in part, be fortuitous, and other methods are certainly more accurate, the new method has value in that it can easily be applied to systems where other methods are difficult if not impossible to use. 2. Conversely, quantitative estimation of cage effect efficiency is possible. Even in systems in which k_R and D can be estimated only within wide limits, it is possible to decide whether or not the cage effect is an order of magnitude large enough to be important. 3. Since the Samuel–Magee model works in a comparatively simple chemical system, its extension to the more complex systems of radiation chemistry becomes

more confident. 4. The technique of varying the density at constant temperature in the vicinity of the critical region provides a method of changing the initial distribution of radicals and their diffusion coefficients. This should prove useful in characterizing radiation chemistry systems.


Cage Effects in Thermal Decomposition Reactions in Solution

By Harold P. Waits and George S. Hammond

Decomposition of an azonitrile (azo-1-cyanocyclohexane) and the related ketenimine (N-(1-cyanocyclohexyl)pentamethyleneketenimine) has been carried out in solutions containing varying amounts of reactive scavengers. In both cases 1,1'-dicyanobicyclohexyl is a principal product of geminate recombination. Decrease in the yield of this product at high scavenger concentrations is taken as a measure of the interference, by scavenger, with geminate recombination. Both the concentration level (~ 0.1 M) at which scavenging of caged pairs begins and the functional form of the dependence of the effect on scavenger concentration show significant deviation from quantitative predictions of approximate theories which emphasize the importance of secondary recombination. An alternative approximate model which emphasizes interference with primary recombination by scavengers which are nearest neighbors at the time of decomposition is developed.

A significant source of contrast between dissociative reactions in liquid solution and in the gas phase arises from the fact that in liquid media collisions occur in sets. Consequently, a pair of reactive fragments produced by either homolytic or heterolytic fission in solution may undergo *geminate recombination* while they are still close neighbors. Since the phenomenon was first discussed by Franck and Rabinowitch,[1] the theory of the "cage effect" has been discussed by a number of authors.[2-4] Emphasis in theoretical treatments has been placed on analysis of the part of the process referred to by Noyes[2b] as *secondary recombination*. Secondary recombination is the sum of all recombinations that occur as a consequence of re-encounters between pairs which have at some time been separated by one or more diffusive displacements. All treatments predict two important characteristics of the interference by scavengers with secondary re-combination: (1) the effect should become measurable at scavenger concentrations of the order of 10^{-2} M or lower; (2) the fractional decrease of the amount of secondary recombination should be a linear function of the square root of the concentration of scavenger. It is also predicted[2b] that, even after secondary recombination has been eliminated, there will be a residual cage effect attributable to *primary recombination*, i.e., recombination of pairs before they have moved from the positions that they occupy immediately after bond breaking.

Good evidence for the reality of the cage effect has been produced in the study of radical-producing decomposition reactions effected thermally, photochemically, and by high energy radiation.[3,5-10] A common method of demonstration is to show that addition of scavenger in low concentration reduces the yields of coupling products to a level that remains constant over a considerable range of larger scavenger concentrations. Although a number of the reports include quantitative treatments which seem to support[3,6,11] the theory based on extensive secondary recombination, none of the studies have involved variation of the concentration of highly reactive scavengers at high scavenger concentrations. We undertook such experiments in the hope of characterizing both primary and secondary recombination. Choice of a thermal decomposition reaction, rather than photolysis, for the study was dictated by our belief that the action of scavengers in thermolysis is less complicated. The radical sources chosen were 1,1'-azocyanocyclohexane (1) and the related ketenimine 2.
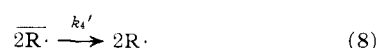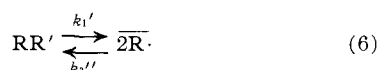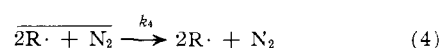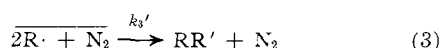

1 – RN_2R　　　　2 = RR'
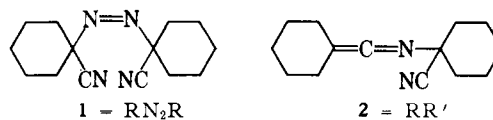
(1) T. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(2) (a) R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954); (b) *J. Am. Chem. Soc.*, **77**, 2042 (1955); (c) **78**, 5486 (1956); (d) *J. Phys. Chem.*, **65**, 763 (1961); (e) "Progress in Reaction Kinetics," G. Porter, Ed., Pergamon Press, London, 1961.

