Chemistry of Diarylazoalkanes. II. Effect of *para* Substituents on the Thermal Decomposition of Azocumenes[1]

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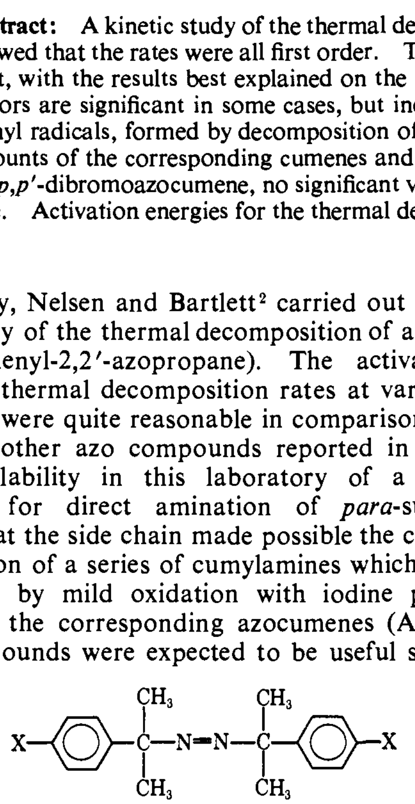
Abstract: A kinetic study of the thermal decomposition in toluene of various *para,para'*-disubstituted azocumenes showed that the rates were all first order. The effects of the *para* substituents upon the rates were small but significant, with the results best explained on the basis of resonance (including hyperconjugative) contributions. Steric factors are significant in some cases, but inductive effects did not appear to be important. The *para*-substituted cumyl radicals, formed by decomposition of the azo compounds, coupled to form the expected dicumyls. Minor amounts of the corresponding cumenes and α-methylstyrenes were also produced by disproportionation. Except for *p,p'*-dibromoazocumene, no significant variation of product distribution was observed with change in temperature. Activation energies for the thermal decompositions were determined.

Recently, Nelsen and Bartlett[2] carried out a detailed study of the thermal decomposition of azocumene (2,2'-diphenyl-2,2'-azopropane). The activation energy and thermal decomposition rates at various temperatures were quite reasonable in comparison with the data for other azo compounds reported in the past. The availability in this laboratory of a synthetic method[3] for direct amination of *para*-substituted cumenes at the side chain made possible the convenient preparation of a series of cumylamines which could be converted by mild oxidation with iodine pentafluoride[2,4] to the corresponding azocumenes (A). These azo compounds were expected to be useful sources of various substituted cumyl radicals which would be of interest in a number of applications, *e.g.*, autoxidation studies.[5]



A, X = H, CH_2, CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$, Br

This investigation was undertaken as part of our continuing interest in the behavior of radical species.[6] The purpose of the present work was to ascertain the effect of the *para* substituent in the azocumene on the rate of thermal decomposition and on product distribution. Unsubstituted azocumene is included as a basis of comparison with prior studies.

Results and Discussion

Thermal Decomposition Rates. Rates of decomposition for the substrates were obtained by investigating the disappearance in the ultraviolet spectrum of the characteristic peak at 367 mμ due to absorption by the azo linkage. No interference by either the solvent or the decomposition products was detected in this region. In contrast, Nelsen and Bartlett determined the kinetics by following nitrogen gas evolution.[2] It is of particular interest that the data (Table I) as obtained by our spectroscopic method at various temperatures for the decomposition of azocumene agree with the prior findings to within 5%. Thus the contribution of photolytic breakdown resulting from irradiation in the spectrometer appears to be negligible under our conditions. Since the spectroscopic technique proved to be simpler to carry out and less subject to experimental variation, it was selected as the preferred general procedure. The kinetic results are summarized in Tables I and II, and one example of an Eyring plot of the rate data is shown in Figure 1 (the other azo compounds gave similar plots).

