of the water molecules to properly solvate the transition state.

This solvation argument might explain why the complex of *p*-nitrophenyl 3-indoleacetate is unreactive hydrolytically. The inhibition found with this substrate could not be electronic in origin because the carbonyl group is separated from the complexing site, the indole ring, by a methylene group. On the other hand, in opposition to the complex of N-(indole-3-acryloyl)imidazole, the complex of *p*-nitrophenyl 3-indoleacetate could show steric hindrance and electrostatic inhibition, and these effects may also contribute to the unreactivity.

Thus, in the search for a synthetic catalyst which will first complex with the substrate and then effect a catalysis, factors such as stereochemical, electrostatic, solvent, and electronic effects on the ground state *vis-a-vis* the transition state must be taken into account.

Azocumene. I. Preparation and Decomposition of Azocumene. Unsymmetrical Coupling Products of the Cumyl Radical

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Abstract: Azocumene (2,2′-diphenyl-2,2′-azopropane) has been prepared from cumylamine and iodine pentafluoride. It undergoes thermal decomposition with $\Delta H^* = 29.0 \pm 0.3$ kcal. and $\Delta S^* = 11.0 \pm 1.0$ e.u. The products of photodecomposition in solution at 20° and of thermal decomposition up to 60° are nitrogen and the result of 5–6% disproportionation and 94–95% coupling of cumyl radicals. A portion of the coupling product, estimated as about 2%, is quinoid dicumyl (III), formed by α-to-*para* coupling of the cumyl radicals. It undergoes thermal redissociation with $\Delta H^* \cong 26$, $\Delta S^* \cong 11$. This quinoid dicumyl is detected by its strong ultraviolet absorption (Figure 2B) which appears during low-temperature photolysis. It reacts rapidly with bromine, and it consumes Koelsch's stable free radical VI at a first-order rate identical with that of its own thermal disappearance, the rate being unaffected by pyridine or by HCl in ether. Similar, but more stable, products are formed when azoisobutane is photolyzed in cumene, ethylbenzene, and toluene (with intensity of absorption decreasing in that order) but not in benzene. Photolysis of azocumene in frozen toluene, in contrast to that in solution, gives more disproportionation than coupling of cumyl radicals by a factor of 1.5–3.

The thermal or photolytic decomposition of azoalkanes (RN=NR) has proved to be a useful source of alkyl radicals, and possesses the advantage that only one type of radical is formed initially. It is generally believed that except in special cases[1] decompositions of azo compounds involve concerted, two-bond cleavages without any intermediate diazoalkyl radical formation.[2] Convincing evidence for this lies in the fact that both groups substituted on the azo linkage substantially affect the decomposition rate. A striking example is phenylazotriphenylmethane, which has a half-life at 50° of 51 min.,[3] while azobenzene does not decompose to radicals thermally, and azotriphenylmethane decomposes so rapidly that it cannot be isolated even at −40°.[4]

Many radical reactions are run in cumene because it is an excellent hydrogen donor and dicumyl, the main reaction product of the cumyl radicals formed, is conveniently handled. The cumyl radical is also of interest in autoxidation work.[5] Azocumene (2,2′-diphenyl-2,2′-azopropane) was expected to be a useful generator of cumyl radicals for study, and also to be free from the side reactions observed in secondary azo compounds (isomerization to hydrazones[6] and induced decomposition by abstraction of α-hydrogen[7]) or in azonitriles (formation of unstable ketenimines by coupling of two α-cyano radicals). The present paper describes the preparation of azocumene and the kinetics and products of its decomposition; the following paper reports a study of factors which influence the cage effect.[8]

The activation parameters for thermal decomposition of some azoalkanes which have been studied previously (Table I[9–13]) form a regular pattern which invites a prediction of the decomposition rate of azocumene.

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(1) As in perester decomposition, phenyl and methyl radicals are not well enough stabilized to contribute to a concerted decomposition. The decomposition of monophenylazomethane, $C_6H_5CH_2N{=}NCH_3$, is initiated by cleavage of the benzyl–N bond alone: S. Seltzer, *J. Am. Chem. Soc.*, **87**, 2628 (1965).

(2) (a) R. K. Lyon, *ibid.*, **86**, 1907 (1964); (b) C. Steel and K. J. Leidler, *J. Chem. Phys.*, **34**, 1827 (1961); (c) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, 77, 3628 (1955).

(3) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 576.

(4) H. Wieland, H. von Hove, and K. Börner, *Ann.*, **446**, 31 (1926).

(5) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963), and references cited there.

(6) S. G. Cohen and C. H. Wang, *ibid.*, 77, 2460 (1955).

(7) T. G. Traylor and R. D. Swigert, unpublished results in these laboratories.

(8) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966).

(9) C. Steel and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 975 (1959).

(10) Reference 2, Table VI.

(11) A. V. Blackham and N. L. Eatough, *J. Am. Chem. Soc.*, **84**, 2922 (1962).

(12) G. Williams and A. S. Lawrence, *Proc. Roy. Soc.* (London), **A156**, 455 (1936).

(13) Calculated from unpublished results of I. V. Berezin in this laboratory. See also ref. 3.