(3) J. C. Roy, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, **76**, 3274 (1954).

(4) L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).

(5) A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 3486 (1955).

(6) F. W. Lampe and R. M. Noyes, *ibid.*, **76**, 2140 (1954).

(7) (a) G. S. Hammond, *et al.*, *ibid.*, **77**, 3244 (1955); (b) **81**, 4876, 4878 (1959); (c) **82**, 5386, 5394 (1960); (d) **85**, 1501 (1963).

(8) R. K. Lyon and D. H. Levy, *ibid.*, **83**, 4290 (1961).

(9) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 543 ff.

(10) G. S. Hammond and J. R. Fox, *J. Am. Chem. Soc.*, **86**, 1918 (1964).

(11) (a) J. Jortner, *et al.*, *J. Phys. Chem.*, **65**, 1232 (1961); (b) **66**, 2039 (1962).

Results

An earlier study[7c] showed that thermal decomposition of 1 and 2 in solutions containing low concentrations of scavengers can be discussed adequately in terms of the mechanisms

$$RN_2R \xrightarrow{k_1} \overline{2R\cdot + N_2} \quad (1)$$

$$\overline{2R\cdot + N_2} \xrightarrow{k_2'} RR + N_2 \quad (2)$$

$$\overline{2R\cdot + N_2} \xrightarrow{k_3'} RR' + N_2 \quad (3)$$

$$\overline{2R\cdot + N_2} \xrightarrow{k_4} 2R\cdot + N_2 \quad (4)$$

$$R\cdot + S \xrightarrow{k_S} RS \quad (5)$$

$$RR' \underset{k_3''}{\overset{k_1'}{\rightleftharpoons}} \overline{2R\cdot} \quad (6)$$

$$\overline{2R\cdot} \xrightarrow{k_2''} RR \quad (7)$$

$$\overline{2R\cdot} \xrightarrow{k_4'} 2R\cdot \quad (8)$$
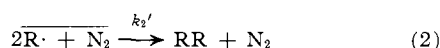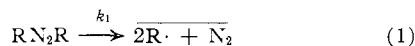
S = a scavenger
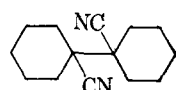
RR = 1,1'-dicyanobicyclohexyl

The notation is that used in the earlier paper although the rate constants, k_2 and k_3, of the coupling reactions of kinetically independent free radicals are not included in this paper. One other type of reaction, radical disproportionation, should be added.
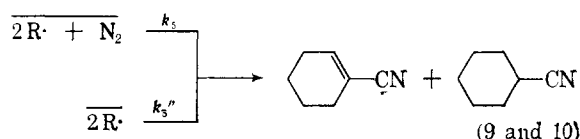
$$\overline{2R\cdot + N_2} \xrightarrow{k_5}$$
$$\overline{2R\cdot} \xrightarrow{k_5''} \longrightarrow$$

(9 and 10)

In the earlier study there was no way of distinguishing between coupling to form RR and disproportionation so the two processes were lumped together. In the present work the yields of RR were determined directly using isotope dilution analysis.

The azo compound 1 was decomposed by heating at 80° in chlorobenzene solutions containing varying amounts of iodine and bromine. The yields of RR were measured and should provide a direct measure of the

