Pulse Radiolysis, Flash Photolysis, and Shock Wave Study of the Recombination $H + Benzyl \rightarrow Toluene$ at 300 and 1300–1650 K

L. Ackermann, H. Hippler, P. Pagsberg, C. Reihs, and J. Troe*

Institut für Physikalische Chemie der Universität Göttingen, Tammannstrasse 6, D-3400 Göttingen, West Germany, and Department of Chemistry, Riso National Laboratory, DK-4000 Roskilde, Denmark (Received: November 6, 1989; In Final Form: February 8, 1990)

Pulse radiolysis, discharge flash photolysis, and laser flash photolysis have been employed to study the recombination reaction $H + benzyl \rightarrow toluene at room temperature.$ Both H atoms and benzyl radicals were monitored. The same reaction was studied directly in shock waves between 1300 and 1650 K. The value of the high-pressure recombination rate constant of $(2.5 \pm 0.8) \times 10^{14}$ cm³ mol⁻¹ s⁻¹ was found to be independent of the temperature between 300 and 1650 K. It is argued that high-pressure rate constants for other recombination reactions should also have very small temperature coefficients over wide temperature ranges. Room temperature rate constants for addition of H atoms to toluene, cycloheptatriene, p-xylene, benzene, phenyl, and *p*-methylbenzyl are also reported.

Introduction

The temperature coefficients, n, of the limiting high-pressure rate constants $k_{rec,\infty}$ of thermal recombination reactions in the gas phase, i.e.

$$k_{\text{rec},\infty} \propto T^n$$
 (1)

are not well understood for two reasons:

(i) Experimental determinations have been inconclusive. Because the absolute values of n are small, n being either positive or negative, experimental studies over wide temperature ranges are required. With increasing temperatures, however, falloff effects become increasingly important. In many cases falloff extrapolations are necessary. Due to the lack of knowledge about collisional energy transfer, particularly at high temperatures, these extrapolations remain unsatisfactorily uncertain. Under the applied conditions it is often difficult to achieve sufficiently high pressures to approach the high-pressure limit. The well-studied recombination of methyl radicals, one of the best studied reactions, at temperatures near 1000 K¹ and above² provides an example. The measured rate constant was so far from the high-pressure limit that falloff extrapolations were inconclusive and suggest quite different temperature coefficients of $k_{rec,\infty}$.³ Derived *n* values were between 0^{2-4} and -2^5 for temperatures between 1000 and 2000 Κ.

(ii) Reliable theoretical predictions are difficult. The value of n (and its temperature dependence) is governed by fine details of the potential energy surface of the reactants which is often not known very accurately. Furthermore, accurate adiabatic channel potential curves for realistic potential surfaces are difficult to calculate. Finalized SACM calculations^{4,6} are still lacking. Other rate calculations have led to quite conflicting results about n; values between -2 and +2 have been obtained (see the recent work of ref 7 and the discussion of earlier work in refs 7-9).

- (3) Troe, J. Symp. (Int.) Combust., (Proc.), 22nd 1988, 843.
 (4) Quack, M.; Troe, J. Ber. Bunsen-Ges. Phys. Chem. 1974, 78, 240.
 (5) Wardlaw, D. M.; Marcus, R. A. J. Chem. Phys. 1985, 83, 3462; J. Phys. Chem. 1986, 90, 5383. Wagner, A. F.; Wardlaw, D. M. J. Phys. Chem. 1988, 92, 2462.
- (6) Troe, J. J. Chem. Phys. 1987, 87, 2773; Ber. Bunsen-Ges. Phys. Chem. 1988, 92, 242; Z. Phys. Chem. (Frankfurt) 1989, 161, 209.
- (7) Darvesh, K. V.; Boyd, R. J.; Pacey, P. D. J. Phys. Chem. 1989, 93, 4772.
- (8) Davies, J. W.; Pilling, M. J. In *Bimolecular Collisions*; Ashfold, M. N. R., Baggott, J. E., Eds.; Royal Society of Chemistry: London, 1989; pp 105-170.
- (9) Hase, W. L.; Wardlaw, D. M. In Bimolecular Collisions; Ashfold, M. N. R., Baggott, J. E., Eds.; Royal Society of Chemistry: London, 1989; pp 171-208.

