

Bond Homolysis in High-Temperature Fluids

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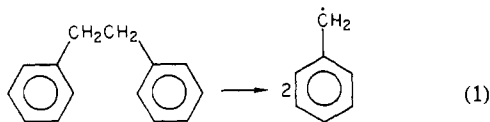
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Abstract: Rate constants for the homolysis of 1,2-diphenylethane have been determined in tetralin, in dodecahydrotriphenylene, and in the gas phase at temperatures above 350 °C. The least-squares-derived Arrhenius expression for this reaction in the gas phase is $k_1/s^{-1} = 10^{(15.25 \pm 0.15) - (62.31 \pm 0.50)/\theta}$ ($\theta = 0.004576T/K$) and is consistent with available thermokinetic data. In liquid tetralin up to its critical temperature and in liquid dodecahydrotriphenylene Arrhenius parameters for this reaction were found to be distinctly higher than gas-phase values, and rate constants to be somewhat lower. These differences between gas- and liquid-phase kinetics are attributed to recombination of nascent free radicals in solution (the "cage effect"), the probability of which decreases with decreasing viscosity.

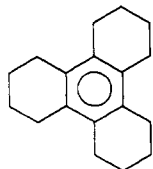
Introduction

The kinetics of reactions in organic fluids at high temperatures has become a subject of major concern in recent years. While the desire to control practical processes such as coal liquefaction has been the primary motivation for much of this interest, the study of chemical reactions under these conditions is very attractive for more general scientific reasons, some of which are the following. (1) Studies of high-temperature liquids can reveal new and unique chemical reactions, especially reactions involving a high activation energy bimolecular step. (2) In high-temperature fluids solvation effects are minimized, thereby simplifying experimental interpretation. (3) Liquid pyrolysis studies may be designed to minimize wall reactions, a common, serious problem in many gas-phase pyrolytic studies.

To better understand reaction kinetics in high-temperature liquids we have determined rates of a single elementary reaction over a wide range of physical conditions. The reaction chosen for study was 1,2-diphenylethane (12DPE) homolysis, reaction 1. This reaction was studied in liquid tetralin up to the critical



temperature of tetralin (444 °C), in dodecahydrotriphenylene (DHTP)



and in the gas phase. These studies show, not unexpectedly, that gas- and liquid-phase homolysis rates are similar in magnitude, but they also reveal interesting differences which can be attributed to a temperature-dependent "cage" effect.

Experimental Section

Two quite different experimental techniques, sealed-tube experiments and very-low-pressure pyrolysis (VLPP) methods, were used in the present studies. Most reactions were studied using the former technique over the range 350–475 °C in evacuated Pyrex tubes containing hydroaromatics. The hydroaromatics, tetralin and DHTP, served as free-radical traps and, in liquid-phase studies, as the solvent. Gas-phase reactions were studied above 600 °C using VLPP techniques.¹

Conventional sealed-tube techniques similar to those described previously for neat 12DPE pyrolysis² were used in experiments involving tetralin. In all liquid-phase runs the liquid:vapor volume ratios at reaction

temperature were at least 3:1. Reactions in the gas phase were simply done by pyrolyzing an amount of reactant mixture small enough to ensure that only vapor was present during pyrolysis.

Because of the high melting point of DHTP (mp 232 °C) and its resulting low room-temperature solubility in organic solvents, the following special procedures were followed in experiments using DHTP. Solid 12DPE and DHTP were independently weighed into reaction tubes. Before evacuation and sealing, a glass rod was inserted into the sample tube to minimize relative vapor/liquid volume. At reaction temperatures this ratio was <0.1. After pyrolysis, the entire reaction tube was crushed while being held inside a Teflon tube and then washed into a sample bottle using highly purified benzene. This mixture was heated and immersed in an ultrasonic bath to ensure complete dissolution of 12DPE and its reaction product, toluene.