Table II demonstrates that the effects of the substituents on the rates of decomposition are relatively small, but significant, which would be expected for a radical mechanism. Except for the *p*-isopropyl and *p*-*t*-butyl groups, both electron-attracting and electron-releasing types increased the rate of decomposition. In contrast, electron-attracting substituents generally produced a decrease in the rate of decomposition of *t*-butyl perbenzoates[7] and benzoyl peroxides.[8]

The ease of decomposition of the *para,para'*-disubstituted azocumenes decreased in the order (Table II) Br > CH_3 > CH_3CH_2 > $(CH_3)_2CH$, $(CH_3)_3C$, H, indicating that resonance interaction outweighs the inductive effect.[9a] Paramagnetic resonance spectra have provided evidence for radical hyperconjugation.[9b,10] The relative standings for the *p,p'*-dialkyl compounds are in the order of the relative contribution to be expected from C–H hyperconjugation. Apparently, with the lone C–H bond in the isopropyl group the effect is negligible. Furthermore, the nearly identical rates for *p,p'*-di-*t*-butyl and the parent member point to no appreciable involvement of C–C hyperconjugation. At the same time, one can conclude that the inductive

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[1] (a) Taken from the M.S. Thesis of C. K. Liang, Case Institute of Technology, 1967; (b) paper I of the series: J. R. Shelton, C. K. Liang, J. F. Gormish, P. L. Samuel, P. Kovacic, and L. W. Haynes, *Can. J. Chem.*, in press.

[2] S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137, 143 (1966).

[3] P. Kovacic and R. J. Hopper, *Tetrahedron*, **23**, 3977 (1967); P. Kovacic, J. F. Gormish, J. W. Knapczyk, and R. J. Hopper, unpublished work.

[4] T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961).

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

[6] For a recent paper in the series see J. R. Shelton and C. W. Uzelmeier, *ibid.*, **88**, 5222 (1966).

[7] A. T. Blomquist and J. A. Berstein, *ibid.*, **73**, 5546 (1951).

[8] A. T. Blomquist and J. A. Buselli, *ibid.*, **73**, 3883 (1951); C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

[9] M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962: (a) p 110; (b) p 90.

[10] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 51.

Table I. Rates and Activation Energies for the Thermal Decomposition of Diarylazoalkanes in Toluene

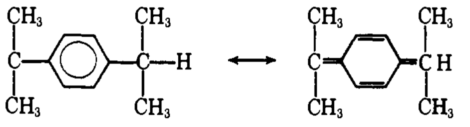
Temp, °C	$K_1 \times 10^5$ sec^{-1}	E_A,[a] kcal/mole
	p,p'-Dibromoazocumene	
42.8 ± 0.25	2.70 ± 0.02[b]	28.1
42.8 ± 0.12	2.72	
48.6 ± 0.12	6.28	
58.0 ± 0.12	21.89	
	p,p'-Dimethylazocumene	
41.0 ± 0.25	1.33	28.8
42.8 ± 0.12	1.66	
44.8 ± 0.25	2.43	
49.5 ± 0.25	5.02	
58.0 ± 0.12	14.19	
58.5 ± 0.25	16.20 ± 0.02[b]	
	p,p'-Diethylazocumene	
42.8 ± 0.12	1.29	26.0
48.6 ± 0.12	3.29	
58.0 ± 0.12	12.40	
	p,p'-Diisopropylazocumene	
42.8 ± 0.12	1.13	29.7
46.7 ± 0.12	2.04	
51.2 ± 0.12	4.26	
58.0 ± 0.12	10.78	
	p,p'-Di-*t*-butylazocumene	
42.8 ± 0.12	1.16	29.5
48.6 ± 0.12	2.58	
58.0 ± 0.12	10.80	
	Azocumene	
41.0 ± 0.25	0.96	29.3
42.8 ± 0.12	1.13	
43.5 ± 0.25	1.65	
44.8 ± 0.25	1.98	
48.6 ± 0.12	3.02	
49.5 ± 0.25	4.16	
58.0 ± 0.12	11.49	
58.5 ± 0.25	12.80 ± 0.02[b]	

[a] The maximum error is estimated to be 1 kcal/mole. [b] Average value of duplicate runs.

Table II. Relative Rates of Decomposition of Various *para,para'*-Disubstituted Azocumenes at 42.8° in Toluene

X in $[p\text{-XC}_6\text{H}_4\text{C(CH}_3)_2\text{N=}]_2$	$K_1 \times 10^5$ sec^{-1}	Relative reactivity
H	1.13	1.00
$(CH_3)_2CH$	1.13	1.00
$(CH_3)_3C$	1.16	1.02
CH_3CH_2	1.29	1.13
CH_3	1.66	1.46
Br	2.72	2.40

effect of *p*-alkyl is not important. It appears that steric factors are involved to some extent, particularly with diisopropyl. Adverse steric interaction in the resonance hybrid (B) between the four methyl groups and the hydrogen atoms on the benzene ring would



B

tend to minimize any resonance contribution. The same general reasoning would apply to all members of the series insofar as the generated radicals are *t*-benzylic (see structure B), but to a lesser degree since only one such group would be involved. The small rate differences within the series are not surprising since even in certain related ionic systems the over-all spread for the range of alkyl groups is quite narrow.[9a] The most probable explanation for the greater reactivity of *p,p'*-dibromoazocumene is that the bromine atom is most effective in resonance stabilization[10] of the cumyl radical.