A way out of this dilemma can be found by studying the reactions of larger molecular systems where falloff effects are less pronounced. There appears to be no fundamental reason for different n values in small or large molecule recombination reactions. In simplified SACM formulations¹⁰ of $k_{rec,\infty}$, partition functions of all except the (at maximum 6) transitional modes cancel. Therefore, apart from very specific potential effects, recombinations of analogous small and large reactants should be characterized by similar n values. Therefore, we started measuring recombination rate coefficients for large polyatomic systems under low-temperature static reactor and high-temperature shock wave conditions. Using these techniques we found¹¹ that the recombination of benzyl radicals over the temperature range 300-1500 K has only a small positive temperature coefficient, n being equal to $+0.4 (\pm 0.4)$. According to the foregoing reasoning, this suggests that the negative n values postulated for methyl recombination should be regarded with scepticism.

We continue our measurements in the present work with a study of H atom combination with benzyl radicals, i.e., with the reaction

$$H + C_7 H_7 \rightarrow C_7 H_8 \tag{2}$$

Studies of the combination of H atoms with smaller radicals such as CH_3 have led to ambiguous conclusions about the value of n. Low-temperature recombination studies of $CH_3 + H$ and hightemperature CH₄ dissociation studies (because of uncertain falloff extrapolations) left unresolvable uncertainties. The value of nwas found to be close to 0^{12} or close to -2^{13} (see also refs 8 and 9, and earlier work cited therein). Our present study of reaction 2 provides information about the temperature coefficient of $k_{rec,\infty}$, in this case for an H + radical combination, which should be transferable from large to small radical systems.

There is a second motivation for the present work. Thermal dissociation studies of toluene have encountered a number of difficulties. These now can be attributed to competition between C-H and C-C bond dissociation in the primary dissociation step, to uncertainties in the dissociation equilibrium constant, and to a relatively fast thermal decomposition of benzyl radicals following the dissociation of toluene. Such complications have led to conflicting interpretations of the various dissociation experiments (see, e.g., the most recent studies of refs 14-19). An independent

- (11) Müller-Markgraf, W.; Troe, J. J. Phys. Chem. 1988, 92, 4899.
- (12) Cobos, C. J.; Troe, J. Z. Phys. Chem. (Frankfurt), in press. (13) Stewart, P. H.; Smith, G. P.; Golden, D. M. Int. J. Chem. Kinet. 1989,
- 21, 923. (14) Braun-Unkhoff, M.; Frank, P.; Just, Th. Symp. (Int.) Combust.,
- (Proc.), 22nd 1988, 1053 (15) Brouwer, L. D.; Müller-Markgraf, W.; Troe, J. J. Phys. Chem. 1988, 92, 4905.

⁽¹⁾ Slagle, I. R.; Gutman, D.; Davies, J. W.; Pilling, M. J. J. Phys. Chem. 1988. 92. 2455.

⁽²⁾ Glänzer, K.; Quack, M.; Troe, J. Chem. Phys. Lett. 1976, 39, 304.

⁽¹⁰⁾ Troe, J. J. Chem. Phys. 1981, 75, 226. Cobos, C. J.; Troe, J. J. Chem. Phys. 1985, 83, 1010.



Figure 1. Absorption-time profiles of benzyl radicals recorded in the pulse radiolysis of toluene/Ar mixtures: observation wavelength 305.9 nm; $[Ar] = 4 \times 10^{-5} \text{ mol cm}^{-3}$; $[toluene] = 1.6 \times 10^{-10} \text{ mol cm}^{-3}$; optical path length = 120 cm; *I* = transmitted light intensity; I_0 = incident light intensity; T = 300 K.

investigation of the recombination reaction (2), therefore, is needed. In the present work we chose conditions where the complications of the toluene dissociation studies were not present.

In this paper we report our high-temperature measurements of $k_{rec,\infty}$ for reaction 2. To within the uncertainties of the experiment our value of $k_{rec,\infty}$ agrees with a series of earlier, room temperature measurements which we also describe here. Our values also agree with a recent room temperature determination²⁰ based on the value of the rate constant for the reference reaction D + CH₃ \rightarrow CH₂D + H.