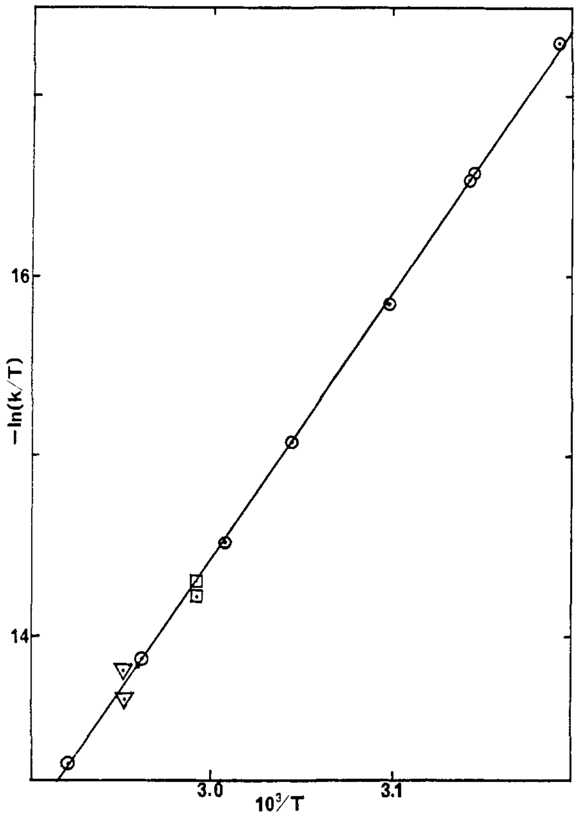

Figure 1. Eyring plot of azocumene decomposition rates: circles, by gas evolution; squares, by disappearance of di-*t*-butyl nitroxide scavenger; triangles, by disappearance of Koelsch radical scavenger.

Azoisopropane is absent from Table I. Cohen and Zand[14] have recently pointed out that the anomalous rate previously reported[15] is in error because the compound isomerizes to acetone isopropylhydrazone, which is also unstable at the temperatures employed. Recently,[16] activation parameters much closer to those expected have been reported, but there still may be some question as to how much of the isomerization is occurring.

Table I. Activation Parameters of Some Azoalkanes

R in RN_2R	ΔH^*, kcal./mole	ΔS^*, e.u.	Phase	Ref.
CH_3	52.3	12.2	Vapor	9
CH_3CH_2	49.5	12.2	Vapor	10
$(CH_3)_3C$	44	16–17	Vapor	11
$PhCH_2$	36	5	Vapor	12
$Ph(CH_3)CH$	32.2	7.2	Dodecane	13

Table I includes numbers found in different phases and solvents, and this would affect the activation parameters of even such nonpolar reactions as these, but it is clear that the effect of symmetrically substituting a pair of methyl groups for α-hydrogen atoms on either methyl or benzyl systems is additive, and the $\Delta\Delta H^*$ is about -2.7 kcal./mole, and $\Delta\Delta S^*$ about $+2$ or 3 e.u. It is not surprising that a second pair of phenyls substituted on azomethane to give azodiphenylmethane does not result in as large an effect as the first pair,[2c] because steric hindrance would not allow both phenyls to be oriented for maximum coplanarity of the benzhydryl group in the transition state. One would expect from the data of Table I that ΔH^* for azocumene should be about 29–30 kcal./mole, and ΔS^* about 9–11 e.u., assuming in both cases that the added methyl groups would not cause tilting of the phenyl rings with loss of benzylic stabilization.

Azocumene, m.p. 86.9–88.7°, was prepared from cumylamine by oxidative coupling with iodine pentafluoride, in a manner similar to Stevens' preparation of azoisobutane.[17] Its properties are discussed in the Experimental section.

Results and Discussion

Thermal Decomposition Rate. Rates of thermal decomposition of azocumene were determined by gas evolution in a constant-volume, variable-pressure, automatic recording device.[18] First-order decomposition was observed, the results being summarized in Table II.

Table II. Rates of Thermal Decomposition of Azocumene

Solvent	Temp., °C.	k (sec.$^{-1}$) $\times 10^5$	Std. error[a]
Toluene	40.04 (±0.05°)	0.946	±0.015
	44.79	1.99	±0.026
	45.01	2.09	±0.047
	49.52	4.33	±0.026
	55.34	9.28	±0.078
	59.42	16.2	±0.16
	64.48	31.6	±0.39
	65.24	32.9	±0.49
	69.23	58.0	±0.99
Dodecane	60.23	14.7	±0.16
3.9 *M* Thiophenol–benzene	58.91	19.4	±0.28

[a] The errors shown represent the limits on k set by the standard deviations of the first and last points in each kinetic plot.

An Eyring plot of the measurements in toluene appears as Figure 1. Activation parameters were $\Delta H^* = 29.0 \pm 0.3$ kcal./mole, $\Delta S^* = 11.0 \pm 1$ e.u. Agreement with the predicted activation parameters is better than might reasonably have been expected. There is some effect of solvent, the decomposition being 21% slower in dodecane, and 27% faster in 3.9 *M* thiophenol–benzene (the thiophenol used as a scavenger) than in toluene.

Photolytic Decomposition. The quantum yield for the photolysis of azocumene was determined using 366-mμ light in a "merry-go-round" apparatus in which samples were continuously rotated about the light source, the actinometer and sample tubes being irradiated at the same time. Benzophenone–benzhydrol actinometers[19] were employed. Decompositions were run in Pyrex test tubes sealed to 1-cm. square Pyrex tubing which allowed ultraviolet analysis without

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(14) S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962).

