Formation of D Atoms in the Pyrolysis of Toluene- d_8 behind Shock Waves. Kinetics of the Reaction $C_7D_8 + H \rightarrow C_7D_7H + D$

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Dilute mixtures (5–20 ppm) of toluene- d_8 in argon were pyrolyzed behind reflected shock waves at temperatures of 1410–1730 K and total pressures of 3 atm. In a second group of experiments, mixtures of 20 ppm toluene- d_8 and 5 ppm neopentane (which acted as a source of H atoms) were similarly pyrolyzed at 1200-1460 K. Progress of the reaction was followed by analysis for H and D atoms by using resonance absorption spectroscopy. For the reaction $C_6D_5CD_3 \rightarrow C_6D_5CD_2 + D$ under the experimental conditions, $k_{1D} = 1.1 \times 10^{14} \exp(-82000 \text{ cal}/RT) \text{ s}^{-1}$. After allowance for isotope effects and unimolecular falloff, the high-pressure rate constant for the reaction $C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H$ is calculated to be $k_{1,\infty} = 2.7 \times 10^{14}$ exp(-83000 cal/RT) s⁻¹ over the range 1000-1800 K. Estimated uncertainties are a factor of 1.5 in k_{1D} and 2 in $k_{1,\infty}$. For the reaction D + C₆D₅CD₃ \rightarrow C₆D₅CD₂ + D₂, $k_{2D2} = 2.1 \times 10^{15} \exp(-15000 \operatorname{cal/RT}) \operatorname{mol}^{-1} \operatorname{cm}^{3} \operatorname{s}^{-1}$ over the range 1300-1800 K, with an uncertainty of a factor of 1.5, while after correction for isotope effects the rate constant for H + C₆H₅CH₃ \rightarrow $C_6H_5CH_2 + H_2$ over the range 600-1800 K can be expressed by the non-Arrhenius equation $k_2 = 7.6 \times 10^{-5} T^{5.5} \exp(-340$ cal/RT) mol⁻¹ cm³ s⁻¹, with an uncertainty of a factor of 2. Data were also obtained on the exchange reaction by which H atoms add to the ring of C₆D₅CD₃, and D atoms are eliminated. For this reaction $k_{4D} = 3.5 \times 10^{13} \exp(-3700 \text{ cal/}RT)$ mol⁻¹ cm³ s⁻¹ in the range 1200–1500 K, with an estimated uncertainty of a factor of 1.5.

Introduction

The main goal of this work has been to obtain rate constant data for the first step in the pyrolysis of toluene- d_8 , which is

$$C_6 D_5 C D_3 \rightarrow C_6 D_5 C D_2 + D \tag{1D}$$

By using the sensitive absorption method to measure D atom concentrations, we have been able to work at very low initial concentrations of toluene and also to obtain data with low conversions of toluene in many of the experiments, thereby minimizing the effects of secondary reactions on the observed D concentrations. However, many of the observed D concentrations do reflect the loss of D by reaction with toluene.

To account for the effects of these other reactions we have used results from papers by Szwarc,¹ Blades, Blades, and Steacie,² Takahasi,³ and Price⁴ published in the 1948-1962 period. Important reactions are

$$C_6H_5CH_3 + H \rightarrow C_6H_5CH_2 + H_2 \tag{2}$$

$$C_6H_5CH_3 + H \rightarrow C_6H_6 + CH_3 \tag{3}$$

$$CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2$$
(6)

Yields of H₂ and CH₄ indicated the relative importance of reactions 2 and 3; Price found the H_2/CH_4 ratio to be 2/1. More recently, Ravishankara and Nicovich⁵ have made further studies of the reactions of H and D with toluene and benzene. These results have also been helpful in interpreting our data.

The only other high-temperature study with which our data can be compared is that of Astholz, Durant, and Troe,⁶ who made spectroscopic studies of the disappearance of toluene and the appearance of benzyl behind reflected shock waves at 1500-1800 K, while the study of benzyl pyrolysis by Astholz and Troe⁷ was helpful in data analysis.