Based on previous experience² and results of separate, short-reaction-duration studies at high temperature, the heat-up time for all sealed-tube experiments is assumed to be 2.5 min.³

The presence of vapor volume in the liquid-phase studies is not expected to noticeably affect observed rates. Using liquid density and 12DPE vapor-pressure estimates² along with the assumption that 12DPE forms ideal solutions with hydroaromatics, the fraction of 12DPE present in the liquid phase is computed to be always greater than 97%.

All chemicals used in these experiments were obtained from commercial sources. Tetralin was purified by spinning-band distillation (purity >99.5% by GC), 12DPE by recrystallization and sublimation, and DHTP by recrystallization.

All analyses were done by gas chromatography using FID detection. To within 5% accuracy relative peak areas were found to be proportional to relative concentrations when corrected for differences in carbon number.

VLPP experiments were done using an apparatus described previously.^{1b} Briefly, these experiments measured 12DPE decomposition rates in a Knudsen-cell, fused-silica flow reactor using mass spectrometric detection. Benzyl radicals (m/e 91) were the only detectable products. The flow rate of 12DPE was deduced from direct pressure measurements in the reactor using a Baratron pressure transducer and controlled by fixing the temperature, hence vapor pressure, of 12DPE in a reactant volume upstream of the reactor.

Results

12DPE pyrolysis was studied under the following conditions: (1) in liquid tetralin from 350 °C to just below its critical temperature of 444 °C; (2) in the gas phase in the presence of tetralin from 375 to 450 °C; (3) in dense, supercritical tetralin; (4) in liquid DHTP between 375 and 475 °C; (5) in the gas phase at very low pressures (<0.1 μ) and high temperatures (613–732 °C).

In all of these reaction systems the rate-controlling step for 12DPE decomposition appears to be unimolecular bond homolysis (reaction 1). In the presence of hydroaromatics, benzyl radicals

(1) (a) D. M. Golden, G. N. Spokes, and S. W. Benson, *Angew. Chem., Int. Ed. Engl.*, **12**, 534 (1973); (b) D. A. Robaugh and S. E. Stein, *Int. J. Chem. Kinet.*, **13**, 445 (1981).

(2) R. E. Miller and S. E. Stein, *J. Phys. Chem.*, **85**, 580 (1981).

(3) We estimate the heat-up time to fall between 1.5 and 3.5 min and to vary somewhat from run to run. This uncertainty can lead to a $\pm 13\%$ error in rate constants derived from a 10-min run.

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Table I. 12DPE Homolysis

A. In Liquid Tetralin									
$T/^\circ\text{C}$	dilution ^a	reaction time/min ^b	% reaction ^c	k_1^d/s^{-1}	$T/^\circ\text{C}$	dilution ^a	reaction time/min ^b	% reaction ^c	k_1^d/s^{-1}
350	10	1440	1.20	1.40×10^{-7}	400	10	240	11.58	8.64×10^{-6}
	10	2880	2.75	1.61×10^{-7}		100	240	10.46	7.75×10^{-6}
	10	2895	2.63	1.53×10^{-7}		500	240	11.57	8.63×10^{-6}
375	100	2880	2.21	1.29×10^{-7}	425	10	30	7.27	4.58×10^{-5}
	10	180	1.08	1.01×10^{-6}		10	30	8.94	5.68×10^{-5}
	10	360	2.21	1.03×10^{-6}		100	30	7.71	4.86×10^{-5}
400	10	360	2.23	1.06×10^{-6}	440	1000	30	7.30	4.59×10^{-5}
	10	60	2.63	7.72×10^{-6}		10	190	39.8	4.51×10^{-5}
	10	127	6.48	8.97×10^{-6}		1000	180	40.3	4.84×10^{-4}
	10	120	5.00	7.27×10^{-6}		10	10	5.2	1.19×10^{-4}
	1000	120	5.52	8.05×10^{-6}		10	90	44.3	1.13×10^{-4}
10	240	10.66	7.91×10^{-6}						

