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# Laser-Induced Kinetics: Arrhenius Parameters for $t\text{-C}_4\text{H}_9 + \text{XI} \rightarrow i\text{-C}_4\text{H}_9\text{X} + \text{I}$ ( $\text{X} = \text{H}, \text{D}$ ) and the Heat of Formation of the $t$ -Butyl Radical

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## Abstract

The metathesis reaction of DI with  $t\text{-C}_4\text{H}_9$  generated by 351-nm photolysis of 2,2'-azoisopropane was studied in a low-pressure reactor (VLPΦ Knudsen cell) in the temperature range of 302–411 K. The data obeyed the following Arrhenius relation when combined with recent data by Rossi and Golden gathered by the same technique ( $t\text{-C}_4\text{H}_9$  by thermal decomposition of 2,2'-azoisobutane):  $\log k_2^{\text{D}}(M^{-1}\text{s}^{-1}) = 9.60 - 1.90/\theta$ , where  $\theta = 2.303RT$  kcal/mol for  $302 \text{ K} < T < 722 \text{ K}$ . The metathesis reaction of HI with  $t\text{-C}_4\text{H}_9$  was studied at 301 K and resulted in  $k_2^{\text{H}}(M^{-1}\text{s}^{-1}) = (3.20 \pm 0.62) \times 10^8$ . An analogous Arrhenius relation was calculated for the protiated system if the small primary isotope effect  $k_2^{\text{H}}/k_2^{\text{D}}$  was assumed to be  $\sqrt{2}$  at 700 K. It was of the following form:  $\log k_2^{\text{H}}(M^{-1}\text{s}^{-1}) = 9.73 - 1.68/\theta$ .

Preliminary data of Bracey and Walsh indicate that earlier Arrhenius parameters determined for the reverse reaction are somewhat in error. Their value of  $\log k_1(M^{-1}\text{s}^{-1}) = 11.5 - 23.8/\theta$  yields  $\Delta H_{f,300}^0(t\text{-butyl}) = 9.2$  kcal/mol and  $S_{300}^0(t\text{-butyl}) = 74.2$  cal/mol·K when taken in conjunction with this study.

## Introduction

The values of the thermochemical parameters of the prototypical  $t$ -butyl radical ( $t\text{-C}_4\text{H}_9$ ) are still an unsettled question despite the efforts of many laboratories trying to find definitive answers. The emphasis on the heat of formation  $\Delta H_{f,298}^0$  and the standard entropy  $S_{298}^0$  of the  $t$ -butyl radical stems from the fact that, besides its pivotal role in many areas of physical chemistry, the stated discrepancies between the various experimental results are the most pronounced compared to the other prototypical hydrocarbon radicals. In general one cannot average the set of parameters for  $t$ -butyl in isolation without affecting the ones for the other prototypical hydrocarbon radicals ( $i$ -propyl,  $n$ -propyl, ethyl, and methyl). In the interest of brevity and due to the recent publication of a review article highlighting the  $t$ -butyl controversy [1], we present the bare essentials of the previous conflicting evidence regarding the values for  $\Delta H_{f,298}^0(t\text{-C}_4\text{H}_9)$

and  $S_{298}^0(t\text{-C}_4\text{H}_9)$  in order to put the present work into proper perspective.

"High" values, that is,  $\Delta H_{f,298}^0(t\text{-C}_4\text{H}_9)$  ranging from 10.5 to 12.0 kcal/mol, are the result of bond scission studies which obtain the Arrhenius parameters for the bond scission of hexamethylethane over some temperature range [2-4]. The thermochemical parameters are then extracted by computing the equilibrium constant using the recombination rate constant (suitably extrapolated a small amount to the measurement temperature [5,6]) and an appropriate value for the standard entropy  $S_{298}^0(t\text{-C}_4\text{H}_9)$  which has been recently determined from matrix isolation spectra for  $t\text{-C}_4\text{H}_9$  [7]. It is seen that this method amounts to a third-law determination of  $\Delta H_f^0(t\text{-C}_4\text{H}_9)$  subject to the entropy choice. A "low" value for  $\Delta H_{f,298}^0(t\text{-C}_4\text{H}_9)$  of  $8.5 \pm 1$  kcal/mol has been quoted as the result of iodination kinetics [8].

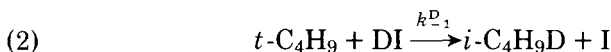
Many bond strengths of organic molecules have been determined using the iodination technique [8] where the Arrhenius parameters of  $k_1$  were measured:



Together with *estimated* Arrhenius parameters for the reverse reaction  $k_{-1}$ , this method yielded both  $\Delta H_1^0$  and  $\Delta S_1^0$  (second-law determination), and therefore  $\Delta H_{f,298}^0(t\text{-C}_4\text{H}_9)$  and  $S_{298}^0(t\text{-C}_4\text{H}_9)$  in view of the known thermochemistry of RH, I, and HI.

As a means of investigating the possible causes of the discrepancy between high and low values of  $\Delta H_{f,298}^0(t\text{-C}_4\text{H}_9)$  we embarked on a program to test the estimated Arrhenius parameters for reaction (-1) by measuring this fast metathetical reaction using our low-pressure photolysis technique.

Some time ago we reported Arrhenius parameters for reaction (-1) over a limited temperature range (644-722 K) [9]. When the



rate at 700 K (corrected for the small isotope effect) was combined with the extrapolated value of  $k_1$  [10], we obtained  $\Delta H_{f,298}^0(t\text{-C}_4\text{H}_9) = 8.4 \pm 1.0$  kcal/mol using a third-law entropy of  $S_{298}^0(t\text{-C}_4\text{H}_9) = 72.2$  eu (a value which now seems too low in light of a recent experimental study by Pacansky and Chang [7]). When the Arrhenius parameters for reaction (-1) (corrected for the isotope effect) were combined in a second-law evaluation with the corresponding parameters for the forward reaction [10], even lower values of 7.2 kcal/mol and 70.6 eu for  $\Delta H_{f,298}^0(t\text{-C}_4\text{H}_9)$  and  $S_{298}^0(t\text{-C}_4\text{H}_9)$  resulted.

The high heat of formation of the  $t$ -butyl radical has the interesting

implication of a negative activation energy ( $-1$  to  $-4$  kcal/mol) for reaction ( $-1$ ) on the basis of the measured activation energy of 21.4 [10] or 22.6 kcal/mol [11] for reaction (1) ( $R = i\text{-C}_4\text{H}_{10}$ ). We pointed out earlier [9] that negative activation energies for metathetical reactions were without precedent and that the  $A$  factor derived for the measured rate constant at 700 K was too low by one to one and one-half orders of magnitude in comparison with measured  $A$  factors for similar reactions. There are only two ways out of this dilemma: either the activation energy of [10] or of [11] is too low by 2–3 kcal/mol, or the low heat of formation of 8.4 kcal/mol for the *t*-butyl radical is correct.

