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The Reinvestigation of the Kinetics of the Metathesis Reactions $t\text{-}C_4H_9^\bullet + HBr\ (HI) \rightarrow i\text{-}C_4H_{10} + Br^\bullet\ (I^\bullet)$ and of the $t\text{-}C_4H_9^\bullet$ Free Radical Thermochemistry

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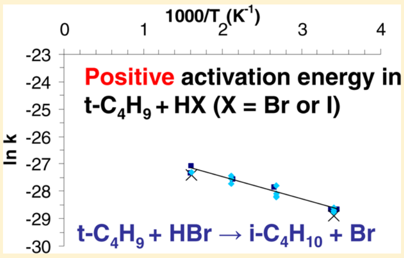
Supporting Information

ABSTRACT: A reinvestigation of the absolute rate constant of the metathesis reactions $t\text{-}C_4H_9^\bullet + HBr \rightarrow i\text{-}C_4H_{10} + Br^\bullet$ (1) and $t\text{-}C_4H_9^\bullet + HI \rightarrow i\text{-}C_4H_{10} + I^\bullet$ (2) was performed thanks to a recently developed apparatus consisting of a Knudsen reactor coupled to detection based on single-photon (VUV) photoionization mass spectrometry (SPIMS). It enables the generation of thermalized hydrocarbon free radicals owing to a source upstream of and external to the Knudsen reactor. The following Arrhenius expressions were obtained: $k_1 = 5.6(\pm1.4) \times 10^{-12} \exp(-6.76(\pm0.94)/(RT))$ and $k_2 = 2.0(\pm0.6) \times 10^{-11} \exp(-8.48(\pm0.94)/(RT))$ with $R = 8.314$ J mol^{-1} K^{-1} over the range 293 to 623 K. The mass balance of the reaction system based on closed shell product detection (CSPD) was checked in order to ensure the accuracy of the used reaction mechanism and as an independent check of k_1 and k_2. The wall-loss rate constants of the *t*-butyl free radical, $k_w^{C_4H_9}$, were measured and found to be low compared with the corresponding escape rate constant, $k_e^{C_4H_9}$, for effusion of $t\text{-}C_4H_9^\bullet$ out of the Knudsen reactor. On the basis of the present results, the free radical standard heat of formation $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 44.3 \pm 1.7$ kJ mol^{-1} was obtained when combined with the kinetics of the inverse halogenation reaction taken from the literature and using $S^\circ_{298}(t\text{-}C_4H_9^\bullet) = 322.2$ J K^{-1} mol^{-1} following a "Third Law" evaluation method. The standard enthalpy for *t*-butyl free radical is consistent for both the bromination and iodination reactions within the stated uncertainties.



■ INTRODUCTION

In the past, the chemical kinetics of halogenation equilibria of the type $R^\bullet + HX \rightleftarrows RH + X^\bullet$, where X is a halogen atom, was thoroughly investigated with the goal to determine the standard enthalpy of formation of hydrocarbon free radicals, $\Delta_f H^\circ_{298}(R^\bullet)$. Indeed, if the rate parameters of both the forward and the reverse reactions are known, this thermochemical quantity may simply be derived using the so-called "Second Law" or "Third Law" treatments. Whereas acceptable agreement between the many previous investigations of the kinetics for the reverse reaction was obtained, two opposite sets of data for the forward reaction exist, for example, for the halogenation reactions involving $C_2H_5^\bullet$, $n\text{-}C_3H_7^\bullet$, or $i\text{-}C_3H_7^\bullet$ summarized in two recent papers.[1,2] Indeed, some investigators measured a low rate constant at ambient temperature associated with a positive activation energy, whereas other workers obtained the opposite trend in experimental studies, namely, rate constants higher by as much as a factor of 50 or more associated with negative activation energies. The source of these discrepancies has so far never been satisfactorily explained. This leaves open the debate about the kinetics of these halogenation reactions as well as some unacceptably large uncertainties about the standard enthalpy of formation of some prototypical hydrocarbon free radicals.

Part of a larger measurement campaign, the present paper focuses on the results obtained for two halogenation reactions involving the transfer of a hydrogen atom to the $t\text{-}C_4H_9^\bullet$ radical:

$$t\text{-}C_4H_9^\bullet + HBr \rightarrow i\text{-}C_4H_{10} + Br^\bullet \quad (1)$$

$$t\text{-}C_4H_9^\bullet + HI \rightarrow i\text{-}C_4H_{10} + I^\bullet \quad (2)$$

Table1 presents a review of the literature in past investigations of reactions 1 and 2. In all studies, the free radical was generated by UV-laser photolysis of different suitable precursors: photodissociation of 4,4-dimethyl-1-pentene at 193 nm,[3,4,7,10] 2,2,4,4-tetramethyl-3-pentanone at 193 nm,[3,10] 3,3-dimethyl-2-butanone at 248 nm,[7] $t\text{-}C_4H_9Br$ at 248 nm,[8] $t\text{-}C_4H_9I$ at 266 nm,[5] or 2,2′-azoisobutane at 351 nm.[6,9,11] For the reaction with HBr, all previous studies reported rather elevated rate constants coupled to a negative temperature dependence. The rate constants were measured by monitoring the temporal decay of the *t*-butyl free radical at selected conditions,[3,7,8] with the exception of three measurements, for which the rate constants were derived either from the accumulation of atomic Br, the open-shell reaction product in reaction 1,[5,6] or the corresponding closed shell product, namely, isobutane ($i\text{-}C_4H_{10}$).[4] The oldest investigation[3] reported a rate constant for reaction 1 at ambient temperature that is approximately three times lower than the more recent studies.[4−8] In the case of the results published by Russell et al.,[3] a problem of contamination of HBr with a substantial amount of H_2 was later judged to be

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Table 1. Obtained Rate Parameters for t-$C_4H_9^\bullet$ + HX (X = I, Br) → i-C_4H_{10} + $X^\bullet$ and Recommended Value for $\Delta_fH°(R^\bullet)$ Based on the Rate Constants for the Inverse Reaction $X^\bullet$ + C_4H_{10} from the Corresponding References

authors	A (cm^3 molecule^{-1} s^{-1})	E_a (kJ mol^{-1})	k_{298} (cm^3 molecule^{-1} s^{-1})	$\Delta_fH°_{298}$(t-$C_4H_9^\bullet$) (kJ mol^{-1})
		t-$C_4H_9^\bullet$ + HBr → i-C_4H_{10} + $Br^\bullet$		
Russell et al.[3]	9.86×10^{-13}	−5.8	1.0×10^{-11}	48.6 ± 1.7[a]
Richards et al.[4]			1.0×10^{-11}	
Nicovich et al.[5]	1.07×10^{-12}	−8.0	2.7×10^{-11}	50.6 ± 2.9[b]
Seakins and Pilling[6]			3.2×10^{-11}	50.9 ± 3.5[c]
Seakins et al.[7]	1.37×10^{-12}	−7.8	3.2×10^{-11}	51.3 ± 1.8[d]
Seetula and Slagle[8]	1.2×10^{-12}	−8.3	3.4×10^{-11}	51.8 ± 1.3[e]
Müller-Markgraf et al.[11]			2.6×10^{-13}	38.5 ± 2.1[f]
		t-$C_4H_9^\bullet$ + HI → i-C_4H_{10} + $I^\bullet$		
Rossi and Golden[9]	8.92×10^{-12}	7.0	5.3×10^{-13}	38.5 ± 5.0[g]
Richards et al.[4]	1.98×10^{-12}	−6.3	2.5×10^{-11}	48.1 ± 3.3[h]
Seetula et al.[10]	3.10×10^{-12}	−6.3	3.9×10^{-11}	48.3 ± 2.0[i]
Müller-Markgraf et al.[11]			6.0×10^{-13}	44.2 ± 2.1[j]

[a] "Second Law" value. The "Third Law" value yields $\Delta_fH°$(t-$C_4H_9^\bullet$) = 47.8 ± 3.0 kJ mol^{-1} at 300 K using $S°(298)$ = 313 ± 10 J mol^{-1} K^{-1} computed from data of ref 12. [b] Average of "Second" and "Third Law" values using the Arrhenius parameters of k_{-1} from ref 3. The individual "Second Law" result is $\Delta_fH°$(t-$C_4H_9^\bullet$) = 49.4 ± 2.3, $S°(298)$ = 311.2 ± 6.9 evaluated at T_m = 375 K, the "Third Law" yields $\Delta_fH°$(t-$C_4H_9^\bullet$) = 50.8 ± 4.0 kJ mol^{-1}, $S°(298)$ = 315.7 ± 11.3 J K^{-1} mol^{-1}. [c] "Third Law" value using $S°(298)$ = 314 ± 10 J K^{-1} mol^{-1} (refs 12 and 13) and the equilibrium constant k_1/k_{-1} at 298 K. When combined with measurements at 573 K (44.2 ± 4.0 kJ mol^{-1}) and 641 K (48.1 ± 4.0 kJ mol^{-1}), the average value is $\Delta_fH°$(t-$C_4H_9^\bullet$) = 47.3 ± 3.5 kJ mol^{-1}. [d] "Third Law" value using $S°(298)$ = 313 ± 6 J K^{-1} mol^{-1} evaluated at T_m = 359 K (listed) is identical to "Second Law" value ($\Delta_fH°$(t-$C_4H_9^\bullet$) = 51.3 ± 1.7 kJ mol^{-1}, $S°(298)$ = 313 ± 5 J K^{-1} mol^{-1} at T_m = 359 K). The extensive reinvestigation of both forward and reverse rate constants presented in ref 3 yields identical results for the free radical thermochemical parameters except for the absolute rate constants, which are higher by a factor of 2 or 3 across the investigated temperature range. [e] "Second Law" value obtaining $S°(298)$ = 315 ± 4 J K^{-1} mol^{-1}. Listed value of $\Delta_fH°$(t-$C_4H_9^\bullet$) is the average of 51.0 ± 1.1 and 52.7 ± 1.6 kJ mol^{-1} using refs 3 and 7 at T_m = 415 and 503 K, respectively, for k_{-1}. [f] "Third Law" value using k_{-1} of ref 3 at 298 K and $S°(298)$ = 313 ± 10 J K^{-1} mol^{-1} (refs 12 and 13). $\Delta_fH°$(t-$C_4H_9^\bullet$) = 41.4 ± 2.5 kJ mol^{-1} is obtained when k_{-1} of ref 14 is used at 298 K. The measured rate constant k_1 has been multiplied by $(3)^{0.5}$ = 1.73 in order to account for the measured primary H/D isotope effect at T = 298 K according to ref 9. [g] "Second Law" approach using data for k_{-2} of ref 15 after correction of k_2 with the measured primary isotope effect for H/D abstraction at 600 ($k_2^H/k_2^D = 2^{0.5}$ = 1.41, assumed) and 300 K (k_2^H/k_2^D = 1.75, measured, see ref 16) resulting in $S°(298)$ = 310.4 ± 4 J K^{-1} mol^{-1}. In comparison, Weitz and co-workers (ref 4) measure a primary H/D isotope effect for the reaction t-$C_4H_9^\bullet$ + HBr/DBr of 1.25 in contrast to a false claim by Seetula et al. (ref 10) reporting 4.0. The results based on the measurements of k_{-2} in refs 17 and 18 were rejected on the basis that they resulted in unrealistically low values of $S°(298)$. The significant uncertainty in the displayed value of $\Delta_fH°$(t-$C_4H_9^\bullet$) stems from the small T-range for the measurement of k_{-2} published in ref 37 and the uncertainty in the H/D primary isotope effect. [h] "Second Law" value. Inverse rate constant k_{-2} taken from refs 15, 17, and 18 and averaging of values of $\Delta_fH°$(t-$C_4H_9^\bullet$). [i] "Third Law" value using k_{-2} from refs 15 ($\Delta_fH°$(t-$C_4H_9^\bullet$) = 50.0 ± 3.0 kJ mol^{-1}), 17 ($\Delta_fH°$(t-$C_4H_9^\bullet$) = 47.0 ± 3.0 kJ mol^{-1}), and 18 ($\Delta_fH°$(t-$C_4H_9^\bullet$) = 48.0 ± 3.0 kJ mol^{-1}) using $S°(298)$ = 313 ± 10 J K^{-1} mol^{-1} (ref 12). "Second Law" treatment obtains $\Delta_fH°$(t-$C_4H_9^\bullet$) = 50.0 ± 5.0 kJ mol^{-1} evaluated at T_m in midrange of k_{-2}. [j] k_2 has been multiplied by a factor of $(3)^{0.5}$ = 1.73 in order to account for the primary H/D isotope effect at T = 298 K using the measured value from ref 9 (see also footnote g). "Third Law" value displayed uses extrapolation to 300 K of $\log k_{-2} = -(9.18 \pm 0.1) - (99555 \pm 1255)/(2.303RT)$ (R = 8.314 kJ mol^{-1}) of unpublished work of Bracey and Walsh (ref 15) cited and used in refs 9 and 10 with $S°(298)$ = 322.2 ± 2.1 J K^{-1} mol^{-1} (Millennium database). Using $S°(298)$ = 310.4 ± 2.1 J K^{-1} mol^{-1} as a lower limit, we obtain $\Delta_fH°$(t-$C_4H_9^\bullet$) = 40.7 ± 2.5 kJ mol^{-1} at 300 K. Using the same procedure at T = 300 K for k_{-2} published in refs 17 and 18 yields values in the brackets of 34.3–37.8 and 37.4–40.9 kJ mol^{-1} for $\Delta_fH°$(t-$C_4H_9^\bullet$) at T = 300 K.

