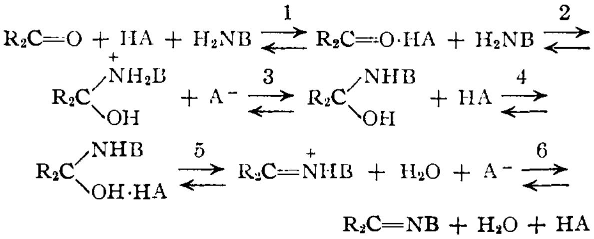
mum and then decreases as the reactive base (NH_2OH) is converted to its unreactive conjugate acid (NH_3^+OH). Furthermore, in no case did the effect of acidity ever increase the rate by as much as one order of magnitude. Therefore, since the effect of pressure on this reaction is very much greater than one could reasonably expect from mere increase in acidity, we conclude that the rate-determining step in the formation of these oximes proceeds by formation of a highly polar activated complex from uncharged reactants. Any proposed mechanism of oxime formation should be examined in the light of this observation.

It was suggested by Bartlett[4] that carbonyl addition reactions of this type have some such mechanism as



$$R_2C{=}O + HA + H_2NB \underset{}{\overset{1}{\rightleftarrows}} R_2C{=}O{\cdot}HA + H_2NB \overset{2}{\rightleftarrows}$$
$$R_2C\begin{matrix}\nearrow \overset{+}{N}H_2B \\ \searrow OH\end{matrix} + A^- \overset{3}{\rightleftarrows} R_2C\begin{matrix}\nearrow NHB \\ \searrow OH\end{matrix} + HA \overset{4}{\rightleftarrows}$$
$$R_2C\begin{matrix}\nearrow NHB \\ \searrow OH{\cdot}HA\end{matrix} \overset{5}{\rightleftarrows} R_2C{=}\overset{+}{N}HB + H_2O + A^- \overset{6}{\rightleftarrows}$$
$$R_2C{=}NB + H_2O + HA$$

and that steps 2 or 5 are rate determining rather than other steps which involve simple proton transfers. Hine[3] proposed a similar mechanism. Hammett[5] and others[6] suggest the converse; that the rate-determining step is a proton transfer or at least involves the participation of charged intermediates in the formation of a charged or neutral activated complex.

The large acceleration of rate by increasing pressure demonstrated in the present work supplies strong evidence that either step 2 or 5 is in fact rate determining as suggested by Bartlett. Furthermore, recent work by Jencks[14] provides evidence that step 5 rather than 2 is rate determining since with more reactive carbonyl compounds at atmospheric pressure the equilibria as far as step 3 were shown to be practically instantaneous. Thus the pressure effect on rate with hindered carbonyl compounds is compatible with Jencks' conclusions.

The technique of carrying out liquid phase ionic reactions at high pressure not only enables one to prepare compounds which are difficult to obtain by more conventional methods, but also provides a useful approach to the study of reaction mechanisms.

Acknowledgment.—We are indebted to Mr. R. W. Walker for the development and performance of the quantitative infrared spectrographic analyses, and to Mr. R. N. Boos for microanalytical data.

[14] W. P. Jencks, Abst. 134th Amer. Chem. Soc. Meeting, Chicago, Ill., Sept. 7-12, 9P (1958).

RAHWAY, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

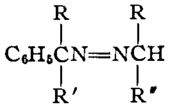
Azo Compounds. XXIX. Decomposition Study of α-Alkyl- and α,α-Dialkylbenzylazoalkanes[1]

BY C. G. OVERBERGER AND A. V. DIGIULIO[2]

RECEIVED SEPTEMBER 15, 1958

The four unsymmetrical benzylazoalkanes, α-phenylethylazoisopropane (I), α-cumylazoisopropane (II), α,α-diethylbenzylazo-3-pentane (III) and α,α-methylisobutylbenzylazo-2-(4-methylpentane) (IV) were decomposed in diphenyl ether. First-order kinetics were observed and the E_A and $\Delta S^{\ddagger}$ were determined in each case. Similar rates were obtained in the presence of benzoquinone. Comparisons between I, II, III and IV are made as well as with azo-bis-isopropane, and 1-azo-bis-1-phenylalkanes. Differences in reactivity are discussed in terms of hyperconjugation and "B"-strain. Additional evidence has been obtained that indicates that in the thermal decomposition of azo compounds, probably both radicals assist in the elimination of nitrogen in the rate-determining step.

