) and mixtures used to measure rates of diffusion ($CHBr_3$ and Ar) were prepared and allowed to mix in reservoir bulbs. The mixtures were flowed through the reaction cell at a rate sufficient to replenish its contents after two or three photolytic flashes so that complications from reaction product accumulation would be avoided.

Under first-order conditions, bromine atom decay is represented by $\ln [Br] = -k_{obsd}\, t + \ln [Br]_0$, while k_{obsd}, the observed pseudo-first-order decay constant, is given by $k_{obsd} = k_{-4}[i\text{-}C_4H_{10}] + k_d$. k_d is the decay constant for Br atom diffusion from the analytical zone viewed by the photomultiplier. The diffusion correction k_d was determined independently for each experiment by flash photolyzing mixtures of $CHBr_3$ and Ar at the respective pressures and temperatures used to obtain k_{obsd}. These diffusional corrections were typically much less than 10% for the vast majority of the experiments and ≤20% for the remainder, which were usually the experiments run at the lowest pressure at a temperature. Since accumulated fluorescent counts are proportional to [Br], slopes from linear least-squares plots of the logarithm of accumulated counts vs t yield k_{obsd} values. The semilogarithmic plots of Br atom fluorescence decays were strictly linear over the range of conditions employed. k_{-4} is determined by using the experimentally measured values of k_{obsd} and k_d. Examples of these plots are shown in Figure 2.

The results obtained from the NASA-GSFC experiments at each of the eight temperatures are summarized in Table II.

The values of k_4 and k_{-4} obtained both at IIT and at NASA-GSFC are plotted in Figure 3. Where more than one rate constant was determined at a given temperature, the mean value is plotted.

Reagent Sources and Purification Procedures. Argon (Cryogenic Rare Gas Labs, 99.9995%) and helium (Air Products, 99.9999%) were used without further purification. Br_2 (Baker, 99.9%), $CHBr_3$ (Fisher, 99%), and $i\text{-}C_4H_{10}$ (Matheson, 99.995%) were each purified by degassing at 77 K for several freeze-pump-thaw cycles.

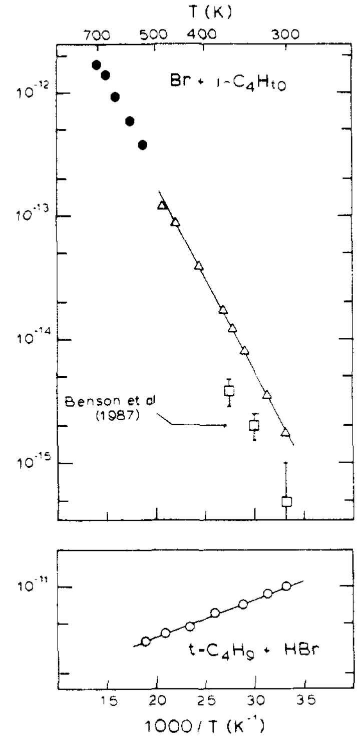

Figure 3. Plot of measured values of k_4 and k_{-4}. Lines are Arrhenius expressions fit to the rate constants (see text). Open and closed circles, photoionization mass spectrometer experiments; open triangles, atomic resonance fluorescence experiments; open squares, from Benson et al.[13]

III. Assessment of Accuracy of Kinetic Measurements. The most probable error in *each* measured value of k_4 and k_{-4} measured at IIT is ±15% and ±10% for the measured values of k_{-4} determined at NASA-GSFC. This assessment takes into account the accuracies of the measured gas flow rates and total pressure, the accuracy of each determination of the radical decay constant, and the data analysis procedures used to calculate k_4 and k_{-4} from the laboratory measurements.

An additional assessment was made of the accuracy of the temperature dependencies of each rate constant (expressed by an Arrhenius activation energy) because of the importance of this information for assessing the accuracy of the determination of the $t\text{-}C_4H_9$ heat of formation. The estimated most probable uncertainty at 370 K (near the middle of the temperature range of the study of reaction 4 at IIT and reaction −4 at NASA-GSFC) for E_4 is ±0.9 kJ mol^{-1} and that for E_{-4} is ±0.8 kJ mol^{-1}. This assessment takes into account the temperature range of the study, the random error in each rate constant determination, and the realization that most possible systematic errors would have a reduced effect on the calculated Arrhenius activation energy.