responsible for this difference[5] and led to a thorough reinvestigation of both k_1 and k_{-1} by Seakins et al.[7] However, no sound explanation has been proposed for the disagreement between the referenced kinetic results[3] and the results of Richards et al.[4] whose experiments were moreover carried out under nominally identical experimental conditions compared with recent investigations,[5,7,8] with the exception that the gas mixture used as a buffer gas by Richards et al.[4] contained a significant fraction of efficient collisional quencher SF_6. The buffer gas absolute pressure typically was on the order of 5 mbar in addition to 0.5 mbar HBr used in 100−300-fold excess over the free radical concentration at 1% decomposition of its corresponding precursor. This study is characterized by an exceptionally large concentration of t-butyl free radicals in the range $(0.2{-}1.0) \times 10^{14}$ cm^{-3} compared with most other studies listed in Table 1.

The previous investigations of the kinetics of the reaction t-$C_4H_9^\bullet$ + HI are also presented in Table 1. These data constitute another explicit example of two opposite trends obtained for such reactions. Indeed, a positive activation energy and a small rate constant initially obtained by Rossi and Golden[9] is opposite to the later, more recent measurements performed by Richards et al.[4] and Seetula et al.[10] The reaction between t-butyl free radical and HI is one for which the extent of the disagreement is the largest among hydrocarbon free radical metathesis reactions of this kind. The discrepancy is a factor 75 at ambient temperature between the two extreme values of k_{-1} or k_{-2}, namely, the "low" values presented in ref 9 vs the "high" values highlighted in refs 4 and 10. The difference between the previously used experimental approach and the present study essentially lies in the free radical generation scheme and in the type of reactor. A laminar flow reactor was used by both Richards et al.[4] and Seetula et al.,[10] whereas Rossi and Golden[9] and Müller-Markgraf et al.[11] conducted their experiments using a Knudsen flow reactor. The results obtained on the $R^\bullet$ + HX reaction by Rossi and Golden[9] also differ from all other recent measurements leading to a negative activation energy of k_{-1} and k_{-2} by the fact that the used photon energy was the least energetic at a wavelength of 351 nm, in comparison to the 193, 248, and 266 nm wavelengths used in other studies with the exception of the study by Seakins and Pilling.[6] As we have already emphasized in our previous publications,[1,2] the large rate constants at ambient temperature, associated with small, but significant negative activation energies, were exclusively obtained under conditions of UV photolysis (<266 nm) of a free radical precursor for all investigations of the kinetics of the reaction of the type $R^\bullet + HX \rightleftarrows RH + X^\bullet$. Notable exceptions are two experiments on $CH_3^\bullet + HBr$ and $C_2H_5^\bullet + HBr$, each at ambient temperature, in which the free radical was generated using H-abstraction by atomic chlorine from the corresponding hydrocarbons upon laser irradiation at 355 nm.[5] Owing to the weak exothermicity of H-abstraction from CH_4 and C_2H_6 by atomic chlorine, we expect no or at best only a minor degree of molecular excitation in the resulting free radical. The same is true for the reaction $Br + i\text{-}C_4H_{10} \rightarrow t\text{-}C_4H_9^\bullet + HBr$ performed by Seakins and Pilling mentioned above.[6]

This is a remarkable exploratory study of reaction 1 combining ambient temperature kinetics of photolytically generated $t\text{-}C_4H_9^\bullet$ with HBr leading to the measurement of k_1, with an equilibration study at 573 and 641 K leading to the extraction of both k_1 and k_{-1} using the time-dependent relaxation rate of a pulse of atomic bromine generated through excimer laser photolysis from a suitable atomic bromine precursor (CF_2Br_2). It is the only study combining photolytic generation of the radical followed by reaction with HBr at ambient temperature with direct equilibration/relaxation at high temperature initiated by reaction −1, namely, H-abstraction from $i\text{-}C_4H_{10}$ by atomic $Br^\bullet$. The measurement of the relaxation kinetics enables the measurement of both high-temperature rate constants, k_1 and k_{-1}, over a narrow temperature range. It is obvious that the mode of $t\text{-}C_4H_9^\bullet$ formation is very different at ambient and high temperatures, namely, photolysis of the free radical precursor (azo-isobutane, $t\text{-}C_4H_9{-}N{=}N{-}C_4H_9\text{-}t$) vs thermal H abstraction by atomic $Br^\bullet$ from the corresponding hydrocarbon, $i\text{-}C_4H_{10}$.

The thermochemical calculations from the studies associated with a negative activation energy result in $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet)$ lying in the range 48.1−51.8 kJ mol^{-1} associated with a high value of k_1 at ambient temperature. The value of the standard enthalpy of formation $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 38.5$ kJ mol^{-1} obtained by Rossi and Golden[9] and Müller-Markgraf et al.[11] is affected by the Arrhenius parameters of the measured rate constant for reaction i, namely, k_i with $i = 1, 2$, which is associated with a positive activation energy and a low value of k_i at ambient temperature. This renders the free radical of $t\text{-}C_4H_9^\bullet$ more stable in the above equilibrium, everything else being equal, compared with studies proposing high values of k_i. This has been recognized a number of times by the proponents of the high values of k_i in the past who attributed the disparity of $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet)$ between high and low values exclusively to that fact, namely, the absolute magnitude of k_i.[3−5,10,19] Nevertheless, the above range of 38−52 kJ mol^{-1} for the standard heat of formation of $t\text{-}C_4H_9^\bullet$ lies in the middle of the extremes of other results for $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet)$ obtained by other nonkinetic experimental techniques and *ab initio* electronic structure calculations. Indeed, lower values were measured, such as the recommended value of $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 35.1 \pm 4.6$ kJ mol^{-1} obtained by Houle and Beauchamp[20] from a photoelectron spectroscopic study of t-butyl free radical. However, this value has been superseded by $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 43.1 \pm 5.0$ kJ mol^{-1} resulting from a reevaluation of the same spectroscopic data[11] using more recent ancillary thermochemistry.[21] Castelhano and Griller[22] obtained a value of $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 39.3 \pm 4.2$ kJ mol^{-1} using the free radical buffer technique by measuring the equilibrium constants for the exchange reaction $CH_3^\bullet + t\text{-}C_4H_9I \rightleftarrows CH_3I + t\text{-}C_4H_9^\bullet$ in solution. From an extensive shock tube study on *t*-butyl free radical using different precursors, Tsang reported $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 45.6 \pm 3.0$, 50.6 ± 4.0, and 47.7 ± 3.0 kJ mol^{-1} using the "Third Law" approach from experiments involving the equilibria $(t\text{-}C_4H_9)_2 \rightleftarrows 2\ t\text{-}C_4H_9^\bullet$, $C(CH_3)_4 \rightleftarrows CH_3^\bullet + t\text{-}C_4H_9^\bullet$, and $t\text{-}C_4H_9^\bullet \rightleftarrows t\text{-}C_4H_8 + H^\bullet$, respectively.[23,24] The "Third Law" treatment performed by Benson et al.[14] based on the experimental measurement of the equilibrium constant $HBr + t\text{-}C_4H_9^\bullet \rightleftarrows Br^\bullet + i\text{-}C_4H_{10}$ and the kinetics of the forward reaction led to a value of $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 45.1$ kJ mol^{-1}. This value is in good agreement with $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 44.2 \pm 4.0$ and 48.1 ± 4.0 kJ mol^{-1} from similar studies of the bromination equilibrium after generation of atomic $Br^\bullet$ from a suitable precursor (CF_2Br_2) using pulsed 193 nm laser radiation at 573 and 641 K reported by Seakins and Pilling.[6] As briefly mentioned above, these authors managed to separately measure both reaction rate constants (k_1 and k_{-1}) using resonance fluorescence detection of atomic $Br^\bullet$, once as the open-shell product of the forward reaction (k_1) and once as the reactant for the backward reaction (k_{-1}). Müller-Markgraf et al.[11] investigated the kinetics of $t\text{-}C_4H_9^\bullet + DX$ (X = Br, I) $\rightarrow i\text{-}C_4H_9D + X^\bullet$, and derived the rate constant for $t\text{-}C_4H_9^\bullet + HBr \rightarrow i\text{-}C_4H_{10} + Br^\bullet$ from their results using DI after application of a correction for the primary H/D kinetic isotope effect based on experimental data.[9] A "Third Law" treatment led to the recommended value $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 38.5 \pm 2.1$ kJ mol^{-1} and $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 41.4 \pm 2.5$ kJ mol^{-1} by using the results of Russell et al.[3] and Benson et al.,[14] respectively, for the inverse reaction (k_{-i}).