TABLE I

YIELD OF RR PRODUCED BY DECOMPOSITION OF RN_2R IN CHLOROBENZENE CONTAINING VARYING AMOUNTS OF BROMINE

$[RN_2R]_0 = 1.00 \times 10^{-5}$ mole l.$^{-1}$ at 80.0° for 8 days

$(Br_2)_0$, mole l.$^{-1}$	Yield RR, %	$(Br_2)_0$, mole l.$^{-1}$	Yield RR, %
3.30×10^{-5}	9.36	3.80×10^{-2}	9.18
6.61×10^{-5}	9.45	5.65×10^{-2}	9.18
9.91×10^{-5}	9.36, 9.45	6.61×10^{-2}	9.00
3.30×10^{-4}	9.27	8.48×10^{-2}	8.88
6.61×10^{-4}	9.18	9.91×10^{-2}	9.09
9.91×10^{-4}	9.27, 9.36	1.23×10^{-1}	9.23
3.30×10^{-3}	9.36	1.70×10^{-1}	8.80
6.61×10^{-3}	9.18	1.73×10^{-1}	8.88
8.48×10^{-3}	9.27	2.24×10^{-1}	8.45
9.91×10^{-3}	9.00	2.87×10^{-1}	7.97
1.13×10^{-2}	9.36	3.56×10^{-1}	8.11
1.70×10^{-2}	9.45	5.89×10^{-1}	7.47
1.90×10^{-2}	8.96	1.02	4.91
3.30×10^{-2}	9.00		

importance of reaction 2. Since RR' is rapidly destroyed by either bromine or iodine, the results are uncomplicated by decomposition of RR' formed in reaction 3. The results are presented in Tables I and II and are plotted in Fig. 1.

TABLE II

YIELD OF RR PRODUCED BY DECOMPOSITION OF RN_2R IN CHLOROBENZENE CONTAINING VARYING AMOUNTS OF IODINE

$[RN_2R]_0 = 1.00 \times 10^{-5}$ mole l.$^{-1}$ at 80.0° for 8 days

$(I_2)_0$, mole l.$^{-1}$	Yield RR, %	$(I_2)_0$, mole l.$^{-1}$	Yield RR, %
3.31×10^{-5}	9.20	6.63×10^{-2}	9.33
9.94×10^{-5}	9.23	9.52×10^{-2}	9.04
9.94×10^{-4}	8.58	9.94×10^{-2}	9.20
3.31×10^{-3}	9.47	2.00×10^{-1}	8.91
6.63×10^{-3}	9.09	4.17×10^{-1}	7.81
9.94×10^{-3}	9.13	5.75×10^{-1}	6.89
3.31×10^{-2}	9.23	1.03	4.36

Decomposition of RR' was studied using α,α-diphenyl-β-picrylhydrazyl (DPPH) as the scavenger. The yields of RR are reported in Table III and Fig. 1.

TABLE III

YIELD OF RR PRODUCED BY DECOMPOSITION OF RR' IN CHLOROBENZENE CONTAINING VARYING AMOUNTS OF DPPH

$[RR']_0 = 1.72 \times 10^{-5}$ mole l.$^{-1}$ at 80.0° for 14 days

$(DPPH)_0$, mole l.$^{-1}$	Yield RR, %	$(DPPH)_0$, mole l.$^{-1}$	Yield RR, %
1.67×10^{-5}	24.3	1.67×10^{-2}	28.6
3.33×10^{-5}	25.3	3.33×10^{-2}	25.7
6.67×10^{-5}	24.3	6.67×10^{-2}	26.4
1.00×10^{-4}	26.5	1.00×10^{-1}	24.8
1.67×10^{-4}	25.1	1.62×10^{-1}	23.6
3.33×10^{-4}	26.8	2.90×10^{-1}	21.7
6.67×10^{-4}	26.8	3.85×10^{-1}	20.0
1.00×10^{-3}	28.1	5.70×10^{-1}	17.4
1.67×10^{-3}	28.5	7.52×10^{-1}	15.8
3.33×10^{-3}	28.6	1.02	14.3
6.67×10^{-3}	27.3	1.24	13.2

The concentrations of RN_2R and RR' were $\sim 10^{-5}$ M in all experiments. Use of low concentrations was necessitated by the requirement that the scavengers be present in essentially constant concentrations throughout the runs. The yields of dinitrile measured at 10^{-5} M in the absence of scavengers were substantially lower than those obtained by decomposition of more concentrated solutions. Data are shown in Table IV. Since the concentrations of RN_2R and RR' were very low, the steady-state concentrations of radicals were much lower than is common in such experiments. Consequently, reactions with the solvent or with impurities are relatively likely to occur if the reactions are first order with respect to radicals. We are inclined to believe that the reaction involves attack on the solvent, chlorobenzene, since impurities were removed by careful purification including heating at 80° with RN_2R for 3 days followed by conventional purification. There is an indication that surface effects are of some consequence in determining the fate of cyanocyclohexyl radicals when they have a long lifetime since the yield of RR was decreased by packing the reaction ampoule with glass wool. In one experiment with glass wool the yield of RR was reduced to the same value as was observed in the presence of DPPH, indicating that RR was formed only by geminate recombination reactions. The yield of RR from RN_2R is larger in the presence of DPPH than in the presence of the halogens since the latter destroy ketenimine. By taking account of the