B. In the Gas Phase (Tetralin Carrier) ^e								
$T/^\circ\text{C}$	reaction time/min	% reaction	k_1/s^{-1}	$T/^\circ\text{C}$	reaction time/min	% reaction	k_1/s^{-1}	
375	360	3.47	1.64×10^{-6}	425	20	6.34	6.24×10^{-5}	
	1440	12.39	1.53×10^{-6}		440	15	9.63	1.35×10^{-4}
	1440	14.03	1.75×10^{-6}		30	19.64	1.33×10^{-4}	
400	60	3.95	1.17×10^{-5}	60	38.13	1.39×10^{-4}		
	60	3.63	1.07×10^{-5}	90	53.09	1.44×10^{-4}		
	120	6.94	1.02×10^{-5}					
	120	7.64	1.13×10^{-5}					

C. In Supercritical Tetralin ^f									
$T/^\circ\text{C}$	density ^g / g cm ⁻³	reaction time/min	% reaction	k_1/s^{-1}	$T/^\circ\text{C}$	density ^g / g cm ⁻³	reaction time/min	% reaction	k_1/s^{-1}
450	0.01	20	25.7	2.82×10^{-4}	475	0.13	20	70.1	1.15×10^{-3}
	0.06	20	25.9	2.85×10^{-4}		0.3	10	38.2	1.07×10^{-3}
	0.14	20	25.1	2.75×10^{-4}		0.5	20	66.9	1.05×10^{-3}
	0.5	10	9.84	2.30×10^{-4}					
	0.5	10	10.7	2.52×10^{-4}					
0.5	20	25.7	2.82×10^{-4}						

D. In Liquid DHTP ^h							
$T/^\circ\text{C}$	reaction time/min	% reaction	k_1/s^{-1}	$T/^\circ\text{C}$	reaction time/min	% reaction	k_1/s^{-1}
375	240	1.08	7.54×10^{-7}	425	60	10.92	3.35×10^{-5}
	1027	4.42	7.35×10^{-7}		60 ⁱ	9.17	2.79×10^{-5}
	1740	6.05	5.99×10^{-7}		450	30	24.0
400	120	3.52	5.07×10^{-6}	475	10	32.6	8.77×10^{-4}
425	15	2.35	3.17×10^{-5}	15	46.5	8.34×10^{-4}	
	60	10.22	3.12×10^{-5}	15	45.7	8.14×10^{-4}	

^a [tetralin]/[12DPE]. ^b This is the total time tubes were in the oven. Times used for computing k_1 are 2.5 min less (see text). ^c $100([\text{toluene}]/2[12\text{DPE}] + [\text{toluene}])$. ^d These rate constants show somewhat more scatter than do values obtained in the gas phase and DHTP studies (Table IB,C). This is because these studies were performed over a period of ca. 1 year during which time minor changes in experimental conditions may have occurred; the other studies were done over a single, short period of time. ^e [tetralin]/[12DPE] ~ 10; total pressures were in the range 0.5–10 atm. ^f [tetralin]/[12DPE] ~ 10. ^g These are rough estimates ($\pm 20\%$); estimated critical density of liquid tetralin is 0.3 g/cm³ (see reference in footnote 14). ^h DHTP = dodecahydrotriphenylene; except where noted. DHTP:12DPE = 20:1 w/w. ⁱ DHTP:12DPE = 200:1 w/w.

generated in this reaction rapidly abstract hydrogen atoms to form toluene. In VLPP experiments benzyl radicals were directly observed as the only major products. The lack of mechanistic complexity in 12DPE pyrolysis is due to the presence of only one low-energy reaction channel and the absence of facile chain reaction pathways.²

In reaction systems containing hydroaromatics (sealed-tube experiments), k_1 values were derived from relative amounts of 12DPE and toluene in the reaction mixture using the equation

$$k_1 = \frac{1}{t} \ln \left\{ 1 + \frac{[\text{toluene}]}{2[12\text{DPE}]} \right\} \quad (2)$$

where t is the reaction duration. Table I contains k_1 values obtained using this expression. Implicit in this expression are the assumptions that 12DPE decomposed solely through reaction 1, that all benzyl radicals were converted to toluene, and that all toluene originated from 12DPE dissociation. The following observations of 12DPE pyrolysis in tetralin support these assumptions

and indicate that eq 2 is a reliable means of obtaining k_1 . (1) Empirical k_1 values are independent of dilution and reaction duration (Table I). (2) Observed activation energies for 12DPE decomposition are comparable to the estimated bond strength of the central C–C bond in 12DPE (see later). (3) Toluene was the only major decomposition product of 12DPE.⁴ (4) Toluene was not found as a product in the pyrolysis of pure tetralin.⁵ (5) The fractional decomposition of 12DPE as measured by relative tetralin/12DPE concentrations before and after reaction agreed with

