increased in intensity throughout the course of the experiment.

Decomposition of RR'.—All the runs without scavengers were made using sealed ampoules except for one run at 100° which was conducted under a nitrogen atmosphere by the batch-sampling technique. The rate constants obtained by the two techniques agree well as is shown by Table II. Decomposition under oxygen at 100° could be performed only by batch sampling. Decomposition at 80° was too slow to make batch sampling feasible because excessive amounts of solvent were lost to the gas stream during the periods necessary to obtain good rate constants. Therefore, rates were not measured in the presence of oxygen at 80°. The sealed-tube technique was used to study decomposition of RR' in the presence of DPPH and HDPPH.

Efficiency of Radical Production from RN_2R and RR'.—Efficiencies measured by the oxidation method utilized essentially the same procedure as was described earlier.[6] The reaction mixtures consisted of 4 ml. of chlorobenzene and 2 ml. of cumene containing small amounts of initiator (0.5-1.0×10^{-3} molar) and inhibitor (1.0-2.0×10^{-5} molar DBPC). The ratio of the amount of initiator to inhibitor was so adjusted that $kt_l << 1$, where k is the rate of decomposition of the initiator and t_l is the inhibition period. A 50:1 ratio of initiator to inhibitor was suitable at 80°. It was convenient to add the inhibitor as an aliquot from a stock solution in benzene and the initiators were added either as solids or in solution. The rate of oxygen uptake was measured long enough to determine the steady rates of oxidation after the inhibition periods.

The rate of radical production from RN_2R was also measured by the iodine method.[7] The rate of disappearance of iodine was followed spectrophotometrically and was found to be zero order with respect to the iodine concentration. All runs at 80° were carried out by the batch-sampling technique Both $[I_2]_0$ and $[RN_2R]_0$ were varied from run to run in such a way as to maintain the condition, $kt_l << 1$, and to keep t_l large enough to measure with precision. The rate of decomposition of RN_2R at 100° was so fast that satisfaction of the condition $kt_l << 1$ would require t_l to be too short for accurate measurement. Therefore, a was estimated either by using the integrated expression for $[RN_2R]$ or by measuring the rate of disappearance of I_2 early in the run (see Results section). The sealed-tube technique was used since this procedure facilitated accurate timing of sampling at short intervals. In runs in which t_l was determined many samples were taken in order to provide data for meticulous documentation of t_l. Plots of $[I_2]$ *versus* time curved appreciably because of the substantial decay of RN_2R over the course of a run.

Decomposition of RN_2R in the Presence of Bromine.—Runs at 80° were followed by the batch-sampling technique under nitrogen. Samples were withdrawn every 5 to 7 minutes and were analyzed spectrophotometrically for bromine. Experiments were discontinued after the bromine was completely gone. The plots of $[Br_2]$ *versus* time were almost linear. However, b-values calculated from the equation $b = [Br_2]_0/[RN_2R]_0kt_l$ were usually greater than one and showed far less reproducibility than was obtained in measurements of a by the iodine method.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY (NO. 2556), PASADENA, CALIF., AND FROM THE DEPARTMENT OF CHEMISTRY AT IOWA STATE UNIVERSITY]

The Mechanism of Decomposition of Azo Compounds. II. Cage Effects in the Decomposition of α,α'-Azoisobutyronitrile and Related Compounds

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The rate of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') from α,α'-azoisobutyronitrile (RN_2R) has been studied in carbon tetrachloride, benzene and styrene. A particularly detailed study was made in carbon tetrachloride solution at 62.5°. The yield of tetramethylsuccinonitrile (RR) from RN_2R in the presence of bromine has also been estimated. The results, coupled with other available information concerning the decomposition of RN_2R and RR', show that the ketenimine is produced by coupling of both primary and secondary decomposition fragments. Application of the theory of the cage effect as an important part of the mechanism of decomposition of azonitriles and ketenimines is justified.

There have been a number of studies of the rate[2,3] of decomposition of α,α'-azoisobutyronitrile (ABN, RN_2R) and of the rates at which radicals are produced[4-7] during the decomposition using variations of the scavenger lifetime method. The latter studies all show that the decomposition is measurably inefficient in producing radicals.[6,8] The same conclusion has been indicated by study of ABN as an initiator for vinyl polymerization[9-11] and by product analysis under various conditions.[10c,12,13] The principal final product of decomposition in inert solvents is tetramethylsuccinonitrile.[12] However, it is also known that substantial amounts of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') are formed and decomposed during the reaction.[14-16]

We have continued our study of this system by following the formation of RR and RR' from ABN. Much of the work parallels that reported in the accompanying paper[17] for the system based on 1,1'-azocyanocyclohexane. All of the equations developed for the latter system are applicable to the ABN problem and will be used in this presentation without repetition.