(15) H. C. Ramsperger, *ibid.*, **50**, 714 (1928).

(16) B. G. Gowenlock, P. Jones, and D. R. Sneeling, *Can. J. Chem.*, 41, 1911 (1963).

(17) T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961).

(18) Built by Dr. I. V. Berezin; to be described in a future publication.

(19) W. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

opening of the tubes. The initial rate of decomposition of azocumene (analyzed at 420 mμ) was found from the best line through four or five points. The quantum yields observed are shown in Table III.

Table III. Quantum Yields for Azocumene Decomposition in Benzene

Temp., °C.	$(\text{Azo})_0$, M	Φ_{azo}
26.3 ± 0.5	0.101	0.60 ± 0.05
24.7	0.051	0.56 ± 0.05

This may be compared with reported values of Φ = *ca.* 0.42 for ethyl azoisobutyrate in benzene,[20] and 0.17 for azomethane in isooctane.[21]

Products. The organic products of azocumene decomposition are the coupling and disproportionation products of the cumyl radical. The following decomposition scheme will be useful in discussing them.

$$\text{Ph(CH}_3)_2\text{CN{=}NC(CH}_3)_2\text{Ph} \xrightarrow{k_{\text{dec}}} [\text{Ph(CH}_3)_2\text{C}^{\cdot}, \text{N}_2, {}^{\cdot}\text{C(CH}_3)_2\text{Ph}]_{\text{cage}}$$

$$[\text{Ph(CH}_3)_2\text{C}^{\cdot}, \text{N}_2, {}^{\cdot}\text{C(CH}_3)_2\text{Ph}]_{\text{cage}} \xrightarrow{k_{\text{cage}}} \text{cage products}$$

$$[\text{Ph(CH}_3)_2\text{C}^{\cdot}, \text{N}_2, {}^{\cdot}\text{C(CH}_3)_2\text{Ph}]_{\text{cage}} \xrightarrow{k_{\text{diff}}} 2\text{Ph(CH}_3)_2\text{C}^{\cdot} + \text{N}_2$$

$$2\text{Ph(CH}_3)_2\text{C}^{\cdot} \xrightarrow{k_{\text{disp}}} \text{Ph(CH}_3)\text{C{=}CH}_2 + \text{Ph(CH}_3)_2\text{CH}$$

$$2\text{Ph(CH}_3)_2\text{C}^{\cdot} \xrightarrow{k_{\text{comb}}} \text{Ph(CH}_3)_2\text{CC(CH}_3)_2\text{Ph}$$

Cumyl radicals are formed in a solvent cage, and a competition is set up between their diffusion apart and geminate (cage) reaction. Cumyl radicals inside or outside the solvent cage can either combine to dicumyl or disproportionate to α-methylstyrene and cumene. Discussion of the "cage effect" and evidence that the same products are formed in the same relative amounts inside and outside the cage are presented elsewhere.[8]

Degassed benzene solutions of azocumene were decomposed both thermally and photolytically and the products analyzed by vapor phase chromatography. Only dicumyl, cumene, and α-methylstyrene (AMS) were observed, although slightly less AMS than cumene was observed in the thermal decompositions, presumably because of polymerization. $k_{\text{disp}}/k_{\text{comb}}$ ratios were determined from the amount of cumene formed, with p-methylanisole (PMA) as an internal standard. Relative sensitivities for cumene, AMS, and PMA were 1:1:1, but dicumyl, which had to be eluted from the v.p.c. column at 100° higher temperature, had a relative peak area of about 1.35, which seemed to be somewhat less reproducible than the other areas. Table IV shows the analytical results and the derived values of $k_{\text{disp}}/k_{\text{comb}}$ from 20 to 60° and also on direct injection of the azocumene solution into the v.p.c. injection port at 170°.

No significant variation of the amounts of disproportionation and combination was observed with temperature, which indicates that the activation energies for the two processes must be very close. Equal activation energies for disproportionation and combination have been reported for ethyl, isopropyl, and t-butyl radicals,[22] among others, although recently a careful reinvestigation of the ethyl radical gave $E_{\text{disp}} - E_{\text{comb}} = -0.3$ kcal./mole.[23]

Table IV. Disproportionation and Combination of Cumyl Radicals Generated from Azocumene in Benzene Solution

Temp., °C.	—V.p.c. peak areas—			Initial azocumene, mmole	$k_{\text{disp}}/k_{\text{comb}}$	(Cumene)/(AMS)
	Cumene	AMS	PMA[a]			
20.5[b]	26.1	32.7	44.1	0.0436	0.054	0.80
	41.8	41.5	71.0		0.055	1.01
20.5[b]	52.3	52.6	90.9	0.0436	0.054	0.99
	45.1	45.6	78.9		0.054	1.00
46.8	40.5	31.0	68.1	0.0436	0.056	1.31
	49.2	36.0	73.2		0.063	1.36
46.8	42.0	33.0	63.5	0.0436	0.062	1.27
60.0	26.4	22.7	52.2	0.0413	0.046	1.17
	30.2	...	56.2		0.049	...
60.0	30.5	23.6	49.5	0.0413	0.056	1.30
	55.0	45.8	93.7		0.054	1.20
"170"[c]	34.1	33.6	57.0	0.0413	0.054	1.01
	63.4	63.5	81.5		0.072	1.00

[a] 0.0356 mmole of p-methylanisole was used as internal standard in all runs. [b] Photolytic decomposition using a 450-w. Hanovia lamp and Corning 7–37 filter. [c] Direct injection into v.p.c. injection port at 170°; temperature control is not good, but a very rapid thermal decomposition must have taken place in the injection port.