(4) The only other product resulting directly from 12DPE decomposition was 1,1-diphenylethane which was also a product in the pyrolysis of neat 12DPE.² In the present experiments this product was generally found at a concentration of 2–3% that of toluene. Benzyl-tetralyl adducts, if formed, were present only in trace amounts (<1% that of toluene). Naphthalene was the major dehydrogenation product of tetralin although trace quantities of 1,2-dihydronaphthalene were also observed.

(5) No toluene was detected as a product of tetralin pyrolysis at 425 °C for 3 h. It is difficult to imagine a free-radical mechanism converting tetralin into toluene at low extents of reaction.

Table II. 12DPE Homolysis via VLPP

T/ °C	flow rate ^a		k_1 - (low pres)/ s ⁻¹ ^c	k_1 - (high pres)/ s ⁻¹ ^d	k_1 - (tetralin) ^e / k_1 - (high pres)
	10 ¹³ molecules/s	% decom- position ^b			
613	4	9.5	0.91	1.41	0.55
633	4	16.1	1.7	2.76	0.61
660	4	30.7	3.9	7.00	0.65
660	13	32.6	4.28	7.68	0.59
660	13	31.4	4.06	7.29	0.62
660	13	31.8	4.13	7.41	0.61
694	4	55.8	11.4	23.4	0.63
694	13	56.1	11.5	23.6	0.63
694	13	56.1	11.5	23.6	0.63
715	4	69.3	20.6	46.0	0.64
732	4	78.0	32.6	78.2	0.64

^a At 100 °C a flow rate of 10¹³ molecules/s generated a pressure of 9 × 10⁻⁵ torr; these flow rates are sufficiently low to ensure minimal effects on measured k_1 values due to benzyl radical recombination. Using k_{-1} (high pres) = 10^{9.4} M⁻¹ s⁻¹ (see text), in all cases the probability of escape of benzyl radicals from the reactor is computed to be ten times that of recombination. ^b Derived from relative parent-ion peak intensities for 12DPE with and without reaction. ^c k_1 (low pres)/s⁻¹ = (% decomposition)0.290 (T/K)^{1/2}/(100 - % decomposition); the factor 0.29 is derived from reactor geometry and the molecular weight of 12DPE. ^d Derived from k_1 (low pres) and RRKM calculations.⁸ RRKM and calculations used a vibrational model consistent with $A = 10^{15.25}$ s⁻¹ and the estimated entropy of 12DPE at reaction temperatures.¹³ It is well known that derived high-pressure values are insensitive to details of this model.⁸ ^e k_1 (tetralin) is obtained by extrapolation of sealed-tube gas-phase results to VLPP temperatures.

values obtained from toluene/12DPE ratios.⁶ (6) Pyrolysis of neat 12DPE liquid has been shown to be a nonchain process whose rate-limiting step is simple bond homolysis.²⁷ (7) Rate constants previously obtained for reaction 1 in a kinetic analysis of neat 12DPE pyrolysis² are in good agreement with values obtained in the present work. (8) Derived rate constants are found to be independent of pressure in both the gas phase (Table IB) and supercritical phase (Table IC).

Pyrolysis in DHTP was not as thoroughly examined as pyrolysis in tetralin owing to the formation of unidentified products from DHTP thermolysis and the low solubility of DHTP in organic solvents. However, no toluene was generated in neat DHTP pyrolysis, and derived k_1 values were found to be independent of dilution and reaction duration (Table ID). Moreover, the similar chemical nature of tetralin and DHTP suggests that the 12DPE pyrolysis mechanisms in these two solvents are very similar.