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(1) Division of Chemistry, California Institute of Technology.

(2) F. M. Lewis and M. S. Matheson, THIS JOURNAL, **71**, 747 (1949).

(3) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

(4) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

(5) M. C. Ford and W. A. Waters, *J. Chem. Soc.*, 1851 (1951).

(6) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

(7) G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3238 (1955).

(8) C. Walling, *J. Polymer Sci.*, **14**, 214 (1954).

(9) L. M. Arnett, THIS JOURNAL, **74**, 2027 (1952); L. M. Arnett and J. H. Peterson, *ibid.*, **74**, 2031 (1952).

(10) (a) J. C. Bevington, J. H. Bradbury and G. M. Burnett, *J. Polymer Sci.*, **12**, 469 (1954); (b) J. C. Bevington, *Trans. Faraday Soc.*, **51**, 1392 (1955); (c) J.C. Bevington, *J. Chem. Soc.*, 3707 (1954).

(11) B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).

(12) A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 1490 (1950).

(13) J. C. Bevington and N. A. Ghanem, *J. Chem. Soc.*, 3506 (1956).

(14) M. Talât-Erben and S. Bywater, THIS JOURNAL, **77**, 3710, 3712 (1955).

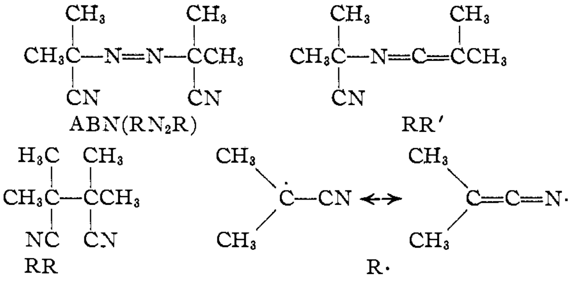
(15) G. S. Hammond, O. D. Trapp, R. T. Keys and D. L. Neff, *ibid.*, **81**, 4878 (1959).

(16) P. Smith and S. Carbone, *ibid.*, **81**, 6174 (1959).

(17) C.-H. S. Wu, G. S. Hammond and J. M. Wright, *ibid.*, **82**, 5386 (1960).

Results

The species involved in the study are ABN, (RN_2R), RR', RR and the cyanopropyl radical, R·.



ABN(RN_2R)

RR'

RR

R·

Rates of Formation of RR' from RN_2R.—The rates of formation of RR' from RN_2R were followed by infrared analysis for RR'. The z-values were estimated, both by measurement of initial slopes and by observation of the time and value of $[RR']_{max}$. Rates of decomposition of RR', needed for the calculations, have been reported elsewhere.[15] Table I summarizes the data. The rate of formation of RR' in carbon tetrachloride containing various radical scavengers has also been measured and the results are reported in Table II. As was observed in the similar measurements with 1,1'-azocyanocyclohexane,[17] addition of scavengers reduces the yield of RR' significantly but does not prevent its formation entirely except in the presence of oxygen with no added antioxidant.

TABLE I

RATES OF FORMATION OF RR' FROM RN_2R

Solvent	Temp., °C.	z	Method of estimation[a]
Carbon tetrachloride	62.5	0.58	A
Carbon tetrachloride	62.5	.57	A
Carbon tetrachloride	69.6	.47	A
Carbon tetrachloride	80.9	.56	A
Carbon tetrachloride	80.9	.54	A
Benzene	62.5	.48	A
Benzene	62.5	.48	A
Benzene	69.6	.47(0.50)	A(B)
Benzene	70.0	.53	B
Benzene	80.9	.43(0.49)	A(B)
Benzene	80.9	.44	A
Styrene	70.0	.26	A
Styrene	70.0	.23	A

[a] Method A: Estimated by measurement of initial rate; $z = (d[RR']/dt)_{t \to 0}/k_1[RN_2R]_0$; method B: estimated by location of $[RR']_{max}$; z calculated from eq. 14 of previous paper.[17]

TABLE II

RATES OF FORMATION OF RR' FROM RN_2R IN THE PRESENCE OF SCAVENGERS IN CARBON TETRACHLORIDE AT 62.5°

$[ABN]_0$ × 10^2, mole l.$^{-1}$	[S][a] × 10^2, mole l.$^{-1}$	z'
6.095	None	0.56[b]
6.093	DPPH, 1.456	.35[c]
6.092	DBPC + O_2, 18.2	.35[c]
6.09	DPPD, 3.02	.35[c]
6.09	O_2	0

[a] S is radical scavenger; DPPH, α,α-diphenyl-β-picrylhydrazyl; DBPC, 2,6-di-*t*-butyl-*p*-cresol; DPPD, N,N'-diphenyl-*p*-phenylenediamine. [b] Without scavenger, the number represents z-value. [c] Method of estimation of z'-value: $z' = (d[RR']/dt)_{t \to 0}/[ABN]_0 k_1$; k_1 is the rate constant of ABN at 62.5°, 1.18 × 10^{-5} sec.$^{-1}$.