Experimental Section

Our apparatus and techniques have been described in an earlier paper.⁸ Briefly, we used a stainless steel shock tube with a test

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section 7.6 cm in diameter and 4.5 m long. Concentrations of H and D atoms were measured by resonance absorption behind the reflected shock wave. The microwave discharge lamp used to produce the Lyman- α radiation (source B of ref 8, with 0.1% H_2 or D_2 in helium at a lamp pressure of 2.5 torr and with 40-W microwave power) had been characterized in terms of emitted line shape and also calibrated empirically. We isolated the Lyman- α line by using the filter system described in ref 8. Temperatures were calculated from the incident shock speed, while the reflected shock pressure was also monitored. Within our 2-3% accuracy of measurement, the observed reflected shock pressures were the same as those calculated from the incident shock speed, and pressure did not vary more than 2-3% throughout an experiment. Accordingly, we have estimated that the uncertainty in temperature is no more than 1.4%, or 20-30 K over the experimental range

The toluene- d_8 was from Kor Isotopes and was stated to have 99.96 atom % D. Neopentane was from Matheson Co. It was found by gas-chromatographic analysis to contain 2.0% butane, and no other significant impurity. As discussed in an earlier paper9 the effect of the butane or production of H atoms could easily be accounted for. Argon was from Airco, Inc., Research Grade, 2 ppm total impurity, with less than 0.5 ppm hydrocarbons reported as methane.

Experimental Results

Two groups of experiments were carried out, the first involving pyrolysis of toluene- d_8 and the second the pyrolysis of mixtures of neopentane (which served as a source of H atoms) and toluene- d_8 . Because both toluene and neopentane absorb Lyman- α radiation rather strongly, all of our mixtures were quite dilute. We used 5 and 20 ppm of toluene- d_8 for the first group, and a mixture of 5 ppm neopentane and 20 ppm toluene- d_8 for the second group. The absorption coefficient of toluene- d_8 vapor at Lyman- α (121.5 nm) and 1300 K is $(4.4 \pm 0.5) \times 10^7 \text{ mol}^{-1} \text{ cm}^2$.

In each experiment the Lyman- α intensity dropped suddenly when the reflected shock wave passed the observation station, because of the molecular absorption. This sudden change was followed by slower changes due to the appearance of atoms, and the two effects could usually be distinguished. The arrival of the reflected shock wave, as recorded by a pressure transducer located at the same position along the shock tube as the optical system,

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Figure 1. Dependence of D atom concentration on time for shock tube experiment with $T_5 = 1478$ K, $P_5 = 3.37$ atm, 5 ppm toluene- d_8 in argon: (--) best estimate of initial slope; (---) calculated concentrations using four-reaction scheme.



Time, microseconds

Figure 2. Dependence of D atom concentration on time for shock tube experiment with $T_5 = 1492$ K, $P_5 = 3.14$ atm, 20 ppm toluene- d_8 in argon: (---) best estimate of initial slope; (---) calculated concentrations using four-reaction scheme.

typically matched the drop of light intensity within the time constant of our optical system $(5-20 \ \mu s)$ so that our zero of time was confirmed within that accuracy. We used a time constant of 5 μs for higher temperature experiments where total experimental times were less than 300 μs , and 20 μs for lower temperature experiments where times extended to 1000 μs or more. The longer time constant gave a better signal-to-noise ratio.

A 20 ppm mixture with 3.0-atm total pressure at 1400 K absorbs 16% of the light by molecular processes. Since the fractions of neopentane and toluene that reacted were generally small, and since the pyrolysis products (benzyl radical, diacetylene, acetylene, and isobutene) would also absorb Lyman- α , we assumed that the molecular absorption remained constant throughout each experiment. We also assumed that boundary layer cooling had no effect on the results. The only effect would be loss of a few percent of the atoms near the windows, and since the effect would also occur during our empirical calibrations, it seemed reasonable that the errors would largely cancel.

While our total data analysis took into consideration all of our measurements over the experimental times, it seemed worthwhile to make a first estimate of the rate constant for toluene- d_8 dissociation from the initial slopes of the curves.

In the pyrolysis of 5 ppm toluene- d_8 , concentrations of D atoms rose linearly with time for a few hundred microseconds, and then



Figure 3. First-order rate constants for the initial step in toluene pyrolysis: (Δ) 5 ppm toluene- d_8 in argon, from initial slopes; (\bigcirc) 20 ppm toluene- d_8 in argon, from initial slopes; (\bigcirc) best least-squares line from initial slopes; (--) best fit from a match with all of the data.