Determination of Thermodynamic Properties of $t\text{-}C_4H_9$

I. Second-Law Determination of $t\text{-}C_4H_9$ Heat of Formation and Entropy. Measurements of $k_4(T)$ and $k_{-4}(T)$ were used to obtain $\Delta H^\circ_f(298)$ and $S^\circ(298)$ for $t\text{-}C_4H_9$. The procedure used was as follows (the units used for k_4 and k_{-4} in this section are cm^3 $molecule^{-1}$ s^{-1}):

1. The measured values of k_4 from the IIT study and those of k_{-4} from the NASA-GSFC investigation cover nearly the same temperature range. They were separately fit to Arrhenius expression.[21]

$$k_4(296\text{–}532) = 9.86\ (\pm 1.3) \times 10^{-13} \exp\{5.8\ (\pm 0.9)\ \text{kJ mol}^{-1}/RT\}$$

$$k_{-4}(298\text{–}478) = 1.83\ (\pm 0.18) \times 10^{-10} \exp\{-28.7\ (\pm 0.8)\ \text{kJ mol}^{-1}/RT\}$$

(These expressions are plotted together with the measured rate constants in Figure 3.)

2. The Arrhenius activation energies, which are taken as accurate measurements of the actual activation energies at a tem-

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[21] Weighting factors were used at each temperature to take into account the number of experiments and variance in measured rate constants.

Table II. Summary of Rate Data from the Flash Photolysis–Resonance Fluorescence Study of the Br + i-C_4H_{10} Reaction

$[i\text{-}C_4H_{10}]$,[a] 10^{15} cm^{-3}	P_{total}, Torr	no. of expts.[b]	k_{-4},[c] 10^{-14} cm^3 s^{-1}
		298 K	
6.29	25	2	0.190 ± 0.006
16.3	30	4	0.164 ± 0.008
16.2	40	6	0.179 ± 0.014
24.5	45	3	0.155 ± 0.004
12.6	50	3	0.176 ± 0.010
32.6	60	4	0.161 ± 0.006
40.8	75	4	0.168 ± 0.018
32.4	80	4	0.164 ± 0.010
22.7	90	3	0.172 ± 0.009
40.5	100	4	0.185 ± 0.014
31.5	125	4	0.184 ± 0.007
37.8	150	4	0.196 ± 0.006
		45	0.174 ± 0.015[d]
		318 K	
7.35	20	3	0.352 ± 0.005
13.7	30	5	0.351 ± 0.018
14.7	40	4	0.342 ± 0.018
20.5	45	5	0.345 ± 0.009
27.3	60	4	0.365 ± 0.011
25.7	70	5	0.344 ± 0.009
33.0	90	4	0.357 ± 0.021
		30	0.350 ± 0.015[d]
		344 K	
7.50	30	3	0.777 ± 0.020
10.0	40	4	0.825 ± 0.023
15.0	60	3	0.784 ± 0.010
11.8	75	4	0.775 ± 0.038
20.0	80	3	0.804 ± 0.031
25.0	100	3	0.802 ± 0.023
18.9	120	4	0.797 ± 0.027
23.7	150	4	0.809 ± 0.024
28.4	180	3	0.822 ± 0.015
		31	0.800 ± 0.028[d]
		360 K	
2.70	20	2	1.41 ± 0.01
4.53	20	2	1.23 ± 0.02
5.39	40	3	1.25 ± 0.03
10.2	45	4	1.22 ± 0.03
8.09	60	4	1.21 ± 0.03
17.0	75	4	1.20 ± 0.04
20.4	90	4	1.23 ± 0.02
13.5	100	4	1.16 ± 0.02
24.9	110	2	1.28 ± 0.01
20.2	150	3	1.20 ± 0.03
		32	1.23 ± 0.06[d]
		373 K	
4.12	15	5	1.69 ± 0.03
6.88	25	4	1.75 ± 0.06
5.89	45	5	1.69 ± 0.09
13.8	50	4	1.73 ± 0.06
7.85	60	4	1.66 ± 0.07
19.3	70	3	1.73 ± 0.03
13.1	100	2	1.75 ± 0.09
18.3	140	3	1.70 ± 0.03
		30	1.71 ± 0.06[d]
		408 K	
1.98	15	4	3.86 ± 0.14
3.30	25	3	3.81 ± 0.10
2.65	40	5	3.87 ± 0.09
5.28	40	3	3.78 ± 0.02
3.31	50	4	3.99 ± 0.09
9.24	70	3	3.80 ± 0.02
5.97	90	1	3.81
13.2	100	3	4.00 ± 0.06
8.29	125	2	3.90 ± 0.12
10.6	160	4	4.06 ± 0.10
		32	3.90 ± 0.12[d]
		450 K	
1.34	25	6	8.50 ± 0.52
2.68	50	4	8.58 ± 0.40
3.29	50	3	9.10 ± 0.19
4.93	75	4	8.61 ± 0.08
6.57	100	4	8.93 ± 0.20
6.44	120	2	8.58 ± 0.22
9.86	150	4	8.66 ± 0.24
10.7	200	3	8.50 ± 0.59
		30	8.67 ± 0.38[d]
		478 K	
3.94	75	4	12.2 ± 0.51
4.09	100	4	12.0 ± 0.30
5.25	100	3	12.3 ± 0.53
		11	12.1 ± 0.43[d]