In contrast, a high value $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 53.1 \pm 12$ kJ mol^{-1} was obtained by Király et al.[25] thanks to a new evaluation of the group additivity value for $\Delta_f H^\circ_{298}(C{-}(C)_3)$ by means of experimental measurements of the equilibrium process $CH_3^\bullet + (CH_3)_2CCH(CH_3) \rightleftarrows (CH_3)_2C^\bullet CH(CH_3)_2$. This higher value of the standard heat of formation of $t\text{-}C_4H_9^\bullet$ is consistent with the results of several theoretical *ab initio* electronic structure calculations with the used quantum-chemical method given inside the parentheses: $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 52.3 \pm 18.0$ kJ mol^{-1} (CBS-q),[26] 54.4 ± 8.5 kJ mol^{-1} (G3),[27] 57 ± 7 kJ mol^{-1} (variety of theoretical methods),[28] $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 44.8$ kJ mol^{-1} (CBS-4),[29] and $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet) = 51.4$ kJ mol^{-1} (CBS-4 corrected by using an empirical expression in order to deal with the experimental results of Seetula and Slagle[8]) and 55.3 kJ mol^{-1} (G3MP2B3).[30]

A review of literature relevant to $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet)$ reveals that this thermochemical quantity remains quite uncertain. Most of the experimental measurements of $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet)$ are based on kinetic results of photolytic studies in the recent past leading to high values of the rate constants k_1 or k_2 associated with negative activation energies[3−8,10] that have been questioned as a result of our recent invesigations[1,2] as well as the results previously published by Rossi and Golden[9] and Müller-Markgraf et al.[11] In fact, the opposite, namely a positive temperature dependence of k_1 was obtained in these two studies for $t\text{-}C_4H_9^\bullet + HI$ by using a softer photolytic generation of the radical coupled to a high frequency of hard-sphere collisions of $t\text{-}C_4H_9^\bullet$ against the vessel walls inside the Knudsen flow reactor. Qualitatively similar results have been obtained in our recent investigations pertaining to reactions involving a number of other hydrocarbon free radicals. The most recent studies have been performed using a newly developed experimental apparatus, which notably enables a novel method of generation of the free radical in question external to the Knudsen flow reactor. Therefore, the remaining uncertainties of the rate constant and $\Delta_f H^\circ_{298}$(t-$C_4H_9^\bullet$) motivated the use of this new tool for the reinvestigation of the kinetics of the reactions t-$C_4H_9^\bullet$ with HBr or HI reported in the present manuscript.

■ EXPERIMETAL METHODOLOGY

The main features of the recently developed experimental apparatus were detailed in a recent publication.[31] Additional information about the experiment, as well as the used data treatment, was also described in both papers on the reactions between ethyl and the propyl free radicals reacting with hydrogen halides HX (X = Br, I).[1,2] Therefore, only a brief overview focusing on *t*-butyl free radical is presented here.

Experimental Apparatus. Briefly, the experiment consists of a Knudsen flow reactor coupled to single-photon (VUV) photoionization mass spectrometry (SPIMS) in "line-of-sight" geometry. The t-$C_4H_9^\bullet$ free radicals were generated before introduction into the Knudsen reactor thanks to a reactor consisting of two glass tubes in series. A flow of 20% H_2/Ar mixture was established across the first tube excited by a 2.45 GHz (λ = 12.2 cm) microwave discharge. When the μ-wave discharge was turned on and powered at 40 W, approximately 50% H_2 underwent bond scission and generated $H^\bullet$ atoms. Subsequently, these $H^\bullet$ atoms flowed into the second tube across a 1 mm diameter Teflon capillary and reacted with the radical precursor flowing into the tube from a separate inlet. In the present case, the used precursor was t-C_4H_9I, so that the chemical generation scheme consisted of the two following reactions:

$$H_2 + h\nu(\mu\text{-wave}) \rightarrow 2H^\bullet \tag{3}$$

$$H^\bullet + \text{t-}C_4H_9I \rightarrow \text{t-}C_4H_9^\bullet + HI \quad (\Delta_r H^\circ_{298} = -75.2\ \text{kJ/mol}) \tag{4}$$

It was experimentally verified that no products other than t-$C_4H_9^\bullet$ and HI were present in the radical generation tube in order to exclude parasitic reaction pathways. This ascertained that no unwanted reactions occurred in this part of the apparatus and that the performed experiments were thus safe from potential artifacts, especially when t-butyl iodide or HI were used.

Subsequently, all the gases, namely, the t-$C_4H_9^\bullet$ free radical but also the remaining t-C_4H_9I and H_2 as well as Ar and the product HI from reaction 4, flowed from the second tube into the Knudsen reactor across another 1 mm diameter Teflon capillary. The t-C_4H_9I flow was always kept in excess compared with the $H^\bullet$ atom flow, typically higher by a factor of 7−10, in order to prevent the admission of significant quantities of $H^\bullet$ to the reactor. Finally, the t-$C_4H_9^\bullet$ reacted in the Knudsen reaction vessel with controlled amounts of the titrant introduced directly using a separate inlet. We note that $[HI]_0$, the concentration of HI in the absence of titrant, which comes from its production in reaction 4, was at least 80 times lower than the smallest HI concentration used for titration in the case of the investigation of the t-$C_4H_9^\bullet$ + HI reaction. All operating conditions, including the inlet flow of each chemical compound, for each individual rate constant measurement are given in Tables A1 and A2 in the Supporting Information. The used gases and liquids were provided by Messer (Ar ≥ 99.998%, H_2 ≥ 99.995%, HBr ≥ 99.98%, and i-C_4H_8 ≥ 99.00%), by the Fairfield Chemical Company (2,2,3,3-tetramethylbutane (C_8H_{18})) and by Carbagas (i-C_4H_{10} ≥ 100%) and liquid t-C_4H_9I of purity ≥95% whose gas phase above the liquid t-C_4H_9I was stabilized with copper (Sigma-Aldrich). Gas phase HI was set free from concentrated solution (Sigma-Aldrich) according to the method described by Dillon and Young.[32] All condensable gases (HI, HBr, and t-C_4H_9I) were purified and degassed by using several freeze (77.36 K)−pump−thaw cycles.

The experiments were performed in two different Knudsen reactors between 293 and 623 K. The main properties of the two reactors are listed in Table 2. These reactors and the close upstream tube where the radicals are generated were FEP-Teflon coated in order to minimize wall losses of the *t*-butyl free radical. The upper limiting temperature of 623 K was chosen in order to prevent significant depolymerization of the thin FEP-Teflon coating. The duplication of experiments in two reactors of differing escape rate constants (k_e) and therefore gas residence or reaction times, enabled the measurement of small radical wall losses (see below). Finally, the gases flowed out of the reactor in an effusive molecular beam across an orifice of 3.5 or 7 mm diameter into the ionization volume of the mass spectrometer and were identified and quantitatively analyzed using single-photon VUV photoionization mass spectrometry, VUV-SPIMS.[31] Photoionization was obtained thanks to VUV photons emitted from a pure H_2 discharge lamp (Lyman-α radiation at 10.20 eV).

Table 2. Important Parameters of the Knudsen Reactor

	reactor a	reactor b
volume (cm^3)	213	286
internal area (cm^2)	256	275.5
Φ exit aperture (mm), nominal diameter	3.5	7.0
k_e (s^{-1}) (measured)	$1.034(T/M)^{1/2}$	$2.367(T/M)^{1/2}$
ω (s^{-1}) (calculated)	$4386(T/M)^{1/2}$	$3509(T/M)^{1/2}$

This experimental apparatus embodies some major improvements compared with previously used techniques because it enables, without any doubt, thermal generation of t-$C_4H_9^\bullet$ free radicals for essentially two reasons: (i) the precursors of the radical, namely, t-C_4H_9I, never interacted with the diffuse microwave plasma in the first tube of the external free radical generation system, and (ii) the numerous collisions of t-$C_4H_9^\bullet$ with the wall of the second tube, as well as with the internal walls of the Knudsen reactor, removed the potential excess of internal energy in t-$C_4H_9^\bullet$. It is therefore expected that all radicals are thermalized.

Data Treatment. The data treatment must consider all reactions occurring in the reactor, namely:

$$\text{t-}C_4H_9^\bullet + HBr \rightarrow \text{i-}C_4H_{10} + Br^\bullet \tag{1}$$

or

$$\text{t-}C_4H_9^\bullet + HI \rightarrow \text{i-}C_4H_{10} + I^\bullet \tag{2}$$

$$\text{t-}C_4H_9^\bullet \rightarrow \text{wall loss} \tag{5}$$

$$\text{t-}C_4H_9^\bullet + \text{t-}C_4H_9^\bullet \rightarrow \text{i-}C_4H_8 + \text{i-}C_4H_{10} \tag{6}$$

$$\text{t-}C_4H_9^\bullet + \text{t-}C_4H_9^\bullet \rightarrow (CH_3)_3CC(CH_3)_3 \tag{7}$$

Table 3. Kinetic Parameters Obtained in the Two Reactors a and b and the Evaluation of k_w and Ratio k_w/k_e

reactor	A (cm^3 molecule^{-1} s^{-1})	E_a (kJ mol^{-1})	k_w (s^{-1}) 298 K	373 K	473 K	623 K	k_w/k_e min−max
		$t\text{-}C_4H_9^\bullet + HBr \rightarrow i\text{-}C_4H_{10} + Br^\bullet$					
a	$(5.05 \pm 1.94) \times 10^{-12}$	6.68 ± 1.22	0.20	0.25	0.31	0.38	0.086−0.11
b	$(5.42 \pm 2.62) \times 10^{-12}$	6.12 ± 2.92					
		$t\text{-}C_4H_9^\bullet + HI \rightarrow i\text{-}C_4H_{10} + I^\bullet$					
a	$(1.73 \pm 0.78) \times 10^{-11}$	7.98 ± 1.42	<0	<0	<0	0.16	<0−0.048
b	$(2.02 \pm 1.04) \times 10^{-11}$	8.64 ± 0.67					

In addition to the two reactions of interest, reactions 1 and 2, the $t\text{-}C_4H_9^\bullet$ may be consumed by disproportionation (reaction 6, k_d), recombination (reaction 7, k_r), and first-order loss on the reactor surface (reaction 5, $k_w^{C_4H_9}$). Two data procedures were used to derive the rate constants of interest. The first is based on the measured decay of the free radical MS signal and enables the determination of the free radical wall-loss constant, $k_w^{C_4H_9}$; the second uses the quantitative measurement of the accumulated closed shell products ($i\text{-}C_4H_8$, $i\text{-}C_4H_{10}$, and $(CH_3)_3CC(CH_3)_3$) in the presence of HX. This is tantamount to measuring the perturbation of the closed shell product concentration in the presence of increasing concentrations of HX, or in other words, the increasing competition of reactions 1 or 2 for t-butyl free radicals compared with reactions 6 and 7.