In this paper we are reporting the kinetics of reaction ( $-1$ ) at room temperature and at some higher temperatures in order to obtain Arrhenius parameters over a wide range of temperatures (300–744 K) in conjunction with our earlier work. The results enable us to comment on the issue of a negative activation energy for the metathesis reaction ( $-1$ ) and on a second-law value for  $\Delta H_{f,298}^0(t\text{-C}_4\text{H}_9)$  if we accept the Arrhenius parameters for reaction (1) ( $RH = i\text{-C}_4\text{H}_{10}$ ) put forward in [10,11].

Since the completion of this work we have been apprised of preliminary work by Bracey and Walsh [12] who have restudied the temperature dependence of  $k_1$ . Their values [ $\log k_1(M^{-1}\cdot s^{-1}) = 11.6 - 23.8/\theta$ ] ease the problem somewhat.

## Experimental

The basic very-low-pressure-pyrolysis (VLPP) method [13] was modified to accommodate photochemical activation. This method has been called very-low-pressure photolysis (VLP $\Phi$ ), and the design of the flow system has been described in a recent review article [14].

In short, the precursor gases are mixed in a low-pressure Knudsen cell that is equipped with an irradiation section. Even at the highest flow rates of the titrant (DI or HI) Knudsen flow conditions were maintained in the VLP $\Phi$  cell so that mixing was complete and rapid compared with the escape out of the reaction vessel and the chemical reaction of interest. The gases are formed into an effusive molecular beam leaving the Knudsen cell. The effusive molecular beam passes two differentially pumped vacuum chambers before it penetrates into the ion source of a quadrupole mass spectrometer (Balzers QMG 311). The beam is chopped by a tuning fork (150 Hz), and the modulated portion of the total ion current is recovered in a lock-in amplifier (PAR 128 A) and converted into a dc current which is transformed into a voltage signal by a preamplifier (Balzers QME 301). Two different Knudsen cells made of Pyrex glass were used in the course of this work. Reaction vessel 1 (130-cm<sup>3</sup> volume) was halocarbon-wax coated and had the following escape rate constants  $k_e$  for a gas of molecular weight  $M$  at temperature  $T$ :  $k_e^S = 0.512 \times (T/M)^{1/2} \text{ s}^{-1}$  and  $k_e^B = 2.81 \times$

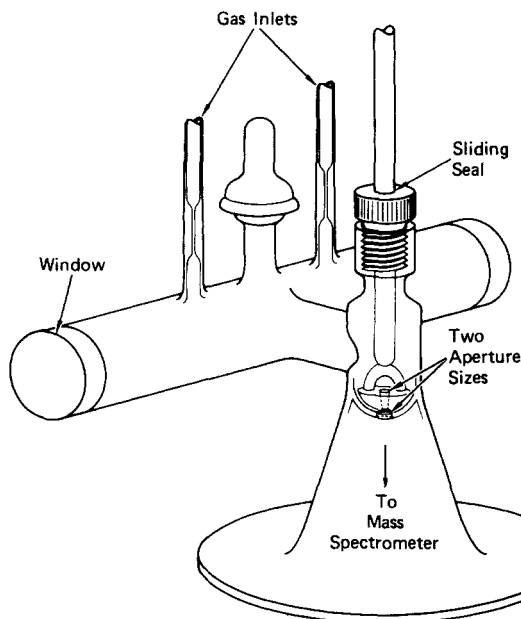


Figure 1. Dual-aperture low-pressure photolysis cell (Pyrex) with 20-cm-long and 1-in.-diameter irradiation section.

$(T/M)^{1/2} \text{ s}^{-1}$ , where  $S$  and  $B$  represent the small and large orifices. Reaction vessel 2 had a volume of  $105 \text{ cm}^3$ , and was uncoated (Pyrex walls), and had the following escape rate constants:  $k_e^S = 0.832 \times (T/M)^{1/2} \text{ s}^{-1}$  and  $k_e^B = 3.381 \times (T/M)^{1/2} \text{ s}^{-1}$ . Both reaction vessels were calibrated by determining the static pressure inside the reactor by means of an absolute pressure gauge (Baratron HA 227-A-1) as a function of the flow rate of  $i\text{-C}_4\text{H}_{10}$ . The flow rates were determined by measuring the pressure drop as a function of time by means of a calibrated pressure transducer (Validyne DP 15).

The irradiation section (20 cm long, 2.54 cm wide) of the Knudsen cell (Fig. 1) was fitted with two Viton O-ring-sealed Suprasil windows (2 mm thick and 2 in. in diameter, Heraeus Amersil). Reaction vessel 2 was wrapped with a four-wire heating tape and insulated with glass wool. The temperature was measured at three different locations on the outside of the reaction vessel by means of a chromel-alumel thermocouple. Temperatures up to  $220^\circ\text{C}$  were achieved with reasonable uniformity ( $10^\circ\text{C}$  spread at the highest temperature). However, the temperature of the Suprasil windows could not be measured in the present setup, and assumption of thermal equilibration was made.

The rate constants for the title reaction obtained in the two different reaction vessels were identical to within 10% of each other. It was con-

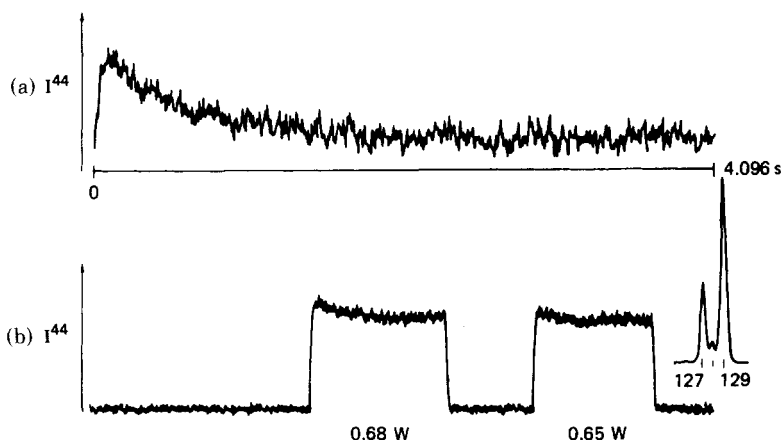
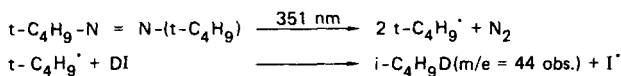


Figure 2. Mass spectrometric traces at  $m/e = 44$  ( $i\text{-C}_4\text{H}_9\text{D}$ ) in the presence of DI. (a) Pulsed mode ( $0.25\text{ s}^{-1}$  pulse repetition rate and averaged for 300 pulses). (b) Continuous mode ( $40\text{ s}^{-1}$ ) of the 351-nm photolysis of 2,2'-azoisobutane ( $F_{\text{azo}}^i = 3.25 \times 10^{15}$  molecules/s). The time scale in (b) is of the order of 10 min and the mass spectrum in the lower right corner represents the HI/DI ratio at  $F^i = 9.4 \times 10^{15}$  molecules/s.

cluded (see below) that wall reactions were not important under our reaction conditions.