[a] Range in $[CHBr_3]$ generally (4–30) × 10^{14} cm^{-3} for experiments at each temperature. [b] Number of first-order decays measured over a range of flash energies, typically 20–56 J. [c] Uncertainty in k_{-4} is one standard deviation. [d] Mean value of k_{-4} at that temperature.

perature nearly midway between the temperature extremes (370 K), were used to obtain $\Delta H°(370)$ for reaction 4:

$$\Delta H°(370) = E_4 - E_{-4} = \{-5.8\ (\pm 0.9) - 28.7\ (\pm 0.8)\} = -34.5\ (\pm 1.7)\ \text{kJ mol}^{-1}$$

3. $\Delta H°(298)$ was calculated by using $\Delta H°(370)$ and the molar heat capacities of the reactants and products in reaction 4:[22]

$$\Delta H°(298) = -35.2\ (\pm 1.7)\ \text{kJ mol}^{-1}$$

4. $K_4(298)$, the equilibrium constant for reaction 4 at 298 K, was obtained from the Arrhenius expressions for k_4 and k_{-4}:

$$K_4(298) = k_4(298)/k_{-4}(298) = 5.92\ (\pm 0.84) \times 10^3$$

5. $\Delta G°(298) = -RT \ln K_4(298)$ and $\Delta G° = \Delta H°(298) - T\Delta S°(298)$ were in turn used to obtain the free energy and entropy changes for reaction 4 at 298 K:

$$\Delta G°(298) = -21.5\ (\pm 0.4)\ \text{kJ mol}^{-1}$$

$$\Delta S°(298) = -45.9\ (\pm 7.0)\ \text{J mol}^{-1}\ \text{K}^{-1}$$

6. The heat of formation and entropy of t-C_4H_9 at 298 K were determined by using these values of $\Delta H°(298)$ and $\Delta S°(298)$ for reaction 4 and the heats of formation and entropies for Br, HBr, and i-C_4H_{10}:[22]

$$\Delta H°_f(298) = 48.6\ (\pm 1.7)\ \text{kJ mol}^{-1}$$

$$S°(298) = 316\ (\pm 7)\ \text{J mol}^{-1}\ \text{K}^{-1}$$

Some explanations regarding the procedure are in order. It was decided to use only the measurements of k_{-4} up to 478 K for these thermochemical calculations for two reasons. Knowledge that reaction −4 involves only the abstraction of the tertiary hydrogen in i-C_4H_{10} has been verified experimentally only up to 421 K.[23,24] Kinetic data on H-atom abstraction from n-C_5H_{12} suggests that abstraction of the primary hydrogens in i-C_4H_{10} by bromine atoms should not be significant even at the highest temperature of the current study.[23] Nevertheless, the possibility

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(22) Temperature-dependent functions for $C°_p$, $\Delta H°_f$, and $S°$ of H, Br, HBr, and i-C_4H_{10} were taken from: Burcat, A. In *Combustion Chemistry*; Gardiner, W. C., Jr., Ed.; Springer-Verlag: New York, 1984; Chapter 8.

(23) Fettis, G. C.; Knox, J. H.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1960**, *82*, 4177.