Finding a temperature-independent value of $k_{rec,\infty}$ between 300 and 1650 K for reaction 2 strengthened the suspicion that negative *n* values in previous studies of small-molecule recombinations, such as CH₃ + CH₃ and H + CH₃, are artifacts due to unidentified or inadequately represented falloff effects.

Experimental Techniques

In the present work the recombination reaction (2) was studied at room temperature by pulse radiolysis, discharge flash photolysis, and laser flash photolysis. H atom and benzyl radical concentrations were monitored. The reaction was also studied in shock waves over the temperature range 1300 and 1650 K by monitoring benzyl radical concentrations. The different experimental techniques will be described briefly in the following.

1. Pulse Radiolysis Experiments. In the pulsed radiolysis experiments, 1 bar of Ar with traces of toluene (between 4×10^{-3} and 0.5 mbar) was irradiated by 30-ns pulses of 2-MeV electrons from a Febetron 705B field emission accelerator. The reaction was followed by monitoring the absorption of benzyl radicals near 300 nm in a White cell arrangement with 12 beam passages and a total path length of 120 cm. The light source for absorption measurements was a pulsed Varian 150-W high-pressure Xe arc lamp. The light was dispersed by a 1-m Hilger and Watts grating spectrograph (1 mm) slit. This slit width corresponds to ≈ 0.4 nm spectral resolution. Signal detection was performed with a Hamamatsu R928 photomultiplier and recorded with Biomation 8100 transient recorder. Further details of the setup are described in refs 21 and 22.

The optical detection of the recombination of H with benzyl, after dissociation of toluene in collisions with electronically excited Ar from pulse excitation, was achieved by absorption measurements of benzyl radicals at 305.3 nm. Figure 1 shows the example of a benzyl absorption trace. During the excitation pulse practically all toluene is destroyed and converted into benzyl + H.



Figure 2. Calibration curve for Lyman- α absorption at 121.6 nm: X, calibration by laser flash photolysis at 193 nm of N₂O + H₂ mixtures; •, calibration by laser flash photolysis at 193 nm of HBr; path length 12 mm; log (I_0/I) = initial H atom absorption.



Figure 3. Absorption-time profile of H atoms recorded in the laser flash photolysis of cycloheptatriene: laser wavelength 193 nm; pulse energy 6 mJ cm⁻²; Lyman- α absorption, absorption length = 12 mm; [cycloheptatriene]_{t=0} = 3.2×10^{-10} mol cm⁻³; [H]_{t=0} = 3.2×10^{-11} mol cm⁻³; [Ar] = 3.4×10^{-5} mol cm⁻³; I = transmitted light intensity, I_0 = incident light intensity, T = 300 K.

The disappearance of benzyl under our conditions is completely governed by reaction 2. The absorption trace in Figure 1, therefore, directly leads to the ratio k_2/ϵ . The benzyl radical has an absorption coefficient of $\epsilon = 7000 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$ at this wavelength. The value of ϵ was determined in the laser flash photolysis studies of ref 16 using benzyl bromide precursors. The value of ϵ agrees closely with the results from ref 23. The addition of H atoms to toluene can produce methylcyclohexadienyl. Perturbations by this reaction can be estimated by using the absorption coefficient of methylcyclohexadienyl at 305.3 nm which is equal to²⁴ 4000 L mol⁻¹ cm⁻¹.

2. Laser Flash Photolysis Experiments. Our flash photolysis experiments used a rectangular reaction cell irradiated from the side with laser pulses of 6×13 mm rectangular profile. For photolysis, 15-ns-long pulses from an ArF excimer laser operating at 193 nm (EMG 200, Lambda Physik) with fluences between 2 and 25 mJ cm⁻² were employed. After the photodissociation pulse, H atoms were detected by Lyman- α absorption perpendicular to the irradiation. The photolysis windows were quartz, and the analysis windows were all MgF₂. The design of the Lyman- α lamp followed ref 25. A 40-W microwave discharge was applied to a 0.1% H₂-He mixture, flowing with a flow rate of about 600 cm s⁻¹. The H atom detection chain consisted of the Lyman- α lamp, a 12-cm-long filter cell with flowing synthetic air, the 13-mm-long reaction cell, a cell with flowing Ar, a Lyman- α interference filter (Oriel 122-N), another cell with flowing Ar, and a solar-blind photomultplier (EMI G26E314LF).