It is of interest to compare the ratio $k_{\text{disp}}/k_{\text{comb}}$ for the cumyl radical with that of the t-butyl radical, the only other tertiary radical which has received much study. A value of 4.6 was reported for the vapor phase reaction of t-butyl radicals from ketone photolysis over a wide temperature range.[22] We found this ratio to be 4.5 in the photolytic decomposition of 2,2′-azoisobutane in benzene solution under the same conditions used for azocumene. The difference between cumyl radicals, which couple to an extent of 94%, and t-butyl radicals, which disproportionate about 80% of the time, is striking.

In the comparison of isobutyl, *sec*-butyl, and t-butyl radicals the relative values of $k_{\text{disp}}/k_{\text{comb}}$ found by Kraus and Calvert[22] were 1:5.4:11.0, close to the statistical ratio (1:5:9) of the number of β-hydrogen atoms on the radicals. If, as these figures suggest, all radical couplings occurred at the same rate, the statistically predicted $k_{\text{disp}}/k_{\text{comb}}$ ratio for the cumyl radical should be 3.07 instead of 0.06 as observed. This factor of 50 favoring coupling over disproportionation in the cumyl as compared with the t-butyl radical may be connected with the benzylic delocalization of the odd electron in the former. Perhaps this delocalization diminishes the importance of hyperconjugation in the transition state for disproportionation. However, we might also expect a lowering of the coupling rate from the same cause, and we could not have predicted the direction of the change in the $k_{\text{disp}}/k_{\text{comb}}$ ratio on going from t-butyl to cumyl radical.

When azocumene was decomposed photolytically at about −8° in frozen benzene, $k_{\text{disp}}/k_{\text{comb}}$ ratios of 0.93 and 1.05 were found in two runs, and the ratio of cumene to AMS was 1.10 ± 0.05. The change in value of $k_{\text{disp}}/k_{\text{comb}}$ cannot be a temperature effect, in view of the constancy of this ratio in all the liquid phase runs. At

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(20) G. S. Hammond and J. R. Fox, *J. Am. Chem. Soc.*, **86**, 1918 (1964).
(21) R. F. Hutton and C. F. Steel, *ibid.*, **86**, 745 (1964).
(22) J. Kraus and J. Calvert, *ibid.*, **79**, 5921 (1957).
(23) P. S. Dixon, A. P. Stefani, and M. Szwarc, *ibid.*, **85**, 2551 (1963).

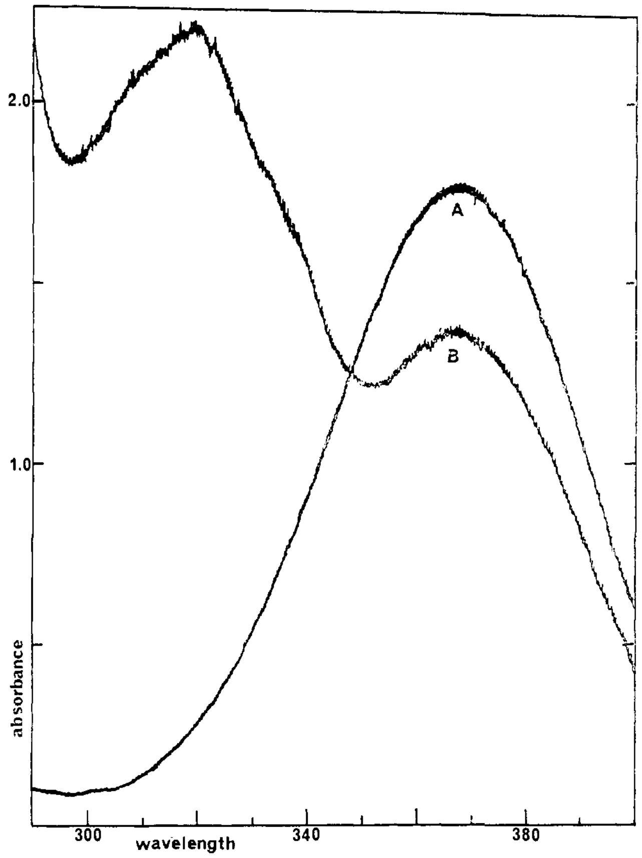

Figure 2. Ultraviolet spectrum of azocumene in cyclohexane: A, before irradiation; B, after 13 min. of irradiation at 366 mμ.

