## Thermal Decomposition of Benzyl Iodide and of Benzyl Radicals in Shock Waves

W. Müller-Markgraf and J. Troe\*

Institut für Physikalische Chemie der Universität Göttingen, Tammannstrasse 6, D-3400 Göttingen, West Germany (Received: September 9, 1987; In Final Form: February 17, 1988)

The thermal decomposition of benzyl iodide into benzyl radicals + I was studied in shock waves by UV absorption spectroscopy. Rate constants  $k_1 = 10^{14.78} \exp(-181 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$  for the dissociation, and  $k_2 = 10^{13.70} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the reverse recombination of benzyl radicals and iodine atoms, were derived over the range 750  $\leq T \leq 950$  K. For the subsequent recombination of the formed benzyl radicals to dibenzyl, a rate constant  $k_7 = 10^{12.60} (T/1000 \text{ K})^{0.4} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  was obtained together with a dibenzyl dissociation rate constant of  $k_8 = 10^{14.9} \exp(-250 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$  (temperature range 900  $\leq T$  $\leq$  1500 K). The UV absorption spectra and dissociation rate constants  $k_{11}$  of benzyl radicals were then studied from 1250 up to 1900 K.  $k_{11}$  is represented as the sum  $k_9 + k_{10}$  with  $k_9 = 10^{10.22} \exp(-187 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$  and  $k_{10} = 10^{15.30} \exp(-349.6 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ . The spectroscopic and kinetic properties at high temperatures of benzyl radicals derived from several different precursor molecules agree.

## Introduction

Benzyl radicals play a key role in the high-temperature pyrolysis of alkyl-substituted benzene molecules (for a discussion of earlier work, see the subsequent articles, ref 1 and 2). Their kinetic properties are not yet well understood. However, without this knowledge many high-temperature studies of the pyrolysis of aromatic molecules cannot be interpreted unambiguously.<sup>1,2</sup> For this reason, we have undertaken an extensive series of studies of benzyl radicals in order to arrive at a better characterization of their high-temperature properties. We have chosen several different precursor molecules and monitored benzyl radical kinetics by UV absorption spectroscopy. In doing this, the decomposition kinetics of the precursor molecules has to be analyzed as well. In the major part of the present work we investigated the precursor molecule benzyl iodide. This system showed the smallest mechnistic complications. A limited amount of work was also done on benzyl chloride and methyl benzyl ketone without going too much into the details of their individual decomposition kinetics. The derived benzyl properties from the present work are consistent with the results of a more involved parameter fitting procedure for the thermal decomposition of toluene<sup>1</sup> and ethylbenzene.<sup>2</sup> Although the benzyl iodide results stand by themselves, the agreement between different benzyl precursor systems suggests that we now possess reliable benzyl radical data.

The thermal decomposition of benzyl radicals, such as studied in the present work, turned out to be unexpectedly fast (our earlier results<sup>3</sup> had to be reinterpreted, see ref 1). On the basis of the known marked resonance stabilization of this radical, we (and others) expected smaller reaction rates. Not too much is known about the reasons for this behavior and about the decomposition pathways. Two channels, leading either to  $C_3H_3 + C_4H_4$  or  $C_2H_2$ +  $C_5H_5$  fragments, have been identified by Knudsen mass spectrometry.<sup>4</sup> An independent verification of such experiments is urgently required. The present kinetic results clearly indicate a change of the decomposition mechanism at temperatures around 1650 K. Although our data appear well characterized, the present work does not reveal the nature of the dissociation pathways. Again more work using other techniques is required.