(24) Fettis, G. C.; Knox, J. H. In *Progress in Reaction Kinetics*; Porter, G., Ed.; Pergamon: New York, 1964; Chapter 1.

of a more complex reaction than that indicated by reaction −4 above 500 K, although remote, does exist.

There is ample evidence that the temperature dependencies of simple atom-transfer reactions are often not well represented by simple Arrhenius expressions over wide temperature ranges.[25] A good example is that of a related reaction, Cl + CH_4.[26] The high-temperature measurements of k_{-4} (see Figure 3) establish the fact that there is only a minor departure from an Arrhenius temperature dependence of k_{-4} over the full temperature range of this study, 298–710 K. Therefore an Arrhenius expression can provide an accurate representation of the temperature dependence of k_{-4} over a reduced portion of the temperature range covered in this study, such as the temperature range in which k_4 was also measured. It is for these reasons that only the measurements of k_{-4} from the NASA–GSFC study were used for obtaining E_{-4} near 370 K.

II. Third-Law Determination of the Heat of Formation of *t*-C_4H_9. A third-law determination of the heat of formation of *t*-C_4H_9 is presented here to demonstrate that it yields a value in agreement with that obtained directly from the kinetic data. The estimated accuracy of this third-law-based heat of formation is below that of the more directly obtained value given above because the probable uncertainty in the calculated entropy of *t*-C_4H_9 is not below that of the measured value reported above. A lingering uncertainty exists in the exact entropy of *t*-C_4H_9, which is associated with the lack of precise knowledge of the rotation barriers for the three methyl groups in *t*-C_4H_9 and of the vibration frequency of the umbrella mode in this radical.[3,7]

Experimental and theoretical studies by Pacansky and coworkers provide the current state of knowledge of the structure and internal motions of *t*-C_4H_9.[27-29] Using this knowledge (which includes a calculated 6.3 kJ mol^{-1} rotational barrier for the CH_3 rotations[29] and an estimated 200-cm^{-1} energy for the pyramidal bending mode),[27] one calculates a value of $S°(298) = 313 \pm 10$ J mol^{-1} K^{-1}. (The uncertainty is estimated from a 2 kJ mol^{-1} uncertainty in the rotational barrier and the fact that the pyramidal bending mode is most probably in the range 100–200 cm^{-1}).[30]

Using $\Delta G°(298)$, which was calculated above, and the calculated entropy of *t*-C_4H_9 to determine $\Delta S°(298)$, one can calculate the enthalpy change for reaction 4:

$$\Delta H°(298) = -34.4\ (\pm 3.0)\ \text{kJ mol}^{-1}$$

Again, using $\Delta H°(298)$ and the known heats of formation of the other species in reaction 4,[22] one obtains the third-law value of the heat of formation of *t*-C_4H_9:

$$\Delta H°_f(298) = 47.8\ (\pm 3.0)\ \text{kJ mol}^{-1}$$

This value for the *t*-C_4H_9 heat of formation is in excellent agreement with the directly determined one.

Discussion

I. Comparison of k_4 and k_{-4} with Values Obtained in Prior Studies. In the prior investigation of reaction −4, Benson, Kondo, and Marshall report values of k_{-4} that were determined at three temperatures between 298 and 363 K.[13] These values are between a factor of 3 and 5 below the values obtained in this study at these same temperatures (see Figure 3). This reinvestigation[13] was motivated by the discovery that there were unrecognized complexities in the original study of this reaction by Islam and Benson.[12] Excited bromine atoms produced in the Br-atom source (a microwave discharge through Br_2) were carried into the very low pressure reactor. To obtain the value of k_{-4} for thermal bromine atoms, apparent values of k_{-4} were measured at higher values of $[Br]_0$ and then extrapolated to infinite $[Br]_0$, the extrapolated value being associated with the thermal rate constant. The stated uncertainty in these three new values of k_{-4} (which varied between 25 and 100%) does not account fully for the differences between the values of k_{-4} obtained by Benson et al.[13] and those obtained in the current investigation. No explanation of the disparity between the results of this study and the current one is apparent. The new mechanism and assumptions used in the study of Benson et al. that were required to separate the effects of thermal and excited bromine atom reactions have not been tested on other systems.

The values of k_4 reported by Islam and Benson that were inferred from their apparent measurement of k_{-4} and K_4 are no longer supported by the authors[13] for the reason discussed above.