−8° frozen benzene solutions may have pockets of concentrated azocumene solution within the frozen material[24]; however, high concentration might be expected to affect both competing bimolecular reactions alike in this case. For work at lower temperatures toluene was chosen because of the opacity of frozen benzene solutions. A toluene solution was cooled to well below its freezing point of −95° by directing a blast of nitrogen gas (cooled by passing through a heat exchange coil of $^1/_8$-in. aluminum tubing immersed in a 3-l. dewar flask of liquid nitrogen) over an n.m.r. tube containing the sample. Temperature control by this method was not very reliable, and values of k_{disp}/k_{comb} varied from 1.48 to 3. N.m.r. was used to determine when the photolyses were finished, but not for accurate analysis of the amounts of cumene and dicumyl, since the toluene C^{13} satellite coincides with the upfield cumene methyl peak. In the run with k_{disp}/k_{comb} = 1.48 one new product was formed, of v.p.c. area about 2% of that of the cumene. In the runs yielding higher ratios the products were more complex. Probably cumyl radicals begin to attack toluene when held so rigidly that the orientation for attacking other cumyl radicals is not readily attained. It may be noted that many more orientations of a cumyl radical pair are suitable for the disproportionation reaction than for combination. During freezing, rotational motion of cumyl radicals must persist long after their diffusion is halted.

A Quinoid Dicumyl. Examination of the ultraviolet spectra of partially photolyzed azocumene solutions revealed enhanced low wave length ultraviolet absorption (Figure 2). Subtraction of the spectrum of unphotolyzed azocumene yielded a difference spectrum with a maximum at 315 mμ, and quite low absorbance at 366 mμ and above. There is also increased absorption at lower wave length, where azocumene and the other products of the reaction also absorb strongly. It was possible to observe a broad maximum at 250–265 mμ about five to seven times as intense as the 315-mμ maximum. This "photointermediate" is quite unstable to ultraviolet light, and careful filtration was required so that the azocumene absorbed almost all of the light in order to build up the new absorption.

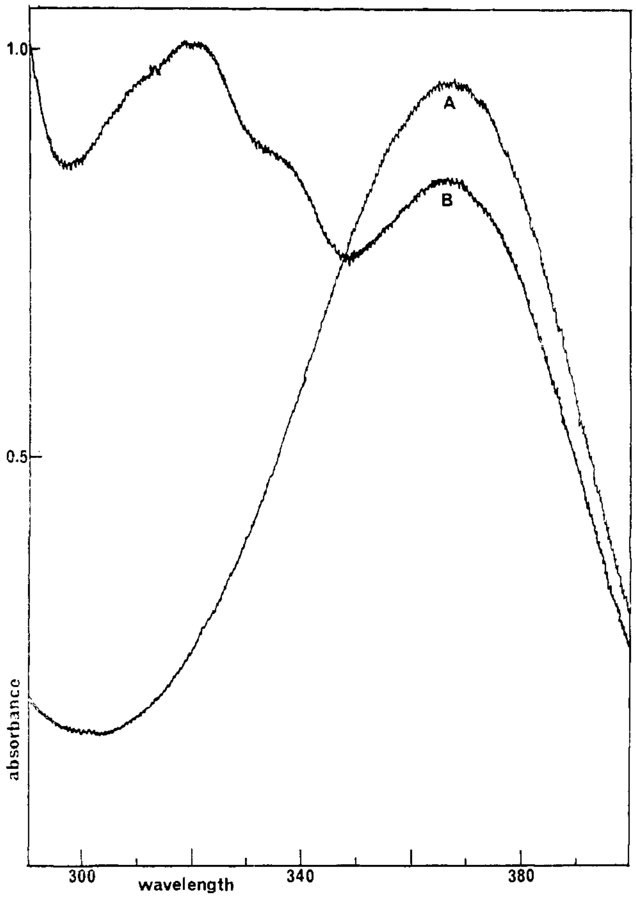

Figure 3. Ultraviolet spectrum of 2,2′-azoisobutane in cumene: A, before irradiation; B, after 6 min. of irradiation at 366 mμ.

Recently azomethane has been shown to undergo spectral changes upon irradiation,[21] caused by a *cis–trans* photoequilibrium (*trans*, λ_{max} 343 mμ (ϵ 14); *cis*, λ_{max} 353 mμ (ϵ 240)). The λ_{max} of the azocumene "photointermediate" absorption is much too short for it to be *cis*-azocumene, and such a compound, if capable of existence at room temperature, would surely be much more unstable than *cis*-azomethane with respect to isomerization back to the *trans* form. Furthermore, irradiation of 2,2′-azoisobutane in benzene or cyclohexane did not result in any enhanced low wave length absorption; the azoisobutane absorption maximum simply faded out. Because of the structural similarity in the two compounds, it seemed likely that the low wave length absorption from azocumene had nothing to do with the azo linkage, but arose from the cumyl radicals.

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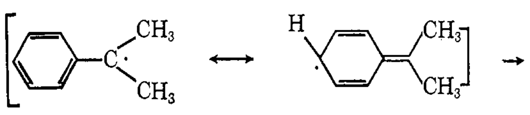
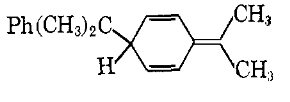
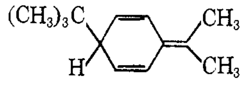
[24] R. E. Pincock and T. E. Klovsky, *J. Am. Chem. Soc.*, 87, 2072 (1965).