⁽¹⁶⁾ Brand, U.; Hippler, H.; Lindemann, L.; Troe, J. J. Phys. Chem., in press.

⁽¹⁷⁾ Rao, V. S.; Skinner, G. B. J. Phys. Chem. 1989, 93, 1864.

 ⁽¹⁸⁾ Pamidimukkala, K. M.; Kern, R. D.; Patel, M. R.; Wei, H. C.; Kiefer,
 J. H. J. Phys. Chem. 1987, 91, 2148.

⁽¹⁹⁾ Hippler, H.; Troe, J. J. Phys. Chem., in press.

 ⁽²⁰⁾ Bartels, M.; Edelbüttel-Einhaus, J.; Hoyermann, K. Symp. (Int.)
 Combust., (Proc.), 22nd 1988, 1053.
 (21) Barcherg, B. B. Einhaus, L. Christener, H. C. J. Blue, Chem. 1970.

⁽²¹⁾ Pagsberg, P. B.; Eriksen, J.; Christensen, H. C. J. Phys. Chem. 1979, 83, 582.

⁽²²⁾ Nielsen, O. J.; Sillesen, A.; Luther, K.; Troe, J. J. Phys. Chem. 1982, 86, 2929.

⁽²³⁾ Ikeda, N.; Nakashima, N.; Yoshihara, K. J. Phys. Chem. 1984, 88, 5803.

⁽²⁴⁾ Hippler, H.; Luther, K.; Pagsberg, P.; Troe, J. Unpublished results. (25) Lifshitz, A.; Skinner, G. B.; Wood, D. R. *Rev. Sci. Instrum.* 1978, 49, 1322.



Figure 4. Absorption-time profile of benzyl radicals recorded in shock waves; benzyl formed via pyrolysis of benzyl iodide, H atoms formed via pyrolysis of ethyl iodide; observation wavelength = 260 nm, observation length = 10 cm; [benzyl]_{i=0} = 1.3×10^{-9} mol cm⁻³; [H]_{i=0} = 6.9×10^{-10} mol cm⁻³; [Ar] = 2.5×10^{-5} mol cm⁻³; T = 1480 K; I = transmitted light intensity, $I_0 =$ incident light intensity; benzyl absorption coefficient = 1.0×10^{4} L mol⁻¹ cm⁻¹.

The quantitative detection of H atoms by Lyman- α absorption required a calibration curve. This was obtained by producing known quantities of H atoms via laser photolysis of HBr or of N₂O-H₂ mixtures in 1 bar of Ar at $\lambda = 193$ nm. The photolysis quantum yields of HBr and N₂O were taken as unity; the absorption coefficients at 193 and 121.6 nm of HBr and N₂O were measured separately. On the basis of the known laser fluences, calibration curves, such as given in Figure 2, were obtained. Three orders of magnitude of concentration are covered in these curves. Deviations of this calibration curve from Lambert-Beer's law are quite obvious. In addition to the effective absorptions of H atoms at 121.6 nm, the absorption coefficients of toluene, cycloheptatriene, and benzene had to be measured for 193 and 121.6 nm.

The example of a Lyman- α absorption-time profile is shown in Figure 3. During the major part of the decay, the absorption trace follows a second-order rate law (although the oscillogram looks like a first-order profile which is due to the nonlinear calibration curve of figure 2). At later times, addition of H to cycloheptatriene has to be accounted for, see below.

3. Discharge Flash Photolysis Experiments. In addition to laser flash photolysis experiments, discharge flash photolysis experiments were also performed. The spatial profiles of the photolysis light are quite different in the experiments. Capacitors of 5 μ F and 15 nH were fired at 20 kV voltage producing flash lengths of about 2 μ s. Although in these experiments quite small H atom concentrations were produced, calibration curves like Figure 2 had to be employed.