Besides kinetic data, the present work is concerned with UV absorption spectra at high temperatures. The careful investigation of these spectra forms the basis for studies of the pyrolysis aromatic hydrocarbons by UV absorption spectroscopy. Although several

CHART I				
	${T_{ m incident}}/{ m K}$	$rac{T_{ m reflected}}{ m K}$	([benzyl iodide]/ [Ar]) <sub>r=0</sub>	λ/ nm
	534	828	63.5	260
b	571	913	100.0	260
с	672	1152	35.2	255
d	740	1315	66.0	260
e	803	1455	70.0	255
f	828	1522	63.5	255
g	870	1620	65.9	260

absorption continua overlap, the spectra can be separated and provide a sensitive analytical tool for monitoring the reaction mechanisms in situ. There is an additional strong interest in the high-temperature absorption spectra of aromatic molecules and radicals because of extensive recent laser-photochemical work.5-10 Our own group has monitored energy-resolved unimolecular reactions and collisional energy transfer of vibrationally highly excited aromatic molecules by their hot UV absorption spectra.5-This work has been extended more recently,<sup>8-10</sup> also with particular emphasis on the spectrum of hot benzyl radicals.<sup>10</sup> The comparison of the UV absorption of vibrationally highly excited benzyl radicals after thermal and photochemical preparation provides an important cross-check for the present interpretation.

#### **Experimental Technique**

We have investigated the thermal decomposition of benzyl iodide, benzyl chloride, methyl benzyl ketone, and the benzyl radicals formed from these three precursor molecules, by heating these substances in incident and reflected shock waves. Reactant, intermediate, and product concentrations, under high dilution by the bath gas argon, were monitored by UV absorption spectroscopy over the spectral range 190-330 nm. In order to improve signal-to-noise ratios of the absorption measurement, a Xe highpressure lamp (Osram XBO, 250 W) served as the light source under pulsed operation. Details of our shock tube, the determination of the individual experimental conditions, and the shock wave technique have been given earlier.<sup>11</sup> Since we used the

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Figure 1. Absorption-time profiles in the thermal decomposition of benzyl iodide in shock waves. Lower traces indicate absorption base lines from pulsed lamp. Initial absorption level due to benzyl iodide absorption in incident shock. Absorption step indicates arrival of reflected shock; spikes at the step due to schlieren signals. Data relating to parts a-g are given in Chart I.

standard shock wave procedure, the reader is referred to this for any more experimental details.

#### Absorption-Time Profiles in the Benzyl Iodide Decomposition

Our measurements of absorption-time profiles from shockheated benzyl iodide-argon mixtures produced a large variety of characteristically different traces. We illustrate our observations at first by a series of oscillograms recorded for varying temperatures, and second by a series with varying concentrations.

For the observation wavelengths  $\lambda = 255$  and 260 nm, which are close to the maximum of the benzyl radical absorption, and ([benzyl iodide]/[Ar])<sub>t=0</sub> = 50-100 ppm, Figure 1a-g shows oscillograms with temperatures in the range 530-1620 K, realized in either incident or reflected shock waves. (Chart I shows data relating to parts a-g of Figure 1.) Measurements where the same temperature was established either in incident or in reflected waves (reflected wave in Figure 1a and incident wave in Figure 1f) show the same behavior. At low temperatures one observes the decomposition of benzyl iodide via the formation of the strongly absorbing benzyl radicals. Absorption signals behind the reflected wave are dominated by benzyl radical absorption. The observed kinetics certainly does not correspond only to a simple benzyl radical formation at low and benzyl radical decomposition at high temperatures. Instead, there are large variations in the time profiles, which are so characteristic that the mechanism can be identified relatively easily.

For a fixed temperature of 1160 K and an observation wavelength of 255 nm, Figure 2a–d shows the influence of varying the benzyl iodide concentration. Again, marked concentration effects are observed which are characteristic for the reaction mechanism.

Before the reaction mechanism of the present system is analyzed in detail below, we identify the main properties of Figures 1 and 2 in terms of the dominant features of the mechanism. At low temperatures, benzyl iodide decomposes with the formation of strongly absorbing species which tentatively (and most plausibly) are identified as benzyl radicals (see below). With increasing temperature a partial removal of the benzyl radicals becomes apparent. From the concentration dependence one can clearly attribute this removal to the approach of the benzyl-dibenzyl equilibrium. At still higher temperatures, this equilibrium is shifted completely to the benzyl side. Finally, at even higher temperatures, benzyl thermally decomposes. However, one observes a residual absorption, which even at the highest temperatures does not disappear, indicating the superposition of benzyl



**Figure 2.** Absorption-time profiles in the thermal decomposition of benzyl iodide in shock waves at  $T_{\text{reflected}} = 1160 \pm 10 \text{ K}$ ,  $\lambda = 255 \text{ nm}$  ([benzyl iodide]<sub>*i*=0</sub> (mol cm<sup>-3</sup>) = 4.8 × 10<sup>-9</sup> (a), 1.7 × 10<sup>-9</sup> (b), 7.5 × 10<sup>-10</sup> (c), and 3.4 × 10<sup>-10</sup> (d)).