yield of RR from RN_2R in the presence of low concentrations of bromine or iodine (9.4%) and in the presence of DPPH (15.4%) and the known efficiency of formation of RR' from RN_2R by geminate recombination,[7c] one can calculate the yield of RR expected from RR' in the presence of low concentrations of DPPH. The calculated value, 28.6%, agrees well with the average experimental value, 27.0%.

TABLE IV

YIELD OF RR PRODUCED BY DECOMPOSITION OF RN_2R IN CHLOROBENZENE AT 80.0° FOR 8 DAYS

$(RN_2R)_0$, mole 1.$^{-1}$	$(DPPH)_0$, mole 1.$^{-1}$	Yield RR without glass wool, %	Yield RR with glass wool, %
1.00×10^{-5}	1.00×10^{-2}	15.7, 15.6	...
5.00×10^{-4}	1.00×10^{-2}	15.3, 14.9	...
1.00×10^{-5}	...	36.9, 35.6	21.2, 15.3
5.00×10^{-4}	...	59.0	59.4, 61.6
5.00×10^{-3}	...	64.5, 63.9	63.3
1.00×10^{-1}	...	68.2	...

Experiments to test the stability of RR under the various reaction conditions showed that the dinitrile is destroyed by heating at 80° with chlorobenzene solutions containing more than 1.0 M bromine, either with or without RN_2R. However, the dinitrile is recovered in near quantitative yield if the bromine concentration is less than 1.0 M. Although the result limits the range of significant scavenging experiments, it leaves uncomplicated the very important range of scavenger concentrations between 0.1 and 1.0 M. The loss of dinitrile in solutions containing 1.0–3.0 M bromine is somewhat surprising since the compound is not destroyed by heating in liquid bromine. However, a good deal of bromination of the solvent occurs in concentrated solutions of bromine in chlorobenzene. Hydrogen bromide produced in the reaction with solvent is probably a primary reactant or a catalyst in the destruction of RR. Data are shown in Table V. Similar experiments showed that RR is not destroyed by heating with DPPH.

TABLE V

RECOVERY OF RR AFTER HEATING IN CHLOROBENZENE CONTAINING VARYING AMOUNTS OF BROMINE

$[RR]_0 = 1.01 \times 10^{-2}$ mole 1.$^{-1}$ at 80.0° for 8 days

	Without RN_2R	With $(RN_2R)_0 = 1.00 \times 10^{-2}$ mole 1.$^{-1}$	
$(Br_2)_0$, moles 1.$^{-1}$	Recovery RR, %	$(Br_2)_0$, moles 1.$^{-1}$	Recovery RR, %
0.0787	98.3	0.0341	98.6
.450	98.6	.408	97.3
.800	99.9	.850	96.8
1.13	95.1	1.07	94.8
1.35	92.3	1.32	89.3
1.51	86.8	1.50	74.3
1.75	65.7	1.77	41.5
1.95	33.9	1.95	21.2
2.50	2.63	2.50	2.34
2.90	0.00	2.90	0.00

The reduction of the yield of RR could be accounted for if RN_2R were destroyed by direct reaction with the halogens. Consequently the rate of decomposition of the azo compound in chlorobenzene containing 0.819 M bromine was measured using isotope dilution analysis. Although the data are not as accurate as those obtained by measuring rates of nitrogen evolution, the rate constant 1.33×10^{-5} sec.$^{-1}$ is only modestly larger than the value 8.42×10^{-6} sec.$^{-1}$ in neat chlorobenzene. A
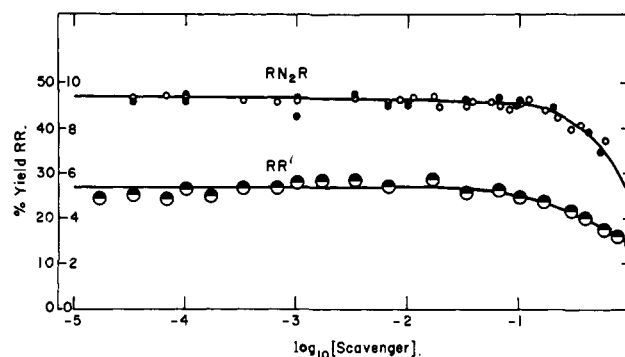