The first method uses the MS signals of the radical as a function of the concentration of titrant, [HX]. This was the signal measured at m/z 57 corrected for the contribution from the fragmentation of $i\text{-}C_4H_{10}$ and $t\text{-}C_4H_9I$ at m/z 57. Using the flow balance equations, it may be shown[1] that the ratios between the MS signals of $t\text{-}C_4H_9^\bullet$ in the absence and presence of titrant HX ($I^0_{C_4H_9}/I_{C_4H_9}$) and for any concentration of HX, depend on [HX] according to

$$\frac{I^0_{C_4H_9}}{I_{C_4H_9}} = \left(\frac{R^{\text{in}}_{C_4H_9} - 2\left(1 + \frac{k_d}{k_r}\right)R^{\text{out},0}_{C_8H_{18}}}{R^{\text{in}}_{C_4H_9} - 2\left(1 + \frac{k_d}{k_r}\right)R^{\text{out}}_{C_8H_{18}}}\right)\left(1 + \frac{k_i}{k_w^{C_4H_9} + k_e^{C_4H_9}}[\text{HX}]\right) \qquad i = 1, 2 \tag{8}$$

where R^{in} and R^{out} are the specific flows of the chemical compounds mentioned in the subscript into or out of the Knudsen reactor and are expressed in molecules s^{-1} cm^{-3}. The superscript 0 refers to initial conditions, namely, in the absence of titrant. Moreover, it was verified in the study involving ethyl radical[1] that the first term in the brackets on the right-hand side of the equation remains close to unity at the prevailing experimental conditions. This is the case because either R^{in} of the radical significantly exceeds $2R^{\text{out}}$ of the recombination products or the experimental conditions were kept within a range for which R^{out} of the recombination product did not vary significantly. The first cited condition is in any case constrained by the mass balance equation governing the present system:

$$2R^{\text{out}}_{C_8H_{18}} = R^{\text{in}}_{C_4H_9} - R^{\text{out}}_{C_4H_9} - R^{\text{out}}_{C_4H_8} - R^{\text{out}}_{C_4H_{10}} \tag{9}$$

Several checks of the accuracy of this assumption were made in the case of the ethyl study,[1] which are also valid in the present case in view of the similarity of the operating conditions. It must be even more accurate in the present case in view of the smaller recombination rate constant compared with ethyl free radical. Indeed, smaller concentrations of the recombination product are expected here because $k_{r,\text{ethyl}} = 1.42 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},[33] whereas the corresponding rate constant is ten times lower for t-butyl radical with $k_{r,t\text{-butyl}} = 1.66 \times 10^{-12}$ cm^3 molecule^{-1}.[34] Therefore, eq 8 may be simplified as follows:

$$\frac{I^0_{C_4H_9}}{I_{C_4H_9}} = \left(1 + \frac{k_i}{k_w^{C_4H_9} + k_e^{C_4H_9}}[\text{HX}]\right) \tag{10}$$

If for one given operating condition the experimental measurement of $I^0_{C_4H_9}/I_{C_4H_9}$ is plotted as a function of HX concentration, a linear regression line is obtained with a slope (S) equal to $k_i/(k_w^{C_4H_9} + k_w^{C_4H_9})$. Because $k_e^{C_4H_9}$, the escape rate constant of $t\text{-}C_4H_9^\bullet$ out of the Knudsen reactor, is known from a previous calibration, two unknowns remain, namely, $k_w^{C_4H_9}$ and k_i. Therefore, k_i, the rate constant of interest, may be determined together with the wall-loss rate constant by using two different sets of data. These two sets are the measurements obtained in the two reactors, namely, reactors a and b. These two reactors differ by their respective values of $k_e^{C_4H_9}$, and at a given temperature, the obtained slopes for reactors a or b are equal to

$$S^{\text{a}} = \frac{k_i}{k_e^{C_4H_9,\text{a}} + k_w^{C_4H_9}} \tag{11}$$

$$S^{\text{b}} = \frac{k_i}{k_e^{C_4H_9,\text{b}} + k_w^{C_4H_9}} \tag{12}$$

Using S^{a}, S^{b}, and $k_e^{C_4H_9}$ measured experimentally, one can calculate $k_w^{C_4H_9}$ and k_i using eqs 13 and 14 derived from eqs 11 and 12:

$$k_w^{C_4H_9} = \frac{S^{\text{b}}k_e^{C_4H_9,\text{b}} - S^{\text{a}}k_e^{C_4H_9,\text{a}}}{S^{\text{a}} - S^{\text{b}}} \tag{13}$$

$$k_i = \frac{S^{\text{a}}S^{\text{b}}}{S^{\text{a}} - S^{\text{b}}}\left(k_e^{C_4H_9,\text{b}} - k_e^{C_4H_9,\text{a}}\right) \tag{14}$$

Table 3 reports results of obtained values of $k_w^{C_4H_9}$ for the four investigated temperatures and the two reactions of interest. It appears that the wall-losses are rather small in all cases, thus reaching 11% of the value of $k_e^{C_4H_9}$ in reactor a (note that $k_e^{\text{a}} < k_e^{\text{b}}$) at most. This parameter is even slightly negative in the range 298−473 K, according to the measurements performed in the $t\text{-}C_4H_9^\bullet$ + HI experiments. These negative terms have no physical reality and are set to zero. This means that the wall losses are too small to be accurately determined because the small random variations of the measurement may lead to unphysical values of $k_w^{C_4H_9}$.

Because the wall-loss measurements reveal that the numerical value of $k_w^{C_4H_9}$ is very small, Table 3, columns 2 and 3, displays the Arrhenius parameters for k_1 and k_2 that may be individually

Table 4. Main Experimental Conditions and Measured Rate Constants for t-$C_4H_9^{\bullet}$ + HBr → i-C_4H_{10} + $Br^{\bullet}$[a]

T (K)	inlet flow of t-C_4H_9 (molecules s^{-1})	$[t\text{-}C_4H_9]_0$[b] (molecules cm^{-3})	$[total]_0$[c] (molecules cm^{-3})	$[HBr]_{max}$[d] (molecules cm^{-3})	k_1 (cm^3 s^{-1} molecule^{-1})	error[e] (%)
		Reactor a (V = 213 mL, exit aperture = 3.5 mm, k_{esc} (s^{-1}) = $1.034(T/M)^{1/2}$)				
293	5.79×10^{13}	1.16×10^{11}	1.71×10^{12}	6.55×10^{12}	3.52×10^{-13}	60
293	1.86×10^{13}	3.73×10^{10}	9.81×10^{11}	5.15×10^{13}	3.58×10^{-13}	57
293	1.62×10^{14}	3.24×10^{11}	5.40×10^{12}	3.72×10^{13}	2.80×10^{-13}[f]	33
373	6.05×10^{13}	1.07×10^{11}	1.47×10^{12}	2.62×10^{13}	7.87×10^{-13}	53
473	6.10×10^{13}	9.62×10^{10}	1.27×10^{12}	2.47×10^{13}	1.05×10^{-12}	62
623	3.90×10^{13}	5.35×10^{10}	7.84×10^{11}	1.60×10^{13}	1.75×10^{-12}	41
623	3.32×10^{13}	4.56×10^{10}	7.53×10^{11}	1.71×10^{13}	1.34×10^{-12}	29
623	6.00×10^{13}	8.24×10^{10}	2.85×10^{12}	2.37×10^{13}	1.26×10^{-12}[f]	19
		Reactor b (V = 287 mL, exit aperture = 7.0 mm, k_{esc} (s^{-1}) = $2.367(T/M)^{1/2}$)				
293	1.28×10^{14}	8.34×10^{10}	1.09×10^{12}	3.23×10^{13}	3.19×10^{-13}	44
293	1.63×10^{13}	1.06×10^{10}	5.16×10^{11}	2.26×10^{13}	3.46×10^{-13}	88
293	1.93×10^{13}	1.26×10^{10}	5.10×10^{11}	1.35×10^{13}	3.79×10^{-13}	53
373	1.38×10^{14}	7.97×10^{10}	1.01×10^{12}	1.03×10^{13}	5.71×10^{-13}	36
373	1.31×10^{14}	7.58×10^{10}	1.00×10^{12}	1.55×10^{13}	8.54×10^{-13}	80
373	1.27×10^{14}	7.35×10^{10}	1.10×10^{12}	2.64×10^{13}	6.39×10^{-13}	74
373	8.90×10^{13}	5.14×10^{10}	8.07×10^{11}	1.76×10^{13}	5.50×10^{-13}	64
473	6.80×10^{13}	3.49×10^{10}	7.33×10^{11}	5.58×10^{12}	1.09×10^{-12}	59
473	1.38×10^{14}	7.08×10^{10}	9.36×10^{11}	7.15×10^{12}	9.10×10^{-13}	33
473	1.25×10^{14}	6.41×10^{10}	9.39×10^{11}	1.11×10^{13}	1.22×10^{-12}	42
623	2.09×10^{13}	9.34×10^{9}	3.19×10^{11}	6.33×10^{12}	1.40×10^{-12}	46

[a] Arrhenius expressions for the whole data set: $k_1 = 5.62(\pm 1.41)\ 10^{-12} \exp(-6.761(\pm 0.936)/(RT))$; A in cm^3 molecule^{-1} s^{-1} and E_a in kJ mol^{-1}. [b] Obtained by dividing the inlet flow of t-$C_4H_9^{\bullet}$ by Vk_w. The steady state concentration, $[t\text{-}C_4H_9^{\bullet}]_{ss}$, is lower due to consumption of t-$C_4H_9^{\bullet}$ by disproportionation and recombination reactions. [c] Initial total concentration (without any titrant) based on the measured initial inlet flows of stable species and the known decays of the radical precursors when the μ-wave discharge is switched on ($[total]_0 = [t\text{-}C_4H_9^{\bullet}]_0 + [t\text{-}C_4H_9I]_0 + [HI]_0 + [H_2]_0 + [Ar]_0$). [d] Maximum [HBr] in the investigated range. [e] Relative error in the rate constants in % of the absolute value of the rate constants. [f] Rate constant based on the detection of closed shell products (CSPD).

calculated in each reactor by making the assumption that $k_w^{C_4H_9} = 0$. It appears that for both investigated reactions, the obtained Arrhenius parameters for the two reactors are quite close to each other which is an indication of the small value of $k_w^{C_4H_9}$.

The rate constants k_i determined from eq 14 are given and discussed below in Results and Discussion, together with the combined set of Arrhenius parameters (Tables 4 and 5).

The second method of data evaluation used to determine the rate constants of interest is based on the observation of the closed shell products of reactions 1 or 2 and 6 and 7, namely, i-C_4H_8, i-C_4H_{10}, and $(CH_3)_3CC(CH_3)_3$. This method will be called "closed shell product detection" or CSPD. Using the steady-state equations that describe the production and the reactive as well as nonreactive (effusive) loss of these closed-shell compounds in the reactor, the following expression has been derived:[1]

$$\frac{R^{out}_{C_4H_{10}}}{R^{out}_{C_4H_8}} = 1 + \frac{k_i[HX]}{\left(\frac{k_d}{\sqrt{k_r}}\right)\sqrt{R^{out}_{C_8H_{18}}}} \qquad (15)$$

The R^{out} terms are the specific flows of the closed shell recombination and disproportionation products out of the Knudsen reactor that were determined using a suitable calibration of the MS signal of authentic chemical compounds. The rate constant of disproportionation (k_d) and recombination (k_r) were previously determined in several studies. The following values given in the review of Warnatz[34] were used in the present study: $k_{d,t\text{-butyl}} = 4.15 \times 10^{-12}$ cm^3 molecule^{-1}, $k_{r,t\text{-butyl}} = 1.66 \times 10^{-12}$ cm^3 molecule^{-1}.[34] The steady state value of [HX] may also be easily calculated from the measured inlet flow using its escape rate constant, k_e^{HX} and the volume V of the reactor. Therefore, for a given experiment, a plot of the ratio $R^{out}_{C_4H_{10}}/R^{out}_{C_4H_8}$ as a function of $[HX]/(k_d/\sqrt{k_r})(R^{out}_{C_4H_{18}})^{1/2}$ results in a straight line whose slope is equal to the rate constant k_i of interest according to eq 15.