4. Shock Wave Experiments. The recombination of H with benzyl was also studied behind reflected shock waves. Details of our shock tube equipment have been described before^{26,27} and are not repeated here. Well-defined concentrations of benzyl radicals were prepared by the thermal dissociation of benzyl iodide whose rapid thermal decomposition at temperatures above 1300 K leads to benzyl radicals and I atoms.¹¹ At these conditions the reaction follows a simple mechanism.¹⁵ A suitable H atom source was found in the thermal dissociation of ethyl iodide. Under our conditions this reaction predominantly leads to $C_2H_5 + I$ (with about 85% yield²⁸). The C_2H_5 rapidly dissociates²⁹ to C_2H_4 and H. The presence of I atoms, HI, and C_2H_4 in the experiment for the temperature range 1300–1650 K was not found to perturb the recombination of H atoms with benzyl. Experiments were done with mixtures of 20–40 ppm ethyl iodide and 40–60 ppm benzyl iodide. The progress of the reaction was followed by

TABLE I:	Recombination Rate Constants for $H + C_7 H_7 \rightarrow C_7$	-Η,
from Pulse	Radiolysis Experiments at 300 K	

G	10	10		
$ C_7H_8 /mol\ cm^{-3}$	1.6×10^{-10}	8.1×10^{-10}	4×10^{-9}	2 × 10 ⁻⁸
$k_{\rm s}/{\rm cm}^3$ mol ⁻¹ s ⁻¹	2.3×10^{14}	2.6×10^{14}	26 × 1014	2.2 × 1014
	2.5 7. 10	2.0 1 10	2.0 1 10	2.2 × 10

time-resolved measurements of the benzyl absorption at 260 nm. Extensive measurements of the benzyl spectrum in ref 11 served as the basis for the analysis of the benzyl absorption profiles.

Figure 4 shows a typical benzyl absorption profile. Because of the excess of the benzyl over the H concentration, there is a residual absorption due to unreacted benzyl. The absorption decay can be interpreted exclusively by reaction 2. The result of this analysis is again the ratio k_2/ϵ which is then evaluated by using the known absorption coefficient.

Results

1. Pulse Radiolysis Experiments. Mixtures of 1 bar of Ar with traces of toluene (in the range $(0.02-2) \times 10^{-8}$ mol cm⁻³) at room temperature were irradiated. At the lowest toluene concentrations the benzyl yields, by absorption at 305.3 nm, corresponded to complete dissociation; at the highest toluene concentrations only a few percent were dissociated. Hence, the recombinations started with initial benzyl concentrations of (1.5-5) \times 10⁻¹⁰ mol cm⁻³. A stoichiometry of 1:1 for benzyl and H concentrations was assumed. Only at the highest toluene concentrations were minor corrections for the reaction of H with toluene and subsequent processes involving CH_3 and C_6H_5 applied. Modeling of the corresponding mechanism was done. A maximum of 10% of the initial benzyl did not recombine with H. These manifest themselves by a residual absorption at 305.3 nm. The correction for these processes amounted to an increase of about 20% to the measured rate constant. For smaller concentrations, these corrections were unnecessary. Table I shows a summary of the derived second-order rate constants for benzyl disappearance which are directly attributed to the recombination (2) of H and benzyl. After the described minor corrections to the high concentration measurements, all derived rate constants agreed very well, leading to an average value of

$$k_2 = (2.4 \pm 0.2) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 300 K.

2. Laser and Discharge Flash Experiments. Our experiments were conducted at such high inert gas pressures $((0.4-4) \times 10^{-5} \text{ mol cm}^{-3} \text{ of Ar})$ that the photolysis products were cooled down rapidly and thermal conditions near 300 K were realized. Furthermore, H atom disappearances were only monitored over the first one to two half-lifes such that mechanistic complications of secondary reactions were not important. Experiments with laser flash photolysis led to initial H atom concentrations near 10^{-10} mol cm⁻³ whereas discharge flash photolysis only produced about 10^{-12} mol cm⁻³ of H atoms. The molecules toluene, cycloheptatriene, *p*-xylene, and benzene were studied, with initial concentrations in the range $10^{-9}-10^{-8}$ mol cm⁻³. In all cases, for the investigated range of conditions, a simple mechanism of the type

$$\mathbf{P} + h\nu \to \mathbf{H} + \mathbf{R} \tag{3}$$

$$H + P \rightarrow HP \tag{4}$$

$$H + R \to HR \tag{5}$$

was obeyed, where P denotes the parent molecule, HP the H adduct of the parent molecule, and R the produced primary radical. Branching of the primary photolysis via processes other than C-H bond split occurs to a minor extent.¹⁶ The primary photolysis, over the investigated range of laser energies of 2-20 mJ cm⁻², not only undergoes single-photon but also two-photon dissociation.³⁰ However, other channels still are of minor importance.