Fig. 1.—Yield of RR produced by decomposition of RN_2R and RR' at 80.0° in chlorobenzene containing varying amounts of scavengers: O, bromine, inner ordinate scale; ●, iodine, inner ordinate scale; ◐, DPPH, outer ordinate scale.

small increase can be easily attributed to a solvent effect such as has been observed many times in the decomposition of compounds such as azobisisobutyronitrile (ABN) and benzoyl peroxide. If all of the increase in rate were real and due to a direct reaction between the azo compound and bromine, the effect would be insufficient to account for the decrease in the yield of RR. The fact that iodine and bromine give essentially identical results also speaks strongly against the view that the halogens exert their effects by direct reaction with the azo compound.

Discussion

Distribution Functions for RN_2R and RR'.—The distribution functions as defined previously[7c] should be modified to take account of the disproportionation process. The following are appropriate functions for description of the fate of geminate radicals formed in the decomposition of RN_2R where a = efficiency of radical production, z' = fraction of geminate radicals that form RR', w' = fraction of geminate radicals that form RR, and x' = fraction of geminate radicals that disproportionate.

$$a = \frac{k_4}{k_2' + k_3' + k_4 + k_5'}$$

$$z = \frac{k_3'}{k_2' + k_3' + k_4 + k_5'}$$

$$w' = \frac{k_2'}{k_2' + k_3' + k_4 + k_5'}$$

$$x' = \frac{k_5'}{k_2' + k_3' + k_4 + k_5'}$$

The analogous functions, a'', z'', w'', and x'' apply to radical pairs formed in the decomposition of RR'.

The quantities a and z' have been measured directly[7c] although there was some uncertainty as to which of the two values of a was most accurate. Scavenging with iodine gave 0.67, whereas the oxidation–inhibition method gave 0.61. The value of w' determined in this study is 0.094. Choice of the value of 0.61 for a gives a value of 0.086 for x'. This would indicate that the relative rates of coupling to RR and disproportionation in the solvent cage are 1.09:1. In a run in which RN_2R was heated long enough to decompose essentially all the azo compounds, but in which 12% RR' should have remained, a yield of 68% RR was produced. This
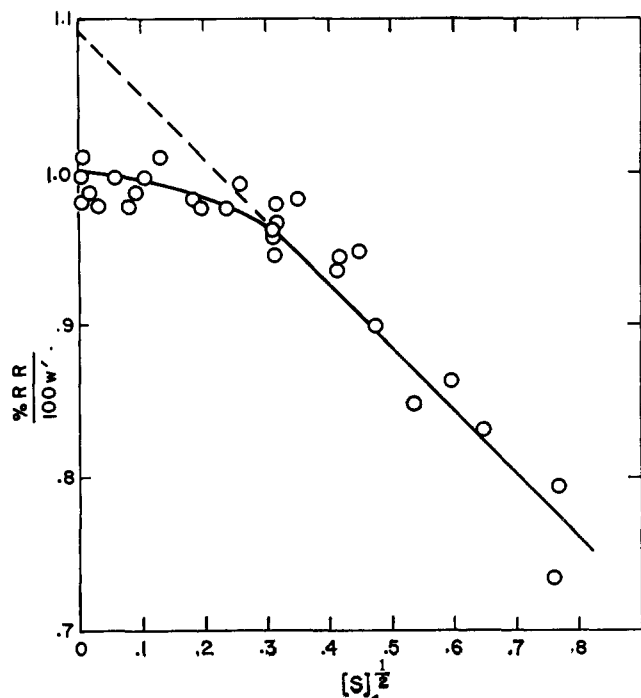
Fig. 2.—Dependence of RR yield on the square root of the scavenger concentration for RN_2R decomposition.