Figure 3. Absorption spectrum of benzyl radicals from benzyl iodide at  $1600 \pm 20 \text{ K}$  ( $\bullet$ ) and  $1160 \pm 30 \text{ K}$  ( $\circ$ ); benzyl from toluene ( $\Box$ ) and ethylbenzene ( $\times$ ) at 1600 K; —, laser flash photolysis results from ref 10 at estimated temperature 1300 K.

and unidentified "benzyl fragment" spectra.

#### **Contributing Absorption Spectra**

According to the previous section, our absorption traces contain contributions from benzyl iodide, benzyl radicals, and "benzyl fragments". The high-temperature absorption spectrum of the parent molecule benzyl iodide can easily be characterized for temperatures where the reaction is too slow to be observed. When the reaction sets in, the strong absorption of benzyl radicals dominates completely. In order to quantitatively study the benzyl radical spectrum and its wavelength dependence, one has to choose conditions where the benzyl iodide decomposition is sufficiently rapid, the benzyl-dibenzyl equilibrium is completely on the benzyl side, but benzyl decomposition is still slow enough such that the benzyl concentration can be extrapolated back to the time zero. These conditions are well realized at temperatures around 1600 K, where one obtains the absorption spectrum of benzyl radicals shown in Figure 3. There is a lot of structure in this spectrum with maxima at  $\lambda \approx 315$ , 260, 230, and  $\leq 190$  nm. The present "hot" UV absorption spectrum has roughly similar properties to the known "cold" room temperature spectrum of benzyl (see ref 10 and earlier work cited therein). However, the details can only be compared with "hot" spectra such as that recorded in laser excitation experiments before vibrational excitation has been



Figure 4. Absorption coefficients of benzyl radicals at 255 ( $\bullet$ ) and 260 nm ( $\blacksquare$ ) as a function of temperature. Flash photolysis data and model results from ref 10: INY,  $\Box$ , O, ---.



Figure 5. Absorption spectrum of "benzyl fragments" at 1600 K. Precursors: benzyl iodide  $(\bullet)$  and toluene  $(\circ)$ .

removed by collisional cooling. Benzyl spectra of this type are available from the laser flash photolysis of benzyl chloride in ref 10. They are compared in Figure 3 with the present results. Apart from minor differences, particularly a wavelength shift by 10 nm, the two spectra show a remarkably good agreement in absolute value of  $\epsilon$  and detailed structure. The minor differences should not be taken too seriously, since the effective vibrational temperature of benzyl from the laser flash photolysis of benzyl chloride at 193 nm is not well-known. From the time evolution of the spectrum during the collisional deactivation process and a modified Sulzer-Wieland representation of the shape of the spectrum, a vibrational temperature of 1300 K was attributed to the laser spectrum shown in Figure 3. Although this procedure will certainly be roughly adequate, minor details may well differ from the spectrum of genuine thermal benzyl such as obtained in the present work. Figure 3 also shows absorption coefficients from this work for the lower temperature 1160 K. In the measurements at this temperature one has to take into account the establishment of the benzyl-dibenzyl equilibrium. There does appear to be a minor blue shift of the spectrum with decreasing temperature such as suggested by the comparison with the measurements from ref 10. Figure 3 also includes absorption coefficients from other benzyl precursors, see below. The general agreement of the absorption coefficients from quite different benzyl sources confirms the identification of genuine benzyl radical spectra. We have investigated the temperature dependence of the benzyl absorption coefficients over a limited range. Figure 4 shows the effects for the main observation wavelengths 255 and 260 nm of this work. There is only a small change of  $\epsilon$  over the range 850–1650 K. The modified Sulzer-Wieland representation of ref 10 would suggest much stronger effects for  $\lambda = 260$  nm. This confirms that the effective temperature of the flash photolysis spectrum in Figure 3 is not too well-defined and the minor differences between the present work and ref 10 are understandable.