The precursor of  $t\text{-C}_4\text{H}_9$ , 2,2'-azoisobutane, was photolyzed by a high-power rare-gas halide excimer laser (Lambda Physik EMG101) delivering between 100 and 120 mJ per pulse at 351 nm using a Xe-F<sub>2</sub>-He gas mixture.

The pulse repetition rate of the laser was either very low ( $0.25\text{ s}^{-1}$ ) so that after each uv pulse the reaction products would leave the reaction cell and the next uv pulse would irradiate a fresh sample [Fig. 2(a)], or high ( $10\text{--}50\text{ s}^{-1}$ ) in order to produce a steady-state concentration of  $t$ -butyl radicals and therefore a steady-state concentration of all reaction products [Fig. 2(b)]. All the reaction rate constants were obtained using the steady-state irradiation mode because of the higher duty cycle and shorter signal acquisition times. A 1.0-m focal length quartz lens was positioned at 25 cm from the output coupler of the excimer laser, such that the beam waist was positioned in the middle of the irradiation tube of the Knudsen cell. The beam had to be steered into the reaction vessel by means of two Suprasil 90° prisms, and the irradiated area measured at the cell entrance window was a rectangle of 2.2 cm by 6 mm ( $1.32\text{ cm}^2$ ). After passage through the cell, the beam entered a power meter (Scientech 362, surface absorber) after

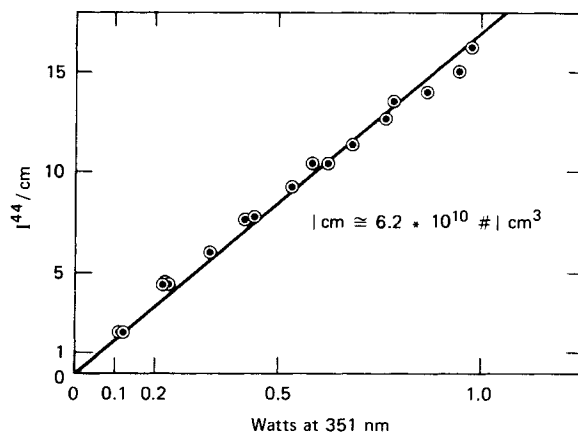


Figure 3. Plot of the mass spectrometric signal at  $m/e = 44$  ( $i\text{-C}_4\text{H}_9\text{D}$ ) upon 351-nm irradiation of 2,2'-azoisobutane ( $F_{\text{azo}}^i = 3.14 \times 10^{15}$  molecules/s) in the presence of DI ( $F^i = 6.1 \times 10^{15}$  molecules/s) as a function of transmitted power. The ordinate has been corrected for 100% titration of  $t\text{-C}_4\text{H}_9$ , and the calibration was established using an authentic sample of  $i\text{-C}_4\text{H}_{10}$  at  $m/e = 43$ , assuming equal mass spectral sensitivities at  $m/e = 43$  and 44 for  $i\text{-C}_4\text{H}_{10}$  and  $i\text{-C}_4\text{H}_9\text{D}$ , respectively.

reflection off a front surface aluminum mirror. The actual measurement was performed by monitoring the steady-state mass spectrometric signal due to  $i\text{-C}_4\text{H}_9\text{D}$  at  $m/e = 44$  ( $i\text{-C}_4\text{H}_{10}$  at  $m/e = 43$ ) as a function of the flow rate of DI (HI) at a constant pulse repetition rate of the 351 nm radiation (10–50 Hz). The transmitted power was monitored simultaneously on the power meter, and all the runs were normalized for constant transmitted power. 2,2'-Azoisobutane (Polysciences, Inc.) was the precursor for  $t$ -butyl radicals and was purified by trap-to-trap distillation. Mass spectrometric analysis of the radical precursor in the flowing system revealed no impurities at a level higher than 2% of 2,2'-azoisobutane. Deuterium iodide (99 atom-%, Merck, Sharp, and Dohme, Ltd., Canada) and hydrogen iodide (Matheson) were used without further purification.

## RESULTS

$t$ -Butyl radicals ( $t\text{-C}_4\text{H}_9$ ) were generated through photolysis of 2,2'-azoisobutane at 351 nm. This frequency was chosen in order to avoid secondary photolysis of the primary photoproduct  $t\text{-C}_4\text{H}_9$  which has been found devoid of any significant absorption above 280 nm [5]. Notably irradiation at 248 nm would generate a much higher concentration of  $t$ -butyl radicals, but probably would also cause significant photochemical decomposition of the  $t$ -butyl radical even in view of the large difference in the absorption coefficient for the azo precursor relative to  $t\text{-C}_4\text{H}_9$ . The

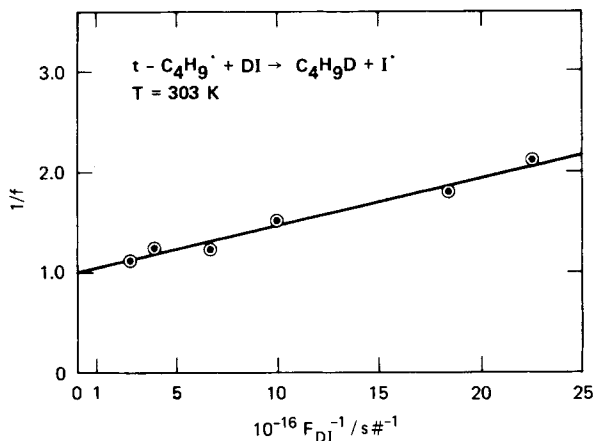
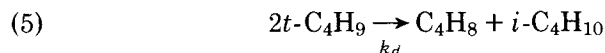
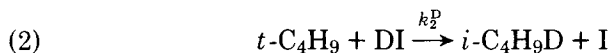
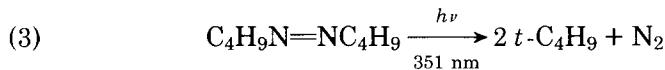
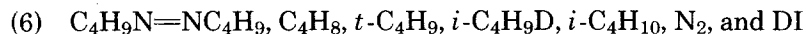