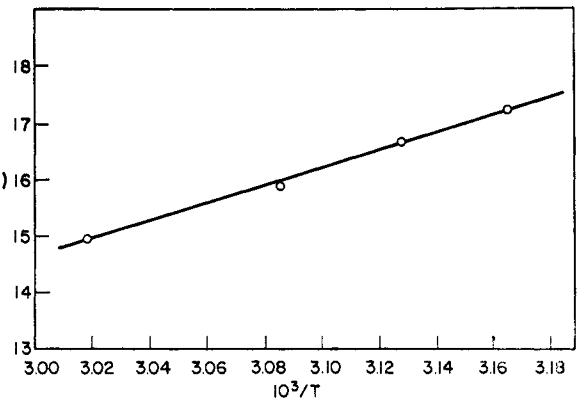


Figure 1. Eyring plot for decomposition of *p,p'*-diisopropylazocumene.

The differences in the activation energies for decomposition of the members in this series were found to be minor (Table I), probably not significant in most cases. Our E_A value for azocumene corresponded nicely to that found by Nelsen and Bartlett.[2]

The effects of substituents in the aromatic nucleus are often independent of the reaction involving the side chain and can be correlated by the Hammett relation. However, this situation does not pertain if there is conjugation between the substituent and the side-chain functionality. In the cases where the simple Hammett relation does not apply, this type of conjugation is involved.[11,12] Taft[12-14] has considered the inductive and resonance effects of substituents separately in a large number of reactions, taking into account the fact that the resonance contribution must depend on the demands of the reaction center. A number of parameters, σ_I, σ_R, were determined for substituents (Table III), and the corresponding ρ values were evaluated for various reactions. The corresponding conventional σ constants, calculated from these values, generally agree quite well with the experimentally determined data. From Table III it is seen that the σ_R value, the capability of a substituent

Table III. Values[a] of σ_I and σ_R

Substituent	σ_I	σ_R
NH_2	0.10	−0.76
OMe	0.23	−0.50
Br	0.45	−0.22
Me	−0.046	−0.102
Et	−0.055	−0.094
i-Pr	−0.064	−0.086
t-Bu	−0.074	−0.078

[a] See ref 12–14.

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(11) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 78 (1963).

(12) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959).

(13) R. W. Taft, Jr., *ibid.*, **74**, 3120 (1952).

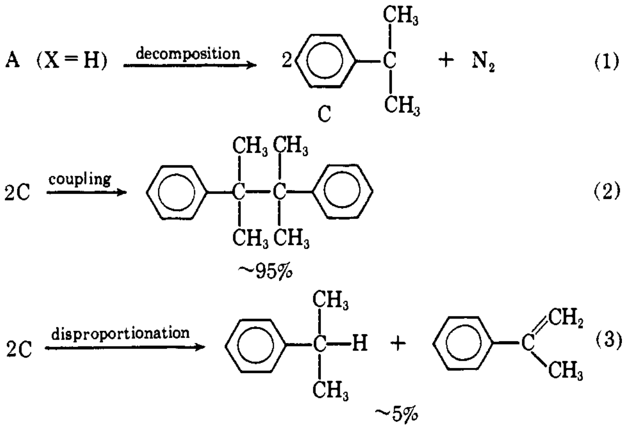
(14) R. W. Taft, Jr., and I. C. Lewis, *ibid.*, **80**, 2436 (1958); *Tetrahedron*, **5**, 210 (1959).

to donate electrons into the benzene ring and thus participate in resonance interaction with the reaction center, decreases in the sequence: Br > Me > Et > *i*-Pr > *t*-Bu. The behavior of the *para,para'*-disubstituted azocumenes is thus consistent, at least qualitatively, with Taft's evaluation of the resonance contribution of these groups. A similar situation apparently prevails in the thermal decomposition of *para,para'*-disubstituted 1,1'-diphenyl-1,1'-azoethanes.[15]