Formation of RR from RN_2R.—It is known that the principal final product of ABN decomposition is tetramethylsuccinonitrile. This compound must be formed by a number of paths: (1) in the inefficient (cage) reaction of RN_2R, (2) in the inefficient reaction of RR', and (3) by coupling of "free" cyanopropyl radicals. For reasons which will be explained later, it becomes important to sort out process 1. This was done by estimation of the yield of RR from RN_2R in the presence of bromine or oxygen. Bromine reacts rapidly with both free radicals and RR'. Oxygen is a good radical scavenger, as is shown by the fact that the rates of oxidation reactions initiated by RN_2R and RR' are independent of the pressure of oxygen above the solutions. Furthermore, spectrophotometric measurements show that no RR' is formed from RN_2R in the presence of oxygen. Since RR' is formed if an antioxidant is added to the solution, the result must indicate that RO_2· reacts with RR'.[15,17] Yields of RR formed under these conditions were estimated by the isotope dilution method using perdeuterio-ABN, and by vapor phase chromatography. No corrections for fractionation of the isotopic mixtures were made and the v.p.c. analysis was not expected to be highly precise. However, the results indicate that approximately 20% RR is formed from RN_2R in the presence of scavengers capable of destroying both R· and RR'.

Measurement of Bromine Lifetimes.—Since bromine reacts stoichiometrically with RR', it was expected that the lifetime of bromine in the presence of decomposing ABN would be shorter than iodine lifetimes in similar experiments. The difference between the two measurements was expected to be a measure of the rate of formation of RR' in the inefficient decomposition of ABN. The results were, however, disappointing. As is shown by the data in Table III, the lifetimes are not a linear function of the initial concentrations of bromine, but increase rapidly as the bromine concentration is increased. The values of b, calculated from the following equation, varied from 0.79 to 1.26. Furthermore, the values of b,

$$b = [Br_2]_0/[ABN]_0 k_1 t_l$$

at the higher bromine concentrations, exceed 1.00. This indicates that some of the decomposing ABN

TABLE III

BROMINE LIFETIMES IN PRESENCE OF DECOMPOSING ABN IN CARBON TETRACHLORIDE AT 62.5°

Run	$[ABN]_0$, mole l.$^{-1}$	$[Br_2]_0$ × 10^{-3}, mole l.$^{-1}$	Lifetime of Br_2, min.	b[b]
1	0.0608[a]	2.90	77	0.87
2	.0608[a]	2.45	72	0.79
3	.0487[a]	4.73	112	1.22
4	.0609[a]	3.8	72	1.04
5	.0488[a]	4.38	101	1.26
6	.0615[c]	2.53	48	1.2
7	.0615[c]	2.76	61	1.01
8	.0610[c]	2.88	66	1.02

[a] Sealed-tube experiment. [b] Factor b was calculated from the equation $b = [Br_2]_0/[ABN]_0 k_1 t_l$; k_1 = 1.18 × 10^{-5} sec.$^{-1}$, the rate constant decomposition of ABN in carbon tetrachloride at 62.5°, and t_l = lifetime of bromine. [c] Batch sampling experiment under nitrogen atmosphere.

molecules must cause the destruction of more than one molecule of bromine. This shows that some secondary reaction, such as bromine substitution must occur.

Discussion

The Key Reactivity Ratios ($k_3/k_2 + k_3$) and ($k_3'/k_2' + k_3'$).—As was done in the previous paper,[17] the rate of coupling to form RR′ relative to radical–radical interactions to give other products was analyzed in terms of k_2 and k_3, rate constants for coupling to give RR and RR′ (or other stable products), respectively. Similar analysis of the coupling reactions, occurring by primary recombination, is expressed in terms of the rate constants k_2' and k_3'. Sufficient data for complete analysis are available only for carbon tetrachloride solutions at 62.5°. The data used were the rate constant for decomposition of RN_2R, the rate constant for decomposition of RR′ and the efficiency factors a and a' for radical production from RN_2R and RR′, and the values of z and z' reported in Tables I and II. Calculation of $k_3/k_2 + k_3$ and $k_3'/k_2' + k_3'$ is straightforward and requires no disturbing assumptions. The alternative method for obtaining $k_3/k_2 + k_3$ involves the increase in the rate of decomposition of RR′ in the presence of scavengers and the value of a' which is determined by dividing the measured rate of radical production by the rate of decomposition in the presence of scavengers.