In previous work Overberger and co-workers[3a,b,c,d,e] prepared a number of symmetrical aliphatic azonitriles and investigated the effect of structure on the rate of decomposition to nitrogen and two free radicals. The purpose of this present work was to extend the study of the effects of structure on the homolytic dissociation of unsymmetrical aliphatic azo compounds particularly where the two radicals attached to the azo linkage were of considerable difference in stability. It was anticipated that a study of this type of azo compound would shed some light on the problem as to whether both carbon–nitrogen bonds were ruptured simultaneously[4,5] in the rate-determining step or occurred in a stepwise manner[6,7] in the thermal decomposition of unsymmetrical azoalkanes and arylazoalkanes. The unsymmetrical benzylazoakanes of the general structures[1,25] were decomposed thermally



$$C_6H_5\overset{\overset{R}{|}}{\underset{\underset{R'}{|}}{C}}N{=}N\overset{\overset{R}{|}}{\underset{\underset{R''}{|}}{C}}H$$

I, $R = R'' = CH_3$, $R' = H$
II, $R = R' = R'' = CH_3$
III, $R = R' = R'' = C_2H_5$
IV, $R = CH_3$, $R' = R'' = iC_4H_9$

and then rates of decomposition studied.

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[1] This is the 29th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series see C. G. Overberger and A. V. DiGiulio, THIS JOURNAL, **81**, 1194 (1959).

[2] This paper comprises a portion of a thesis presented by A. V. DiGiulio in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate School of the Polytechnic Institute of Brooklyn.

[3] (a) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, **71**, 2661 (1949); (b) C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951); (c) C. G. Overberger and H. Biletch, *ibid.*, **73**, 4880 (1951); (d) C. G. Overberger and A. Lebovits, *ibid.*, **76**, 2722 (1954); (e) C. G. Overberger, W. F. Hale, M. B. Berenbaum and A. B. Finestone, *ibid.*, **76**, 6185 (1954).

[4] H. C. Ramsperger, *ibid.*, **51**, 2134 (1929).

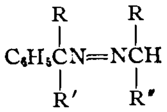
[5] S. G. Cohen and C. H. Wang, *ibid.*, **77**, 3628 (1955).

[6] M. Page, H. O. Pritchard and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3878 (1953).

[7] G. L. Davies, D. H. Hey and G. H. Williams, *ibid.*, 1397 (1956).

TABLE I

DECOMPOSITION OF UNSYMMETRICAL BENZYLAZOALKANES IN DIPHENYL ETHER



$$C_6H_5\overset{R}{\underset{R'}{C}}N{=}N\overset{R}{\underset{R''}{C}}H$$

Compound	Temp., ±0.05°C.	$k \times 10^4$, sec.$^{-1}$	Gas evolved, %	Concn. of quinone, mole/l.	Gas evolved in presence of quinone, %	$k \times 10^4$, sec.$^{-1}$
I, R = R″ = CH_3, R′ = H	143	1.74 ± 0.04	105 ± 1[a]	0.115	92[a]	1.54
	152	4.43 ± .05	109.5 ± 0.5	.115	100	4.24
	165.5[b]	16.63 ± .17	111 ± 1	.234	101	15.70
II, R = R′ = R″ = CH_3	120	1.06 ± .01	110.5 ± 0.5			
	125	1.95 ± .04	110 ± 3			
	135	5.94 ± .11	114 ± 2			
	143	14.21 ± .08	111.5 ± 1.5	.0923	101	14.08
	130[c]	3.77	108	.0923	101	3.79
III, R = R′ = R″ = C_2H_5	120.05	0.78 ± .02	98.5 ± 0.5			
	125	1.37 ± .01	95 ± 0			
	130	2.63 ± .00	97.5 ± 0.5			
	139	7.38 ± .04	95.5 ± .5			
	147	19.06 ± .02	97.5 ± .5	.115	91 ± 1	19.38 ± 0.5
IV, R = CH_3, R′ = R″ = $i C_4H_9$	103	1.17 ± .01	96.5 ± .5			
	110	2.52 ± .01	96.5 ± 1.5			
	120	8.51 ± .05	96.5 ± 1.5			
	125	15.75 ± .47	99 ± 0	.139	97 ± 1	16.16 ± .24
	130	26.18	88[d]			
		25.95	97	.139	93	25.17

[a] A less pure sample. [b] Temp. ±0.3°. [c] Mesitylene solvent. [d] Known to be less pure.

Kinetic Results

The rates of the thermal decomposition of the four azo compounds in diphenyl ether over a range of temperatures were determined. The apparatus used was essentially the same as described by Overberger and Berenbaum,[3b] and the same precautions were taken to exclude oxygen from the reaction. The rate of gas evolution was recorded with a gas buret and the rate constant, k, calculated as the product of 2.303 and the slope of a plot of $\log (V_\infty/V_\infty - V_t)$ *vs.* time, where V_t is the total volume of gas evolved at time, t. The value of V_∞ was taken as the observed value obtained after an elapsed time equivalent from 7 to 10 half-lives. In all cases a small induction period was noted at the beginning of every decomposition.

In determining the rate of decomposition of compound I at 165.5° a modified reaction flask was utilized as described by Overberger and Gainer.[8] The flask was maintained at a constant temperature by the vapors of boiling mesitylene and a mercury gas buret was utilized rather than a water gas buret. The volume of gas evolved in the apparatus was of the order of 12–15 ml. as compared to 25–50 ml. in all the other decompositions. Duplicate runs were carried out in all cases, and typical first-order rate plots are shown in Figs. 1 and 2.