Fig. 3.—Dependence of RR yield on the square root of the scavenger concentration for RR' decomposition.

compares well with the value of 72% reported for complete reaction.[12] The results appear to indicate that disproportionation of geminate radicals is somewhat more important than is the case with pairs of radicals that re-encounter after having been independent. Although there is a precedent for such behavior,[7c] the present evidence, which depends upon measurement of x' as a difference between unity and the sum of the experimental values of a, w', and z', is probably insufficiently precise to be an accurate measure of the variation in reactivity between "newly born" and "old" radicals. Choice of the value of 0.67 as the efficiency factor for RN_2R does not improve the agreement. Presumed values of the distribution functions are listed in Table VI.

TABLE VI
DISTRIBUTION OF RADICAL PAIRS FROM RN_2R AND RR' AT 80° IN CHLOROBENZENE SOLUTION

Function	RN_2R	RR'
a or a''	0.61	0.27
z' or z''	.21	.38
w' or w''	.094	.17
x' or x''	.086	.18

There are insufficient data for calculation of the distribution functions for radical pairs for RR'. However, values can be calculated if we assume that the ratio z''/w'' is 2.23, the same as the value for pairs formed from RN_2R. The yield of RR from RR' in the presence of low concentrations of DPPH is related to w'' as

$$0.27 = (\% \text{ RR}/100) = w'' + w''z'' + \ldots +$$
$$w''z''^n + \ldots = w''/(1 - z'') \quad (11)$$

Similarly, the relationship between a'' and the previously reported[7c] value of a', the *apparent* efficiency of radical production from RR', is

$$0.43 = a' = a''/(1 - z'') \quad (12)$$

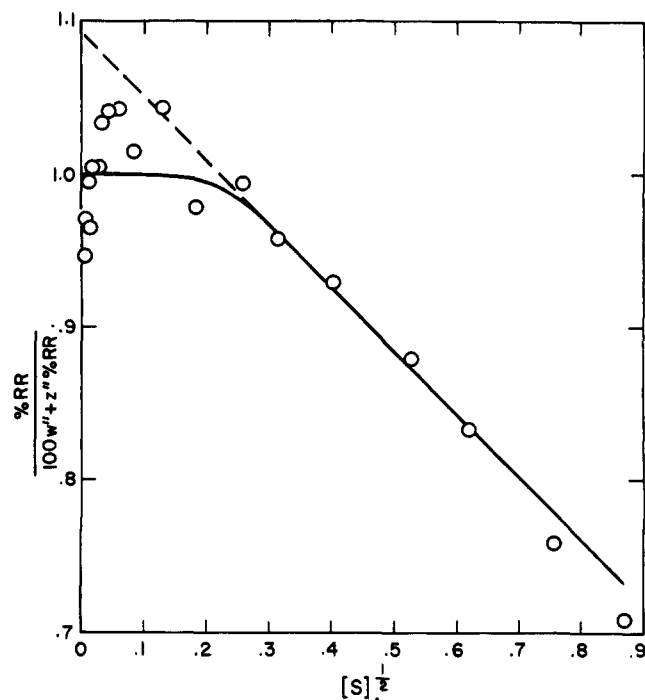(12) C. G. Overberger, *et al.*, *J. Am. Chem. Soc.*, **75**, 2078 (1953).

Use of these relationships gives the values of the distribution functions listed in Table VI. It is interesting to note that the ratio w''/x'' is close to unity, as was w'/x', although no restriction that would require this result has been introduced.

Dependence of RR Yields on Scavenger Concentrations.—The pertinent variables for use in comparison of our data with predictions based on theories of diffusion controlled kinetics are w' and w''. The probability, ϕ, that a radical pair, which would otherwise have recombined, will react with a scavenger is given by the relationships