Data reported in our earlier paper[15] were interpreted as indicating that the rate of decomposition of RR′ was the same in the presence and in the absence of scavengers. This conclusion was reached because several runs in the presence of oxygen and di-*t*-butyl-*p*-cresol in 2:1 carbon tetrachloride–cumene gave rates of decomposition very close to those observed in the same solvent using degassed solutions (both $\sim 1.0 \times 10^{-5}$ sec.$^{-1}$). On the other hand, parallel measurements of the rates in pure carbon tetrachloride and in carbon tetrachloride containing α,α-diphenyl-β-picrylhydrazyl (DPPH) gave 0.84×10^{-5} sec.$^{-1}$ and 1.00×10^{-5} sec.$^{-1}$, respectively. The assumption that regeneration of RR′ occurred *only* by coupling of "caged" radicals seemed obvious at the time but is totally inconsistent with the data reported in this paper which *demand* the assumption that "free" cyanopropyl radicals combine to give RR′. To understand this enigma we must look at the magnitude of the effects to be expected. Using the data from ABN decomposition we arrive at 0.46 for the value of $k_3/k_2 + k_3$. This predicts that the increase in rate of RR′ decomposition in the presence of a scavenger should be $1/(1-0.46a')$. The value of a' depends upon our choice of the value of the rate constant in the presence of scavengers. If we choose a rate constant *measured* in the oxidation mixture, the value of a' is 0.41 and the predicted increase in rate is a factor of 1.2. While the calculated increase is almost exactly that observed if the experiment with DPPH is considered accurate, it is clear that the magnitude of the effect is too small to become a valuable tool in our analysis. This is one of our reasons for seeking a different system for study.[17] In retrospect we have come to the conclusion that there was probably an error in the measurement of the rate in the presence of oxygen and an antioxidant. The reactions were carried out in a three-necked flask with the necks extending above the surface of the constant temperature bath. The oxygen supply was replenished periodically by purging briefly with oxygen. The combination of cooling by the cold gas and by conduction probably lowered the temperature enough to compensate for the increase in rate due to the scavenging effect. If this is the case, the efficiency factor, a', should be reduced by about 16%, giving a tentative value of 0.34.

The amount of RR formed in the presence of low concentrations of bromine in carbon tetrachloride provides an alternative estimate of the distribution of the radicals in primary recombination reactions. The total inefficient reaction is 54%. If 20% RR is formed, the yield of RR′, neglecting disproportionation, is 34%. This agrees very well with the measured value of 35% and confirms the estimate of $k_3'/k_2' + k_3'$. The values of the reactivity ratios are summarized in Table IV.

Table IV

Distribution of Radicals in Decomposition of α,α'-Azoisobutyronitrile and Dimethyl-N-(2-cyano-2-propyl)-ketenimine in Carbon Tetrachloride at 62.5°

Compound	a or a'	z	z'	$yk_1'/y'k_1'$	$k_3/(k_2 + k_3)$	$k_3'/(k_2' + k_3')$
ABN	0.46[a]	0.56	0.35		0.46	0.65
CPK	0.35[b]			0.84	0.46	

[a] Efficiency factor determined by oxidation-inhibition period and by iodine-lifetime measurement. [b] Efficiency factor determined by oxidation-inhibition period (see text).

Reaction in Styrene.—It was previously reported[15] that the rate of decomposition of RR′ is 1.6 times faster in styrene than in benzene. This was attributed to a decrease in the cage effect due to solvation of cyanopropyl radicals by formation of charge-transfer complexes of cyanopropyl radicals with styrene. The sharp reduction in the rate of formation of RR′ from ABN (Table I) is also consistent with this view.

Cage Effects in Thermal Decomposition Reactions.—We believe there is little reasonable doubt that we have been able to measure, with fair accuracy, the efficiency of radical production in the thermal decomposition of ABN, 1,1′-azocyanocyclohexane (ACC) and the two related ketenimines. We now feel that it is possible to advance compelling arguments in support of the view that the inefficiency is due to primary recombination of radicals before they have been separated by diffusion. The most cogent arguments in favor of this view are: (1) The ratios $k_3/k_2 + k_3$ and $k_3'/k_2' + k_3'$ are either very similar or identical in both systems which we have studied. (2) Tetramethylsuccinonitrile is produced from ABN even in the presence of very reactive scavengers when the latter are present in relatively low concentration but none is produced when ABN is decomposed in liquid bromine.[18] (3) Altogether too many coincidences are required by the assumption that all inefficient reactions are cyclic, non-radical process. (4)

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[18] O. D. Trapp and G. S. Hammond, This Journal, **81**, 4876 (1959).