Equation 15 shows that the independent variable $R^{out}_{C_4H_{10}}/R^{out}_{C_4H_8}$ depends on the ratio $s = k_d/(k_r)^{0.5}$ for t-butyl free radical disproportionation (reaction 6) and recombination (reaction 7), which have been repeatedly measured in the past using a variety of experimental techniques. We are making a choice in that we adopt the values from molecular modulation spectroscopy (MMS)[35−37] that are consistent with the corresponding values from the Warnatz review.[34] The ratio s has the following values in units of $cm^{1.5}$ $s^{-0.5}$ molecule$^{-0.5}$: 3.22×10^{-6},[34] 4.96×10^{-6},[35] 3.75×10^{-6},[36] and 3.60×10^{-6},[37] which are all based on the ratio $r = k_d/k_r$ of 2.3[38] except for the Warnatz value, which returned r = 2.5. The value r = 2.3 originates from the review by Kerr,[38] is based mostly on the analysis of stable hydrocarbon products from radical recombination and disproportionation and is considered a consensus value that is independent of temperature in the range of most experiments. Taking the most recent MMS results[36,37] with r = 2.3, we obtain satisfactory agreement of the resulting rate constant of interest, k_i, when using the values of the Warnatz review that uses r = 2.5. If we take the Warnatz kinetics as a baseline, the Arthur[36] and Anastasi and Arthur[37] s ratios increase the measured rate constant k_i by 12−14%. The increase in k_i based on the Arthur and Anastasi and Arthur data[36,37] is lower than the calculated uncertainties of the measurements. However, the Parkes and Quinn data[35] lead to an increase of k_i by a factor of 1.54 and 1.74 using r = 2.3 from Kerr[38] and their measured r of 2.8,[35] respectively. In conclusion, we take the Warnatz[34] values of k_d

Table 5. Main Experimental Conditions and Measured Rate Constants for $t\text{-}C_4H_9^\bullet + HI \rightarrow i\text{-}C_4H_{10} + I^\bullet$[a]

T (K)	inlet flow of $t\text{-}C_4H_9$ (molecules s^{-1})	$[t\text{-}C_4H_9]_0$[b] (molecules cm^{-3})	$[total]_0$[c] (molecules cm^{-3})	$[HI]_{max}$[d] (molecules cm^{-3})	k_2 ($cm^3\ s^{-1}\ molecule^{-1}$)	error[e] (%)
Reactor a (V = 213 mL, exit aperture = 3.5 mm, k_{esc} (s^{-1}) = $1.034(T/M)^{1/2}$)						
293	3.93×10^{13}	7.87×10^{10}	1.75×10^{12}	3.12×10^{13}	5.66×10^{-13}	69
293	3.16×10^{13}	6.32×10^{10}	1.64×10^{12}	4.23×10^{13}	6.42×10^{-13}	67
293	8.92×10^{13}	1.79×10^{11}	5.00×10^{12}	3.84×10^{13}	7.45×10^{-13}[f]	73
373	6.19×10^{13}	1.10×10^{11}	1.88×10^{12}	2.90×10^{13}	1.28×10^{-12}	27
473	4.85×10^{13}	7.65×10^{10}	1.42×10^{12}	1.20×10^{13}	2.66×10^{-12}	29
623	2.02×10^{13}	2.77×10^{10}	6.41×10^{11}	8.32×10^{12}	5.08×10^{-12}	27
623	3.74×10^{13}	5.13×10^{10}	9.00×10^{11}	7.08×10^{12}	3.37×10^{-12}	34
623	1.40×10^{14}	1.92×10^{11}	3.57×10^{12}	7.08×10^{12}	3.49×10^{-12}[f]	48
Reactor b (V = 287 mL, exit aperture = 7.0 mm, k_{esc} (s^{-1}) = $2.367(T/M)^{1/2}$)						
293	7.65×10^{13}	4.99×10^{10}	9.95×10^{11}	4.34×10^{13}	6.34×10^{-13}	18
373	5.27×10^{13}	3.04×10^{10}	8.03×10^{11}	2.66×10^{13}	1.17×10^{-12}	60
373	1.01×10^{14}	5.82×10^{10}	7.79×10^{11}	2.83×10^{13}	1.13×10^{-12}	28
473	3.92×10^{13}	2.01×10^{10}	5.16×10^{11}	2.36×10^{13}	2.53×10^{-12}	61
473	1.09×10^{14}	5.59×10^{10}	8.22×10^{11}	2.72×10^{13}	2.07×10^{-12}	53
623	4.53×10^{13}	2.02×10^{10}	4.96×10^{11}	1.85×10^{13}	4.20×10^{-12}	73

[a] Arrhenius expressions for the whole data set: $k_2 = 2.02(\pm 0.58)\ 10^{-11} \exp(-8.483(\pm 0.940)/(RT))$; A in $cm^3\ molecule^{-1}\ s^{-1}$ and E_a in kJ mol^{-1}. [b] Obtained by dividing the inlet flow of $t\text{-}C_4H_9^\bullet$ by $Vk_{w.}$ The steady state concentration, $[t\text{-}C_4H_9^\bullet]_{ss}$, is lower due to consumption of $t\text{-}C_4H_9^\bullet$ by disproportionation and recombination reactions. [c] Initial total concentration (without any titrant) based on the measured initial inlet flows of stable species and the known decays of the radical precursors when the μ-wave discharge is switched on ($[total]_0 = [t\text{-}C_4H_9^\bullet]_0 + [t\text{-}C_4H_9I]_0 + [HI]_0 + [H_2]_0 + [Ar]_0$). [d] Maximum [HBr] in the investigated range. [e] Relative error in the rate constants in % of the absolute value of the rate constants. [f] Rate constant based on the detection of closed shell products (CSPD).

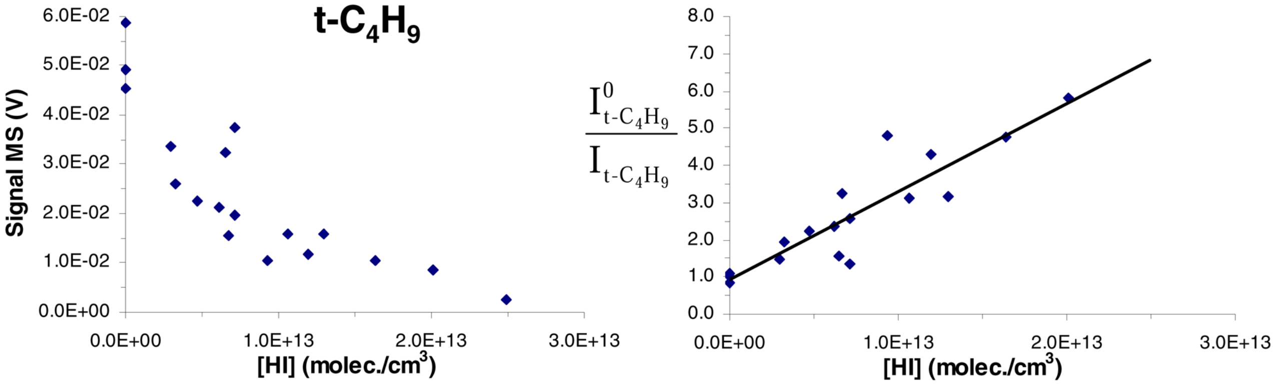

Figure 1. Functional dependence of $t\text{-}C_4H_9^\bullet$ SPIMS signals (left) and ratio I^0/I as a function of HI concentration (reactor a, 293 K, entry 1 in Table 5). Correlation line parameters: $y = (2.39 \times 10^{-13})x + 0.9312$.

and k_r as the most suitable values with the understanding that it constitutes a lower limiting value of k_i. The most recent MMS measurements[36,37] support this contention. Both rate constants (k_d, k_r) have been independently evaluated using the resulting r = 2.5[34] being close to the consensus value of 2.3.[38]

In comparison to the first, this second method presents the advantage that the measurement of k_i is independent of the determination of the radical wall-loss rate constant, $k_w^{C_4H_9}$. However, this second method requires the additional calibration of the evaluated MS signals of two closed shell products ($i\text{-}C_4H_8$ and 2,2,3,3-tetramethylbutane or hexamethylethane, C_8H_{18}) in terms of exit flows. The main advantage of the dual data evaluation method is the welcome opportunity to check the mass balance between the loss of the free radical and the closed-shell product formation in the same experiment, which has never been performed to date. Indeed, if the rate of disappearance of the radical with increasing amounts of titrant agrees with the accumulation or reaction yield of the products for the considered reactions involving this radical, we may claim that the reaction mechanism is completely understood and accurate within the uncertainty limits of the experiment. This means that no major chemical reaction is missing or has failed to be taken into account in the corresponding reaction mechanism.

■ RESULTS AND DISCUSSION

The Absolute Value of the Measured Rate Constants. Tables 4 and 5 present the results of all individual rate constant determinations obtained using the data evaluation procedure described above. For the two investigated reactions, the rate constants were measured at four different temperatures in the range 293−623 K in several individual measurements based on the disappearance of the $t\text{-}C_4H_9^\bullet$ SPIMS signals. Figure 1 displays an example of typical data on *t*-butyl free radical decay with increasing HI concentration leading to a rate constant determination. Results such as these are relevant for the rate constant measurement of the reaction of $t\text{-}C_4H_9^\bullet$ with HI at 293 K in reactor a, for which the operating conditions are listed in the first data row in Table 5. It clearly appears that the $t\text{-}C_4H_9^\bullet$ MS signal decreases when the amount of HI increases.