Figure 4. Inverse of fractional yield  $1/f$  of  $C_4H_9D$  ( $m/e = 44$ ) versus inverse of flow rate of DI ( $1/F_{DI}$ ) into the reactor for run No. 1 (Table I).  $F_{azo}^i = 1.50 \times 10^{15}$  molecules/s,  $20 \text{ s}^{-1}$  at 351 nm.

kinetic scheme relevant to our reaction system, using DI as radical trapping agent, is as follows:



and escape of



The resulting isobutane- $d_1$  or isobutane were monitored at  $m/e = 44$  or 43, respectively. It was assumed that the mass spectral sensitivity of the monodeuterated isobutane at  $m/e = 44$  was identical to the one for isobutane at  $m/e = 43$  in view of the fact that  $M^+ - 15(\text{methyl}) = 43$  is the base peak for isobutane. This assumption, however, does not affect the kinetic results because our formalism uses only relative (mass spectrometric) signal strengths. Only the mass balance data which make use of absolute sensi-



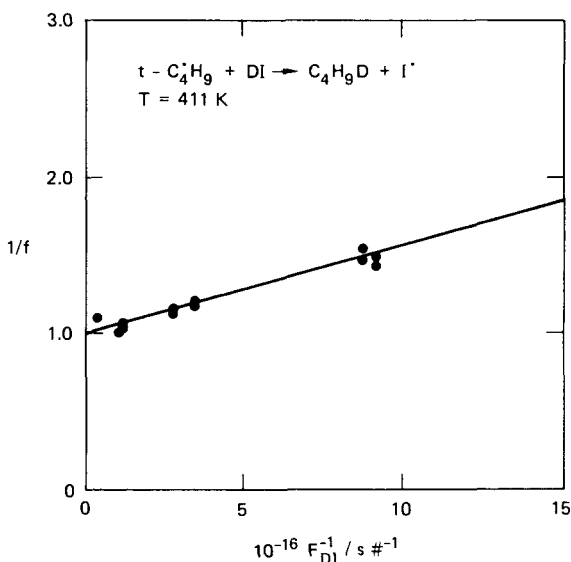


Figure 5. Inverse of fractional yield  $1/f$  of  $i$ - $C_4H_9D$  ( $m/e = 44$ ) versus inverse of flow rate of DI ( $1/F_{DI}^i$ ) into the reactor for run No. 9 (Table I).  $F_{azo}^i = 2.85 \times 10^{15}$  molecules/s,  $40 s^{-1}$  at 351 nm.

tivities for isobutane, and thus for isobutane- $d_1$ , depend on the validity of the above assumption (see below).

Figure 3 shows that the yield of  $t$ -butyl radicals measured as the yield of isobutane- $d_1$  at  $m/e = 44$  at a given DI concentration is linearly proportional to the power of the laser radiation in the continuous-wave mode [Fig. 2(b)] of the experiment. The sensitivity factor of  $6.2 \times 10^{10}$   $t$ - $C_4H_9$  molecules/cm<sup>3</sup> for each cm in the graph was calculated using  $k_2^D = 1.83 \times 10^8 M^{-1} \cdot s^{-1}$  and  $[DI] \rightarrow \infty$ . This means that the raw data were corrected for 100% titration using the measured rate constant for reaction (2) (see below). The good linearity of the data in Figure 3 shows that  $[t$ - $C_4H_9]$  in fact scales linearly with the laser power.

The rate constant  $k_2^X$  ( $X = H, D$ ) was determined by measuring the yield of  $i$ - $C_4H_9X$  at  $m/e = 44$  or 43 as a function of the flow rate of XI into the reactor in the continuous-wave irradiation mode at constant laser power. The functional dependence of the fraction of radicals titrated ( $f$ ) on the flow rate of XI ( $F_{XI}^i$ ) has the following form [9]:

$$(7) \quad \frac{1}{f} = 1 + \frac{k_e^{C_4H_9} k_e^{XI}}{k_2^X F_{XI}^i}, \quad X = H, D$$

where  $k_e$  is the corresponding escape rate constant for the indicated species and  $k_2^X$  is the desired rate constant for the protiated ( $X = H$ ) or deuterated ( $X = D$ ) system. Due to the relatively low value of  $k_2^X$ , only the small ap-

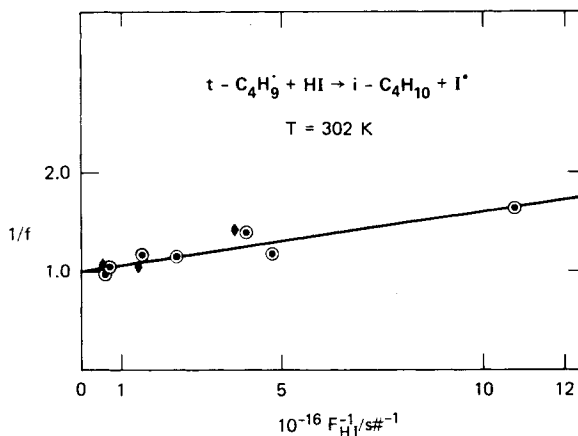


Figure 6. Inverse of fractional yield  $1/f$  of  $i\text{-C}_4\text{H}_{10}$  ( $m/e = 43$ ) versus inverse of flow rate of HI ( $1/F_{\text{HI}}^i$ ) into the reactor for run No. 10 (Table I).  $F_{\text{azo}}^i = 2.22 \times 10^{15}$  molecules/s,  $30 \text{ s}^{-1}$  at 351 nm.

erture was used in collecting the kinetic data because the extent of reaction (2) in the large-aperture reactor was generally too low for flow rates leading to Knudsen flow conditions.