Competing hypotheses which have been raised are easily disposed of by logical arguments.

We will consider the details of the above points in turn. In the ABN system we have two measurements of $k_3/k_2 + k_3$ which are in tolerably good agreement, although the value estimated from data for the decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine (CPK) in the presence and absence of scavengers is based upon a single measurement and involves rejection of the data obtained from decomposition of CPK in the presence of oxygen and an antioxidant. The agreement of the two values obtained in the study of the cyanocyclohexyl system[17] is excellent, and, in the latter case, definitive measurements are easy to make because relatively large amounts of ketenimine are produced by coupling of "free" radicals. Specifically, this makes the difference between the rates of decomposition of N-(1-cyanocyclohexyl)-pentamethyleneketenimine (CHK) in the presence and absence of scavengers large enough to be measured easily.

In neither system are the values of $k_3/k_2 + k_3$ and $k_3'/k_2' + k_3'$ close enough together to be considered identical within the limits of the precision of our measurements. Discovery of small errors in our assumptions concerning stoichiometry could, of course, change the picture and make the two quantities appear identical in either or both cases. Even assuming that the small differences are real, we are impressed with the similarity in the values. It appears that factors which govern the relative rates of formation of RR and RR' in the inefficient reactions of the azo compounds are cut from the same fabric as those which determine the relative rates of the coupling reactions of "free" cyanoalkyl radicals. In the cyanohexyl system this similarity has been extended to include the fact that there is only a small and similar variation in both ratios with an increase in the reaction temperature. It is very much easier to fit these facts with the notion that all of the reactions are radical–radical reactions than by the hypothesis that RR and RR' are formed from RN_2R by cyclic, non-radical reactions which just happen to have the same activation energy as that required for the thermal decomposition.

Perhaps the most direct proof of our hypothesis comes from the experiments with bromine as a scavenger. It was found that no RR was formed by the decomposition of ABN in liquid bromine.[18] However, we now know that a substantial amount of this product is formed by decomposition of the azo compound in a dilute solution of bromine in carbon tetrachloride. Although the stoichiometry of bromine consumption is variable, as has been described, we know that iodine gives concentration-independent stoichiometry when it is present at comparable concentrations. This implies that the anomalies do not arise from incomplete scavenging of "free" cyanopropyl radicals by bromine and that RR must be one of the products of the inefficient decomposition reaction. Since this reaction disappears in liquid bromine, we know that the reaction *must* involve an intermediate which is scavengeable by reactive species which are in continual contact with the azo compound. Stepwise, radical dissociation accounts well for the facts.

The matter of required coincidences in non-radical mechanisms for decomposition was touched on above in the discussion of $(k_3/k_2 + k_3)$, $(k_3'/k_2' + k_3')$ and the small effect of temperature variations on these ratios. The coincidence is compounded by consideration of the results of the photolysis of ABN reported by Smith and Rosenberg.[19] They found that the yield of RR' from RN_2R in photolysis at room temperature was similar to the yields in thermal decomposition[16] at higher temperatures. The results were not dissected in terms of primary and secondary reactions but imply that there is no great change in the balance in either process, unless some more coincidences have arisen or the inefficient process has disappeared altogether. Still further coincidences will have to be evoked to account for the effects of styrene, which decreases the rate of formation of RR' from RN_2R and accelerates RR' decomposition, if the cage hypothesis is not accepted.

Talât-Erben and Isfendiyaroğlu[20] have recently suggested that decomposition of CPK does not involve radicals at all. Such a hypothesis is entirely untenable in view of the fact that the compound initiates oxidation and polymerization reactions.[15] Talât-Erben concluded, from a fragmentary report of evidence, that radicals in styrene are only produced by reaction of the ketenimine with styrene. It is true that the rate of initiation falls as the styrene concentration is decreased, but the rate does not approach zero and the rate of decrease is smaller with CPK than with ABN.[21] The positive evidence presented in favor of the non-radical decomposition was the *failure of the rate of formation of RR to deviate from the relationship predicted by the mechanism presented in these papers.* Deviation was expected on the basis of the fact that a small amount of disproportionation has not been taken into account. Actually the amount of disproportionation is very small[6] (∼10% in total decomposition of ABN), and detection of the expected deviation would require very precise analysis. Furthermore, the analytical method used (weight of a residue after removal of ketenimine) would be expected to include part of the disproportionation products anyway since Bickel and Waters[12] showed that non-volatile material, probably a low polymer of methacrylonitrile, is produced from disproportionation products.