 ⁽²⁶⁾ Astholz, D. C.; Troe, J.; Wieters, W. J. Chem. Phys. 1979, 70, 5107.
 (27) Brouwer, L. D.; Müller-Markgraf, W.; Troe, J. Ber. Bunsen-Ges. Phys. Chem. 1983, 87, 1031.

⁽²⁸⁾ Yang, J. H.; Conway, D. C. J. Chem. Phys. 1965, 43, 1296.

⁽²⁹⁾ Benson, S. W.; O'Neal, H. E. Kinetic Data on Gas Phase Unimolecular Reactions; NSRDS-NBS 21; National Bureau of Standards: Washington, DC, 1970; pp 105 and 517.

⁽³⁰⁾ Hippler, H.; Riehn, Ch.; Troe, J.; Weitzel, K.-M. J. Phys. Chem., in press.



Figure 5. Pseudo-first-order rate constants of H atom disappearance in H + cycloheptatriene (CHT) mixtures (300 K): (•) discharge flash photolysis; (O) laser flash photolysis.



Figure 6. Pseudo-first-order rate constants of H atom disappearance in H + toluene (\bullet) and H + p-xylene (O) mixtures; [RH] = toluene or p-xylene concentration; discharge flash photolysis at 300 K

Measurements of the concentration dependence of the apparent rate constants of disappearance of H atoms allowed us to separate k_4 and k_5 . The procedure is illustrated in Figures 5-7. At low H concentrations, e.g., one may plot the first-order rate constants of H atom decay as a function of the initial concentration. Figures 5 and 6, for cycloheptatriene and toluene photolysis, demonstrate the concentration dependence of these apparent decay constants of H atoms. According to the mechanism of reactions 3-5, these measurements are most studied for the determination of k_4 values for adduct formation. Experiments at higher H concentrations were characterized by only minor contributions of adduct formation and dominant second-order disappearance rates of H via reaction 5. Figure 7 demonstrates the concentration dependence of the apparent second-order rate constants for H atom disappearance in H + cycloheptatriene mixtures.

Table II summarizes the obtained values from discharge and laser flash photolysis experiments. For the toluene system, the radical R was shown earlier to correspond predominantly^{16,30} to the benzyl radical. The adduct HP corresponds to methylcyclohexadienyl. The reaction $H + HP \rightarrow HPH$ is known²⁴ to have nearly the same rate constant as H + R. However, under the present conditions, this process interfered only at later times. For the cycloheptatriene system, the radical R is known again to correspond³¹ to benzyl, since after light absorption cycloheptatriene undergoes instantaneous internal conversion to toluene.



Figure 7. Pseudo-second-order rate constants of H atom disappearance in H + cycloheptatriene (CHT) mixtures (laser flash photolysis at 300 **K**)

TABLE II: Recombination and Addition Rate Constants for Flash Photolysis Experiments at 300 K and 1 bar

reaction	$k/cm^3 mol^{-1} s^{-1}$	ref
$H + benzyl \rightarrow toluene$	$(2.6 \pm 0.3) \times 10^{14}$	this work
	$(3.3 \pm 1) \times 10^{14}$	20
$H + toluene \rightarrow$	$(1.1 \pm 0.5) \times 10^{11}$	this work
methylcyclohexadienyl	1×10^{11}	33
H + cycloheptatriene →	$(1.8 \pm 0.5) \times 10^{12}$	this work
cycloheptadienyl	≥5 × 10 ¹¹	24
$H + p$ -methylbenzyl $\rightarrow p$ -xylene	$(2.3 \pm 1.0) \times 10^{14}$	this work
$H + p$ -xylene \rightarrow	$(1.1 \pm 0.7) \times 10^{11}$	this work
p-dimethylcyclohexadienyl	$(3.5 \pm 0.7) \times 10^{11}$	34
H + phenyl → benzene	$(2.2 \pm 0.8) \times 10^{14}$	this work
$H + benzene \rightarrow cyclohexadienyl$	$(1.7 \pm 0.5) \times 10^{10}$	this work
	$(3 \pm 2) \times 10^{10}$	34