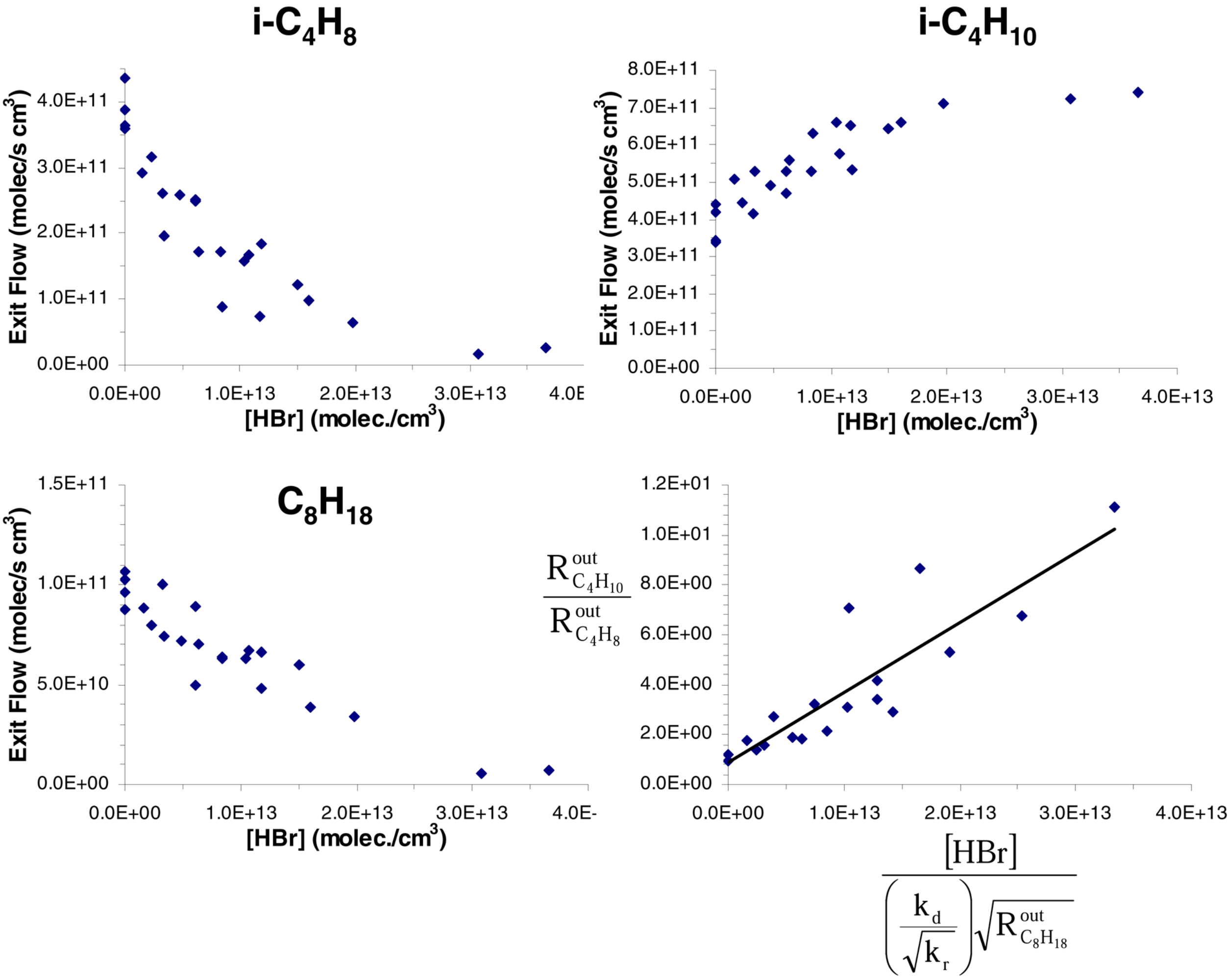

Figure 2. Functional dependence of i-C_4H_8, i-C_4H_{10}, and C_8H_{18} calibrated exit flows as a function of the concentration of HBr in the Knudsen flow reactor (reactor a, 293 K, entry 3 in Table 4), and the linear fit for the measurement of the rate constant based on the closed shell products (CSPD) method. Correlation line parameters: $y = (2.80 \times 10^{-13})x + 0.8082$.

Moreover, as shown on the right panel of Figure 1, a plot of $I^0_{C_4H_9}/I_{C_4H_9}$ as a function of HI concentration leads to a linear regression line whose slope is equal to $k_i/(k_w^{C_4H_9} + k_e^{C_4H_9})$, according to the data treatment procedure described above. Taking these results as an example, the obtained slope is equal to 2.39×10^{-13}. Multiplying this value by the known values of k_e and k_w leads to a rate constant of 5.66×10^{-13} cm^3 s^{-1} molecule^{-1} for the conditions of the example. It may be noted that the linear regression line has an intercept close to unity as expected for eq 10.

In both cases, two additional measurements were also performed based on the observations of the closed shell products (isobutene, hexamethylethane) for two different temperatures. These closed-shell products experiments were always performed in reactor a characterized by a larger residence time compared with reactor b and, therefore, at equivalent inlet flows, by a greater value of [t-$C_4H_9^\bullet$] and higher importance of the radical−radical reaction compared with reactions 1 or 2. As expected, a MS signal for the recombination product that clearly stands out above the baseline could not be measured in reactor b owing to its lower free radical concentration at equal or comparable inlet flow of t-butyl free radicals. An example of an experiment performed for a measurement of the rate constant is presented in Figure 2, which corresponds to results displayed in entry 3 of Table 4 corresponding to data measured at 293 K for the reaction t-$C_4H_9^\bullet$ with HBr. When the concentration of HBr increases, the exit flows of i-C_4H_8 and C_8H_{18} decrease, whereas the exit flow of i-C_4H_{10} becomes more important due to the production of this chemical compound in the reaction t-$C_4H_9^\bullet$ + HBr. The linear fit obtained for a rate constant determination using the closed shell product method (see above) is shown at the bottom right of Figure 2 and led to a rate constant of 2.80×10^{-13} cm^3 s^{-1} molecule^{-1} in the present case. Once again, it may be noted that the intercept is close to unity as expected in view of eq 15. The errors listed in the last column to the right of Tables 4 and 5 are given in terms of a percentage of the rate constant and were determined by means of an appropriate 2σ least-squares analysis of the slopes of the experimental fits of each individual rate constant determination.

In addition to the t-$C_4H_9^\bullet$, i-C_4H_8, i-C_4H_{10}, and $(CH_3)_3CC(CH_3)_3$ MS signals required for the evaluation of the rate constants k_1 and k_2, the MS signals of Ar, t-C_4H_9I, HBr, and HI were also monitored. The Ar MS signals were always constant over a set of experiments and therefore validate the fact that the H_2/Ar flows in the discharge tube were always maintained at a constant rate. Moreover, this observable served as an internal standard and is a good indication that each set of experiments was performed under controlled and stable photoionization conditions. The MS signals for the free radical precursor, t-C_4H_9I, also remained constant. This ensures that the rate of free radical generation by the reaction t-C_4H_9I + $H^\bullet$ was kept constant during each individual set of experiment. This notably indicates that there was no HX counterflow from the Knudsen reactor into the t-$C_4H_9^\bullet$ generation tube. Indeed, if this would not have been the case, HX would react with the $H^\bullet$ atoms in the rather fast $H^\bullet + HX \rightarrow H_2 + X^\bullet$ reactions ($k_{298,\text{H+HBr}} = 6.31 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_{298,\text{H+HI}} = 2.09 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1})[39,40] and therefore compete with the t-$C_4H_9^\bullet$ generation reaction. This may finally lead to a lower decrease of the t-C_4H_9I MS signal and therefore decreasing initial *t*-butyl free radical concentration with increasing HX. Such behavior has never been observed. Another conclusion that may be reached from this observation is that there was no additional consumption of the precursor in the Knudsen reactor with $X^\bullet$ atoms released from the titration by the reaction t-C_4H_9I + $X^\bullet$ → t-$C_4H_9^\bullet$ + XI, as expected from the slow kinetics of this reaction ($k_{298,\text{t-C4H9I+I}} = 2.41 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}).[17] Finally, the titrant signals were also monitored, and it appears that HI flowing out the radical generation tube was negligible in comparison to the flow of HI used as titrant. Recombination and disproportionation of *t*-butyl free radicals taking place already in the upstream free radical generation tube could be ruled out because the analysis of the closed-shell reaction products in reactor b revealed the complete absence of the corresponding reaction products, namely, 2,2,3,3-tetramethylbutane and isobutylene. The t-$C_4H_9^\bullet$ concentration in reactor b is expected to be lower by the factor $k_e^{C_4H_9,b}/k_e^{C_4H_9,a} = 2.3$, which sufficiently slows these radical−radical reactions 6 and 7 compared with reactions 1 and 2. All the observations discussed in this paragraph are regarded as an additional check of the used experimental procedure.

Figures 3 and 4 display the experimental results as an Arrhenius plot using the rate constants presented in Tables 4 and 5. On each graph, the dark and light blue points are all measurements of individual rate constants obtained using the free radical detection method and the black crosses are the results of the closed shell product analysis. The latter method was used for two sets of experiments located at the two extremes of the investigated temperature range for both reactions. The kinetic results obtained from the two data treatments are in good agreement with each other. This ensures a mass balance check of the used chemical system to which we attach great importance.

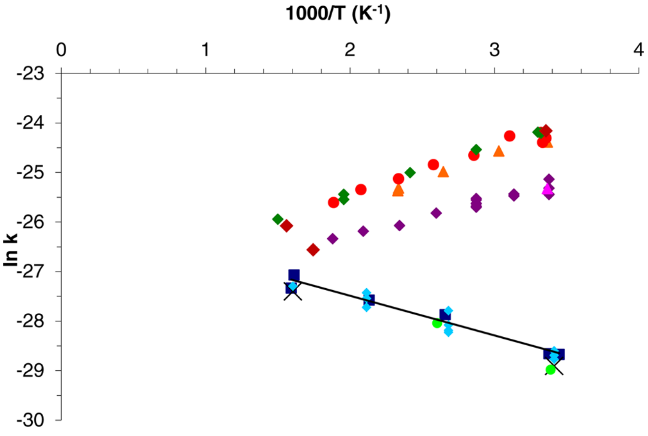

Figure 3. Arrhenius plot (solid line) of current data in comparison with previously published results for k_1 (t-$C_4H_9^\bullet$ + HBr → i-C_4H_{10} + $Br^\bullet$) under the experimental conditions presented in Table 4 (experimental uncertainties of individual data points). Dark blue squares, light blue diamonds, and black crosses correspond to the present work for radical decay in reactor a, radical decay in reactor b, or closed shell product analysis, respectively; purple diamonds, Russell et al.;[3] pink triangle, Richards et al.;[4] orange triangles, Nicovich et al.;[5] red circles, Seakins et al.;[7] dark green diamonds, Seetula and Slagle;[8] brown diamonds, Seakins and Pilling;[6] light green circles, Müller-Markgraf et al.[11]

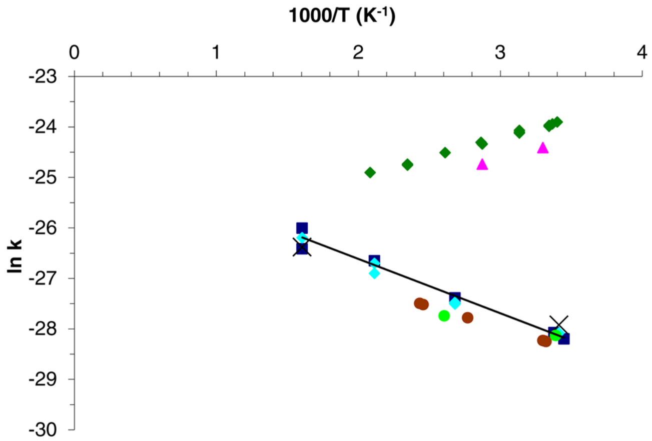

Figure 4. Arrhenius plot (solid line) of current data in comparison with previously published results for k_2 (t-$C_4H_9^\bullet$ + HI → i-C_4H_{10} + $I^\bullet$) under the experimental conditions presented in Table 5 (experimental uncertainties of individual data points). Dark blue squares, light blue diamonds, and black crosses correspond to the present work for radical decay in reactor a, radical decay in reactor b, or closed shell product analysis, respectively; pink triangles, Richards et al.;[4] brown circles, Rossi and Golden;[9] dark green diamonds, Seetula et al.;[10] light green circles, Müller-Markgraf et al.[11]

The two sets of measurements exhibit linearity in the Arrhenius plot for both studied reactions and may be correlated to the following Arrhenius expressions:

$$k_1 = 5.6(\pm 1.4) \times 10^{-12} \exp(-6.76(\pm 0.94)/(RT)) \qquad (16)$$

$$k_2 = 2.0(\pm 0.6) \times 10^{-11} \exp(-8.48(\pm 0.94)/(RT)) \qquad (17)$$

where the units are cm^3 molecule^{-1} s^{-1} for preexponential factors and kJ mol^{-1} for the activation energies with $R = 8.314$ J mol^{-1} K^{-1}. The uncertainties reported in the two Arrhenius expressions were obtained from a 2σ statistical evaluation of the random errors, enabling the determination of the standard deviation associated with the slope and intercept of the linear Arrhenius plot.