When azoisobutane was photolyzed in *cumene* solution, a low wave length absorption similar to that observed from azocumene in a wide variety of solvents (cyclohexane, ether, benzene, toluene) appeared (Figure 3). This photoproduct was also unstable to unfiltered ultraviolet light. Since the *t*-butyl radical will abstract a hydrogen atom from cumene, it is clear that the presence of cumyl radicals is a sufficient condition for formation of a compound which absorbs at 310–320 mμ. The most reasonable such process is dimerization of cumyl radicals at the *para* position to form the quinoid compound III. In the case of azoisobutane decomposition in cumene, one would expect either III or a quinoid product incorporating a *t*-butyl radical, IV. Evidence that the product formed is principally IV is given below.



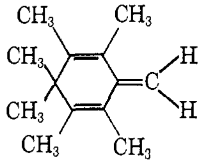


III



IV

Although quinoid products from *para* attack of radicals on triphenylmethyl radical have been in the literature for a long time,[25] there is little known concerning such attack on less hindered radicals. Kice and Taymoorian[26] observed an absorption maximum at 290–310 mμ in the product of polymerization of methacrylate with 1,1-diphenylethylene as a chain-transfer agent, which they attributed to a quinoid structure in the termination product. A well-characterized compound comparable to III and IV is the ultimate methylation product of benzene, methylenehexamethylcyclohexadiene (V).[27] This compound had a maximum at 257 mμ (log ϵ 4.27). As noted above, III and IV do have strong absorption in this region, but the maximum is difficult to locate. III reacts rapidly with bromine, but it has not yet been possible to isolate III, IV, or a product derived from them.



V

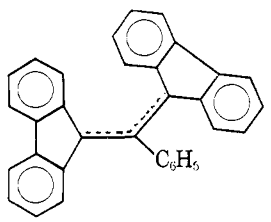
The 315-mμ absorption due to III shows a strictly first-order thermal disappearance. A degassed solution of azocumene in cyclohexane was photolyzed in a 1-cm. square Pyrex cuvette, and the cuvette was placed in a thermostated Beckman DU compartment. The disappearance of the 315-mμ absorption was then followed with time. Rates observed appear in Table V.

Table V. Rate Constants for Thermal Decomposition of III in Cyclohexane

Temp., °C. (±0.05°)	k (sec.$^{-1}$) × 10^4	Std. dev. × 10^2	Half-life, sec.
26.0	2.43	0.78	2900
28.3	2.70	0.99	2600
30.61	3.73	1.83	1900
36.35	10.1	1.50	690
39.94	15.6	0.71	440
	$\Delta H^* \cong 26$ kcal./mole	$\Delta S^* \cong 11$ e.u.	
26.35[a]	2.91	1.57	2400
39.8[b]	19.2		360

[a] Solvent was 0.12 M pyridine in cyclohexane; not degassed. [b] In toluene, rate determined by disappearance of Koelsch radical; see text.

It would not be unreasonable to expect III to undergo acid- or base-catalyzed rearrangement and give *p*-cumylcumene, the aromatized product, by a hydrogen shift. The normal rate in 0.12 M pyridine showed, however, that the reaction in the other cases was not being catalyzed by adventitious acid or base. Similarly, rough rate measurements in ether and ether saturated with HCl showed extremely little effect on the rate (half-life about 78 min. in ether, 74 min. in ether saturated with HCl). Although v.p.c. spectra of decomposed azocumene solutions were run at very high gain, no *p*-cumylcumene could be detected in them.



VI

Polymerization and aromatization are ruled out as pathways for disappearance of III. Homolytic cleavage to two cumyl radicals seemed the most likely possibility remaining, and it was found that radical scavengers do disappear as III decomposes. By use of a known amount of a dilute scavenger, it was possible to get a rough estimate of how much III was present. The Koelsch radical (1,1,3,3-dibiphenylene-2-phenylallyl, VI) was selected for a quantitative study of the decomposition of III, since it has a high absorptivity, and was shown to be effective in scavenging cumyl radicals.[8] One difficulty is the presence of azocumene in the reaction mixture, as it also decomposes thermally, although much more slowly. By using an amount of Koelsch radical greater than the amount of scavengeable III, but less than the amount of azocumene left, we observed a rapid first-order decline in absorbancy caused by decomposing III superposed upon a slow zero-order decline due to decomposition of azocumene.[8] It then was possible to extrapolate the zero-order line back to zero time and separate the two components of the rate. The rate of decomposition of III calculated by disappearance of Koelsch radical appears in Table V and, considering the solvent change, gives reasonable agreement with the runs determined by

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[25] F. Ullmann and U. Borsum, *Ber.*, **35**, 2877 (1902).

[26] J. L. Kice and F. Taymoorian, *J. Am. Chem. Soc.*, **81**, 3405 (1959).