Table I summarizes the results obtained in this work. Inspection of the columns under "gas evolved" shows that these decompositions produce nitrogen and a hydrocarbon gas. Actually compounds I and II both yield a mixture of propane and propylene along with nitrogen, depending upon the amount of coupling. The assumption is made that the ratio of nitrogen molecules to propane (or propylene) molecules formed is essentially

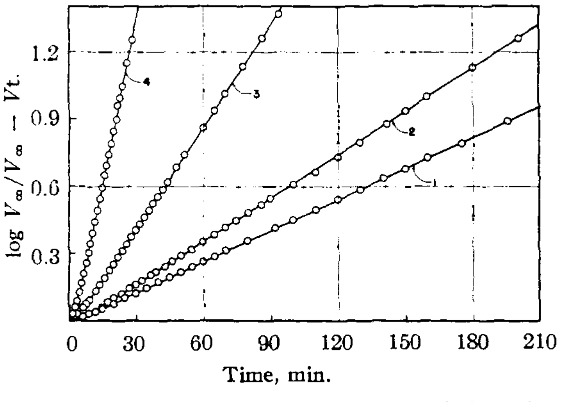


Fig. 1.—Decomposition of unsymmetrical benzylazoalkanes in diphenyl ether: (1) 143°, α-phenylethylazoisopropane; (2) 110°, α,α-methylisobutylbenzylazo-2-(4-methylpentane); (3) 135°, ∞-cumylazoisopropane; (4) 147°, α,α-diethylbenzylazo-3-pentane.

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(8) C. G. Overberger and H. Gainer, THIS JOURNAL, **81**, in press (1959).

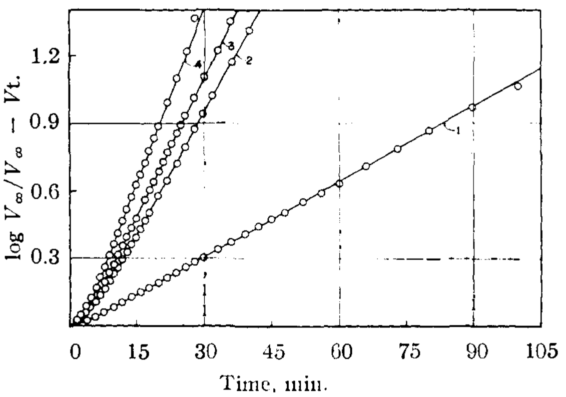
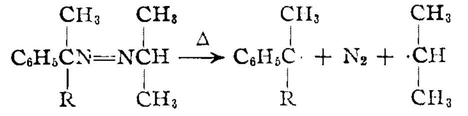


Fig. 2.—Decomposition of benzylazoalkanes in diphenyl ether in presence of benzoquinone: (1) 152°, α-phenylethylazoisopropane; (2) 143°, α-cumylazoisopropane; (3) 125°, α,α-methylisobutylbenzylazo-2-(4-methylpentane); (4) 147°, α,α-diethylbenzylazo-3-pentane.

constant throughout the reaction. If this is correct then the volume of gas evolved is a measure of the decrease in concentration of the azo compound and the first-order rate equation is valid. In order to test this assumption a few decompositions were conducted in the presence of benzoquinone, an efficient radical scavenger, (see last three columns of Table I) for compound I at 143, 152, and 165.5° and at 143° for compound II.



$$\mathrm{C_6H_5\overset{CH_3}{\underset{R}{C}}N{=}N\overset{CH_3}{\underset{CH_3}{C}}H \xrightarrow{\Delta} C_6H_5\overset{CH_3}{\underset{R}{C}}\cdot + N_2 + \cdot\overset{CH_3}{\underset{CH_3}{C}}H}$$

I, R = H; II, R = CH_3

Also in the table are reported initial results obtained in mesitylene solvent at 130° with and without the presence of benzoquinone for compound II. It can be seen that the quinone is an efficient radical scavenger and removes the isopropyl radicals formed in the decomposition rapidly; thus the volume of gas measured is essentially due to the evolved nitrogen. Smid and Szwarc[9] have shown, however, in the case of the thermal decomposition of butyryl peroxide that a small fraction of C_3-hydrocarbons form as a result of a "cage" disproportionation independently of the concentration of quinone. It is very probable that the same effect would be present in the azo decomposition, but on the basis of Smid and Szwarc's results this is only a small fraction of the total and probably does not account for more than 1 or 2% of the gas evolved in the azo decomposition. The last column in Table I shows that except in the case where a slightly impure compound was used, the evolved volume of gas in these cases was stoichiometric for the theoretical evolution of nitrogen and the rate constants were essentially the same as those obtained in the decomposition where benzoquinone was absent.