These Arrhenius expressions clearly indicate that the two reactions of interest are occurring with a rather low rate constant associated with a positive temperature dependence when the present experimental apparatus was used. This is obviously in distinct contrast with most of the previous determinations, which are also shown in Figures 3 and 4.[3−5,7,8,10] Indeed, the high rate constants and negative activation energies obtained in studies in which the free radical was generated by highly energetic photolysis of a suitable precursor at 193, 248, or 266 nm are not obtained in the present case. However, for the reaction with HI, the present results are in rather good agreement with the previous measurements performed by Rossi and Golden,[9] as well as Müller-Markgraf et al.,[11] both in terms of the absolute rate

Table 6. Thermochemical Parameters of *t*-Butyl Free Radical from $t\text{-}C_4H_9^\bullet + HX \leftrightarrows i\text{-}C_4H_{10} + X^\bullet$ Equilibria Using k_1 and k_2 from This Work and k_{-1} and k_{-2} from Work of Listed Authors[a]

		Second Law		Third Law[b]	
authors for k_{-i}	T range for k_{-i} (K)	$\Delta_f H^\circ_{298}$	S°_{298}	$\Delta_f H^\circ_{298}$ (K_i at T_m)[c]	$\Delta_f H^\circ_{298}$ (K_i at 298 K)[d]
		$i\text{-}C_4H_{10} + Br^\bullet$			
Fettis et al.[42]	423−483	38.8 ± 1.2	286 ± 0.8	53.2 ± 2.0	48.0 ± 1.9
Islam and Benson[43]	295−305	30.6 ± 2.7	311 ± 0.5	33.9 ± 1.7	33.9 ± 1.6
Choo and Choe[44]	299−328	35.3 ± 0.9	292 ± 0.5	44.6 ± 1.7	44.2 ± 1.5
Benson et al.[14]	298−363	34.2 ± 2.7	288 ± 2.0	45.2 ± 1.7	44.1 ± 1.7
Russell et al.[3]	298−478	35.4 ± 1.2	301 ± 0.6	42.9 ± 1.9	41.1 ± 1.9
Seakins et al.[7]	423−621	37.1 ± 1.7	299 ± 1.1	45.9 ± 2.2	41.5 ± 2.0
average		**35.2 ± 3.5**	**296 ± 11.6**	**44.3 ± 7.7**	**42.1 ± 5.9**
		$i\text{-}C_4H_{10} + I^\bullet$			
Teranishi and Benson[17]	525−583	29.8 ± 8.0	285 ± 1.4	44.9 ± 3.6	38.1 ± 2.9
Knox and Musgrave[18]	503−618	34.0 ± 8.3	293 ± 2.9	44.8 ± 6.1	39.9 ± 4.7
Bracey and Walsh[15e]	573−614	36.6 ± 2.3	299 ± 2.5	41.7 ± 2.8	43.6 ± 3.5
average		**31.1**	**288.8**	**44.8**	**39.0**
total average		**34.4 ± 2.7**	**294 ± 7.9**	**44.4 ± 4.7**	**41.3 ± 3.8**

[a] Units of $\Delta_f H^\circ_{298}$ in kJ mol^{-1} and S°_{298} in J K^{-1} mol^{-1}. [b] Thermochemical quantities for other products and reactants, including S°_{298} of $t\text{-}C_4H_9^\bullet$ = 322.2 J K^{-1} mol^{-1} for the "Third Law" calculations, are based on data from the Millennium database.[37] From the listed maximum least-squares error of $C_p(t\text{-}C_4H_9^\bullet)$ of 0.64% at 1300 K, we obtain an uncertainty in S°_{298} of $t\text{-}C_4H_9^\bullet$ of ±2.1 J K^{-1} mol^{-1} assuming that the error in C_p is independent of temperature. [c] Calculation based on the equilibrium constant K_i at the mean temperature (T_m) using the measured inverse reaction rate constant, k_{-i}. T_m is the algebraic (unweighted) average over the given temperature range. [d] Calculation based on the equilibrium constant K_i at 298 K using the extrapolated rate constant k_{-1} or k_{-2}. [e] The thermochemical parameters obtained by using k_{-2} of Bracey and Walsh (ref 15) have not been used to establish the displayed average for $\Delta_f H^\circ(t\text{-}C_4H_9^\bullet)$ at 300 K.

constant and its temperature dependence. This precursor study also used photolytic generation of the free radical albeit using less energetic photons (351 nm). These authors even added a caveat at the end of the more recent publication regarding the use of 248 nm radiation when an azo precursor of *t*-butyl free radical was used.[11] The study performed by Rossi and Golden[9] presents another important common feature with the present work, namely, the use of a Knudsen flow reactor in contrast to the flow tube reactors used in most other investigations. The good agreement between the current data set and the results of Rossi and Golden[9] and Müller-Markgraf et al.[11] displayed in Figure 4, the latter after correction of k_i for the measured primary H/D isotope effect, does perhaps not come as a surprise in view of the similar experimental technique used in both investigations.

It is well-known that the Knudsen reactor is a system characterized by many "hard" collisions of the molecules with the vessel wall, as is the case here, at collision frequencies of ω (s^{-1}) = $4386(T/M)^{1/2}$ and ω (s^{-1}) = $3509(T/M)^{1/2}$ in reactors a and b, respectively. This may ensure efficient removal of any potential excess internal energy in the $t\text{-}C_4H_9^\bullet$ free radical before reaction with HX. The thermalization by numerous wall collisions achieved in such a reactor is in distinct contrast to collisions with weak colliders such as He and N_2 used as bath gases in flow reactors used in other studies.[3−5,7,8,10] Regarding the role of collisions, it is interesting to note that the study performed by Richards et al.,[4] in which the hard collider SF_6 was used at a significant partial pressure in the buffer gas mixture leads to a lower rate constant among the photolytic studies conducted in tubular reactors. This observation may be interpreted as an indication that the thermalization of the radical is a key feature in such a kinetic study. By the same token, the two high temperature experiments of Seakins and Pilling[6] addressing the generation of *t*-butyl free radical using H-abstraction by atomic bromine may not be comparable to their ambient temperature experiments where *t*-butyl radical was generated through photolysis of azoisobutane at 351 nm. The two high-temperature rate constants have a positive temperature dependence (Figure 2 in ref 6; see also Figure 3) akin to our present results. In the analysis of Seakins and Pilling, all kinetic data are treated using a common Arrhenius line and result in a significant negative temperature dependence by virtue of the large value of k_1 at ambient temperature. Future work will reveal whether there are systematic errors not accounted for when comparing two sets of rate constants obtained from very different experimental techniques. It may be speculated that a potential excess of internal energy in the free radical may significantly affect the absolute value of the obtained rate constant in cases characterized by a low reaction barrier.

However, as mentioned in our previous papers[1,2] that showed similar discrepancies for identical H-transfer reactions involving ethyl and propyl radicals, an unambiguous explanation about the origin of this disagreement cannot be proposed with certainty at this point. We can only underline our confidence in our results owing to the major improvement brought about by resorting to an advanced experimental technique, mainly the external and "soft" chemical generation of the free radicals used in the present case. Moreover, the current study is the only one that investigated the effect of the HX addition on both the radical and the closed shell products, which clearly leads to consistent results.

Thermochemical Consequences for $t\text{-}C_4H_9^\bullet$ Free Radical. The present Arrhenius parameters may be used with those previously published for the inverse reactions to perform thermochemical calculations. Two methods may be used in this regard that enable the calculation of the enthalpy of reaction, from which the $t\text{-}C_4H_9^\bullet$ standard enthalpy of formation may be derived if this parameter is known for the other chemical compounds involved in the reaction. The first is called the "Second Law" method and uses the difference between the activation energy (E_a) of the forward and reverse reaction in order to obtain the enthalpy of the reaction:

$$\Delta_r H^\circ_{298} = E_{a,i} - E_{a,-i} - \int_{298}^{T_m} \left(\sum C_{p,prod} - \sum C_{p,react}\right) dT \tag{18}$$

where T_m is the mean temperature of the smallest investigated temperature range corresponding to the inverse reaction (k_{-1} and k_{-2}) in the present case. This "Second Law" method also enables the determination of the entropy of reaction from the ratio between the two preexponential terms according to

$$\Delta_r S_{298} = R \ln\left(\frac{A_i}{A_{-i}}\right) - \int_{298}^{T_m} \frac{\left(\sum C_{p,prod} - \sum C_{p,react}\right)}{T} dT \tag{19}$$

The alternative treatment, named "Third Law" method, enables the calculation of the enthalpy of reaction at a given temperature (T) from the rate constants measured in both directions and thus from the equilibrium constant $K_{eq} = k_i/k_{-i}$ at some temperature T_m:

$$\Delta_r H^\circ_{298} = T\left(\Delta S^\circ_r - R \ln \frac{k_i}{k_{-i}}\right) - \int_{298}^{T} \left(\sum C_{p,prod} - \sum C_{p,react}\right) dT \tag{20}$$

This second method requires knowledge of the entropy of reaction, ΔS°_r, either from a measurement or from an *a priori* estimate or guess. Both methods obtain the thermochemical quantities at a given temperature (T_m or T) and must be corrected to 298 K for the calculation of the standard thermochemical parameters by using the known heat capacities of each chemical compound. From the so obtained enthalpy of reaction, the t-$C_4H_9^\bullet$ enthalpy of formation is calculated by using known enthalpies of formation for the other chemical species:

$$\Delta_f H^\circ_{298}(\text{t-}C_4H_9) = -\Delta_r H^\circ_{298} - \Delta_f H^\circ_{298}(HX) + \Delta_f H^\circ_{298}(X) + \Delta_f H^\circ_{298}(\text{i-}C_4H_{10}) \tag{21}$$

For the calculations presented below, all required thermochemical parameters except for *t*-butyl free radical were taken from the Millennium database.[41] Table 6 presents the results of "Second Law" and "Third Law" calculations using all available measurements for the kinetics of the inverse reaction, which are referred to in the first column of Table 6. Two "Third Law" treatments were performed, the first at T_m, the mean temperature of the investigated ranges for the inverse reaction that are listed in second column of Table 6, and the second at 298 K. The results presented in Table 6 show that a general agreement between all of these evaluations cannot be obtained within reasonable uncertainty limits. The "Second Law" treatment often leads to smaller values of $\Delta_f H^\circ_{298}(\text{t-}C_4H_9^\bullet)$ compared with the "Third Law" method for reasons that are well and widely known. One exception is the work of Seakins et al.,[7] which leads to perfect agreement of the thermochemical parameters obtained using the "Second Law" and "Third Law" methods. These authors apparently have managed a flawless separation of the reaction entropy from enthalpy from the temperature dependence of the equilibrium constant $K = k_{-1}/k_1$, which leads to identical values of the thermochemical parameters as mentioned in footnote d of Table 1. An open but perhaps a minor problem is the apparent disagreement between the "Second Law" entropy S°_{298} = 314 ± 6 kJ mol^{-1} K^{-1} mentioned in footnotes c, d, and f of Table 1, which agrees with both measurement and numerical calculation of the structure of *t*-butyl free radical,[12,13] and the value from the Millennium database of $S^\circ(298)$ = 322.2 ± 2.1 kJ mol^{-1} K^{-1}[41] (footnote b of Table 6). In the present work, we have preferred to use the value given in the Millennium database in order to use heat capacities (C_p) that are consistent with the absolute entropy of *t*-butyl. It seems, however, that the uncertainty limits of $S^\circ_{298}(\text{t-}C_4H_9^\bullet)$ may be unduly optimistic in this case.