At high temperatures, benzyl radicals decompose into a variety of fragments. These fragments produce a residual absorption such as recognized in Figure 1f,g. We have studied this spectrum in detail since it also contributes to the observed high-temperature absorptions in the pyrolysis of toluene and ethylbenzene.<sup>1,2</sup> Figure



Figure 6. Room temperature UV spectra of species important in benzyl pyrolysis systems (see text).

5 shows the wavelength dependence of the benzyl fragment spectrum at temperatures around 1600 K. The value of the absorption coefficient is defined by using a 1:1 conversion of benzyl radicals into benzyl fragments, whatever their chemical nature may be. Figure 5 also demonstrates the agreement between the benzyl fragments from the present system, and benzyl fragments from toluene pyrolysis such as studied in ref 1.

The present observations clearly are dominated by the strong absorption from benzyl radicals. Nevertheless, one has to ask whether other species appearing in the mechanism may also contribute to the recorded absorption traces. For this purpose, Figure 6 compares room temperature spectra of benzyl iodide, molecular iodine, and dibenzyl (in nonpolar liquid solvent). Because of the low vapor pressure at room temperature, we had difficulties obtaining reliable high-temperature absorption coefficients for dibenzyl in shock waves. However, the small room temperature values of  $\epsilon$  at our main observation range 250-270 nm, and the distance from the stronger absorptions at  $\lambda \leq 220$ nm, suggest that the expected high-temperature broadening of the short-UV spectra does not produce values of  $\epsilon$  which, at temperatures around 1300 K, are of comparable magnitude as the benzyl values. As a matter of fact, the detailed analysis of the absorption traces of Figures 1 and 2 for most conditions indicated no other contributions besides those from benzyl iodide, benzyl radicals, and benzyl fragments. Only for low temperatures could a minor contribution from dibenzyl just be identified with  $\epsilon \approx 500 \text{ L mol}^{-1} \text{ cm}^{-1}$  at T = 1200 K and  $\lambda = 255 \text{ nm}$  (see below).

### Absorption-Time Profiles in the Benzyl Chloride and Methyl **Benzyl Ketone Decomposition**

Some experiments have also been done with the benzyl radical precursor molecules benzyl chloride and methyl benzyl ketone. Here, the absorption from the undissociated parent molecules at 250-260 nm is even weaker than for benzyl iodide such that the benzyl absorption is completely dominant. Figure 6 includes the room temperature spectrum of benzyl chloride which, compared to the benzyl iodide spectrum, is shifted to shorter wavelengths.

The disappearance of benzyl radicals at temperatures around 1700 K and the appearance of the residual absorptions from benzyl fragments with benzyl radicals from the precursors benzyl chloride and methyl benzyl ketone agree in all details with those observed in benzyl iodide experiments. Figure 7 shows examples of the corresponding absorption-time profiles. The times for disappearance of benzyl radicals are the same, and the spectra of the benzyl radicals and their "fragments" are identical (one should note that different absorption levels of the parent molecules before the reflected waves are present in Figures 7, a and b). The results of such experiments are included in the representations for benzyl iodide experiments.

#### **Reaction Mechanism**

To analyze our observations, we have considered the following reaction mechanism based on the qualitative appearance of Figures



Figure 7. Absorption-time profiles of benzyl fragmentation: a, benzyl precursor = benzyl chloride, reflected shock wave with T = 1725 K,  $[\text{benzyl chloride}]_{t=0} = 3.3 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ nm}, [\text{Ar}] = 2.9 \times 10^{-9} \text{ mol cm}^{-3}, \lambda = 260 \text{ mol cm}^{-3}, \lambda$  $10^{-5}$  mol cm<sup>-3</sup>; b, benzyl precursor = methyl benzyl ketone reflected shock wave with T = 1725 K, [methyl benzyl ketone]<sub>t=0</sub> =  $3.6 \times 10^{-9}$ mol cm<sup>-3</sup>,  $\lambda = 255$  nm, [Ar] =  $3 \times 10^{-5}$  mol cm<sup>-3</sup>.