The same effects are noted in the decomposition of III and IV, where a low boiling product, a pentane or pentene (b.p. ~36°) and a hexane or hexene (b.p. ~60°), are side products which may affect the total volume of gas measured, along with the nitrogen. In compound III, the effect is greater than in IV, since the presence of benzoquinone produces a decrease of about 6% in the total amount of gas evolved, whereas in IV the decrease is only about 3 or 4%. This is interpreted as meaning that more of the pentane escapes the reaction solution as vapor in the non-quinone-containing decompositions, whereas the hexane produced in the decomposition of IV only partially escapes as a vapor adding therefore only slightly to the total gas volume. This second fact seems to be verified in the study of the products of decomposition of IV[1] where only ~20% of the total hexane fraction which was isolated was obtained in a cold trap between the reaction flask and the gas trap. The remainder was obtained by fractionally distilling the reaction solution, using high bath temperature to obtain the low boiling fraction. In any event the fact that the rates are essentially the same when benzoquinone is present or absent justified the use of the data obtained without benzoquinone added.

In decompositions studied in this work, it was observed that the time for the completion of the reaction was essentially the same at the same temperature for the same azo compounds with considerable differences in purity. Calculations of the rate constants determined by using the observed final volume for V_∞ (since this should always be a measure of the initial concentration of the azo compound) for a decomposition run of an impure sample of IV at 130° gave a rate constant which agreed with one determined on a pure azo compound. Cohen and Wang[10] have also noted that the rate constants determined from an impure sample of azo-bis-diphenylmethane yielded essentially the same results as a pure sample.

In Table II is summarized the kinetic results along with pertinent data from other workers. The slope of the line determining the activation energies for the azo compounds I through IV were determined by a least square calculation and were found to be in close agreement with the values obtained by a plot of log k *vs.* $1/T$. The entropies of activation were determined in the usual fashion according to the transition state theory[11] using an experimental value of k at 125° for compounds II, III and IV, and the experimental value of k at 143° for the compound I.

The rate constants for compounds V, VI and VII were extrapolated to 120° from the values of k reported at 110.3° for these compounds[12] using the integrated form of the Arrhenius equation, whereas the rate constant for VIII was extrapolated to 120° from the rate equation given in reference 13 and the rate constant for IX was obtained from the rate equation given in reference.[14a]

Discussion.—The problem as to whether both carbon–nitrogen bonds are ruptured simultaneously

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(9) J. Smid and M. Szwarc, This Journal, **79**, 1534 (1957).

(10) S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955).

(11) S. Glasstone, K. J. Laidler, H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

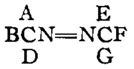
(12) S. G. Cohen, S. J. Groszos and D. B. Sparrow, *ibid.*, **72**, 3947 (1950).

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

(14) (a) H. C. Ramsperger, This Journal, **50**, 714 (1928); (b) **49**, 912, 1495 (1927).

TABLE II

DECOMPOSITION OF ARALKYL AZO COMPOUNDS



$$\mathrm{B}\overset{\mathrm{A}}{\underset{\mathrm{D}}{\mathrm{C}}}\mathrm{N{=}N}\overset{\mathrm{E}}{\underset{\mathrm{G}}{\mathrm{C}}}\mathrm{F}$$

A	B	D	E	F	G	$k \times 10^4$, sec.$^{-1}$ t, 120°	E_A, kcal./mole	ΔS^{++}, cal. mole^{-1} deg.$^{-1}$
I, CH_3	C_6H_5	H	CH_3	H	CH_3	0.132[d,g]	36.5	9.3
II, CH_3	C_6H_5	CH_3	CH_3	H	CH_3	1.06[d]	36.7	14
III, C_2H_5	C_6H_5	C_2H_5	C_2H_5	H	C_2H_5	0.78[d]	39.0	19
IV, CH_3	C_6H_5	i-C_4H_9	CH_3	H	i-C_4H_9	8.51[d]	35.2	15
V,[a] CH_3	C_6H_5	H	CH_3	C_6H_5	H	4.85[e,g]	32.6	7
VI,[a] C_2H_5	C_6H_5	H	C_2H_5	C_6H_5	H	2.06[e,g]	32.3	
VII,[a] i-C_4H_9	C_6H_5	H	i-C_4H_9	C_6H_5	H	7.11[e,g]	33.3	9
VIII,[b] H	C_6H_5	H	H	C_6H_5	H	0.045[f,g]	35.0	5
IX,[c] CH_3	H	CH_3	CH_3	H	CH_3	0.00001	40.9	1

[a] Ref. 12. [b] Ref. 13. [c] Ref. 14. [d] Decomposed in diphenyl ether. [e] Decomposed in ethylbenzene. [f] Vapor phase decomposition. [g] Extrapolated to 120°.