Roy, *et al.*,[22] have questioned the view that the cage effect is responsible for the inefficiency of radical production in ABN decomposition. They photolyzed ABN in solutions containing varying amounts of iodine and measured the amount of iodine fixed in the products as organoiodide. Since the amount of iodine incorporated in the organic products increased monotonously with increasing iodine concentration up to 0.3 *M*, they reasoned that iodine must be capable of reacting with geminate radical pairs before they were separated by diffusion. They also extended the study of

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(19) P. Smith and A. M. Rosenberg, THIS JOURNAL, **81**, 2037 (1959).

(20) M. Talât-Erben and A. N. Isfendiyaroğlu, *Can. J. Chem.*, **37**, 1165 (1959).

(21) R. T. Keys, Doctoral Dissertation, Iowa State University, 1958.

(22) J. C. Roy, J. R. Nash, R. R. Williams and W. H Hamill, THIS JOURNAL, **78**, 519 (1956).

iodine scavenging in the thermal decomposition to experiments involving similar, high iodine concentrations and obtained efficiency factors which agreed well with those previously measured at lower iodine concentrations.[6] They reasoned that the low-efficiencies must be due to some non-radical reaction. We believe that it is more likely that some anomaly is involved in the photochemical experiments. For example, iodine may react with a long-lived excited state of the azo compound. The authors reported that quantum yields were determined using nitrogen evolution as an internal actinometer. This procedure might preclude detection of increases in the quantum yield of nitrogen with increasing iodine concentration and would eliminate the cage effect since decomposition would occur with the molecule in contact with iodine.

In summary, we conclude that diffusion control of the chemistry of geminate radical pairs, formed in the first step of thermal dissociation, provides by a wide margin the most acceptable basis for explanation of all available data.

Hot Radicals.—The suggestion already has been made many times that the first-formed products of a radical decomposition reaction may possess excess energy. This is almost certainly true of most photolyses and could be true of thermal decomposition of azo compounds. The C—N[23] and N=N[24] bond energies are 70 and 100 kcal., respectively; 225 kcal. is the heat of formation of nitrogen and 32 kcal. is the heat of activation for the decomposition of an azonitrile. This indicates that if nitrogen and the radicals are produced in their ground electronic states, they should have an excess energy of 17 kcal. plus the resonance energy of two cyanoalkyl radicals. Most of this excess will probably be vibrational, and it is conceivable that coupling recombination may occur while the radicals are still sufficiently excited to have a typical chemical reactivity. Another difference between freshly formed radicals and those which live long enough to be separated by diffusion may derive from the fact that the former may not have achieved equilibrium solvation.

If the indicated small differences between $(k_3/k_2 + k_3)$ and $(k_3'/k_2' + k_3')$ turn out to be genuine, they will have to be attributed to some sort of hot radical phenomenon. While we shall continue study of this interesting problem, we believe the present results indicate that no very dramatic effects on reactivity are likely to be attributable to special reactivity of hot radicals.

Stages of Diffusive Separation.—We have analyzed the problem as though there were only two conditions of radicals produced by decomposition, separated and unseparated. In developing the theory of diffusion controlled reactions, Noyes[25] has defined two stages of separation, one in which the radicals are still in molecular contact and a second in which they have been separated by at least one molecular diameter. It is clear that the difference between a factors (for RN_2R) and a' factors (for RR′) may be due to the fact that radicals from the azo compound are produced already separated by a nitrogen molecule. It is particularly interesting that, even without taking account of primary recombination to regenerate RR′, the values of a' are smaller than those of a in both systems.

We have not attempted to distinguish two stages of separation because we have no data bearing on the problem. In reporting the interesting kinetics of the decomposition of phenylphenylsulfonyl diimide, Rosenthal and Overberger[26] have suggested that the difference between the behavior of iodine and other radical scavengers may indicate that iodine interferes with primary recombination and that less reactive scavengers are only capable of reacting with "solvent separated" radicals. If this is the correct interpretation of their data, and alternatives were suggested, the differences between the magnitudes of primary and secondary cage effects must be even larger than we would guess from the comparison of azo compounds and ketenimines. In order to unravel the details of the stages of separation, it will be necessary to extend studies of the type reported in these papers to include much higher concentrations of scavengers than we have used heretofore.

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Experimental

Commercial Materials. **Bromine, carbon tetrachloride** and **2,6-di-*t*-butyl-*p*-cresol**, were purified as described in the previous paper.[15] **Benzene** (Fisher Chemical Co., Reagent Grade, thiophene-free) was dried with sodium and fractionated through a 4-ft. Oldershaw column. The fraction boiling at 80.2° was used. **α,α′-Azoisobutyronitrile** (Westville Laboratories, recrystallized grade) was recrystallized twice from the methanol; m.p. 101–2° dec. Purification of styrene was described previously.[15] **N,N′-Diphenyl-*p*-phenylene-diamine** (B. F. Goodrich) was recrystallized from chlorobenzene; m.p. 144–144.2°.