1 and 2 as well as on independent knowledge about some of the reaction steps. Benzyl iodide unimolecularly decomposes via

$$\mathbf{BI} \to \mathbf{B} + \mathbf{I} \tag{1}$$

(B = benzyl radicals). For the low temperatures, where this reaction is observable, we did not notice any pressure dependence of the derived first-order rate coefficients of reaction 1. The recombination between benzyl and iodine atoms

$$B + I \to BI \tag{2}$$

must always be taken into account. However, its contribution decreases with increasing temperature.

The iodine atoms formed by reaction 1 can liberate more benzyl radicals via

$$I + BI \rightarrow B + I_2 \tag{3}$$

Reliable rate data for this reaction, as well as for the reverse reaction

$$\mathbf{B} + \mathbf{I}_2 \to \mathbf{I} + \mathbf{B}\mathbf{I} \tag{4}$$

are available.<sup>12,13</sup> Simulations show that reaction 4 contributes only when I<sub>2</sub> and benzyl radicals are present in similar concentrations. Therefore, particular care had to be taken not to have any  $I_2$  in the reaction mixture introduced into the shock tube. The  $I_2$  produced in reaction 3 may thermally dissociate

$$I_2 + M \rightarrow 2I + M \tag{5}$$

This well-known reaction<sup>14</sup> as well as the reverse recombination (equilibrium constant from ref 15)

$$I + I + M \rightarrow I_2 + M \tag{6}$$

also were included in our modelling.

At low temperatures, the dominant benzyl radical sink is the recombination forming dibenzyl

$$2B \to B_2 \tag{7}$$

An equilibrium with the dibenzyl dissociation

$$\rightarrow 2B$$
 (8)

is established. The present work provides a direct access to the

 $B_2$ 

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<sup>(14)</sup> Troe, J.; Wagner, H. Gr. Z. Phys. Chem. NF 1967, 55, 326 and references given there. (15) "JANAF Thermochemical Tables"; Natl. Stand. Ref. Data Ser. 1971,

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**Figure 8.** Rate coefficients of benzyl iodide decomposition. Reaction 1,  $[Ar] = (3.0 \pm 1.0) \times 10^{-5}$  mol cm<sup>-3</sup>; O, incident shock ([benzyl iod-ide]/[Ar])<sub>t=0</sub> = 64 ppm; •, reflected shock, 101 ppm; •, reflected shock, 66 ppm.

rate constants of reactions 7 and 8 and to the equilibrium constant of the benzyl-dibenzyl equilibrium.

At high temperatures, when the benzyl-dibenzyl equilibrium is increasingly on the benzyl side, benzyl fragmentation sets in. Studies by Knudsen mass spectrometry<sup>4</sup> have suggested the two reaction channels

$$B \to C_5 H_5 + C_2 H_2 \tag{9}$$

$$\rightarrow C_4 H_4 + C_3 H_3 \tag{10}$$

Since our experiments only provide information on the rate of disappearance of benzyl radicals and the simultaneous appearance of an absorption from benzyl fragments, at present we cannot go beyond a global characterization of the benzyl fragmentation by a process

$$B \rightarrow benzyl fragments$$
 (11)

Reactions 1–8 and 11 provide the minimum set of reactions required to represent the present observations. The many details and the characteristic variations of the observed absorption-time profiles allow for a unique determination of several rate parameters and absorption coefficients. We demonstrate below that the results of this parameter-fitting procedure are remarkably unique and that the observed profiles were represented in all details for a large variety of conditions. We are therefore confident about the derived results and the analysis of the mechanism.

#### **Derived Rate Coefficients**

We evaluated our experiments by deriving rough first guess parameters for the unknown reaction rates from the oscillograms such as shown in Figure 1. A detailed simulation of the reaction mechanism 1–8 and 11 was then performed using a stiff-stable integrator routine of a modified Gear type.<sup>16</sup> Extensive sensitivity tests were performed as a control of the analysis. The calculated concentration profiles were converted into the observed absorption-time profiles. A fine-tuning was then done in order to accurately reproduce the experimental results. The procedure rapidly produced general agreement; see the next section.