in the rate-determining step or in a stepwise fashion in the thermal decomposition of unsymmetrical aliphatic azoalkanes or arylazoalkanes is still a subject of question. Ramsperger[4,14a,b] had studied the vapor phase thermal decompositions of azomethane, azoisopropane and methylazoisopropane and on the basis of their relative reactivities and the intermediate activation energy of methylazoisopropane suggested that both carbon–nitrogen bonds were ruptured simultaneously. However, Page, Pritchard and Trotman-Dickenson[6] have proposed arguments that azomethane may decompose in a stepwise fashion and suggested that the rather "abnormal" pre-exponential or A factors obtained by Ramsperger and later Rice[15] may be caused by a chain decomposition. Cohen and Wang[5,10] noted that in a comparison of azomethane, azo-bis-isopropane, 1-azo-bis-1-phenylethane and azo-bis-diphenylmethane, that symmetrical substitution of a pair of methyls or a pair of phenyls for α-hydrogens had an approximate additive effect on lowering of activation energy. From this observation and also from a comparison of phenylazodiphenylmethane with phenylazotriphenylmethane and azo-bis-diphenylmethane they suggested that this effect was probably largely the result of resonance stabilization of the radicals, and that symmetrical and unsymmetrical azo compounds may decompose by simultaneous rupture in the rate-determining step of both carbon–nitrogen bonds.[16]

As noted by Cohen and Wang the comparison of phenylazodiphenylmethane and azo-bis-diphenylmethane was not ideal, since the possible conjugation of the phenyl and azo group might markedly affect the strength of the diphenylmethyl–nitrogen bond. Wieland, Ploetz and Indest[17] found that a small amount of benzoylhydrazine was formed in the decomposition of benzoyl-azotriphenylmethane and that the yield of nitrogen was not quantitative. On this basis David, Hey and Williams[7] suggested that benzoylazotriphenylmethane decomposed in a stepwise manner. Since the ease of decomposition of azodibenzoyl, benzoylazobenzene and azobenzene decreased in the order listed, this was considered as indicative that the Ph–N bond was stronger than the $\mathrm{Ph{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}N}$ bond. On this basis they suggested that the decomposition of arylazotriarylmethanes proceeded in an analogous fashion in which the formation of the triphenylmethyl radical and the phenylazo radical was the first stage and the rate-determining step. Hyson, Beasley, Holub, Overbaugh and Schreyer[18] by means of a nomograph have been able to correlate and predict the one minute half-life decomposition temperature of a number of carbamylazonitriles. This nomograph relationship was also found to hold for a benzoylazonitrile series as well as for the azoalkanes studied by Ramsperger. These workers suggest that it would be difficult to reconcile the correlation of the nomograph with an interpretation other than that of a simultaneous rupture of both carbon–nitrogen bonds, with the formation of two radicals and a molecule of nitrogen.

Additional support for the conclusion that both radicals attached to the azo linkage assist in the rate-determining step is obtained from the data in Table II. From a comparison of compounds I, V and IX, it can be seen that replacement of a methyl group in IX by a phenyl (I) has caused a decrease of approximately 4 kcal. in the E_A, and replacement of a pair of methyls in IX by a pair of phenyls (V) has caused an approximate decrease of 8 kcal. Compound I is approximately 10,000 times more reactive than IX[19] and this result is undoubtedly due to both the decrease in E_A and the increase in ΔS^{++}. However, replacement of a methyl group in I by a phenyl group (V) only causes a 37-fold increase in the reactivity. This is undoubtedly due to the fact that the entropy of activation remained almost constant. However, the 37-fold increase is still significant and since both compounds I and V contain the easily formed α-phenylethyl radical, it is unlikely that the cleavage of the α-phenylethyl–nitrogen bond is rate determining in both cases, since if the decomposition occurred in a stepwise manner, the rate of decomposition of I and V

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(15) O. K. Rice and D. V. Sickman, *J. Chem. Phys.*, **4**, 242 (1936).

(16) S. G. Cohen and C. H. Wang, THIS JOURNAL, **75**, 5504 (1953).

(17) H. Wieland, T. Ploetz and H. Indest, *Ann.*, **532**, 166 (1937).

(18) A. M. Hyson, D. K. Beasley, F. F. Holub, S. C. Overbaugh and R. C. Schreyer, Abstracts of the 129th Meeting of the American Chemical Society, Dallas, Tex., April 8 to 13, 1956, p. 6R.

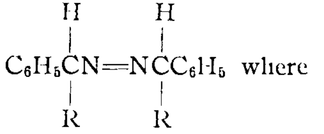
(19) The comparison may not be strictly valid since the data for IX were obtained from vapor phase decompositions and E_A and ΔS^{++} are known to be susceptible to solvent effects, although the rate itself is little affected in many free radical reactions.

should be approximately of the same order except for a statistical factor of two. Cohen and Wang[5] have reached a similar conclusion.

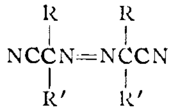
The results are best explained on the basis that both radicals assist or participate in the rate-determining step. These results seem to substantiate Ramsperger's earlier work, and there does not seem to be any question concerning the mode of decomposition of compounds I and V in solution. The complicating factor of possible conjugation present in the phenylazo series is not present here.