A more detailed comparison with related literature examples in both the radical and ionic categories proves instructive. A convincing array of evidence has accumulated which indicates that polar factors can contribute in a significant manner to the transition state in homolytic hydrogen abstraction involving the methyl group of toluene derivatives. The nature of the attacking radical plays a crucial role.[16,17] In a study of aromatic substitution with cyclohexyl radicals in this laboratory,[6] it was found that the ability of a variety of substituents (*e.g.*, CH_3, OCH_3, and Cl) to stabilize the transition state could be correlated with σ values. Furthermore, useful correlations arise from esr determination of proton coupling constants which are believed to be influenced by hyperconjugative effects[18] in the aromatic series.[19] From a study[20] of *p*-alkylnitrobenzene anion radicals the coupling constants (gauss) were found to decrease in the order CH_3 (3.98) > CH_3CH_2 (2.96) > $(CH_3)_2CH$ (1.74). A similar trend was noted by Scheffler[21] for the 4-alkyl-2,6-di-*t*-butylphenoxy radicals, CH_3 (10.7) > $(CH_3)_2CH$ (4.6). Steric interactions, which influence the preferred equilibrium conformations of the alkyl groups, apparently play a significant role.[20]

Considerable effort has been expended in attempts to elucidate the hyperconjugative effects of alkyl groups attached to the aromatic nucleus in polar reactions. Working with the *p*-alkylbenzyl bromide–pyridine system,[22] Baker and Nathan reported the results, $CH_3{:}CH_3CH_2{:}(CH_3)_2CH{:}(CH_3)_3C{:}H = 1.66{:}1.48{:}1.34{:}1.35{:}1$. An important factor contributing to the narrow spread would appear to be the relatively small amount of charge formation in the transition state during the S_N2 displacement. In contrast, appreciably larger differences were noted by Brown and coworkers[23] in the solvolysis of *p*-alkylphenyldimethylcarbinyl chlorides: $CH_3{:}CH_3CH_2{:}(CH_3)_2CH{:}(CH_3)_3C{:}H = 26{:}22{:}18.8{:}14.4{:}1$. In this case a larger degree of carbonium ion character is associated with the charged species. The very similar findings[24] obtained with p-$RC_6H_4CH_2OSO_2C_7H_7$ show that steric barriers associated with structures of type B are comparatively small, at least in the ionic category.

Products. The organic products from decomposition of the azocumenes resulted from coupling and disproportionation of the corresponding cumyl radicals. Identification was accomplished by comparison (glpc) with authentic materials. The reaction scheme employed is the same as that proposed by Nelsen and Bartlett[2] (illustrated with azocumene).



Only dicumyls, cumenes, and α-methylstyrenes were observed in the thermal degradation. The distribution of the cumyl radicals in the products formed is listed in Table IV.

The data reveal that in the decomposition of *p,p'*-dialkylazocumenes, as well as the parent compound, cumyl-type radicals couple to the extent of 90–95% with disproportionation accounting for the remainder, in harmony with the behavior observed previously for azocumene.[2] No significant variation in the amounts of disproportionation and coupling were observed with temperature change, which indicates that the activation energies required for the two processes must be similar, again in keeping with the earlier disclosure.[2] Equal activation energies for disproportionation and coupling have been reported for ethyl, isopropyl, and *t*-butyl radicals,[25] although in a recent more precise study of the ethyl radical $E_{\text{comb}} - E_{\text{disp}}$ was found to be 0.3 kcal/mole.[26] Relative to the unsubstituted case,[2] the alkyl substituents evidently are not important in affecting the product distribution and activation energies of disproportionation and coupling processes. The prior investigators[2] noted a change in $k_{\text{disp}}/k_{\text{comb}}$ when azocumene decomposition was carried out photolytically in a solid matrix.

In the breakdown of *p,p'*-dibromoazocumene, 23% disproportionation and 77% coupling occurred at 46.5°, in contrast with 18% disproportionation and 82% coupling at 64°. In comparison with the other radicals, the more favorable delocalization when bromine is present apparently lowered the rate of coupling to a greater extent than that of disproportionation as the temperature decreased, so that the product distribution was significantly altered. The 5% increase in coupled product with this increase in temperature suggests that the coupling process has a higher activation energy than that of disproportionation.

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[16] A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1**, 31 (1965).

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[22] J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1840 (1935); J. W. Baker, *ibid.*, 1448 (1936).

[23] H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, **79**, 1897 (1957).

[24] J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

[25] J. W. Kraus and J. G. Calvert, *ibid.*, **79**, 5921 (1957).