From RN_2R

$$1 - \phi = \% \text{ RR}/100w' \quad (13)$$

From RR'

$$\frac{\% \text{ RR}}{100} = \frac{w''(1 - \phi)}{[1 - z''(1 - \phi)]}$$

$$1 - \phi = \frac{\% \text{ RR}}{100w'' + z''\% \text{ RR}} \quad (14)$$

Since the theory of secondary recombination[2-4] predicts a linear relationship between ϕ and $[S]^{1/2}$, the functions on the right-hand sides of eq. 13 and 14 were plotted against $[S]^{1/2}$. The results are shown in Fig. 2 and 3. The predicted relationship is not observed in either case. The result is not surprising since casual inspection of the data shows that concentrations of scavengers (*e.g.*, 10^{-2} M) predicted to provide significant interference with secondary recombination actually effect no measurable decrease in ϕ. As will be shown below, the scavenger concentration level is such that interference with primary recombination would be expected. If primary and secondary recombination are merged, theory developed to fit the effect of scavengers on the secondary process could not be expected to fit all the data. In terms of Noyes' discussion,[2d] one
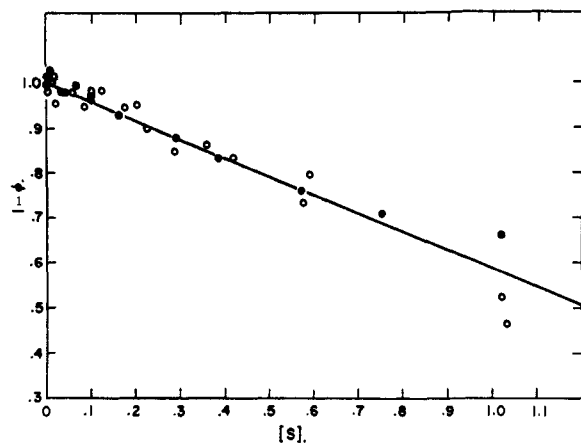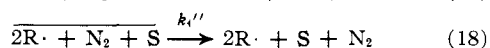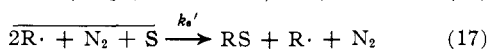
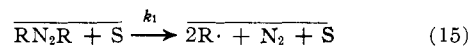Fig. 4.—Dependence of $1 - \phi$ on scavenger concentration for RN_2R and RR' decomposition: O, RN_2R; ●, RR'.

could not hope to account for the results by the use of a single, "long-time" rate constant for the scavenging reaction.

Primary Recombination.—At the very high concentrations of scavengers used in this study some interference with primary recombination seems inevitable since some decomposing molecules must have scavengers as nearest neighbors. At low concentrations of scavenger the fraction of newly formed pairs that will have scavenger molecules as nearest neighbors will be proportional to the concentration of scavenger. At some high concentration level the number will cease to be a linear function of the concentration of scavenger and a significant number of radical pairs will have more than one scavenger as nearest neighbors. Figure 4 shows a plot of $(1 - \phi)$ against scavenger concentration. Data for decomposition of RN_2R in the presence of both bromine and iodine and of RR' in the presence of DPPH are combined in a single plot. This encourages us to investigate the feasibility of developing a model based on the very simple view that geminate recombination will be prevented *only if the radical pair is born with a scavenger as a nearest neighbor.* Consider the reaction scheme

$$\overline{RN_2R + S} \xrightarrow{k_1} \overline{2R\cdot + N_2 + S} \qquad (15)$$

$$\overline{2R\cdot + N_2 + S} \xrightarrow{k_g'''} RR, RR', \text{etc.} \qquad (16)$$

$$\overline{2R\cdot + N_2 + S} \xrightarrow{k_s'} RS + R\cdot + N_2 \qquad (17)$$

$$\overline{2R\cdot + N_2 + S} \xrightarrow{k_4''} 2R\cdot + S + N_2 \qquad (18)$$

Let $k_g''' = $ sum of the rate constants for geminate destruction of radicals, $g = $ fraction of geminate radicals

$$k_g''' = k_2''' + k_3''' + k_5'''$$

which react with each other when formed beside a scavenger, $v = $ fraction of geminate radicals which

$$g = k_g'''/(k_g''' + k_s' + k_4'') = z''' + w''' + x'''$$

react with a scavenger when formed as nearest neighbor to it, and $\alpha_1 = $ fraction of total RN_2R having one

$$v = k_s'/(k_g''' + k_s' + k_4'')$$

scavenger molecule as a nearest neighbor.