Two main factors have been shown to affect the stability of azo compounds, the resonance stability which the radicals attached to the azo linkage can provide for the transition state and steric factors. The importance of the resonance stability of the radicals has been noted by Cohen and Wang.[10]

In the symmetrical azo compounds ($RR'HCN{=}NCHR'R$) the ease of decomposition is facilitated in the order $R,R' = H$, CH_3, C_6H_5, the increased reactivity being attributed largely to decrease in activation energy. They[10] suggested that the differences in activation energies were correlated with differences in the resonance stabilization energies of the radicals, which in turn would be reflected in the resonance stabilization of the transition state. High stabilization energies would lead to lower dissociation energies of the carbon–nitrogen bonds and thus to lower activation energies.

In the series  $C_6H_5\overset{H}{\underset{R}{C}}N{=}N\overset{H}{\underset{R}{C}}C_6H_5$ where R = methyl, ethyl and isobutyl[12] the size of the R groups had only a small but noticeable effect on the rate of decomposition. The effect of substituents in the phenyl ring of azo-bis-1-phenylalkanes[12] was found to be small. Alder and Leffler[20] and Leffler and Hubbard[21] studied the role of solvent in the decomposition of phenylazotriphenylmethane, and showed that although the rate is relatively insensitive to changes in solvent, the effect was shown to be due to a compensating change in the entropies and the enthalpies of activation, and not necessarily due to a lack of interaction of solvent in either the initial or transition state. Both Cohen and Wang[10] and Davies, Hey and Williams[7] have studied the decompositions of substituted phenylazotriphenylmethanes. It was found that both electron-donating and electron-attracting substituents led to decreases in the rates of decomposition. Cohen and Wang suggested that perhaps resonance stabilization of the ground state by both types of substituents was an important factor. However, later work on the *m*-substituted phenylazo-triphenylmethanes[7,22] showed that both types of substituents again had the same effect. Since it was unlikely that *m*-substituents would influence the rate by affecting the resonance stabilization of the ground state or the transition state, Cohen and Wang suggest that the phenyl radical was stabilized by electron accession which tends toward completion of an octet, and destabilized by electron depletion. Davies, Hey and Williams[7] have interpreted these results in terms of desolvation in the transition state.

The effect of steric factors involving strain was demonstrated in the work reported by Overberger and co-workers[3a–c] on the azonitriles of the structure



$$NC\overset{R}{\underset{R'}{C}}N{=}N\overset{R}{\underset{R'}{C}}CN$$

where R and R' are alkyl substituents. It was found that when branching was introduced on the carbon beta to the azo carbon (R' is isobutyl or neopentyl), the rate of decomposition was increased strikingly. When no branching was present in this portion the rates were all quite similar. This effect was attributed to frontal or "F" strain, since models had shown considerable interaction between the two halves of the molecule in the more stable *trans* configuration. However, recent work by Hyson, *et al.*,[18] on the carbamylazonitriles indicate that this interpretation must be modified. They have shown that in the carbamylazonitriles  $(R)(R')(CN)CN{=}N\overset{O}{\overset{\|}{C}}\text{-}NH_2$ where there was no possible steric interaction between the two halves of the molecule, the same type of reactivity relationship existed, and that therefore the observed enhanced decomposition rates for the compounds with β-substituents must be related largely with the specific groups attached to the azo carbon.

Although some of the results obtained in this work are consistent with the "F"-strain theory, this can be only one factor. It appears likely that the results are probably best explained on the basis of hyperconjugation and "B"-strain[23] or a combination of both. These factors were previously considered by Overberger and co-workers in interpreting the decomposition data of the azonitriles. They were not considered to be major factors although it was recognized that these factors contributed to the relative stability of the azo compounds.

When the benzyl hydrogen in compound I in Table II is replaced by a methyl group to give the azo compound II, the reactivity is increased by 8-fold. This appears to be largely due to a hyperconjugation effect, whereby three additional hydrogens are available for resonance stabilization of the tertiary benzyl radical as opposed to the secondary benzyl radical of compound I. B-Strain does not seem to be important here since the models of these two compounds show very little interaction among the groups of the individual secondary and tertiary azo carbons. It is quite interesting to note that the increased resonance stabilization of the benzyl radical of compound II is

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(20) M. G. Alder and J. E. Leffler, This Journal, **76**, 1425 (1954)

(21) J. E. Leffler and R. A. Hubbard, *J. Org. Chem.*, **19**, 1089 (1954)

(22) S. Solomon, C. H. Wang and S. G. Cohen, This Journal, **79**, 4101 (1957).

(23) (a) H. C. Brown, H. Bartholomay and M. D. Taylor, *ibid.*, **66**, 435 (1944); (b) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1815 (1949); (c) H. C. Brown and I. Moritani, *ibid.*, **77**, 3623 (1955).

reflected in the increased entropy of activation rather than in the activation energy. This hyperconjugation effect is even more evident in compounds V and VIII[24] where a pair of methyl groups has replaced a pair of hydrogens with a subsequent increase in reactivity of about 100-fold.