[27] W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

disappearance of 315-mμ absorption. In this reaction 2.08×10^{-4} mmole/ml. of Koelsch radical disappeared because of decomposition of III, and the initial O.D.$_{315}$ was 2.88. In order to convert these numbers to a concentration of III, however, it is necessary to assume a cage effect for decomposition of III. Azocumene shows a 26.5 ± 1.5% cage effect under these conditions, and since the same radicals would be formed closer together by decomposition of III, one might predict a higher cage effect. The situation is somewhat analogous to that of the azonitriles and the related ketenimines; AIBN shows a cage effect of about 35%, while that of the related ketenimine is about 65%.[28] Arbitrarily choosing a value of 50% for the cage effect, one calculates that III was present in about 2×10^{-4} M concentration, and thus would assign a value to ϵ_{315} of 1×10^4. The 250–265-mμ maximum, as stated above, is some five to seven times as strong as the 315-mμ maximum; in view of the 1.9×10^4 maximum observed for V, it seems possible that a 50% cage effect is too high for III, for this would make ϵ at its 250–265 mμ maximum $5\text{–}7 \times 10^4$. If ϵ_{315} were 10^4, the yield of quinoid dicumyl III would be about 1.8%, since when 43.3% of the original 0.15 mmole of azocumene present had been decomposed, O.D.$_{315}$ was 2.78 (corrected for undecomposed azocumene). This photolysis was run at 4.5°; in a similar run at 25° a yield of III calculated in the same manner was 2.2%. The yield of III does not seem to be highly temperature dependent. As implied above, the yields of III calculated with an ϵ_{315} of 10^4 are probably a maximum.

para **Attack on Benzylic Radicals.** As noted above, photolysis of azoisobutane in cumene gives a low wave length absorption quite similar to that of III, and either III or IV could be formed. The compound causing the absorption is much more stable thermally than III, however, as is shown by the data of Table VI. Because the half-life of III is under 8 min. at 40°, it is clear that little III is formed, and the product is presumably IV.

Table VI. Thermal Decomposition of Compound from Irradiated Azoisobutane in Cumene at 40°

Time, min.	O.D.$_{320}$
0	1.56
10	1.47
20	1.47
45	1.45

To see how general formation of quinoid-type products from benzylic radicals might be, azoisobutane was decomposed in ethylbenzene, toluene, diphenylmethane, and p-cymene. Enhanced low wave length absorption was obvious in diphenylmethane and ethylbenzene, and could be detected in toluene, but was absent in p-cymene. The p-cymene result is quite understandable, for the p-methyl group would substantially increase hindrance to *para* attack. It also indicates that *ortho* attack is unimportant. If the crude assumption were made that ϵ_{320} is the same for the products from cumene, ethylbenzene, and toluene, relative yields of 114:12:1 would be calculated. It should be noted that several factors are operating, including decreased steric hindrance at the more reactive benzylic position in toluene, as well as decreased amounts of H abstraction by t-butyl radicals.

IV appears to be stable enough to be isolated, but to date attempts have led only to polymeric material.

Experimental Section

Benzene, toluene, cumene, and dodecane were extracted with sulfuric acid until colorless, washed with water and sodium carbonate, dried with calcium sulfate, and distilled from sodium or lithium aluminum hydride. Cumene was stored in the dark, in ampoules sealed under nitrogen.

2,2′-Azoisobutane was prepared by the method of Stevens[17] except that the iodine pentafluoride employed (Matheson) was simply poured from the cylinder; this did not affect the yield significantly. The minor (2–5%) impurity which is difficult to distill from the product[17] was removed by preparative v.p.c. (Aerograph A 700 with 3/8-in. silicone rubber column, injection port at 150°, column temperature 130°). The n.m.r. spectrum consisted of a sharp singlet at δ 1.12 (in CCl_4, internal TMS). The ultraviolet spectrum showed a maximum at 366 mμ (ε 13).

Azocumene was prepared in a similar manner. Cumylamine[29] (13.5 g., 0.1 mole) in 10 ml. of methylene chloride, was added over 1 hr. to a stirred mixture of 120 ml. of methylene chloride, 18 ml. of pyridine, and 5 ml. of iodine pentafluoride at −10 to −20° (cooled with CCl_4–Dry Ice snow slurry). The mixture was stirred for another hour at −10°, then for 1 hr. at 0°. Water was added, and the mixture was stirred until the yellow solid which precipitates during the reaction was dissolved. The organic layer was extracted with water, 1 N HCl, sodium thiosulfate solution, and water. After drying with magnesium sulfate, most of the solvent was removed by rotary evaporation (at a temperature of under 30°) and the brown solid obtained after cooling was isolated. From this solid was isolated 4.75 g. of faintly yellow azocumene after two recrystallizations from methylene chloride or ether.

Anal. Calcd. for $C_{18}H_{22}N_2$: C, 81.15; H, 8.33. Found: C, 81.08; H, 8.39. The melting point was 86.9–88.7° (sealed tube, 1°/min. heating). The n.m.r. spectrum (Varian A 60) in CCl_4 with internal TMS standard showed the methyl singlet at δ 1.49, and the aromatic region was centered at 7.21. The ultraviolet spectrum (Cary 11) had the maximum for the azo linkage at 367 mμ (ε 44), a minimum at 290 (1.8), and phenyl absorption maxima at 252 (660), 258 (598), and 264 (374), respectively. The phenyl maxima were imbedded in the tailing of intense end absorption.

Irradiation. The Corning 7–37 filter transmits about 28% at 366 mμ, and about 9% at 334 mμ. From the relative intensities of the 450-w. Hanovia lamps used, over 97% of the light transmitted is 366-mμ light and about 2.6% is 334-mμ light.

Decomposition rates were determined by gas evolution in an apparatus described elsewhere.[18] Samples of 0.2–0.25 mmole in 5 ml. of solvent were degassed by three cycles of freezing, pumping, and thawing before a run was started. The Guggenheim method of elimination of the infinity point[30] was used for the slow runs (temperature less than 50°). Least-squares rate constants and activation parameters were calculated[31] on an IBM 1620 computer.