II. Thermochemistry of *t*-C_4H_9. The second-law determinations of the heat of formation and entropy of *t*-C_4H_9 reported here are the most complete determinations of these thermodynamic properties of *t*-C_4H_9. They are based solely on kinetic measurements (with the exception of the heat capacities of reactants and products in reaction 4 that were used to obtain the small −0.7 kJ mol^{-1} correction used to calculate $\Delta H°(298)$ from $\Delta H°(370)$). In this section, these measured thermodynamic properties are compared with those reported by others. Since virtually all prior investigations required additional thermochemical information (e.g., the entropy of *t*-C_4H_9) and/or assumed structural or kinetic parameters (particularly the activation energies of the R + HBr (or HI) reactions), this section includes discussions of these assumptions in an attempt to account for differences between the current and the prior determinations of these thermodynamic properties of *t*-C_4H_9.

Entropy of *t*-C_4H_9. There is very close agreement between the calculated entropy of *t*-C_4H_9 (313 ± 10 J mol^{-1} K^{-1}), which is based on the measured, calculated, and estimated properties of this radical reported by Pacansky,[27,29] and the measured value (316 ± 7 J mol^{-1} K^{-1}). The recommended value of 200 cm^{-1} for the low-frequency pyramidal bending mode of the radical is based on an extrapolation of known barriers to comparable motions of the simpler alkyl radicals.[30] The calculated entropy would be the same as the measured one if this frequency was lowered to 140 cm^{-1}.

The measured entropy with its associated error limits provides some limits on the actual values of the two uncertain frequencies. For the calculated entropy to remain in agreement with the measured value, adjustments of these two frequencies should result in essentially no change in the entropy of *t*-C_4H_9 or a slight increase.

Enthalpy of Formation of *t*-C_4H_9. There is excellent agreement between the heat of formation of *t*-C_4H_9 determined in the current study and the values that are derived from kinetic studies of reactions D and E. However, the current value is above those obtained in the prior study of the same equilibrium and from studies of the iodination of *i*-C_4H_{10}. These and related studies are reviewed in this section.

Tsang has published a comprehensive analysis of kinetic studies that have investigated the kinetics of either the forward or reverse portions of reactions D and E for the *t*-C_4H_9 radical:[8]

$$(t\text{-}C_4H_9\text{-})_2 \rightleftharpoons 2t\text{-}C_4H_9 \qquad (6)$$

$$t\text{-}C_4H_9\text{-}CH_3 \rightleftharpoons t\text{-}C_4H_9 + CH_3 \qquad (7)$$

$$t\text{-}C_4H_9 \rightleftharpoons C_4H_8 + H \qquad (8)$$

Equilibrium constants obtained by combining the results of the many studies considered were all consistent with a *free energy* of formation of *t*-C_4H_9 at 298 K in a very narrow range, −44.0 ± 2.2 kJ mol^{-1}. Tsang's assessment of this free energy of formation is in complete accord with our measured value (−45.6 ± 0.4 kJ mol^{-1}). This agreement suggests that the extrapolations of rate constants for the forward or reverse portions of reactions 6–8 that were required to obtain their equilibrium constants (and the free

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(25) Fontijn, A.; Zellner, R. In *Reactions of Small Transient Species*; Fontijn, A., Clyne, M. A. A., Eds.; Academic: New York, 1983; Chapter 1.

(26) Heneghan, S. P.; Knoot, P. A.; Benson, S. W. *Int. J. Chem. Kinet.* **1981**, 13, 677.

(27) Pacansky, J.; Chang, J. S. *J. Chem. Phys.* **1981**, *74*, 5539.

(28) Schrader, B.; Pacansky, J.; Pfeiffer, U. J. *J. Phys. Chem.* **1984**, *88*, 4069.

(29) Pacansky, J.; Yoshimine, M. *J. Phys. Chem.* **1986**, *90*, 1980.

(30) Although 200 cm^{-1} is recommended by Pacansky as the estimate for the umbrella frequency, it is mentioned as an upper limit in the discussion of this frequency in ref 27.

energy of formation of t-C_4H_9) were as accurate as presumed. Comparison of heats of formation is less meaningful. Tsang reports extreme values for the calculated t-C_4H_9 heat of formation {49.0 (±2.2) - 51.9 (±2.2) kJ mol^{-1}}[31] that result from using assessments of the maximum and minimum possible entropies for this radical. (There is only a 1.6 kJ mol^{-1} difference between the t-C_4H_9 heat of formation obtained from Tsang's recommended free energy and the heat of formation obtained in the current study if the measured entropy obtained here is used to obtain this heat of formation.)