The adduct HP probably corresponds to cycloheptadienyl. For p-xylene, R corresponds²⁴ to methylbenzyl and HP to p-dimethylcyclohexadienyl. For benzene, R probably corresponds to phenyl whereas with high certainty HP corresponds to cyclohexadienyl.

Table II compares the derived rate constants for adduct, HP, formation with literature values. An average value of k_2 from all cycloheptatriene and toluene experiments with laser and discharge flash photolysis gives

$$k_2 = (2.6 \pm 0.3) \times 10^{14} \,\mathrm{cm^3 \ mol^{-1} \ s^{-1}}$$
 (6)

It should be emphasized that the rate constants for H recombination with dimethylbenzyl and with phenyl are quite similar to k_2 , being again close to 2×10^{14} cm³ mol⁻¹ s⁻¹.

3. Shock Wave Experiments. Over the temperature range 1300-1650 K and with Ar concentrations of $(3-5) \times 10^{-5}$ mol cm⁻³, the benzyl decays could well be followed and evaluated with respect to reaction 2. Simulations of the complete mechanism¹⁵ showed that clean conditions were achieved and effects of secondary reactions such as reactions of H atoms with the forming toluene, toluene dissociation, etc. introduced only minor corrections. For the high-temperature conditions of this work, constructions of falloff curves for toluene dissociation¹⁵ suggest that only minor falloff effects are present. They amount to about $k_2/k_{2\infty} \approx 0.85$ under our typical conditions. This factor is mainly attributed to weak collision broadening effects of the falloff curve. Apart from this falloff correction, slight uncertainties about the H atom yield from the dissociation of ethyl iodide have to be considered. We have assumed that this yield amounts to 85% under our average conditions.^{28,29} Applying these two minor corrections, our results are illustrated in Figure 8. The average value of the shock wave results of

$$k_{2\infty} = (2.6 \pm 0.7) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
 (7)

agrees very well with the room temperature result. The uncertainty

⁽³¹⁾ Thrush, B. A.; Zwolenik, J. J. Bull. Soc. Chim. Belg. 1962, 71, 642.

⁽³²⁾ Price, S. J. Can. J. Chem. 1962, 40, 1310.
(33) Sauer, M. C.; Ward, B. J. Phys. Chem. 1967, 71, 3971.
(34) Sauer, M. C.; Mani, I. J. Phys. Chem. 1970, 74, 59.



Figure 8. High-pressure recombination rate constant of the reaction H + benzyl \rightarrow toluene (2): (\triangle) Pulse radiolysis, discharge, and laser flash photolysis experiments from this work; (\triangle) flow system relative rate measurements from ref 20; (O) flow system toluene dissociation experiments from ref 32 converted with equilibrium constant of ref 19; (\bigcirc) shock wave experiments from this work.

reflects the scatter and the amount of the applied corrections.

Discussion

Although there are at present no direct measurements of k_2 at intermediate temperatures between 300 and 1300 K, the agreement between the measured room temperature and hightemperature values of k_2 , and the absence of a temperature dependence between 1300 and 1650 K, strongly indicate a temperature-independent value of k_2 over the full temperature range. The consistency of the various room temperature determinations of the present work appears convincing. The agreement with the flow system result from ref 20 also appears quite satisfactory taking into account that the value of $k_2 = (3.3 \pm 1) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1}$ s⁻¹ was obtained via measurements of the reaction $D + C_7 H_7 \rightarrow$ C_7H_7D relative to the reaction $D + CH_3 \rightarrow CH_2D + H$ and a theoretical conversion from the D + C_7H_7 to the H + C_7H_7 reaction. Some information about k_2 in the range 900-1100 K can be obtained from the old toluene dissociation studies of ref 32 and the new determination of the toluene dissociation equi-librium constant of ref 19. Using $k_{-2} = 10^{14.8} \exp(-356 \text{ kJ} \text{mol}^{-1}/RT) \text{ s}^{-1}$ from ref 30 and $k_{-2}/k_2 = 5 \exp(-360 \text{ kJ mol}^{-1}/RT)$ mol cm⁻³ from ref 19 one obtains a consistent picture with $k_2 \approx$ $(2.6 \pm 0.5) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ also in the range 900–1100 K. We, therefore, conclude that there is no indication of any deviation of k_2 from a final value of