TABLE I: Elementary Reactions Found Important in Data Analysis

		v	
reaction	A, mol cm^3 s	E, cal	ref
$(1D) C_6 D_5 C D_3 \rightarrow C_6 D_5 C D_2 + D$	1.1×10^{14}	82 000	a
(2D) H + C ₆ D ₅ CD ₃ \rightarrow C ₆ D ₅ CD ₂ + HD	2.5×10^{15}	14600	
(2D2) D + $\dot{C}_6\dot{D}_5\dot{C}\dot{D}_3 \rightarrow \dot{C}_6\dot{D}_5\dot{C}\dot{D}_2 + D_2$	2.1×10^{15}	15000	
(3D) H + C ₆ D ₅ CD ₃ \rightarrow C ₆ D ₅ H + CD ₃	3.5×10^{13}	3 700	b
(3D2) D + C ₆ D ₅ CD ₃ \rightarrow C ₆ D ₆ + CD ₃	2.8×10^{13}	3 700	b
(4D) H + C ₆ D ₅ CD ₃ \rightarrow C ₆ D ₄ HCD ₃ + D	3.5×10^{13}	3 700	с
(5) $C_5H_{12} \rightarrow C_4H_8 + CH_3 + H$	2.65×10^{17}	86 300	9

^aBased on overall agreement with D concentrations. ^bActual rate constant given by $A \exp(-E/RT)(0.0018/(0.0018 + \exp(-5000/T)))$. ^cActual rate constant given by $A \exp(-E/RT)\exp(-5000/T)/(0.0018 + \exp(-5000/T))$.

at later times the values fell below the linear behavior. An example is shown in Figure 1. First-order rate constants were calculated for the appearance of D atoms from the initial slopes. For 20 ppm, curvature in the plot of D concentration vs. time appeared within $100 \ \mu$ s (Figure 2), and it was more difficult to obtain the initial slope, so we consider that the rate constants calculated from the initial slopes of the 5 ppm mixtures are more accurate than those from the 20 ppm mixtures. Of a total of 24 experiments, 6 were for 5 ppm toluene and 18 for 20 ppm. In calculating a leastsquares curve, we decided to weight the 5 ppm experiments at 3 compared to 1 for the 20 ppm ones, so that the set of 5 ppm experiments had the same weight as the set of 20 ppm experiments. The average pressure for all 24 experiments was 3.2 atm, with a standard deviation of 0.2 atm, and the temperature range 1410-1730 K.

The least-squares Arrhenius equation, calculated as described above, is

$$k_{\rm D} = 7.5 \times 10^{12} \exp(-74800 \text{ cal}/RT) \text{ s}^{-1}$$

where the standard deviation of the points from the line in terms of log k is 0.10, or a factor of 1.26. The 95% confidence level in E is 6000 cal. A graph of these results is shown in Figure 3. We should emphasize that for the full data analysis a 20 ppm experiment was as valuable as a 5 ppm one, and the final Arrhenius equation given in Table I is based on equal weighting of all the experiments.

One set of seven toluene- d_8 -neopentane experiments was done in which H atom concentrations were measured, while in another set of eight experiments D atom concentrations were measured. The temperature range was 1200–1560 K, with all but two of the experimental temperatures being below the range of pyrolysis experiments, so the observed D atoms came primarily from the reaction of H with toluene- d_8 rather than decomposition of the toluene. Average pressures in the two sets of data were 2.2 \pm 0.4 and 3.0 \pm 0.1 atm, respectively. D atoms appeared quite early in the experiments, as shown in Figure 4, indicating a rapid



Figure 4. Dependence of H and D atom concentrations on time for two shock tube experiments with $T_5 = 1303$ K, 5 ppm neopentane + 20 ppm toluene- d_8 in argon, $P_5 = 2.31$ atm for H atoms, 2.98 atm for D atoms: (O) observed H atom concentration multiplied by 2.98/2.31 for comparison with D experiment; observed D atom concentration; (--) calculated H atom concentration multiplied by 2.98/2.31; (---) calculated D atom concentration.

reaction between H and toluene- d_8 . A kinetic interpretation of these data is given below.

Discussion

Our data can be interpreted reasonably well on the basis of a small number of elementary reactions, which are given in Table I. Of these, only reactions 1D and 2D2 were important in the pyrolysis experiments. A fairly rapid exchange reaction involving D atoms no doubt occurs via reaction 4D2, where one atom adds

$$D + C_6 D_5 CD_3 \rightarrow C_6 D_5 CD_3 + D$$
 (4D2)

to the ring and another comes off, but this is not observable. We considered the possible importance of several other reactions, as described below.