The 8.6 kJ mol^{-1} difference between the heat of formation of t-C_4H_9 obtained by Benson et al.[13] and that of the current study is associated entirely with their use of the usual assumed activation energy for R + HBr reactions to calculate the t-C_4H_9 heat of formation. If this assumed value were replaced with the measured one reported here, there would be complete agreement between heats of formation (this is because both studies obtained the same activation energy for the Br + i-C_4H_{10} reaction).

In the following paper (part 2),[10] the activation energies of other R + HBr reactions were determined. They are all below the assumed value of 8 ± 4 kJ mol^{-1}, decreasing monotonically from -1.3 ± 0.9 kJ mol^{-1} for the CH_3 + HBr reaction to -5.8 ± 0.9 kJ mol^{-1} for the t-C_4H_9 + HBr reaction. This difference between assumed and actual R + HBr activation energies accounts essentially completely for the systematic difference in heats of formation (10–15 kJ mol^{-1}) between those obtained in prior bromination studies (for the C_2–C_4 alkyl radicals) and those obtained in studies of reactions D and E.

Also in part 2[10] the results of the study of additional R + HBr reactions are used to support a comparable explanation for why the heats of formation obtained from studies of iodination processes (reactions A and B) are too low. It is again indicated that the activation energies of R + I_2 (HI) reactions are negative and again 10–15 kJ mol^{-1} below the presumed values.

There have been investigations of the kinetics of an iodination reaction to determine the heat of formation of t-C_4H_9:

$$i\text{-}C_4H_{10} + I \rightleftharpoons t\text{-}C_4H_9 + HI \qquad (9)$$

Measurements have been made of both the forward[32-34] and reverse[35,36] rate constants. Combining this kinetic information in different ways and using various estimates of the entropy of t-C_4H_9 have led to values of the t-C_4H_9 heat of formation from 32 to 38.5 kJ mol^{-1},[3,32-36] the highest values still being 10 kJ mol^{-1} below that determined in the current study. In separate experiments using different experimental methods and covering different temperature ranges, Rossi and Golden obtained values of k_{-9} in two temperature ranges,[35,36] which, when combined, yielded an Arrhenius expression for this rate constant, $k_{-9} = 8.9 \times 10^{-12} \exp(-7.0 \text{ kJ mol}^{-1}/RT)$ cm^3 $molecule^{-1}$ s^{-1}. Rossi and Golden used this information together with earlier determinations of k_9 by others to obtain a heat of formation for t-C_4H_9 in the same direct fashion that was used in the current study of reaction 4. The value obtained[36] (38.5 kJ mol^{-1}) is 10 kJ mol^{-1} below that of the current study.

Since no significant assumptions were required to obtain the t-C_4H_9 heat of formation in the Rossi and Golden study,[35] the source of this difference in heats of formation must be in one or more of the kinetic studies. The choice we make here is based on some evidence but is largely speculation and should be understood as such. It is offered as a means of focusing attention on the final differences that exist in determinations of this important heat of formation.

It appears to us that the t-C_4H_9 + HI rate constants measured by Rossi and Golden[35,36] are much too low, particularly those determined in the second study conducted near ambient temperature, 302–411 K.[36] If this is indeed the case, it can account for the noted disparity in t-C_4H_9 heats of formation. The value of k_{-9} obtained by Rossi and Golden at ambient temperature (301 K) is 5.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.[36] This value is significantly below what would be expected from known trends in R + HBr (HI) rate constants. The constants for these reactions (at a particular temperature) are expected to increase if (1) HI replaces HBr and (2) the size of the free radical R increases. The first trend is supported by the results of Donaldson and Leone,[37] who measured both the CD_3 + HBr and CD_3 + HI rate constants at ambient temperature. The values obtained were 4.7×10^{-12} for the former and 7.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for the latter. Relative rate measurements have also provided an indication that the activation energy for the CH_3 + HBr rate constant is above that of the CH_3 + HI reaction.[38] The second trend is indicated by the results of the measurements of R + HBr rate constants reported in part 2.[10] At ambient temperature, they increase from 1.5×10^{-12} to 1.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1} between the CH_3 + HBr and the t-C_4H_9 + HBr reaction. On the basis of these trends and rate constants, one would expect the t-C_4H_9 + HI rate constant to be greater than 1×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, which is a factor of 20 above the value reported by Rossi and Golden.[36]