Our results on the primary decomposition of benzyl iodide (1) such as derived mainly from the appearance of the benzyl radical absorption, are illustrated in Figure 8. Experiments behind incident and reflected shock waves, and with varying initial concentrations, all fall on the same Arrhenius plot represented by

$$k_1 = 10^{14.77 \pm 0.1} \exp(-181 \ (\pm 10) \text{ kJ mol}^{-1} / RT) \text{ s}^{-1}$$
 (12)



Figure 9. Rate coefficients for benzyl recombination. Reaction 7, this work: (II) incident and ( $\bullet$ ) reflected shock wave. ( $\odot$ ) pulse radiolysis.<sup>19</sup> Insert: [benzyl iodide]/[Ar])<sub>r=0</sub> = ( $\Box$ ) 200 ppm, ( $\bullet$ ) 102 ppm, (II) 64 ppm, ( $\times$ ) 35 ppm, (O) 15 ppm, ( $\blacktriangle$ ) 7 ppm.

 $k_1$  was determined over the range  $750 \le T \le 950$  K at [Ar]  $\approx 3 \times 10^{-5}$  mol cm<sup>-3</sup>. No pressure dependence was noted over the range  $10^{-5} \le [Ar] \le 10^{-4}$  mol cm<sup>-3</sup>. The corresponding recombination rate coefficient was determined mainly from the time dependence of the benzyl radical absorption at later stages. A value of

$$k_2 = 10^{13.70 \pm 0.2} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
 (13)

was obtained.

The measured activation energy from eq 12 fits well to the endothermicity of reaction 1. With enthalpies of formation for benzyl iodide<sup>12</sup> ( $\Delta H_{f}^{\circ}(298 \text{ K}) = 127.3 \text{ kJ mol}^{-1}$ ), benzyl<sup>17</sup>  $(\Delta H_{\rm f}^{\circ}(298 \text{ K}) = 200 \ (\pm 6) \text{ kJ mol}^{-1}), \text{ and } I^{15,18} \ (\Delta H_{\rm f}^{\circ}(298 \text{ K}))$ = 106.7 (±8) kJ mol<sup>-1</sup>), one obtains  $\Delta H^{\circ}(298 \text{ K}) \approx 179.5 (\pm 6)$ kJ mol<sup>-1</sup> for reaction 1. The independent determination of  $k_1$  and  $k_2$  from this work also leads to the equilibrium constant of the  $BI \rightleftharpoons B + I$  equilibrium. The preexponential factor of  $k_1$  is about a factor of 3 lower than that of the related dissociation of toluene.<sup>1</sup> Similarly,  $k_2$  is about a factor 2-3 lower than the corresponding value for recombination of H with benzyl.<sup>1</sup> The similarity of the results indicates that eq 12 and 13 of this work are reasonable. The slightly lower values compared to the toluene bond fission can be rationalized by different centrifugal effects due to the different masses of H and I atoms (see ref 1). Measurements of  $k_1$  and  $k_2$  could only be made at the lower temperatures of our experimental range.

After the primary fragmentation of benzyl iodide, we discuss our measurements for the combination of benzyl radicals and the benzyl-dibenzyl equilibrium, which dominate medium temperature conditions. Here, the partial disappearance of benzyl radical absorption directly leads to  $k_7$ . Figure 9 shows  $k_7$  for a large range of initial concentrations. A slightly positive temperature coefficient of  $k_7$  is noted which leads to a room temperature determination of  $k_7$  from ref 19.  $k_7$  can be represented over the range 300-1500 K as

$$k_7 = 10^{12.60 \pm 0.1} (T/1000 \text{ K})^{0.4} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
 (14)

The measured equilibrium constant for the benzyl-dibenzyl equilibrium, over the temperature range 750-1500 K, follows as

 $K_{\rm c} = k_8/k_7 = 155 \exp(-248.1 \text{ kJ mol}^{-1}/RT) \text{ mol cm}^{-3}$  (15)

The corresponding values of  $k_8$  are plotted in Figure 10. No

<sup>(17)</sup> Rossi, M.; Golden, D. M. J. Am. Chem. Soc. 1979, 101, 1230.

<sup>(18)</sup> Joshi, R. M. J. Macromol. Sci.-Chem. 1974, A8, 861.