Following the approach taken in our recent publications,[1,2] our preferred value for $\Delta_f H^\circ_{298}(\text{t-}C_4H_9^\bullet)$ will be based on the results obtained by the "Third Law" method at T_m. The "Second Law" calculations are discarded because the reliability of the results obtained using this method greatly depends on the accuracy of the measured activation energies. The accuracy of these parameters will essentially depend on the size of the investigated temperature ranges, more specifically, the $1/T$ ranges. These ranges are often quite narrow for the inverse reaction k_{-i} as listed in the second column of Table 6. Therefore, it may be assumed that in most cases, the activation energies are more uncertain than the rate constants measured within a given temperature range, which leads us to prefer the "Third Law" approach. Another reason to reject the "Second Law" approach, is that the resulting entropy is inconsistent with commonly accepted values for this thermochemical parameter, such as $S^\circ_{298}(\text{t-}C_4H_9^\bullet)$ = 322.2 ± 2.1 J K^{-1} mol^{-1} listed in the Millennium database, which seems to be agreed upon by many.[41]

Between the two "Third Law" calculations displayed in Table 6, the one performed at T_m is preferred over the one at 298 K, because the extrapolation of the rate constants k_{-i} using the measured Arrhenius parameters from T_m down to ambient temperature is fraught with larger uncertainties (see above) than the extrapolation of the equilibrium constant K_i from T_m to 298 K. The reader is reminded of the limited accuracy of the Arrhenius parameters of the inverse reaction (k_{-1}) owing to a rather restricted temperature range in most cases over which k_{-1} could be measured owing to a substantial activation energy for k_{-1} in the case of iodination. Therefore, it seemed more suitable to perform the thermochemical calculations by using the rate constants obtained at high temperatures (T_m), and to subsequently apply the correction down to 298 K by using the well-accepted and tabulated heat capacities of the involved chemical compounds including the free radical in question listed in the Millennium database.[41]

A further argument for the justification of a "Third Law" recommendation of a result obtained at T_m may be the agreement between the evaluation of the bromination and iodination system as has been commented on several times.[10,19] The preferred value is therefore $\Delta_f H^\circ_{298}(\text{t-}C_4H_9^\bullet)$ = 44.3 ± 1.7 kJ mol^{-1}, which is the average value among all "Third Law" evaluations at T_m with the exception of the two older bromination studies.[42,43] Both studies seem to be outliers whose results for $\Delta_f H^\circ_{298}(\text{t-}C_4H_9^\bullet)$ are symmetrically located around the average value. In any case, its inclusion in the global average does not significantly affect the preferred value but rather extends its uncertainty limits. Fettis et al.[42] overestimate the standard enthalpy of *t*-butyl free radical by approximately 10 kJ mol^{-1}, whereas Islam and Benson[43] underestimate it by the same amount. This latter work has been superseded by a more recent study[14] because of the significant lifetime of the upper spin state of Br ($^2P_{1/2}$) in the VLPR system.[45] This excited state of atomic bromine lies 3685.4 cm^{-1} over its ground state ($Br(^2P_{3/2})$)[46] and is generated together with its ground state in the microwave discharge of a dilute Br_2/He mixture. The preferred value displayed in Table 6 is notably in perfect agreement with some previous experimental determinations, such as $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet)$ = 45.1 kJ mol^{-1} recommended by Benson et al.[14] and $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet)$ = 44.2 ± 4.0 or 48.1 ± 4.0 kJ mol^{-1} reported by Seakins and Pilling[6] (see also Table 1, as well as Figure 3, for the kinetic results), both studies dealing with experiments involving the equilibrium $Br^\bullet + i\text{-}C_4H_{10} \leftrightarrows HBr + t\text{-}C_4H_9^\bullet$. $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet)$ = 45.6 ± 3.0 and 47.7 ± 3.0 kJ mol^{-1} obtained by Tsang[23,24] from data involving the equilibrium $(t\text{-}C_4H_9)_2 \leftrightarrows 2\ t\text{-}C_4H_9^\bullet$ and $t\text{-}C_4H_9^\bullet \leftrightarrows C_4H_8^\bullet + H$, respectively, also strongly support the present results. The *ab initio* CBS-4 calculations published by Marsi et al.[29] leading to $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet)$ = 44.8 kJ mol^{-1} is also in perfect agreement with the present results when the empirical correction *post factum* is dropped. However, we are aware that the preferred value supported by the present measurements is a few kJ mol^{-1} smaller than some other preferred experimental and theoretical thermochemical parameters as alluded to in the Introduction. It seems that the present results lie at the lower end of the consensus range proposed by W. Tsang,[24] namely, $\Delta_f H^\circ_{298}(t\text{-}C_4H_9^\bullet)$ = 48.0 ± 3.0 kJ mol^{-1} under conditions where both uncertainties overlap. The same may be said for the proponents of the "high" values of the thermochemical parameters for t-butyl free radical: their uncertainty range certainly overlaps Tsang's, and their preferred value is located at the upper end of Tsang's consensus value. However, we would like to stress that this is the first time the halogenation method leads to values as close as they are to the consensus value in terms of overlapping uncertainties across the time history of thermochemical studies.

In retrospect, we have embarked on a program to reinvestigate a couple of fast halogenation reactions, namely, reactions 1 and 2 that have been disputed over the years and for which a consensus on a high value of the rate constant k_1 and k_2 as well as a negative energy of activation seems to have been firmly established. On the other hand, a serious reinvestigation using a different experimental setup has been performed of which the present paper is a part. The disagreement first and foremost concerns the kinetics, much less so the thermochemical consequences, of $\Delta_f H^\circ_{298}$ $(t\text{-}C_4H_9^\bullet)$, the change of which may be regarded as modest for reasons mentioned above.

Obviously, a specific reason for this profound disagreement between the two sets of the halogenation kinetics cannot be given at this time. We first will restrict ourselves to point out areas that apparently do not constitute the likely cause of the problem. In both "camps", kinetic experiments have been performed on both the disappearance of the *t*-butyl free radical and the appearance of products, either atomic bromine, isobutene, or the change in the closed-shell products upon HBr or HI addition as performed in this work. Therefore, the kinetics seems confirmed from a mass balance point of view owing to consistent results. The obvious difference between both camps arise apparently in the manner in which the free radicals are generated and the collisional environment: The group observing fast kinetics exclusively generates the radicals using UV-laser photolysis at pressures of He or N_2 ranging into the hundred millibar regime except for two experiments in which the free radical was generated through H-abstraction from a hydrocarbon precursor by atomic chlorine.[5]

Two areas need to be addressed more closely in future experiments designed to shed light on this profound disagreement: (a) The role and nature of the "loss" processes needed to describe either the real-time decay of the free radical[3,7,8,10] or the accumulation of the atomic Br product.[5] In the first case (molecular beam sampling), we have significant first-order losses in excess of 50 s^{-1}; in the second type of experiments (optical detection using resonance fluorescence), we have diffusion out of the viewing region on the order of 25 s^{-1}.[5] It is clear that radical loss rate constants on the order encountered in Knudsen flow reactors ($k_w < 1\ s^{-1}$) cannot be measured in laminar flow tube and slow-flow optical experiments. At this point, we have to strongly oppose an attempted "explanation" for the shortcomings of the Knudsen flow reactor experiments in terms of the magnitude of k_w.[10,19] Owing to the influence of wall-deactivation processes of free radicals at low pressure conditions all Knudsen flow reactor studies have been conducted under strict inclusion of wall effects of the radical (k_w), which means that redundant experiments have been systematically performed in order to separate k_i from k_w, without exception. This is standard procedure in the application of a method where molecules and radicals predominantly undergo wall collisions except for the fastest gas-phase reactions such as radical−radical recombination and disproportionation. (b) Although the buffer gas pressures in UV-laser photolytic experiments range from a few Torr of He up to 300 Torr of N_2, it would be desirable to learn more about the details of vibrational cooling and energy transfer, especially the seemingly rate-controlling V−T energy transfer at low levels of internal energy as well as its temperature dependence[47] in hydrocarbon free radicals other than methyl free radical. Methyl free radical energy transfer and deexcitation have been investigated as far as its VUV absorption at 216 nm is concerned, but nothing is known about the sensitivity of detection at low internal energies of polyatomic free radicals. It would be beneficial to learn more about low-level energy transfer in complex hydrocarbon free radicals in order to enable the solution of this experimental conundrum or at the very least eliminate a potential problem. In parallel, theoretical methods have to be investigated thoroughly as to their robustness regarding the chemical kinetic significance of stable complexes of the type $HX\cdot R^\bullet$.

■ CONCLUSIONS

The kinetics of the reactions $t\text{-}C_4H_9^\bullet + HBr \rightarrow i\text{-}C_4H_{10} + Br^\bullet$ (1) and $t\text{-}C_4H_9^\bullet + HI \rightarrow i\text{-}C_4H_{10} + I^\bullet$ (2) were reinvestigated by using a newly developed apparatus. This enabled a novel generation of the $t\text{-}C_4H_9^\bullet$ radical by soft chemical reaction in an ancillary flow reactor upstream of the Knudsen flow reactor, which constitutes a major improvement in comparison to past experimental techniques. The treatment of the obtained experimental data enabled the verification that the chemical mechanism takes into account all reactions occurring in the reactor thanks to a suitable mass balance check involving both the decay of the $t\text{-}C_4H_9^\bullet$ free radical and the accumulation of the closed shell products isobutylene, isobutane, and hexamethylethane generated in reactions of the t-butyl free radical with either HBr or HI or by recombination and disproportionation. The obtained rate parameters led to low absolute values of the rate constants associated with a positive temperature dependence for both HBr and HI reactions, as well as to low but expected wall loss rate constants for *t*-butyl free radical. The results may be expressed in the following Arrhenius expressions: $k_1 = 5.6(\pm1.4) \times 10^{-12} \exp(-6.76(\pm0.94)/(RT))$; $k_2 = 2.0(\pm0.6) \times 10^{-11} \exp(-8.48(\pm0.94)/(RT))$. These new kinetic results enabled a thermochemical evaluation of the standard enthalpy of formation of *t*-butyl free radical based on the "Third Law" approach, which led to the following preferred value: $\Delta_f H^\circ_{298}$(t-$C_4H_9^\bullet$) = 44.3 ± 1.7 kJ mol^{-1} using S°_{298}(t-$C_4H_9^\bullet$) = 322.2 J K^{-1} mol^{-1}. In view of the tenacious and persistent disagreement with the results of some other experiments resulting in very different chemical kinetics, we forego at this time a recommended value in favor of a preferred value of $\Delta_f H^\circ_{298}$(t-$C_4H_9^\bullet$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental conditions for reactions 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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