Unusually low rate constants can be obtained in experiments of the type conducted by Rossi and Golden if there are undetected first-order processes that consume the radical (such as heterogeneous loss). In their low-temperature study,[36] Rossi and Golden discussed this matter in detail and concluded, on the basis of experimental tests, that heterogeneous loss of t-C_4H_9 was a negligible process (which would require a first-order rate constant for heterogeneous loss to be $\ll 1$ s^{-1}). In our study, in which we used the same wall coatings employed by Rossi and Golden, typical wall loss rate constants at ambient temperature were 90 s^{-1} (this would translate into a heterogeneous loss rate constant of ≈ 45 s^{-1} in the size of reactor used by Rossi and Golden).[36] If a heterogeneous loss process of this magnitude had escaped detection in these studies of Rossi and Golden, it would have resulted in apparent rate constants for reaction -9 factors of 20–50 too low. Clearly, it will require additional studies of the kinetics of R + HI reactions to test the veracity of this tenuous "explanation". Such investigations would also be very useful for obtaining a clearer understanding of the kinetics and mechanisms of R + HI reactions.

III. Tertiary C–H Bond Energy in i-C_4H_{10}. The tertiary C–H bond energy in i-C_4H_{10} ($\Delta H^\circ(298)$, i-$C_4H_{10} \rightarrow t$-C_4H_9 + H) is now known with more accuracy (401.2 ± 1.7 kJ mol^{-1}). Agreement or disagreement with this value depends entirely on one's choice for the t-C_4H_9 heat of formation. For example, there is complete agreement with Tsang's recommended bond energy[8] (402.5 kJ mol^{-1}) obtained from his assessment of the t-C_4H_9 heat of formation while there is poorer agreement with the lower value recently recommended by McMillen and Golden,[36] 388 kJ mol^{-1}, which is based on their studies of reaction -9.

IV. Mechanism of the t-C_4H_9 + HBr Reaction. As was mentioned above, the significant negative activation energy of the t-C_4H_9 + HBr reaction {-5.8 (±0.9) kJ mol^{-1}} is unprecedented for an apparent H-atom metathesis reaction.[39] Theoretical studies have also concluded that activation energies for elementary reactions that have no potential energy barriers along the reaction coordinate do not have significant negative activation energies (if present, they were generally no lower than -1 kJ mol^{-1}).[40-42] Another explanation for the observed kinetic behavior of the t-C_4H_9 + HBr reaction is indicated.

The Arrhenius parameters for the t-C_4H_9 + HBr reaction, including magnitudes of both the preexponential factor and the

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[31] This is a corrected range of enthalpies and is slightly smaller than the range originally reported in ref 8. Tsang, W., personal communication, 1987.

[32] Teranishi, H.; Benson, S. W. *J. Am. Chem. Soc.* **1963**, *85*, 2887.

[33] Knox, J. H.; Musgrave, R. G. *Trans. Faraday Soc.* **1967**, *63*, 2201.

[34] Bracey, J.; Walsh, R., unpublished results (cited and used in ref 3 and 36).

[35] Rossi, M.; Golden, D. M. *Int. J. Chem. Kinet.* **1979**, *11*, 969.

[36] Rossi, M.; Golden, D. M. *Int. J. Chem. Kinet.* **1983**, *15*, 1283.

[37] Donaldson, D. J.; Leone, S. R. *J. Phys. Chem.* **1986**, *90*, 936.

[38] Kerr, J. A.; Moss, S. J., Eds. *Handbook of Bimolecular and Termolecular Gas Reactions*; CRC: Boca Raton, 1981; Vol. 1, p 240.

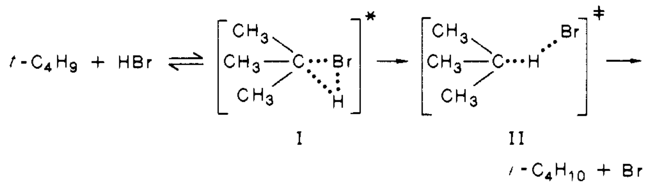
[39] Reference 38, Chapter 1.