$$k_2 = (2.6 \pm 0.7) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
 (8)

being constant within the error limits over the whole temperature range 300-1700 K.

The simplified statistical adiabatic channel model (SACM) of ref 10 provides a convenient means of analysing the value of k_2 . The high-pressure recombination rate constant $k_{rec,\infty}$ is represented by the product of the phase space theoretical contribution $k_{rec,\infty}^{losse}$

$$k_{\rm rec,\infty}^{\rm loose} = \left(\frac{kT}{h}\right) \left(\frac{h^2}{2\pi\mu kT}\right)^{3/2} \frac{Q_{\rm el}({\rm T})}{Q_{\rm el}({\rm B}) Q_{\rm el}({\rm H})} Q^*_{\rm cent} \qquad (9)$$

and a rigidity factor $f_{rec.\infty}^{rigid}$, i.e., by

$$k_{\rm rec,\infty} = k_{\rm rec,\infty}^{\rm loose} f_{\rm rec,\infty}^{\rm rigid} \tag{10}$$

where Q_{el} denotes electronic partition functions of toluene (T), benzyl (B), and H, Q^*_{cent} is the centrifugal partition function, and μ is the reduced mass of H and B. With Morse potentials, Q^*_{cent} usually assumes a temperature dependence of $Q^*_{\text{cent}} \propto T^1$ such that $k_{\text{rec},\infty}^{\text{losse}} \propto T^{0.5}$. In the present case the rigidity factor $f_{\text{rec},\infty}^{\text{rigid}}$ essentially only contains contributions from two deformation vibrations in toluene correlating with two rotations of benzyl. The simplified SACM version of ref 10 usually produces nearly temperature-independent $f_{rec,\infty}^{rigid}$ whereas the more detailed original SACM⁴ tended to lead to small negative temperature coefficients, e.g. compensating the small negative temperature coefficient of k in the $CH_3 + CH_3 \rightarrow C_2H_6$ recombination. Because the fine details of this temperature dependence depend on the fine details of the potential with the corresponding accurate adiabatic channel eigenvalue calculations (see, e.g., ref 6), present theoretical predictions of the temperature coefficient n of $k_{rec,\infty}$ appear to be no better than about $n = 0 \pm 0.5$. In any case, the presently available versions of SACM are consistent with the observed temperature-independent value of n for a recombination system which is characterized by a dominant short range "chemical" potential and only a minor long-range multipole contribution. The present results also suggest a temperature-independent high-pressure recombination rate constant for the $H + CH_3 \rightarrow CH_4$ reaction from the present experiments, the absolute values obtained for $f_{rec.\omega}^{rigid}$ are 0.066 for 300 K and 0.031 for 1500 K. The understanding of these values waits for a further analysis on the basis of better potential models.

Acknowledgment. Assistance with the pulse radiolysis experiments by A. Sillesen, with helpful discussions by H.-G. Löhmannsröben, and financial support by the Deutsche Forschungsgemeinschaft are gratefully acknowledged.

Registry No. H, 12385-13-6; benzyl, 2154-56-5; toluene, 108-88-3; cycloheptatriene, 544-25-2; *p*-xylene, 106-42-3; benzene, 71-43-2; phenyl, 2396-01-2; *p*-methylbenzyl, 2348-52-9; methylcyclohexadienyl, 74622-56-3; cycloheptadienyl, 127254-73-3; 1,4-dimethylcyclohexadienyl, 57406-96-9; 3,6-dimethylcyclohexadienyl, 77323-04-7; cyclohexadienyl, 12169-67-4.