Unimolecular rate constants obtained in VLPP experiments are a function of the collision frequency in the reactor.^{1a} It was therefore necessary to convert empirical VLPP rate constants to collision-frequency independent (i.e., "high pressure") values. RRKM theory was used for this purpose.⁸ Empirical and high-pressure rate constants are given in Table II.

Discussion

Since phase effects on rate constants are best understood using gas-phase values as a point of reference, gas-phase results will be discussed first.

Empirical k_1 (gas) values obtained in the presence of tetralin (375–475 °C) exhibit very straight Arrhenius behavior consistent with the following least-squares-derived expression, k_1 (gas)/s⁻¹ = 10^{(15.25±0.15)-(62.31±0.50)/θ}, where θ = 0.004576T/K. This ex-

(6) In two liquid-phase runs at 425 °C for 3 h, one with 10:1 tetralin:12DPE, the other with 1000:1, percentage decomposition of 12DPE as measured by tetralin:12DPE ratios before and after reaction were 37 and 36%, respectively, while corresponding values derived from toluene:12DPE ratios were 39.8 and 40.3%. These four values are regarded as identical within experimental error.

(7) M. L. Poutsma, *Fuel*, **59**, 335 (1980).

(8) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley, London, 1972.

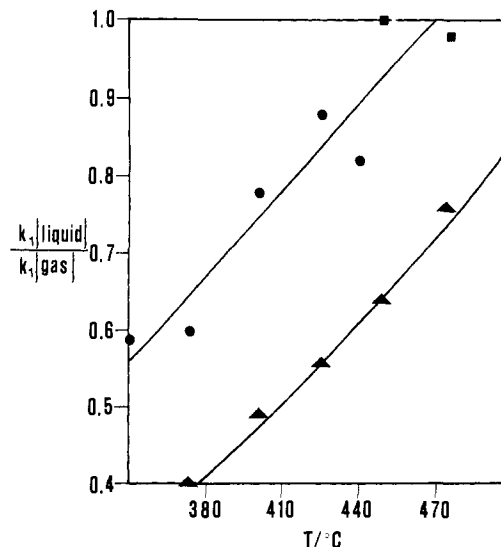


Figure 1. Relative liquid/gas rate constants for homolysis of 12DPE. Data used in this figure are given in Table I: (●) in liquid tetralin, (▲) in liquid dodecahydrotriphenylene. Lines are derived from Arrhenius expressions given in the text.

pression will be used later for computing relative gas/liquid rate constants. In addition to the well-behaved kinetics discussed earlier, the following considerations provide further confidence in the accuracy of this expression.

If it is assumed that radical recombination occurs without an activation energy (in concentration units), then the above parameters yield a bond strength^{9a} of 63.5 kcal/mol (1 kcal = 4.186 kJ) for the central C–C bond in 12DPE and a rate constant for gas-phase benzyl radical recombination, k_{-1} , of 10^{9.4} M⁻¹ s⁻¹.^{9b} This bond strength value is in reasonable agreement with the value of 60.0 kcal/mol based on a recently recommended value for the enthalpy of formation of benzyl radicals of 47.1 kcal/mol¹⁰ and an enthalpy of formation of 12DPE of 34.2 kcal/mol.¹¹ Note that the enthalpy of benzyl radical formation has recently been suggested to be as high as 49 kcal/mol,¹² and the above value for 12DPE is uncertain to at least ±1 kcal/mol. The rate constant derived above for benzyl radical recombination falls in the range generally found for radical recombination.¹³ The key point of these calculations is to show that the Arrhenius parameters in the above expression for k_1 (gas) are within the range expected for this reaction in the gas phase.

VLPP results provide additional support for the accuracy of rate constants obtained in sealed-tube experiments. When extrapolated to temperatures of VLPP experiments, the above expression for k_1 (gas) yields rate constants ~63% of those derived from VLPP experiments (see Table II). We consider this to be good agreement considering the combined uncertainties in our VLPP and sealed-tube experiments as well as possible Arrhenius "curvature".