α,α′-Diphenylpicrylhydrazyl was prepared by the method of Goldschmidt and Renn[27] and recrystallized from benzene; m. 142.3°.

Dimethyl-N-(2-cyano-2-propyl)-ketenimine was prepared and purified as previously described.[15]

α,α′-Azoisobutyronitrile-d_{12}.—Deuterioacetone (0.046 mole), prepared by the method of Condon,[28] was added dropwise to a stirred solution of hydrazine sulfate (0.03 mole) and potassium cyanide (0.06 mole) in 20 ml. of water. After 8 hr. of stirring the product was filtered, washed with water, and dissolved in the minimum amount of 95% alcohol. Bromine water (0.37 M) was added dropwise until the bromine color persisted. The product was separated by filtration, washed with water, and dried. The yield of ABN-d_{12} was 64%. Deuterium analyses[29] gave 100 D/(D + H) = 92.2 and 92.5.

Formation of RR′ from ABN.—The infrared absorbance at 2020 cm.$^{-1}$ of RR′ solutions in carbon tetrachloride is linear with respect to concentration up to 0.1 M. The analytical procedure was essentially the same as those described in the earlier paper[17] except that the base line density technique[30] was used in the determination of absorbance. The apparent extinction coefficient of RR′ was redetermined frequently. The formation of RR′ in the absence of scavengers was followed using the sealed-ampoule technique,[17] and the reaction in the presence of scavengers was carried out by

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[23] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1959, p. 85.

[24] G. E. Coates and L. E. Sutton, *J. Chem. Soc.*, 1187 (1948); values estimated using the higher values for atomization of carbon and nitrogen.

[25] R. M. Noyes, This Journal, **77**, 2042 (1955).

[26] A. J. Rosenthal and C. G. Overberger, *ibid.*, **82**, 108 (1960).

[27] S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

[28] F. E. Condon, This Journal, **73**, 4675 (1951).

[29] Analyses by J. Nemeth, Urbana, Ill.

[30] J. J. Hugh, M. F. Bell and J. V. White, *Anal. Chem.*, **19**, 2936 (1947).

batch sampling.[17] Since the extinction coefficient for RR′ is the same in carbon tetrachloride and in benzene, it was assumed that the same value can also be used for styrene solutions.

The Yield of Tetramethylsuccinonitrile (RR) from ABN in the Presence of Scavengers. (1) **Isotope Dilution Analysis.**—ABN-d_{12} (1.71×10^{-3} mole) was added to 100 ml. of 0.038 *M* bromine in carbon tetrachloride. The solution was degassed three times at −78°, and the flask was filled with dry, oxygen-free nitrogen after each of the first two evacuations; it was finally sealed *in vacuo*. The mixture was heated at 65–74° for 44 hours (at least 7 half-lives). Bromine and solvent were removed by distillation at room temperature under reduced pressure after the addition of 0.3000 g. of tetramethylsuccinonitrile as a carrier. The carrier sample (m.p. 167–168°) was prepared independently by decomposition of unlabeled ABN. The residue from the distillation was sublimed four times yielding 0.313 g. of dinitrile, m.p. 163–165°, having $100\ \mathrm{D}/(\mathrm{D} + \mathrm{H}) = 0.16$. The labeled material was therefore diluted to 0.173 times its original concentration. Since the carrier sample contained 2.21×10^{-3} mole there was 4.608×10^{-4} mole of labeled dinitrile in the reaction mixture, indicating a 26% yield.

A carbon tetrachloride solution (25 ml.) containing 0.171×10^{-3} mole of ABN-d_{12} was heated under gentle reflux for 24 hours. A slow stream of oxygen was passed over the solution, and the solvent was entirely lost after the 24-hour period. A 0.300-g. sample of dinitrile was added and the material was recrystallized from methanol giving 180 mg. of product, m.p. 157–160°, $100\ \mathrm{D}/(\mathrm{D} + \mathrm{H}) = 11.2$; calculated yield of dinitrile in the decomposition, 18%.

(2) **Vapor Phase Chromatography.**—A solution of ABN (0.0558 *M*) in carbon tetrachloride was heated 133.5 hr. (8.2 half-lives) at 62.5°. Oxygen was bubbled slowly through the reaction mixture throughout the reaction. An aliquot from the mixture was subjected to vapor phase chromatography on a silicone column at 155°. A symmetrical peak was obtained at the retention time characteristic of RR. Comparison of the peak area with those obtained in chromatograms of solutions containing known amounts of RR indicated that the nitrile was produced in 20% yield.