<sup>(19)</sup> Pagsberg, P.; Troe, J., unpublished results.



**Figure 10.** Rate coefficients for thermal decomposition of dibenzyl. Reaction 8,  $[Ar] = (3.0 \pm 1.0) \times 10^{-3}$ ,  $([benzyl iodide]/[Ar])_{t=0} = (\bigcirc)$ 102 ppm, ( $\bigcirc$ ) 66 ppm, ( $\times$ ) 35 ppm, ( $\bigcirc$ ) 16 ppm, ( $\Box$ ) 7.3 ppm; (---) ref 20 with uncertainties (...) indicated there.

0.9

06

0.7

0.8

10<sup>3</sup>K/T-

11



Figure 11. Rate coefficients of "fragmentation" of benzyl radicals. Reaction 11, benzyl precursors: □, toluene; ×, ethylbenzene; ●, benzyl iodide; ■, benzyl chloride; O, methyl benzyl ketone.

dependence on [Ar] and on the initial concentration was noted.  $k_8$  is expressed by

$$k_8 = 10^{14.9} \exp(-250 \ (\pm 10) \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$$
 (16)

over the range  $900 \le T \le 1500$  K.  $k_8$  agrees very well with an earlier estimate in ref 20. However, the estimate of  $k_7 \approx 10^{11.1}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> from ref 20 is more than an order of magnitude lower than the present measurement, and so the agreement in  $k_8$  appears



**Figure 12.** Simulation (—) of the absorption  $(E = \log (I_0/I))$ -time profiles observed (×) in the experiment of Figure 1f (arrow = arrival of reflected shock wave).



Figure 13. Calculated concentration-time profiles for the simulation of Figure 12.

fortuitous ( $k_7$  and  $K_c$  were estimated in ref 20). Compared to the recombination of much smaller polyatomic radicals like methyl, there is only about a one order of magnitude decrease of the radical recombination rate constant.

The high-temperature reaction studied in the present work is governed by the thermal decomposition (11) of benzyl radicals. The rate coefficient  $k_{11}$  follows directly from the observed benzyl radical decays. Figure 11 illustrates our results. Data from the various benzyl precursors are all combined. Nevertheless, the Arrhenius plot has a complicated form. There appears to be a change of the benzyl radical dissociation mechanism at temperatures around 1600 K. The low-temperature results can be represented by

$$k_9 \approx 10^{10.22 \pm 0.7} \exp(-187 \ (\pm 15) \text{ kJ mol}^{-1} / RT) \text{ s}^{-1} \ (17)$$

the high-temperature results by

$$k_{10} \approx 10^{15.30\pm0.3} \exp(-349.6 \ (\pm 11) \text{ kJ mol}^{-1} / RT) \text{ s}^{-1}$$
 (18)

The experiments from ref 4 at 1523 K indicate a ratio  $k_9/k_{10} = 4 \pm 2$  which would agree with our ratio  $k_9/k_{10} = 3.15 \pm 0.6$  for this temperature. Separating our measured  $k_{11} = k_9 + k_{10}$  into  $k_9$  and  $k_{10}$ , however, is certainly premature at this stage. Our data should not be interpreted further until more information is available, either experimental information on products and branching ratios or theoretical information on the detailed fragmentation mechanism. In order to rule out bimolecular contributions, we have carefully checked for concentration dependences of  $k_{11}$  in the low-temperature range T < 1600 K. This might have explained the strongly curved Arrhenius plots. However, this search was unsuccessful. Therefore, on the basis of the identical results on benzyl radical spectra, fragmentation rate coefficients, and benzyl fragment spectra, we can empirically characterize the high-temperature properties of benzyl radicals well, but we presently do not understand our results.

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Figure 14. Simulation of absorption-time profiles for the experiment from Figure 2a (a) and Figure 2d (b).