The relative proportion of HI/DI was monitored by mass spectrometer at  $m/e = 128, 129$  for every flow rate of DI into the reactor. Accordingly the total nominal flow rate of DI as measured by the pressure drop in the calibrated volume was converted to an effective flow rate  $F_{\text{DI}}^i$  by means of the experimentally determined ratio of signal intensities at  $m/e = 128$  and 129. Typically the DI/HI ratio varied from 2.85 at a nominal flow rate of  $5.7 \times 10^{14}$  molecules/s to 15.24 at  $3.7 \times 10^{16}$  molecules/s. The isotopic exchange reaction is thought to occur in the low-pressure section of the DI inlet line in the portion between the flow-controlling glass capillary array and the inlet capillary of the reaction vessel. When  $1/f$  is plotted against  $1/F_{\text{XI}}^i$ , a straight line is obtained with unity intercept and slope  $k_e^{\text{C}_4\text{H}_9} k_e^{\text{XI}} / k_2^{\text{X}}$ . The escape rate constants are known quantities from the calibration of the reaction vessel, so that  $k_2^{\text{X}}$  can be computed from the slope of the straight line. Typical  $1/f$  versus  $1/F_{\text{XI}}^i$  plots are shown in Figure 4 ( $T = 303 \text{ K}$ ), in Figure 5 ( $T = 411 \text{ K}$ ) for  $\text{X} = \text{D}$ , and in Figure 6 ( $T = 301 \text{ K}$ ) for  $\text{X} = \text{H}$ . Table I presents the rate constants  $k_2^{\text{X}}$  determined in the small-aperture reactor in the continuous-wave irradiation mode. Each rate constant was determined by monitoring the amount of  $i\text{-C}_4\text{H}_9\text{D}$  (at  $m/e = 44$ ) or  $i\text{-C}_4\text{H}_{10}$  (at  $m/e = 43$ ) at 4 to 8 flow rates of DI or HI ( $F_{\text{DI}}^i$  and  $F_{\text{HI}}^i$ , respectively). Typically  $1/f = 2.050$  at  $F_{\text{DI}}^i = 4.24 \times 10^{14}$  molecules/s ("pure" DI flow rate corrected for the HI contribution), whereas  $1/f$  is 1.061 at  $F_{\text{DI}}^i = 1.19 \times 10^{16}$  molecules/s for run 6. The fraction  $f$  of radicals titrated at a given  $F_{\text{XI}}^i$  was determined as the ratio  $(i\text{-C}_4\text{H}_9\text{X})/(i\text{-C}_4\text{H}_9\text{X})_\infty$  of the mass spectrometric

TABLE I. Measured rate constants ( $M^{-1}\cdot s^{-1}$ ) as a function of temperature for the title reactions.

$t\text{-C}_4\text{H}_9 + \text{DI} \xrightarrow{k_2^{\text{D}}} i\text{-C}_4\text{H}_9\text{D} + \text{I}$		
Run No.	T/K	$k_2^{\text{D}}/M^{-1} s^{-1}$
1	303	$1.55 * 10^8$ <sup>a</sup>
2	303	$1.55 * 10^8$ <sup>a</sup>
3	303	$1.93 * 10^8$
4	303	$2.07 * 10^8$
5	302	$1.80 * 10^8$ <sup>b</sup>
6	302	$2.06 * 10^8$ <sup>b</sup>
7	407	$2.76 * 10^8$
8	361	$2.25 * 10^8$ <sup>b</sup>
9	411	$3.70 * 10^8$
$t\text{-C}_4\text{H}_9 + \text{HI} \xrightarrow{k_2^{\text{H}}} i\text{-C}_4\text{H}_{10} + \text{I}$		
10	302	$2.63 * 10^8$
11	301	$3.11 * 10^8$
12	301	$3.87 * 10^8$

<sup>a</sup> Reaction vessel 1 was halocarbon wax-coated (Wax 15-00).

<sup>b</sup> Experiments for which both small- and large-aperture data are available.

signals, where ( $i\text{-C}_4\text{H}_9\text{X}$ ) was the mass spectrometric signal of the titrated  $i$ -butane at the given  $F_{\text{XI}}^i$ , whereas ( $i\text{-C}_4\text{H}_9\text{X}$ )<sub>∞</sub> was that same quantity at the maximum degree of titration achievable under our experimental conditions. At flow rates larger than  $2.0 \times 10^{16}$  molecules/s the mass spectral signal intensity at  $m/e = 44$  or 43 started to decrease slightly for unknown reasons so that this flow rate represented the upper limit for the HI or DI flow. Due to the slow rate constant  $k_2^{\text{X}}$  (see Table I), the extent of the titration was 96% at  $F_{\text{DI}}^i = 2.0 \times 10^{16}$  molecules/s. Therefore the raw data, that is,  $f$  evaluated at a flow rate smaller than  $2.0 \times 10^{16}$  molecules/s, were corrected by forcing the straight line through the unity intercept in an iterative manner. In all cases this procedure was carried out only once, and this correction led to a maximum decrease of 10% in the rate constant, typical values lying between 2 and 5%. The second iteration led to a 1% decrease in the rate constant and was therefore ignored, indicating that after

one iteration a self-consistent value of  $k_2^X$  was obtained. In any case, this refinement of the raw data resulted in a rate constant  $k_2^X$  which was lower by, at most, 10% of its original value.

A comment concerning the wall deactivation of *t*-C<sub>4</sub>H<sub>9</sub> radicals is in order here. Generally the first-order loss process of a hydrocarbon radical in a Knudsen cell includes escape of the radical out of the reactor ( $k_e^R$ ) and wall loss processes ( $k_w^R$ ) transforming the radical into a stable species by some wall-catalyzed reaction. Accordingly  $k_e^{C_4H_9}$  in eq. (7) has to be replaced by  $k^I = k_e^{C_4H_9} + k_w^{C_4H_9}$  if the wall reaction is competitive with escape and other chemical processes under the given experimental conditions. In this case one has to obtain two independent data sets (usually for a small and a large aperture reaction vessel) in order to determine separately the rate constants of interest (here  $k_2^X$  and  $k_w$ ). We have evidence that under our reaction conditions  $k_w$  is not competitive, so that we have omitted this term in the treatment of the data [eq. (7)]. Our evidence is as follows.

First, the data of inverse yield versus inverse flow rate for the large aperture reaction vessel were consistent with eq. (7) for flow rates of XI larger than  $0.7 \times 10^{16}$  molecules/s. This means that  $k_w^{C_4H_9}$  is much smaller than  $k_e^{C_4H_9}$  under our experimental conditions, and the two independent data sets (large and small aperture) overdetermine the unknown  $k_2^X$ . At lower flow rates the yields of titrated radicals in the large aperture reaction vessel were too high, a fact that possibly could be attributed to a window effect. The predicted straight line for the large reactor aperture data went through the data points (for runs 5, 6, and 8, see Table I) within experimental uncertainty when the rate constant  $k_2^D$  from the small aperture reactor (evaluated excluding  $k_w$ ) was used. The intercept in the plot  $1/f$  versus  $1/F_{DI}^i$  was larger by a factor corresponding to the ratio of  $k_e^M(B)/k_e^M(S)$ , where *B* and *S* correspond to the large and small apertures, and the slope was larger by the square of this ratio  $[(4.064)^2 = 16.51]$ . It is evident that the yields in the large aperture vessel were much smaller than in the small aperture reactor so that the precision of the large aperture data was lower than that of the small aperture data.