Decomposition of ABN in the Presence of Bromine.—Bromine was determined spectrophotometrically using the absorption at 4300 Å. Runs at 62.5° were carried out by both the batch-sampling and sealed-ampoule techniques.[15] Solutions of bromine in carbon tetrachloride were shown to be stable under the reaction conditions. In a typical, sealed-ampoule run the carbon tetrachloride solution containing 0.0608 *M* ABN and 0.00245 *M* bromine was distributed into ampoules which were sealed *in vacuo* after five degassing cycles. The ampoules were placed in the constant temperature bath and removed at intervals, quenched by cooling, and analyzed by transferring part of the solutions to Beckman cells and reading the absorbance at 4300 Å.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAM M. RICE UNIVERSITY, HOUSTON, TEX.]

The Reactions of *p*-Phenylene-bis-diazonium Ion with Water[1]

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In water at *p*H between 2 and 4, *p*-phenylene-bis-diazonium ion (tetrazotized *p*-phenylenediamine) shows a reversible formation of a mono-*anti*-diazohydroxide and a mono-*anti*-diazotate. The mono-*syn*-diazotate is assumed to isomerize at a very rapid rate. The spectrophotometrically undetected mono-*syn*-diazohydroxide is shown to undergo a kinetically first-order reaction to give the phenol, *p*-hydroxybenzenediazonium ion, which is very probably formed by a reaction with a cyclic transition state, a true S$_{\mathrm{N}}$i reaction. The rate problem of a system of two substances interconverted reversibly, each one of which yields a third substance irreversibly as shown in the scheme below, has been integrated exactly in the form of explicit expressions of the concentration of each substance as a function of the four rate constants and time (see Scheme I). It is shown that this system fits within satisfactory precision the case of the tetrazonium salt hydrolysis.

Introduction

The reversible formation of *syn*-diazotates from diazonium salts has been a subject of recent study.[3] In the case of the diazonium ion with the powerfully electron-withdrawing *p*-nitro substituent, two additional features became apparent.[4] First was the rapid first-order reaction of the *syn*-diazotate to give the *anti*-diazotate. Second was the detection of a perceptibly slow kinetically second-order reaction between diazonium ions and hydroxide ion, presumably to give the *syn*-diazohydroxide. The fact that the extent of reaction is sufficient for rate measurement at a *p*H low enough to give a slow rate, with this substituent (which surely increases the rate constant) only means that the diazotate formation equilibrium is even more sensitive to substituents than is the rate constant. Another clearer example of this difference in sensitivity to substituents has also been found.[5] It has been observed recently that the *p*-diazonium ion group is far more powerfully electron withdrawing than is the *p*-nitro group[6]; it became of interest to study the diazonium salt with this influential substituent, especially because this diazonium salt had been reported to be the only *p*-substituted diazonium salt which gives nitrogen more rapidly than unsubstituted benzenediazonium ion.[7] We can anticipate that the *syn*–*anti*-isomerization will be even more rapid than in the case of the *p*-nitro substituted compound, that the diazotates will be formed at a much lower *p*H than with any other known compound, and that an unusual mechanism of decomposition will be involved. We may speculate that the substitution of hydroxide for nitrogen may be a bimolecular reaction[8] activated by the diazonium ion group, which promotes many other nucleophilic substitution reactions on the aromatic ring.[1]

Results

The following results were obtained by studying the absorption spectra of solutions never more than 10^{-4} *M* in tetrazonium salt. The experimental design was controlled by the failure to find a solvent in which the tetrazonium salt was soluble and

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(1) Paper VI of the series, "Reactions of Diazonium Salts with Nucleophiles," paper V, THIS JOURNAL, **82**, 862 (1960).

(2) Robert A. Welch Foundation Postdoctoral Fellow, 1957–1958.

(3) E. S. Lewis and H. Suhr, *Chem. Ber.*, **91**, 2350 (1958).

(4) E. S. Lewis and H. Suhr, THIS JOURNAL, **80**, 1367 (1958).

(5) E. S. Lewis and J. D. Saltiel, Paper presented at the Southwest Regional Meeting, American Chemical Society, Dec., 1959.

(6) E. S. Lewis and M. D. Johnson, THIS JOURNAL, **81**, 2070 (1959).

(7) C. C. Snow, *Ind. Eng. Chem.*, **24**, 1420 (1932).

(8) E. S. Lewis and W. H. Hinds, THIS JOURNAL, **74**, 304 (1952).