An analysis of the liquid-phase rate data in Table I will now be presented. A least-squares fit of these data yields k_1 (tetralin)/s⁻¹ = 10^{(16.58±0.19)-(66.81±0.58)/θ} and k_1 (DHTP)/s⁻¹ = 10^{(16.89±0.17)-(68.37±0.55)/θ}. Arrhenius parameters for these reactions are not only considerably greater than those obtained for k_1 (gas)

(9) (a) By bond strength we mean the enthalpy of bond dissociation at 298 K. (b) Based on $\Delta S^\circ_{\text{reaction}} = 36.3$ cal mol K⁻¹ derived from additivity and estimated values in ref 13a.

(10) M. Rossi and D. M. Golden, *J. Am. Chem. Soc.*, **101**, 1230 (1979).

(11) ΔH_f° (12DPE) is taken as the sum of ΔH_f° (12DPE, solid) as recommended in J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1972, and a recent sublimation enthalpy determination in A. O. Osborn and D. W. Scott, *J. Chem. Thermodyn.*, **12**, 429 (1980).

(12) W. Tsang in "Shock Waves in Chemistry", A. Lifshitz, Ed., Marcel Dekker, New York, 1981, Chapter 2.

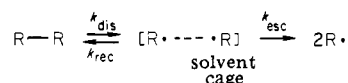
(13) (a) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1976; (b) "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, 1973, Chapters 1 and 2.

but are distinctly greater than are plausible for homolysis in the gas phase. For instance, if one assumes a zero activation energy for radical recombination, then these expressions imply that $k_{-1} \sim 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ and that the bond strength is $\sim 69 \text{ kcal/mol}$. Both of these values are considerably greater than would be plausible for gas-phase 12DPE homolysis. Clearly, Arrhenius parameters for reaction 1 in the liquid phase involve contributions from factors not important in the gas phase. While these factors will be discussed in detail below, we do not wish to overemphasize differences between gas- and liquid-phase homolysis. In our experiments the effect of phase on rate constants is only a factor of 2–3, while temperature changes cause $k_1(\text{liquid})$ to vary by a factor of ~ 200 .

To more closely examine relative gas/liquid rate constants, in Figure 1 the ratios $k_1(\text{tetralin})/k_1(\text{gas})$ and $k_1(\text{DHTP})/k_1(\text{gas})$ are shown as a function of temperature. It is clear from this figure that liquid-phase dissociation rates are always less than gas-phase rates and approach gas-phase rates with increasing temperature. On the basis of the preceding Arrhenius parameters, extrapolated gas- and liquid-phase rate constants would become equal at 464 °C in tetralin ($T_{\text{critical}} = 444 \text{ °C}$) and at 534 °C in DHTP ($T_{\text{critical}} \sim 590 \text{ °C}$).¹⁴

Both the magnitude and temperature dependence of $k_1(\text{liquid})/k_1(\text{gas})$ are consistent with the idea that differences between gas- and liquid-phase homolysis rates are due primarily to "cage" effects in the liquid phase.¹⁵ Solvation effects are expected to be minimal under these high-temperature and nonpolar conditions.

If the effect of cage recombination on bond homolysis rates is represented by the following model,



then the presence of the solvent cage reduces the net dissociation rate by the factor $(1 + k_{\text{rec}}/k_{\text{esc}})$. Reaction of caged radicals with solvent molecules is orders of magnitude slower than escape or cage recombination because of comparatively high activation energies ($10 \pm 5 \text{ kcal/mol}$) for radical-molecule reactions of hydrocarbons.

The observations that $k_1(\text{gas}) > k_1(\text{tetralin}) > k_1(\text{DHTP})$ and that the ratio $k_1(\text{liquid})/k_1(\text{gas})$ increases with increasing temperature are both consistent with the physically reasonable idea that a decrease in viscosity (or an increase in diffusion rate) leads to an increase in k_{esc} relative to k_{rec} .