B-Strain appears to become more important in compound III, where, although the total decrease in the number of hydrogens alpha to the azo carbons is 4 as compared to compound II, the rate is only 1.5-fold slower. The model of this compound shows an appreciable strain or crowding around the tertiary carbon, and also some interaction between the ethyl groups of the secondary radical. The apparent relief of strain in going from the tetrahedral to the planar configuration on decomposition would aid in accelerating the decomposition, and this effect seems to be operating in compound III to offset to a large extent the loss in the number of α-hydrogens. When compound III is compared to I, the total number of α-hydrogens is one less, but the rate is enhanced by 6-fold. Whether this effect is due to increased B-strain in III, or to the possibility that α-hydrogens attached to a benzyl radical may contribute to a greater degree to the stability of a benzyl radical as opposed to its contribution to the stability of a purely alkyl radical is not clear. Although there may be a difference in degree of effective resonance stabilization of the two types of radicals by hyperconjugation, it appears quite likely that B-strain is the chief factor here.

In compound IV, where the total number of α-hydrogens have decreased by two when compared to compound II, the effect of B strain is even more evident. This azo compound is 8 times more reactive than II. This effect is more than likely due to the presence of appreciable B-strain, especially in the tertiary benzyl carbon. The comparison with compound I shows a 64-fold increase in reactivity, whereas compound IV contains only one more α-hydrogen. When compared with compound III, which has two less α-hydrogens, the reactivity is 11-fold greater, apparently due to the substantially greater B-strain present in IV, as well as to the slightly greater resonance stabilization of its radicals.

The comparison of the above four unsymmetrical azo compounds with the symmetrical compounds in Table III gives additional insight on the effect of hyperconjugation and B-strain on reactivity.

In comparing compound II with V, where a phenyl and a hydrogen have been replaced by a pair of methyls, respectively, the increase in the number of α-hydrogens has been 6, whereas the reactivity has decreased 4.6-fold. In comparing III with VI (a pair of ethyls replacing a hydrogen and a phenyl), the number of α-hydrogens increased by 4 and the decrease in reactivity was only 2.6-fold. Likewise in comparing II with III (α-hydrogens decrease by four), there is only a 1.5-fold decrease in reactivity, whereas in comparing V with VI (α-hydrogens decrease by two), there is a 2.4-fold decrease in reactivity.

In comparing II with V, there is very little steric interaction in either compound, and the relative reactivities are probably directly related with the resonance stabilization of the radicals attached to the azo linkage. The same reasoning holds for the difference in reactivities in compounds V and VI, although in VI there is a small amount of interaction between the phenyl and ethyl groups of the individual benzyl radicals, but this effect is apparently small. In comparing III with VI, the decrease in reactivity does not appear as great as one would expect based only on the over-all decrease in stability of the radicals if the relationship between II and V is used as a criterion. In this case one is going from a compound (VI) with no steric interaction to one which exhibits a substantial amount of back strain in the tertiary benzyl radical (III). It is suggested that the increased back strain in compound III probably explains the enhanced reactivity over what would normally be expected if no B-strain were present. The same point of view is supported on consideration of the reactivities of II and III.

The effect is more strikingly demonstrated in compound IV. When IV is compared with VII, the number of α-hydrogens is actually increased by 6 (as compared to 6 for compounds II and V, and 4 for compounds III and VI) by the substitution of a pair of methyls for a phenyl and a hydrogen. Whereas the reactivities were decreased (more so for the non-sterically hindered case) in both other cases, the reactivity of IV was actually slightly greater than VII, and this is probably due to the enhanced B-strain in IV in the tertiary benzyl radical. Since models of VII show that there is some steric interaction between the phenyl and isobutyl groups of the individual benzyl radicals of VII (this probably accounts for the slightly greater reactivity of VII over V), the B-strain introduced by replacing the hydrogen by a methyl along with the 6 hydrogens is sufficient apparently to overcome the loss of a benzyl radical resonance so that compound IV actually is slightly more reactive than VII. The effect must be due primarily to the tertiary radical, since it would not be expected that replacement of a phenyl by a methyl would increase the strain in the secondary radical.

It is interesting to note, then, that when comparing compound II with V, III with VI, and IV with VII, where 6,4 and 6 hydrogens, respectively, capable of hyperconjugation replace a benzyl radical, the difference in rates between the pairs is greatest for the first, where there is no apparent back strain effect in either compound and the effect is probably due to the loss of resonance stabilization of one benzyl radical which is not offset by the increased hyperconjugation effect. The effect is reflected in the difference in activation energies which is compensated for to a large extent by a favorable entropy of activation in compound II. The modifying effect of B-strain is observed in the next two pairs III, VI and IV, VII whereby the hyperconjugation effect is in-

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[24] The comparison may not be rigorous, since the rate equation for VIII was determined by measuring the rate of decomposition in the vapor phase. However, the comparison is probably qualitatively correct.

creasingly modified by B-strain to overcome the loss of a benzyl radical resonance. The effect of the loss of a benzyl radical resonance between III and VI is reflected in the considerable difference in activation energy, which again is compensated for to a large degree by the very favorable entropy of activation of III. The rather high activation energy of III appears anomalous and is also consistent with the anomalous ultraviolet spectrum of this compound.[25] The loss of one benzyl radical resonance between VII and IV is reflected to a certain extent in the differences of the activation energies, but is more than compensated for by the quite favorable increase in the entropy of activation of IV.