[40] Clary, D. C. *Mol. Phys.* **1984**, *53*, 3.

[41] Menon, A.; Sathyamurthy, N. *J. Phys. Chem.* **1981**, *85*, 1021.

[42] Harding, L. B.; Wagner, A. F. *Symp. (Int.) Combust. [Proc.]*, in press.

activation energy, are consistent with a complex mechanism involving the reversible formation of a bound intermediate:[25,43]



The rate constants of both reactions 4 and −4 have no pressure dependence (over the range of conditions used in these studies), which indicates a weakly bound complex, i.e., one with an intrinsic lifetime that is significantly shorter than the collision frequency at the highest pressures used in this investigation.[43] The negative activation energy (and low Arrhenius *A* factor) arises from the facts that the potential energy of the second (and rate-determining) transition state (‡) has a tighter structure than that usually associated with the first step (the initial formation of the adduct) and has a potential energy lower than that of the reactants.[43]

There is abundant evidence that many reactions between free radicals and diatomic molecules containing halogen atoms proceed via the formation of a bound or quasi-bound intermediate. Golden and Benson have suggested that the unusually low activation energies of the reactions between free radicals and I_2 could be associated with the formation of bound intermediates.[9] Grice and co-workers have reported evidence of complex formation in molecular beam investigations of the reaction $CH_3 + ICl$[44] and OH + Br_2.[45] "New compounds" such as CH_3IF[46] and HI_2[47] have been "synthesized" and characterized in other molecular beam studies by Lee and co-workers. A large number of complexes of the form R·HF have been stabilized on cold matricies and their properties reported.[48]

The reactions of H, O, and OH with F_2, Cl_2, Br_2, and I_2 have rate constants that increase from the lightest to the heaviest halogen.[49] This trend is the opposite of that predicted by Evans–Polanyi-type relationships,[50,51] which predict a lowering of the activation energy in a homologous series of atom-transfer reactions with increasing exothermicity. This reverse trend has been cited as evidence of the presence of strong attractive forces between the free radicals and the halogen molecules, which in some instances can lead to actual bound intermediates.[49] (Molecular beam studies by Grice and co-workers have found clear evidence for long-lived bound complexes in the case of reactions of O atoms with halogen molecules.[52]) The R + HBr reaction rate constants (R = CH_3, C_2H_5, and *i*-C_3H_7) display the same inverse relationship between reactivity and exothermicity as do the H, O, and OH reactions described above. This is interpreted here as an indication that comparable intermolecular forces are involved in the R + HBr reactions which are responsible for similar mechanisms.

Plausible structures for the important intermediates in the *t*-C_4H_9 + HBr reaction are indicated above. The loose bound *t*-C_4H_9·HBr adduct must involve some interaction with the bromine atom. Structure I is simply a symbolic way of displaying this interaction. (Strong intramolecular interactions of bound bromine atoms with free-radical centers have been advanced in an entirely different context by Skell and co-workers to account for retention of structure in β-bromoalkyl radicals.[53])

Summary

This investigation has yielded determinations of the rate constants of both the forward and reverse reactions involved in the equilibrium *t*-C_4H_9 + HBr ⇌ *i*-C_4H_{10} + Br as a function of temperature and pressure. These results have been used to directly determine the enthalpy of formation (48.6 ± 1.7 kJ mol^{-1}) and entropy (316 ± 7 J mol^{-1} K^{-1}) of the *t*-C_4H_9 radical at 298 K and the tertiary bond energy DH(*t*-C_4H_9–H), 401.2 ± 1.7 kJ mol^{-1}.

The observation of a significant negative activation energy for the *t*-C_4H_9 + HBr reaction has led to an explanation for the primary source of the disparities that exist between alkyl radical heats of formation determined in prior studies of bromination kinetics and those derived from kinetic studies of dissociation–recombination equilibria—the assumed R + HBr activation energies required in the former studies to determine heats of formation were 10–15 kJ mol^{-1} too high.

A complex mechanism for R + HBr reactions is proposed to account for their kinetic behavior, particularly their negative activation energies.

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Registry No. *t*-C_4H_9, 1605-73-8; HBr, 10035-10-6; *i*-C_4H_{10}, 75-28-5; Br, 10097-32-2.

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