Products were analyzed by v.p.c. An Aerograph 1520 operating with a thermal conductivity detector was used with 10 ft. × 1/8 in. columns packed with 20% FS.1265 on 80–100 mesh Gaschrom S. Inlet temperature was typically 225°, detector temperature 275°, and a column temperature of 75° was used until everything but dicumyl was off; 175° was required to elute dicumyl. Comparison of v.p.c. retention times and n.m.r. spectra with those of authentic samples was used for identification of compounds. p-Cumylcumene was prepared from α-methylstyrene and cumene[32] and it was shown that no compound of this retention time was observable by v.p.c. in spent azocumene decomposition mixtures. Decompositions to examine products and quantum yields were run in

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sealed tubes degassed by three freeze–pump (to 1 μ)–thaw cycles. Use of p-methylanisole as a v.p.c. standard did not result in the detection of any new products.

Actinometer solutions were prepared from recrystallized commercial benzhydrol and benzophenone (0.1 M in each); the amount of decomposition of benzophenone was determined by ultraviolet. The apparatus is described above.

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Azocumene. II. Cage Effects and the Question of Spin Coupling in Radical Pairs

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Abstract: The cage effect in the thermal decomposition of azocumene in toluene at 40° was found to be 27.0–28.4% with di-t-butyl nitroxide, 26.3% with galvinoxyl, and, in benzene with 3 M thiophenol, 26.4–27.4%. Over a range of temperature in toluene the apparent activation energy of the ratio ($R = E/(1 - E) = k_{\mathrm{diff}}/k_{\mathrm{cage}}$) of diffusion to interaction rates of cumyl radicals is 1.3 kcal. In conjunction with the estimate $E_{\mathrm{diff}} \sim 2.6$ kcal. from diffusion theory,[14] this result suggests that E_{cage}, the activation energy for cumyl radical interaction, also has the value 1.3 kcal. Neither thiophenol nor galvinoxyl is a completely satisfactory scavenger for cumyl radicals. In a series of nine solvents (Figure 2) it is shown that kinematic viscosity is not the chief factor determining variation of the cage effect; the cage effects in chlorobenzene and nitrobenzene are higher than expected from their kinematic viscosities. Direct photolysis and decomposition photosensitized by triphenylene and by pyrene show a steeper temperature dependence of the cage effect, and a cage effect at 40° which is 6–7% higher, than in thermal decomposition. No difference was observable between the cage effect for photolysis and that for photosensitized decomposition. In view of evidence that these decompositions proceed from excited singlet and triplet, respectively, it is concluded that electron-spin relaxation in a pair of cumyl radicals is complete before the radicals can diffuse out of the solvent cage.

Inefficiencies in the production of radicals from initiators (cage effects) have received a great deal of study since the first theoretical treatment by Franck and Rabinowitch.[1] Even in the relatively simple case of iodine dissociation, in which many parameters which are unknown for larger molecules have been measured, it is still not possible to calculate the efficiencies observed,[2] yet there is general agreement on the reasons for inefficient radical production.

When radicals are formed by homolytic decomposition of an initiator in solution, a competition is set up between interaction of the radicals and their diffusion apart. If the radicals are reactive enough, a significant fraction will react before diffusion out into the solution where they may be detected by radical scavengers.

It was thought that differences might be observed in the efficiency of radical production depending on the relative spin orientations in the newly formed radical pair. When an azo compound decomposes thermally, its vibrationally excited singlet ground state gives a nitrogen molecule and two radicals, initially with paired spins (eq. 1), while if it could be decomposed from an electronically excited triplet state, the radicals would initially be formed with parallel spins (eq. 2).

$$\mathrm{R{-}N_2{-}R} \longrightarrow {}^1\mathrm{R{-}N_2{-}R}^* \longrightarrow (\mathrm{R}\uparrow,\ \mathrm{N_2},\ \downarrow\mathrm{R}) \qquad (1)$$

$$\mathrm{R{-}N_2{-}R} \longrightarrow {}^3\mathrm{R{-}N_2{-}R}^* \longrightarrow (\mathrm{R}\uparrow,\ \mathrm{N_2},\ \uparrow\mathrm{R}) \qquad (2)$$

At infinite distance, the spins of two separate radicals would not be correlated at all, but there must be some distance of approach inside which there is a significant energy difference between paired and unpaired spins, for a "singlet pair" of radicals could combine directly to form a normal σ bond, while a "triplet pair" could not. The magnitude of the cage effect ought to be a good indicator of how fast the spin inversion occurs, for radical–radical reactions must compete with diffusion in order to give a cage effect. If spin inversion were slower than diffusion rates, one would expect to find a smaller cage effect in a decomposition from an excited triplet initiator (which could be generated by photosensitized azo compound decomposition) than from thermal decomposition.

Azocumene[3] was chosen for this study because it undergoes clean decomposition to identical radicals and also has convenient rates of thermal and photolytic decomposition.

Results

Scavengers. For a study of the cage effect it is important to have a scavenger which will capture all radicals that escape the cage and no others.[4] A scavenger is presumed to meet this condition if the same cage effect is found over a range of scavenger concentration and also with different scavengers. In this study one hydrogen-donating scavenger, thiophenol, and three

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