Second, the absence of a significant wall deactivation process for *t*-C<sub>4</sub>H<sub>9</sub> could be established by observing the yield of isobutene (*i*-C<sub>4</sub>H<sub>8</sub>) as a function of the flow rate of XI. From previous studies of the reactivity of *t*-C<sub>4</sub>H<sub>9</sub> in a low-pressure reaction vessel at elevated temperatures it was concluded that the wall reaction of *t*-C<sub>4</sub>H<sub>9</sub> primarily resulted in *i*-C<sub>4</sub>H<sub>8</sub> rather than *i*-C<sub>4</sub>H<sub>10</sub> [6]. We observe (see the section on mass balance) that the ratio of isobutene (monitored at *m/e* = 56) and isobutane (monitored at *m/e* = 43) amounts to 8.2:1 in the absence of the titrant XI at room temperature under our reaction conditions (reaction vessel 2). This in turn means that roughly 90% of the observed isobutene is the product of the wall deactivation of *t*-C<sub>4</sub>H<sub>9</sub> [reaction (4)], with the remainder being the product of the homogeneous disproportionation reaction [reaction (5),  $k_d$ ]. Thus

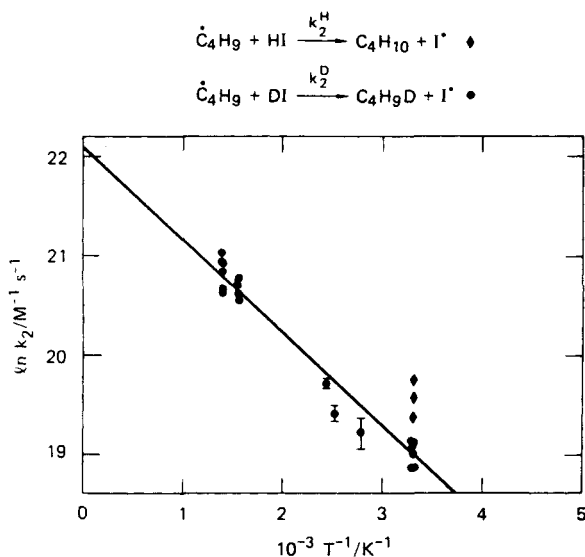


Figure 7. Arrhenius plot for the title reaction (deuterated system). The high-temperature points ( $T$  around 700 K) are from an earlier study by Rossi and Golden [9], whereas the low-temperature points (300–400 K) are the result of the present work. The least-squares fit is represented by  $\log k_2^{\text{D}}(\text{M}^{-1}\text{s}^{-1}) = 9.60 - 1.90/\theta$ , where  $\theta = 2.303RT$  kcal/mol. The diamonds represent the rate constants for the protiated system  $k_2^{\text{H}}$ .

the appearance of isobutene serves as a convenient marker for the occurrence of reaction (4). We make the pertinent observation that at  $F_{\text{DI}}^i = 2.3 \times 10^{14}$  molecules/s the mass spectrometric signal at  $m/e = 56$  (isobutene) is barely visible with an approximate signal-to-noise ratio of 1:1, whereas at  $F_{\text{DI}}^i = 8.2 \times 10^{14} \text{ s}^{-1}$  the signal due to isobutene has vanished completely. This latter value of  $F_{\text{DI}}^i$  was a factor of 2 or so lower than the lowest  $F_{\text{DI}}^i$  used to determine  $k_{\text{D}_1}^{\text{D}}$  [reaction (2)]. For this control experiment we chose a flow rate of 2,2'-azoisobutane higher by a factor of 2 compared to that of the runs of Table I, and the highest pulse repetition rate of  $40 \text{ s}^{-1}$  at 351 nm in order to maximize the production of  $t\text{-C}_4\text{H}_9$  and hence the rate of reaction (5). Therefore we conclude that in the presence of the titrant DI, reaction (4) is not important compared to  $k_e^{t\text{-C}_4\text{H}_9}$  and  $k_2^{\text{D}}$ .

A look at Table I reveals the following results:  $k_2^{\text{D}} = (1.83 \pm 0.24) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  at 303 K and  $k_2^{\text{H}} = (3.02 \pm 0.63) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  at 301 K. The precision of the HI data is lower due to a noisier signal at  $m/e = 43$ , corresponding to  $i\text{-C}_4\text{H}_{10}$ , because of the significant contribution of 2,2'-azoisobutane, the  $t\text{-C}_4\text{H}_9$  precursor. The contribution of the azo precursor to  $m/e = 44$  for the DI titration was an order of magnitude smaller than the corresponding one at  $m/e = 43$  for the HI titration. The primary isotope effect defined as the ratio  $k_2^{\text{H}}/k_2^{\text{D}}$  amounts to  $1.749 \pm 0.409$  at  $T = 302 \text{ K}$ ,

in agreement with one's expectation for the primary isotope effect of exothermic metathetical reactions without significant activation energies [9,15]. When the data of Table I for  $k_2^D$  are combined with the corresponding ones from an earlier VLPP study where the *t*-butyl radical was generated by pyrolysis of the same azo precursor used in this study (2,2'-azoisobutane) [9], the Arrhenius plot in Figure 7 results. The Arrhenius plot can be represented by the following relation:

$$(8) \quad \log k_2^D (M^{-1} \cdot s^{-1}) = 9.60 - 1.90/2.303RT$$

where  $R = 1.99 \times 10^{-3}$  kcal/mol·K. We would like to stress at this point that on the basis of the 19 separate determinations of  $k_2^D$  in the present and previous [9] work, there can be no doubt that reaction (2) has a finite, though small, activation energy. By combining pyrolytic [9] and photolytic experiments (present study) in the present rate constant determination, we were able to achieve a temperature interval of 420 K over which measurements of even small activation energies can be accomplished with some accuracy. It is possible, however, that the present measurements of  $k_2^D$  at  $T = 407, 361$ , and  $411$  K are subject to some systematic error due to the fact that the temperature of the window may have been significantly lower than the temperature of the wall where the temperature measurement was taken. In this case the true values for  $k_2^D$  at these higher temperatures would be larger than presently measured. Omission of the above three values in the Arrhenius plot leaves the  $A$  factor unchanged and results in an activation energy of  $1.86$  kcal/mol, a result which is not significantly different from eq. (8). Incidentally the Arrhenius parameters from eq. (8) are quite close to the one derived in the earlier study [ $\log A_2 (M^{-1} \cdot s^{-1}) = 9.67$ ;  $E_2 = 2.10$  kcal/mol] over a much narrower temperature range (78 K) [9].

The next question is how to correct the Arrhenius parameters measured for the deuterated system [eq. (8)] into the ones for the protiated system in view of the fact that the primary deuterium isotope effect was measured only at one temperature (302 K). We make use of the assumption that the above isotope effect is equal to  $\sqrt{2}$  at temperatures of 600–700 K. With eq. (8) and the measured isotope effect of  $1.75$  at 302 K, as well as the assumed isotope effect of  $\sqrt{2} = 1.41$  at 716 K, we may obtain the Arrhenius expression for  $k_2^H$ :

$$(9) \quad \log k_2^H (M^{-1} \cdot s^{-1}) = 9.73 - 1.68/2.303RT$$

where  $R = 1.99 \times 10^{-3}$  kcal/mol·K. It is evident that both the  $A$  factor and the activation energy are slightly different with respect to the corresponding parameters for the deuterated system because of the (assumed) temperature dependence of the primary deuterium isotope effect. In the following discussion on the heat of formation of *t*-C<sub>4</sub>H<sub>9</sub> we will use eq. (9) rather than ignore the isotope effect on  $k_2$ .