It is informative to examine the relation between bond homolysis and the reverse reaction, radical recombination,

$$\frac{k_1(\text{liquid})}{k_1(\text{gas})} = \left(\frac{K_{\text{liquid}}}{K_{\text{gas}}} \right) \left(\frac{k_{-1}(\text{liquid})}{k_{-1}(\text{gas})} \right) \quad (3)$$

where K is the equilibrium constant for reaction 1. From this viewpoint, the magnitude of the ratio $k_1(\text{liquid})/k_1(\text{gas})$ can be resolved into thermodynamic ($K_{\text{liquid}}/K_{\text{gas}}$) and kinetic ($k_{-1}(\text{liquid})/k_{-1}(\text{gas})$) factors. If we represent the present values of $k_1(\text{liquid})/k_1(\text{gas})$ as 0.6 ± 0.2 and use the implications of previous work that $K_{\text{liquid}}/K_{\text{gas}} = 0.7 \pm 0.2$,¹⁶ then we conclude that over the range of the present experiments, within a factor of about 2, $k_{-1}(\text{liquid}) \sim k_{-1}(\text{gas})$.

We have made an effort to analyze the temperature dependence of $k_1(\text{liquid})/k_1(\text{gas})$ in terms of eq 3. Unfortunately, this analysis was not productive. While it may be most straightforward to attribute this dependence to diffusional (i.e., kinetic) effects, it is not clear to what degree radical recombination is controlled by

diffusion under the present experimental conditions. Moreover, the rather small magnitude of this temperature dependence coupled with possible small temperature dependences of $K_1(\text{liquid})/K_1(\text{gas})$ and $k_{-1}(\text{gas})$ would make such detailed analysis highly speculative. Further, we recognize that small systematic errors in rate determinations could substantially modify the slope of the lines in Figure 1.

Very recently, McMillan et al.¹⁷ reported a brief study of 12DPE homolysis in tetralin in which they obtained $k_1/s^{-1} = 10^{16.4-66.3/\theta}$. This expression is in good agreement with the present results and provides support for our high Arrhenius parameters for reaction 1 in liquids. Cronauer et al.¹⁸ in a survey of reactions in tetralin reported $k_1/s^{-1} = 10^{10.87-48.1/\theta}$. While these rate parameters are in gross disagreement with those obtained here, these rate constants do agree with ours at 440 °C.

Rate constants previously reported for 12DPE dissociation in neat 12DPE are $\sim 30\%$ lower than obtained here for reaction in tetralin. This is in accord with the present findings since the viscosity of 12DPE is expected to fall between that of tetralin and DHTP.¹⁹

Previous studies of homolysis in solution²⁰ have been carried out at considerably lower temperatures than the present studies and generally have involved the formation of oxygen-centered radicals. These reactions are therefore more likely to be influenced by solvation effects than the present studies. While in these previous studies it has been found that dissociation rates in liquids and gases are comparable, actual differences between gas and liquid rate constants and rate parameters were found to vary from reaction to reaction; in some cases rates were actually faster in solution than in the gas phase. This indicates that solvation effects can exert at least as great an effect on rates in solution as cage recombination. Therefore, absolute cage recombination probabilities cannot be obtained from previous homolysis studies. However, in accord with present findings, previous studies have demonstrated that homolysis rates in solution tend to decline with increasing solvent viscosity.^{15,21} Also, there is ample evidence for the influence of viscosity on the "cage" effect from observations of photolysis quantum yields in solution.¹⁵ While the magnitudes of these effects are comparable to the present values, more detailed comparisons are of dubious value owing to vastly different physical conditions between these and our experiments.

In summary, 12DPE homolysis rate constants in high-temperature liquids are of a similar magnitude but smaller than gas-phase values. These differences diminish with increasing temperature, resulting in higher Arrhenius parameters for homolysis in liquids than in the gas phase. Arrhenius parameters for liquid-phase 12DPE homolysis appear to be a superposition of gas-phase values and a temperature- (viscosity) dependent cage effect. The high temperatures and nonpolar conditions of these experiments serve to suppress solvation effects and allow relatively direct determinations of cage effects in thermal reactions.

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Registry No. 1,2-Diphenylethane, 103-29-7; phenylmethyl radical, 2154-56-5.

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