The interpretation given above for the unsymmetrical and symmetrical alkyl azo compounds may also be applied in the same fashion to the linear azonitrile compounds.[3a–e] B-Strain is probably the major strain factor, although F-strain may assist to a lesser degree in accelerating the rate of decomposition of some of the azo compounds.

It should be realized, of course, that the arguments used for explaining the order of reactivity of the four unsymmetrical azo compounds listed in this work would still hold if the decompositions were occurring in a stepwise fashion with the rate determining step being the scission of the benzyl carbon–nitrogen bond, since the same relationships concerning B-strain and hyperconjugation are present among the four pertinent benzyl radicals.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Stereochemistry of Raney Nickel Desulfurizations. I. The 1,3-Disubstituted Cyclohexane and the Bicyclo[2.2.1]heptane Systems

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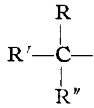
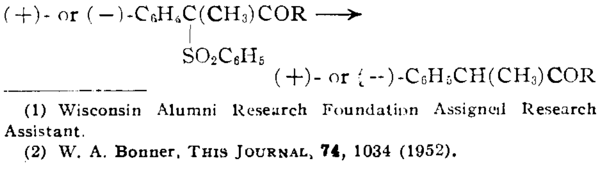
The synthesis and proof of stereochemistry of *trans*- and *cis*-3-methyl-3-mercaptocyclohexanols (IIIa and IIIb, respectively) are described. Suitable derivatives of IIIa and -b were reductively desulfurized with Raney nickel to give mixtures of diastereoisomeric 3-methylcyclohexanol derivatives: *cis*-S-benzyl ether O-β-naphthoate(IXb) → 37% *cis* and 63% *trans;* sulfone (Xb) of IXb → 43% *cis* and 57% *trans; trans*-S-benzyl ether O-β-naphthoate(IXa) → 56% *cis* and 44% *trans;* sulfone(Xa) of IXa → 46% *cis* and 54% *trans.* Phenyl 4-camphyl sulfide and the corresponding sulfone were prepared and were shown to give camphane on desulfurization.

Although the recent literature abounds in examples of the well-known Raney nickel desulfurization reaction, only a few of the reported cases provide information about the stereochemical fate of the carbon atom which becomes hydrogenolyzed. This gap in the body of results being accumulated is due in part to the infrequency of asymmetric S-*t*-carbinyl systems(I), a structural type necessary for retention of asymmetry in a sulfur hydrogenolysis reaction. W. A. Bonner[2] has made a deliberate attempt to study the stereochemistry of the reaction by employing derivatives of 2-phenyl-2-mercaptopropionic acid, substances which conform to the specified type I. Each of the enantiomers of 2-phenyl-2-phenylmercaptopropionamide (or the corresponding sulfoxide) gave on desulfurization racemic 2-phenylpropionamide. By contrast, the antipodal sulfones were converted to the expected products with 90% retention of optical activity; and although the relative configurations of starting material and product were not determined rigorously, inversion was indicated by the method of rotational trends. On the basis of these results, and others, Bonner[2] advanced a concerted mechanism involving coordination of the sulfone oxygen atom on the reagent, accompanied by backside displacement by hydrogen adsorbed on the metal surface. Because of the unusual nature of the Raney nickel desulfurization reaction, we felt it desirable to scrutinize stereochemically other systems and thereby extend and consolidate the grounds upon which mechanistic proposals can be developed.



$$\mathrm{R'{-}\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}{-}S{-}}$$

I, R, R', R'' ≠ H



$$(+)\text{- or }(-)\text{-}C_6H_5\underset{\displaystyle SC_6H_5}{C}(CH_3)CONH_2 \longrightarrow (\pm)\text{-}C_6H_5CH(CH_3)CONH_2$$

$$(+)\text{- or }(-)\text{-}C_6H_5\underset{\displaystyle SO_2C_6H_5}{C}(CH_3)COR \longrightarrow (+)\text{- or }(-)\text{-}C_6H_5CH(CH_3)COR$$

The 3-methyl-3-mercaptocyclohexanol system seemed attractive for desulfurization studies in that the oxygenated carbon atom would serve as a convenient and reliable reference point for gaining stereochemical information about changes at the 3-position; the anticipated desulfurization products, *cis* and/or *trans*-3-methylcyclohexanols, are well-characterized substances to which secure stereochemical assignments have been made.[3] Synthesis of the desired diastereoisomers was ac-

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[1] Wisconsin Alumni Research Foundation Assigned Research Assistant.

[2] W. A. Bonner, THIS JOURNAL, **74**, 1034 (1952).

[3] H. L. Goering and C. Serres, Jr., *ibid.*, **74**, 5908 (1952).