### Mass Balance

Our rate measurements can only be complete if a mass balance in the presence and absence of the titrant DI can be established. A typical mass balance experiment involved the comparison of the whole mass spectrum (mass range 1 to 100) in the presence and absence of DI, as well as in the presence and absence of 351-nm laser radiation. The mass spectral sensitivities at  $m/e = 99$  (tetramethylbutane), 56 (*i*-butene), 43 (*i*-butane), and 57 (2,2'-azoisobutane) were established by leaking in calibrated flows of authentic samples.

At a pulse repetition frequency of  $50 \text{ s}^{-1}/0.9 \text{ W}$  and with  $F_{\text{azo}}^i = 2.5 \times 10^{15}$  molecules/s in experiment A (see Table II), one observes the relative decrease at  $m/e = 57$  upon irradiation in the absence of DI. This procedure almost certainly undercounts the degree of photolysis because of the contributions of tetramethylbutane and  $t\text{-C}_4\text{H}_9$  itself. However, these two contributions to  $m/e = 57$  should be small (see below). In the presence of DI the same irradiation conditions led to  $F_{t\text{-C}_4\text{H}_9}^i = 1.62 \times 10^{14}$  molecules/s based on the yield of  $i\text{-C}_4\text{H}_9\text{D}$  at  $m/e = 44$ , extrapolated to 100% titration using  $k_2^D$  from Table I ( $1.83 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ).

In the absence of DI the following yields were measured at identical irradiation conditions (3.21% photolysis):  $F_{\text{TMB}}^0 = 2.28 \times 10^{12}$  molecules/s for tetramethyl butane measured at  $m/e = 99$ ,  $F_{\text{C}_4\text{H}_{10}}^0 = 1.52 \times 10^{13}$  molecules/s for *i*-butane measured at  $m/e = 43$ , and  $F_{i\text{-C}_4\text{H}_8}^0 = 1.25 \times 10^{14}$  molecules/s for *i*-butene measured at  $m/e = 56$ . All these measurements suffer from the uncertainty of the unknown contribution of  $t\text{-C}_4\text{H}_9$  to the above masses, however small they may be. Furthermore no correction for the small decrease in azo precursor concentration upon irradiation was made when the yield of *i*-butane at  $m/e = 43$  was established. Table II presents the mass balance data for two experiments, A and B, at two different flows of the radical precursor and at two different laser powers.

Based on the simple reaction scheme [reactions (2)–(6)], the mass balance equation assumes the following form:

$$(10) \quad F_{\text{C}_4\text{H}_9\text{D}}^0 = F_{i\text{-C}_4\text{H}_8}^0 + F_{i\text{-C}_4\text{H}_{10}}^0 + 2F_{\text{TMB}}^0 + F_{t\text{-C}_4\text{H}_9}^0$$

The left-hand side of eq. (10) represents the total amount of  $t\text{-C}_4\text{H}_9$  generated upon photolysis of the azo precursor in the presence of DI, in the absence of any complicating loss processes, notably wall losses, and thus represents the true "initial" concentration of *t*-butyl radicals ( $1.62 \times 10^{14}$  molecules/s, experiment A, see Table II). The right-hand side represents the fate of the  $t\text{-C}_4\text{H}_9$  in the absence of DI. The sum of the individual contributions, excluding  $F_{t\text{-C}_4\text{H}_9}^0$  out of the Knudsen cell, amounts to  $1.45 \times 10^{14}$  molecules/s, and this sum allows us to determine the steady-state flux of  $t\text{-C}_4\text{H}_9$ . This flux ( $F_{t\text{-C}_4\text{H}_9}^0$ ) is given in Table II, experiment A, as

TABLE II. Mass balance in flux (molecules/s) for reaction system [eqs. (2)–(6)]. The numbers in parentheses are the molecular masses at which the species was monitored by mass spectrometry.

Run	$C_4H_9N_2C_4H_9(57)$	$C_4H_9D(44)$	$C_4H_8(56)$	$C_4H_{10}(43)$	$C_8H_{18}(99)$	$t-C_4H_9^a$	DI	Photolysis <sup>b</sup>
A	$2.44 \times 10^{15}$	$1.57 \times 10^{14}$	—	—	—	—	—	3.21% at .9W
	$2.56 \times 10^{15}$	$1.62 \times 10^{14}$	$1.25 \times 10^{14}$	$1.52 \times 10^{13}$	$2.28 \times 10^{12}$	$1.72 \times 10^{13}$	$2.09 \times 10^{15}$	—
B	$3.34 \times 10^{15}$	$1.43 \times 10^{14}$	—	—	—	—	—	2.13% at .6W
	$3.34 \times 10^{15}$	$1.71 \times 10^{14}$	$1.52 \times 10^{14}$	$2.48 \times 10^{13}$	<sup>c</sup>	—	$2.18 \times 10^{15}$	—

<sup>a</sup> Calculated according to eq. (10).

<sup>b</sup> Determined using  $m/e = 57$  in the absence of DI. In the presence of DI the apparent photolysis yield was lower, indicating contribution of an additional species at  $m/e = 57$ .

<sup>c</sup> No TMB could be detected due to lower laser power. In experiment A, the signal-to-noise ratio for TMB at  $m/e = 99$  was 3:1.



$1.72 \times 10^{13}$  molecules/s, corresponding to a number density of  $1.12 \times 10^{11}$  molecules/cm<sup>3</sup>.