The rate constants of reactions 2-5 given in Table are based partly on literature data and partly on ours. For reaction 2, Ravishankara⁵ gives

$$k_2 = 1.25 \times 10^{14} \exp(-8400 \text{ cal}/RT) \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

in the range 600-1000 K. We have estimated, on the approximate basis of activated complex theory considerations, that for reaction 2D the corresponding rate constant equation would be

$$k_{2D} = 1.0 \times 10^{14} \exp(-8600 \text{ cal}/RT) \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

while for reaction 2D2 we obtain

$$k_{2D2} = 8.5 \times 10^{13} \exp(-9000 \text{ cal}/RT) \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

By a short extrapolation, the rate constants of the three reactions at 1050 K (the average temperature of the earlier flow reactor studies) are calculated to be 2.23×10^{12} , 1.62×10^{12} , and 1.14 $\times 10^{12}$ mol⁻¹ cm³ s⁻¹, respectively.

It did not seem a good idea to extrapolate these equations into the range of our data, since abstraction reactions of this type typically show non-Arrhenius behavior at higher temperatures, the rate constants rising above the extrapolation of lower-temperature curves.¹⁰ Therefore, if an Arrhenius equation is used to express the rate constant at higher temperatures, the value of E should be higher than at low temperatures. We found that good agreement with our data could be obtained if we let k_{2D} and k_{2D2} be 40% greater than the above values at 1050 K, and have activation energies 4000 cal greater than the low-temperature ones. These are the values given in Table I. Our pyrolysis curves are fairly sensitive to the rate constant for k_{2D} , since that reaction is mainly responsible for the substantial curvature in the graphs of [D] vs. time. Assuming the overall validity of our data analysis, the expression for k_{2D2} is probably accurate within a factor of 1.6 in the temperature range 1450-1750 K. The sensitivity of the neopentane-toluene- d_8 results to reaction 2D is somewhat less, so we would estimate accuracy of a factor of 1.8 in the range 1200–1500 K. A non-Arrhenius equation for k_2 over the range 600-1700 K is

$$k_2 = 7.6 \times 10^{-5} T^{5.5} \exp(-340 \text{ cal}/RT) \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

with an estimated uncertainty of a factor of 2.

For addition of H or D to toluene and subsequent dissociation of the product, Ravishankara's data can be combined with those of Price.⁴ For the addition of H to toluene and toluene- d_8 , Ravishankara found

$$k_{3.3D} = 3.5 \times 10^{13} \exp(-3700 \text{ cal}/RT) \text{ mol}^{-1} \text{cm}^{3} \text{ s}^{-1}$$

in the range 300-1000 K, while for addition of D to toluene- d_8 he found a somewhat smaller value, which we estimate from his graph to be

$$k_{3D2} = 2.8 \times 10^{13} \exp(-3700 \text{ cal}/RT) \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

For reaction 3 at 1050 K, $k_3 = 6.0 \times 10^{12} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$.

Since Price found that, in pyrolysis of toluene at 1050 K, the H_2/CH_4 ratio is 2/1, we can calculate the fraction of addition reactions that lead to CH_3 formation. If this fraction is x, then

$$k_3 x / k_2 = \frac{1}{2}$$

and x = 0.18. This fraction is close to the statistical one of $\frac{1}{6}$ for loss of CH₃ from toluene, but the similarity is probably coincidental. Since the C_6H_5 -H bond is about 10 kcal stronger than the C_6H_5 -CH₃ bond,¹¹ one would expect that there will be a substantial temperature dependence of the H_2/CH_4 ratio, with CH₄ becoming the main product at room temperature^{12,13} and H_2 the main one at higher temperatures. If we assume a 10-kcal difference in activation energy for loss of H compared to loss of CH₃, and also assume the same value for loss of D compared to loss of CD₃, then the equations of Table I, notes a and \hat{b} , result. At temperatures above 1500 K, less than 5% of the D that adds to toluene- d_8 in pyrolysis experiments is replaced by CD₃; 95% of the time a D is added and a D comes off. At our temperatures this reaction is so fast that the steady-state quantities of C₆D₅H- CD_3 and $C_6D_6CD_3$ are extremely small.

The reactions and rate constants of Table I could be used to model our neopentane-toluene- d_8 experiments with reasonable success. The most important process involving toluene is reaction 4D, the exchange reaction that uses up H atoms and produces D. The next most important was usually reaction 2D, followed by reactions 3D, 2D2, and 3D2. Toluene pyrolysis was only important in one or two of the highest-temperature experiments. Figure 4 shows the results of two typical experiments-the extent of agreement between experiment and calculation is also typical. For the H atom measurements, the average ratio of observed to calculated H concentrations for all the data points was 0.96, and the standard error of the ratios was 0.22, while for the D atom measurements the corresponding values were 0.99 and 0.34.