#### Modelling of Observed Absorption–Time Profiles

Finally, the agreement between all measured absorption-time profiles and the modelled results on the basis of the shown rate and absorption coefficients will be demonstrated. Apart from the described absorption coefficients for benzyl iodide, benzyl radicals,

dibenzyl, and benzyl fragments, and from the rate coefficients of eq 12–18, the modelling used literature values of  $k_3 = 10^{11.75}$ exp(-14.6 kJ mol<sup>-1</sup>/RT) and  $k_4 = 10^{7.5}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> from ref 12 and 13, and of  $k_5 = [Ar]10^{13.99}$  exp(-127.2 kJ mol<sup>-1</sup>/RT) cm<sup>3</sup>  $mol^{-1} s^{-1}$  and  $k_5/k_6 = 10^{5.32} exp(-154 \text{ kJ mol}^{-1}/RT)$  atm from ref 14 and 15. With these input data, for example, the absorption signals behind the incident and reflected wave in Figure 1f are reproduced as demonstrated in Figure 12. Figure 13 also shows the calculated concentration profiles of benzyl radical, molecular iodine, dibenzyl, and benzyl fragments behind the reflected shock wave for this experiment. The concentration dependence of the signals in Figure 2 is reproduced equally well as demonstrated with the simulated signals of Figure 14 for the experiments of Figure 2a,d. All other recorded profiles could be simulated in the same manner. Our simulations have always been accompanied by detailed sensitivity tests which are not reproduced here (for details, see ref 21). We, therefore, are confident that our analysis of the present experiments is complete and has led to a reliable characterization of the kinetic and spectroscopic properties of benzyl radicals under high-temperature conditions.

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**Registry No.** Benzyl iodide, 620-05-3; benzyl radical, 2154-56-5; benzyl chloride, 100-44-7; methyl benzyl ketone, 103-79-7.

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# Thermal Decomposition of Toluene: A Comparison of Thermal and Laser-Photochemical Activation Experiments

## L. D. Brouwer, W. Müller-Markgraf, and J. Troe\*

Institut für Physikalische Chemie der Universität Göttingen, Tammannstrasse 6, D-3400 Göttingen, West Germany (Received: September 9, 1987; In Final Form: February 17, 1988)

The thermal decomposition of toluene has been reinvestigated in shock waves detecting toluene, benzyl radicals, and benzyl fragment concentrations by UV absorption spectroscopy in the range 190–320 nm. The experiments are interpreted in terms of a dominant toluene dissociation into benzyl radicals + H fragments with a rate constant  $k_1 = 10^{15.45\pm0.2} \exp(-(371.9 \pm 10) \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$  (at [Ar] =  $(2.6 \pm 0.4) \times 10^{-4} \text{ mol cm}^{-3}$ ) and in terms of a faster benzyl fragmentation which is in agreement with experiments on other benzyl sources. The derived thermally averaged rate constants of toluene dissociation  $k_1$  are consistent with specific rate constants k(E,J) from laser excitation experiments. Similarly, the nature of the dominant product channel is consistently identified in thermal and photochemical experiments, ruling out a recently discussed dominance of fragmentation into the phenyl + methyl channel.

#### Introduction

In spite of intense research over the past 10 years, the thermal decomposition of toluene under high-temperature combustion conditions still presents a series of puzzling uncertainties. Neither the rate of the primary fragmentation and the branching ratio into the two dissociation channels

$$C_7H_8 (+M) \to C_7H_7 + H (+M)$$
 (1)

$$C_7H_8(+M) \rightarrow C_6H_5 + CH_3(+M)$$
 (2)

nor the mechanism of the subsequent reactions is well established. From a practical point of view, this situation is rather unfortunate since simple aromatic hydrocarbons constitute an increasing fraction of unleaded fuel for internal combustion engines. From a more fundamental point of view, laser-photochemical studies of vibrationally highly excited aromatic molecules present attractive opportunities for investigating model unimolecular bond fission processes. Toluene dissociation has been studied over the temperature range 1500–2200 K in shock waves by a variety of detection techniques. UV absorption of the decomposing parent molecule and the forming benzyl radicals,<sup>1-4</sup> atomic resonance absorption of H atoms<sup>5-7,10</sup> (or D atoms in the case of deuterated toluene<sup>5.6</sup>), laser schlieren densitometry,<sup>8</sup> time-of-flight mass spectrometry,<sup>8</sup> and the single-pulse<sup>9</sup> technique have all been employed, leading

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