In the absence of DI the initial flux of *t*-C<sub>4</sub>H<sub>9</sub> was determined from the signal intensity decrease at *m/e* = 57 upon irradiation. In the presence of DI that same quantity was determined from the yield of C<sub>4</sub>H<sub>9</sub>D at *m/e* = 44, corrected for 100% reaction. The agreement is surprisingly good (see Table II) and gives us some confidence that the reaction mechanism put forth in reactions (2)–(6) is valid for our experimental situation. Also the photolysis yield scales linearly with laser power. As discussed above, the predominance of *i*-C<sub>4</sub>H<sub>8</sub> in eq. (10) is believed primarily due to wall deactivation of *t*-C<sub>4</sub>H<sub>9</sub> (no titrant!), a fact that has been found in *t*-butyl recombination studies at higher temperatures [6], and only a minor portion is due to the homogeneous disproportionation reaction (5) of *t*-C<sub>4</sub>H<sub>9</sub>. Likewise, the *i*-C<sub>4</sub>H<sub>10</sub> may also have two origins, the wall reaction of *t*-C<sub>4</sub>H<sub>9</sub> [reaction (4)] and homogeneous disproportionation of *t*-C<sub>4</sub>H<sub>9</sub> [reaction (5)]. The fact that the *t*-C<sub>4</sub>H<sub>9</sub> mostly ends up as *i*-C<sub>4</sub>H<sub>8</sub> in the absence of a titrant during its lifetime in the reactor makes the steady-state concentration of *t*-C<sub>4</sub>H<sub>9</sub> very small with respect to the initial concentration of *t*-C<sub>4</sub>H<sub>9</sub> measured as the yield of *i*-C<sub>4</sub>H<sub>9</sub>D at 100% titration with DI. Taking the difference between the left- and right-hand sides of eq. (10) and assigning it to  $F_{i\text{-C}_4\text{H}_9}^0$ , we obtain  $[t\text{-C}_4\text{H}_9]_{ss} = 1.12 \times 10^{11}$  molecules/cm<sup>3</sup>. The *t*-C<sub>4</sub>H<sub>9</sub> recombination rate constant  $k_r$  is given by eq. (11) following the reaction mechanism (2)–(6):

$$(11) \quad k_r = \frac{k_e^{\text{TMB}}[\text{TMB}]}{[t\text{-C}_4\text{H}_9]_{ss}^2}$$

Using the above value for  $[t\text{-C}_4\text{H}_9]_{ss}$  and  $[\text{TMB}] = 2.10 \times 10^{10}$  molecules/cm<sup>3</sup> (corresponding to  $F_{\text{TMB}}^0 = 2.28 \times 10^{12}$  molecules/s), we obtain  $k_r = 8.4 \times 10^8 \text{M}^{-1}\text{s}^{-1}$ , which is about a factor of 3 lower than the results of two recent studies [5,6]. In any case, the good agreement of the mass balance serves to validate the reaction mechanism. The combination rate constants are uncertain, arising from differences of large numbers in the calculation of the steady-state concentration of *t*-C<sub>4</sub>H<sub>9</sub> ( $[t\text{-C}_4\text{H}_9]_{ss}$ ).

#### *The Heat of Formation of t-C<sub>4</sub>H<sub>9</sub>*

The temperature dependence of the equilibrium constant  $K_1 = k_1/k_{-1}$  yields both the reaction enthalpy and entropy from a van't Hoff plot (second-law determination). For  $k_1$  two slightly different sets of Arrhenius parameters were measured, one by Teranishi and Benson (TB) [10] [eq. (12)] and the other by Knox and Musgrave (KM) [11] [eq. (13)]:

$$(12) \quad \log k_1 (\text{M}^{-1}\text{s}^{-1}) = 10.9 \pm 0.2 - (21.3 \pm 0.5)/\theta$$

TABLE III. Thermochemical values.

	$\Delta H_{f,300}^o$ <sup>a</sup>	$C_{p,300}$ <sup>b</sup>	$C_{p,500}$ <sup>b</sup>	$C_{p,600}$ <sup>b</sup>	$C_{p,700}$ <sup>b</sup>	$S_{600}^o$ <sup>b</sup>	$S_{300}^o$ <sup>b</sup>
$v = 0$		19.3	29.9	35.1	39.0	94.9	76.0
$t\text{-C}_4\text{H}_9$ $v = 1.5$ [9.2] <sup>c</sup>		22.0	31.3	35.7	39.8	[93.5] <sup>c</sup>	[74.2] <sup>c</sup>
HI	6.3	6.97	7.11	7.25	7.40	64.3	49.4
$i\text{-C}_4\text{H}_{10}$	-32.1	23.25	35.62	40.62	44.50	92.4	70.4
I	25.5	4.97	4.97	4.97	4.97	46.7	43.2

<sup>a</sup> kcal/mol.<sup>b</sup> cal/mol<sup>-1</sup>·K<sup>-1</sup> (eu).<sup>c</sup> This work, together with Ref. [12].

$$(13) \quad \log k_1(M^{-1}\cdot s^{-1}) = 11.3 \pm 0.4 - (22.6 \pm 1.1)/\theta$$

where  $525 < T(K) < 583$  and  $\theta = 2.303RT$  in kcal/mol. When we combine the above rate parameters for  $k_1$  with our measured corresponding one for  $k_{-1}$  from eq. (9), we obtain the following values for  $\Delta H_1^0$  and  $\Delta S_1^0$  (at 298 K). From TB we get  $\Delta H_1^0 = 19.6$  kcal/mol,  $\Delta S_1^0 = 5.00$  eu, and from KM we get  $\Delta H_1^0 = 20.9$  kcal/mol,  $\Delta S_1^0 = 7.20$  eu. These values yield  $\Delta H_f^0(t\text{-C}_4\text{H}_9) = 6.65$  kcal/mol and  $S^0(t\text{-C}_4\text{H}_9) = 69.4$  eu from TB and  $\Delta H_f^0(t\text{-C}_4\text{H}_9) = 7.95$  kcal/mol and  $S^0(t\text{-C}_4\text{H}_9) = 71.6$  eu from KM. Both sets of thermochemical parameters seem too low in comparison with even the "low" heat of formation of *t*-butyl radicals and with a recently measured [7] value for  $S^0(t\text{-C}_4\text{H}_9)$ .

The recent preliminary work of Bracey and Walsh [12] mitigates the problem a great deal. They report:

$$(14) \quad \log k_1(M^{-1}\cdot s^{-1}) = 11.6 \pm 0.1 - (23.8 \pm 0.3)/\theta$$

when  $573 < T(K) < 614$ . Combining these values with those reported here for  $k_{-1}$ , we find that  $S_{600}^0(t\text{-C}_4\text{H}_9) = 93.5$  eu. This corresponds to a *t*-butyl radical whose methyl rotors are hindered by about 1.5 kcal. This information allows the calculation of the thermochemical information shown in Table III. Thus we obtain  $S_{300}^0(t\text{-C}_4\text{H}_9) = 74.2$  eu and  $\Delta H_{f,300}^0(t\text{-C}_4\text{H}_9) = 9.2$  kcal/mol,  $DH(t\text{-butyl-H}) = 93.7$  kcal/mol. The value of the entropy is exactly the value currently favored by Pacansky [7b] from the work in [7a], wherein the value of 76.0 eu was promulgated.

The value of  $DH(t\text{-butyl-H}) = 94$  kcal/mol closes the "*t*-butyl gap," but not completely. Values as high as 96 kcal/mol can still be derived from other methods [1].

### Acknowledgment

This work was supported by the Air Force Office of Scientific Research under Contracts F49620-78-C-0107 and F44620-83-K-001.

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Received February 7, 1983

Accepted May 9, 1983