Since benzyl is resonance stabilized, its rate of decomposition is relatively slow. In our range of temperatures and pressures, Astholz and Troe's data⁷ give the first-order Arrhenius equation

 $k = 4.0 \times 10^{16} \exp(-101500 \text{ cal}/RT) \text{ s}^{-1}$

which at 1600 K gives $k = 550 \text{ s}^{-1}$, about a factor of 2 below our first-order rate constant for the pyrolysis of toluene itself. Since this reaction involves breaking of C-C bonds, there should be a

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very small deuterium kinetic isotope effect. In a Knudsen cell/mass spectrometric study, Smith¹⁴ found the main pyrolysis products of benzyl to be C_2H_2 and C_5H_5 , with smaller amounts of C_4H_4 and C_3H_3 . None of these products led rapidly to formation of H atoms, so we do not expect that benzyl decomposition will have a significant effect on our results. As a further check on its importance, we made a calculation at the upper limit in which each benzyl that dissociated produced a H atom instantly. The average increase in D concentration for all the experiments was only 5%, and there were only seven experiments at the highest temperatures for which the final D concentrations were increased by more than 10% when this hypothetical reaction was added. Since the actual production of D from benzyl is expected to be much less than assumed in this calculation, it seemed reasonable to neglect benzyl dissociation in our final calculations.

Reactions found to be unimportant included abstraction of D from the ring, since the C–D bond dissociation energy for ring D atoms is about 25 kcal greater than that for D atoms on the methyl group.¹¹ Reaction 5 represents the net rate of formation of H from neopentane, including minor side reactions such as reaction of H with neopentane. The reaction of D with neopentane was included in our calculations but found to be unimportant.

The best value of k_{1D} from modeling of all of the data is given in Table I. With this value and the other rate constants from Table I, the average ratio of observed to calculated D concentrations is 1.00, and the standard error was 0.20. This Arrhenius equation is shown along with that found from the initial slopes in Figure 3. Clearly the absolute values of the rate constants found by the two approaches are similar, although the Arrhenius parameters differ somewhat.

It can be seen, then, that our data fit very well with lowertemperature data for reactions 2-4, and our rate constant expressions can be used for kinetic calculations up to 1700 K. However, when we compare our results for reaction 1 with those of Astholz, Durant, and Troe,⁶ the only other set that overlaps our experimental range, the agreement is not good at all. At 1600 K, which is included in both sets of experiments, we obtain k_{1D} = 690 s⁻¹, while at a comparable total pressure and slightly larger toluene partial pressure they find $k_1 = 1.0 \times 10^4 \text{ s}^{-1}$, a factor of 19 higher. A factor of 1.5 can be attributed to the isotope effect Another point which Astholz, Durant, and Troe recognized but did not include in their calculations is that some toluene is converted to benzyl by reaction 2. Our calculations indicate an average of 0.34 molecule converted by reaction 2 for each toluene molecule decomposed for the 5 ppm mixtures, and 0.57 molecule for the 20 ppm mixtures. The limit, according to our simplified mechanism, would be 1 molecule converted to reaction 2 for each dissociating toluene molecule, so a factor of up to 2 in the derived rate constant could occur by neglecting reaction 2. Allowing for these two factors, a discrepancy of at least 6 remains between our data and theirs.

One possible reason for our value to be low would be that we had less toluene in our mixtures than we thought. This is a matter for concern since toluene has a fairly low vapor pressure (about 20 torr at room temperature), and Astholz, Durant, and Troe reported loss of up to 20% of their toluene on the walls of their apparatus. We have evidence that a major loss of toluene did not occur. First, an ultraviolet spectrographic analysis of our nominally 20 ppm sample of toluene- d_8 in argon at 200-220 nm and room temperature indicated the presence of 17 ppm of toluene, in good agreement with our expectations. Second, we found an absorption coefficient at Lyman- α of 4.4 \times 10⁷ mol⁻¹ cm², as mentioned above, which compares to the value 3.9×10^7 mol⁻¹ cm² which we found for benzene (room-temperature vapor pressure about 80 torr). Third, in the highest temperature pyrolysis experiment with 5 ppm toluene at 1732 K, we observed a maximum D atom concentration of 5.6×10^{-11} mol cm⁻³, where the initial toluene concentration is considered to be 10.8×10^{-11} mol cm⁻³, directly indicating the presence of at least half the expected concentration of toluene. We therefore consider that our rate constants are no more than 10-20% low because of loss of toluene on apparatus walls. We can offer no simple explanation of the difference between the two groups of data.