[26] P. S. Dixon, A. P. Stefani, and M. Szwarc, *ibid.*, **85**, 2551 (1963).

Table IV. Distribution[a] of Radicals in the Products of Decomposition of *para*-Substituted Azocumenes in Toluene

R in [p-$RC_6H_4C(CH_3)_2N{=}]_2$	Temp, °C	p-$RC_6H_4CH(CH_3)_2$	p-$RC_6H_4C(CH_3){=}CH_2$	[p-$RC_6H_4C(CH_3)_2]_2$	Total yield[b]
H	64.0 ± 0.5	3.1	2.4	94.5	93
	44.5 ± 0.3	3.0	2.3	94.7	84
CH_3	64.0 ± 0.5	2.9	2.7	94.4	99
	44.5 ± 0.5	2.8	2.7	94.5	87
CH_3CH_2	64.0 ± 0.5	3.2	5.6	91.2	99
	46.5 ± 0.3	3.8	5.4	90.8	87
$(CH_3)_2CH$	64.0 ± 0.5	2.7	2.8	94.5	95
	44.5 ± 0.3	3.5	4.5	92.0	85
$(CH_3)_3C$	64.0 ± 0.5	4.8	4.4	90.8	88
	44.5 ± 0.3	5.5	4.7	89.8	84
Br	64.0 ± 0.5	9.0	9.0	82.0	87
	46.5 ± 0.3	8.7	14.0	77.3	77

[a] Mole percentage of total amount of radicals accounted for after five half-lives of decomposition. [b] Percentage of theoretical based on azo compound present at start.

Equivalent amounts of the two disproportionation products were generally formed. However, larger proportions of the substituted α-methylstyrene were observed with the *p*-bromo compound and *p*-ethyl derivative under certain conditions.

Experimental Section

Preparations. Syntheses of the azo compounds and the authentic samples required for product identification are reported elsewhere by Shelton and coworkers.[1b]

Decomposition Rate Measurements. The thermal decomposition rates were measured with an A.P.C. Cary Model 14 recording spectrophotometer. The cell holder was connected with a Forma constant-temperature circulator which was the source of heat. The cell (2 cm, quartz) was fitted with a capillary tube filled with mineral oil, and an iron-constantan thermocouple was inserted and connected to a L. & N. millivolt potentiometer to obtain true reaction temperature readings. A 6.8-ml portion of the reaction solution (~0.0085 *M*) of the azo compound in toluene was introduced into the cell.

The wavelength was fixed at 367 mμ, which is the characteristic absorption region for the azo linkage, and the recording chart speed was set at 387 sec/division. Recording on the chart was started when the cell was placed in the holder. When equilibration at the desired temperature was attained, the chart was marked to indicate the initial point of rate measurement.

Since evaporation of the toluene solvent was significant at the temperatures employed (which woud change the concentration of the solution and, in turn, affect the accuracy of the measurement) only the data for the first few hours from the initial points were used in the calculation of rate constants.

The change of absorbance with concentration of azo compound in the reaction solution followed Beer's law quite well, and thus it was convenient to plot the absorbance directly on semilogarithmic paper. Good first-order straight lines were observed. From these data rate constants were calculated.

Product Analysis. In a flask fitted with a reflux condenser was placed a toluene solution of the *para,para'*-disubstituted azocumene (~0.05 *M*) containing approximately 0.5 mmole of the substrate. The flask was flushed with nitrogen and immersed in the constant temperature bath for five half-lives under a small positive pressure of nitrogen.

The crude reaction mixtures were analyzed by a Matronic Model 500 dual column gas chromatograph with 10 ft × 1/8 in. column packed with 20% silcone QF* 1 on 80–100 mesh Chromosorb W (non-acid wash). Inlet temperature was typically 225°, detector temperature 280°. The column temperatures for glpc analysis of the *para*-substituted α-methylstyrenes and cumenes ranged from 90 to 100°, and for the *para,para'*-disubstituted dicumlys from 185 to 200°. The internal standard for identification of the low-boiling products was *p*-methylanisole, except for the *p*-methyl and *p*-ethyl derivatives (1,2,4-trichlorobenzene). For the high-boiling products, bibenzyl was used in all cases except for the *p*-bromo derivative (dicumyl). Comparison of glpc retention times with those of authentic samples which were either made by other routes or obtained commercially were used for identification of compounds (product peak areas determined with a planimeter).

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