Astholz, Durant, and Troe note that extrapolation of their data to lower temperatures leads to rate constants at 1000–1100 K considerably higher than those found earlier, for example by Price.⁴ They consider that the rate constants reported near 1050 K may be low because of a substantial amount of reverse reaction. However, a steady-state calculation for H using the most important reactions shows that this is not the case. If we consider only

$$C_6H_5CH_3 \stackrel{1}{\underset{-1}{\longleftarrow}} C_6H_5CH_2 + H$$
 (1)

$$H + C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H_2$$
(2)

and apply these to a Price experiment at 1050 K, with 11.8-torr initial pressure, residence time of 1.05 s, conversion of 0.14% and calculated k_1 of $1.3 \times 10^{-3} \text{ s}^{-1}$, the additional data needed are $k_{-1} = 9.0 \times 10^{13} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (calculated from k_1 and thermodynamic data of ref 11) and $k_2 = 2.2 \times 10^{12} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$. The steady-state H concentration is

$$[H]_{ss} = k_1 [C_6 H_5 C H_3] / \{k_{-1} [C_6 H_5 C H_2] + k_2 [C_6 H_5 C H_3]\}$$

and if it is assumed that at the end of the experiment the benzyl concentration is 0.14% of the initial toluene concentration, $[H]_{ss} = 6 \times 10^{-16} \text{ mol cm}^{-3}$. Accordingly, the reverse rate of reaction 1 is $1.1 \times 10^{-11} \text{ mol cm}^{-3} \text{ s}^{-1}$, compared to the forward rate of 2.0 $\times 10^{-10} \text{ mol cm}^{-3} \text{ s}^{-1}$, or only about 5%. Refinements of the calculation, such as allowance for loss of H by addition to the ring followed by elimination of CH₃, will further reduce the percent of reverse reaction. Therefore, the reported rate constants at 1050 K should be valid.

In order to compare high- and low-temperature data it is necessary to consider the extent of unimolecular falloff under the various conditions. Astholz, Durant, and Troe calculated that at 10-torr toluene pressure and 1100 K, k/k_{∞} is 0.75 ± 0.15, while for a dilute mixture of toluene in 3 atm of argon at 1600 K, k/k_{∞} = 0.4. However, a unimolecular falloff calculation that matches our smaller rate constants will have less falloff. We have made calculations by the RRKM approach, allowing for the low collision efficiency of Ar by a method we have described before.¹⁵ If our experimental rate constants are correct, the two k/k_{∞} values should be 0.98 ± 0.02 and 0.85 ± 0.1 , respectively, and the dilute mixture of 3 atm and 1100 K would have $k/k_{\infty} = 0.95 \pm 0.05$. A good Arrhenius curve for toluene in a dilute mixture of 3 atm should extend from the high-temperature data to match the 1050 K data $(1.3 \times 10^{-3} \text{ s}^{-1})$. The equation for reaction 1D of Table I gives a rate constant of 0.94×10^{-3} s⁻¹ at 1050 K, which after an isotope correction of 1.7 gives $1.6 \times 10^{-3} \text{ s}^{-1}$ for reaction 1.

Finally, an equation for k_{∞} for reaction 1 may be calculated by combining rate constants at 1600 and 1050 K. If k/k_{∞} is taken to be 0.85 at 1600 K, and an isotope correction of 1.5 applied, $k_{1,\infty}$ is ((690)(1.5/0.85)) 1.22 × 10³ s⁻¹ at that temperature, while if k/k_{∞} is 0.98 at 1050 K, $k_{1,\infty}$ is 1.4 × 10⁻³ s⁻¹. The Arrhenius equation is then

$$k_{1,\infty} = 2.7 \times 10^{14} \exp(-83000 \text{ cal}/RT) \text{ s}^{-1}$$

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Registry No. H_2 , 1333-74-0; D_2 , 7782-39-0; $C_6D_5CD_3$, 2037-26-5; $C_6D_5CD_2$, 2154-55-4; H, 12385-13-6; D, 16873-17-9; $C_6H_5CH_2$, 2154-56-5; $C_6H_5CH_3$, 108-88-3; neopentane, 463-82-1.

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