At dilute scavenger concentrations ϕ is given by
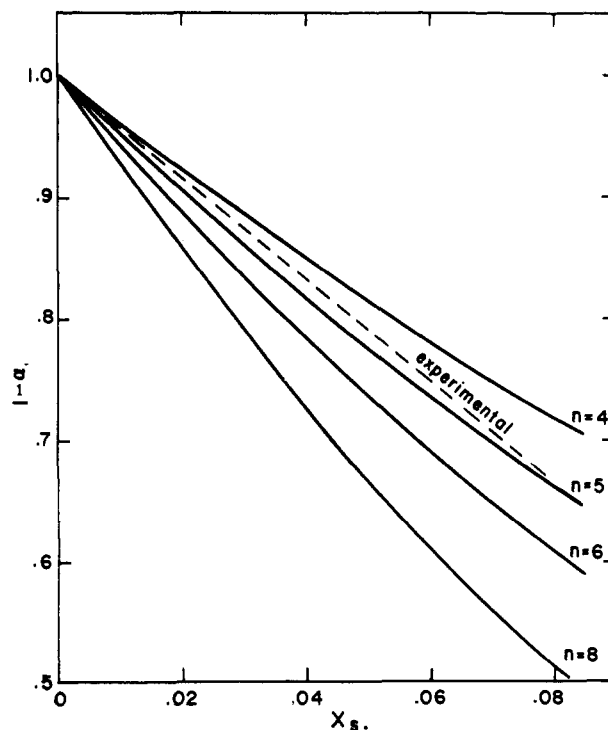
$$\phi = \alpha_1 v \qquad (19)$$

Fig. 5.—Plot of $1 - \alpha$ against x_s.

If we assume random[13] distribution of solvent and scavenger molecules about the substrate before decomposition and make no correction for differences in molar volumes, we can readily calculate α_1 as a function of the average number of nearest neighbors possessed by any substrate molecule.

$$\alpha_1 = nx_s(1 - x_s)^{n-1}$$

$$\cong \alpha \text{ (at small } x_s) \qquad (20)$$

$x_s = $ mole fraction of scavenger, $n = $ average number of nearest neighbors to substrate molecules, and $\alpha = $ fraction of total RN_2R having one or more scavenger molecules as nearest neighbors.

At high concentrations of scavenger, ϕ should be modified to take account of molecules having more than one scavenger molecule as a neighbor.

$$\alpha = \alpha_1 + \alpha_2 + \ldots \alpha_n = [1 - (1 - x_s)^n]$$

$$\alpha - \alpha_1 = [1 - (1 - x_s)^n] - nx_s(1 - x_s)^{n-1} \qquad (21)$$

Table VII shows the values of α_1 and $\alpha - \alpha_1$ calculated for representative values of x_s assuming that $n = 4, 5, 6,$ and 8. The results show that $\alpha - \alpha_1$ begins to be significant at the higher concentrations used in our study. Figure 5 shows plots of $1 - \alpha$ against x_s for four different values of n. The broken line in the figure shows the location of the values of $1 - \phi$ which were also used in Fig. 4. The theoretical lines show slight curvature which might have been buried by small experimental errors in $1 - \phi$. Otherwise the experimental data seem to give an adequate fit if n is assumed to be between 4 and 5 on the average. The fact that a good fit is obtained indicates that it is *possible* to account

(13) The assumption is that the free energies of interaction of scavenger molecules with solvent and with the radical source are equal. While such is probably not the case, both interactions are likely to be small and neglect of selective complexing is probably a reasonable first approximation.

for the effect of scavengers without recourse to any diffusive process by a reasonable, but arbitrary, choice of the number of nearest neighbors. That such a model can fit the data does not exclude the possibility that there is some recombination of radicals after diffusion (secondary recombination) and that some scavenger molecules make small diffusive excursions to capture radical pairs. Such a view could be accommodated by reducing the value of n in the above treatment, thereby leaving some of the scavenging action to be accounted for by nonnearest neighbor scavengers. While the latter part of the process might be expected to fit the half-order law, the over-all deviation from the linear relationship might be negligible.[14] In short, our results indicate that experimental separation of primary and secondary recombination is not experimentally feasible; the results are also compatible with the view that there is no significant amount of secondary recombination.

TABLE VII

x_s	n	α_1	$\alpha - \alpha_1$
0.020	4	0.075	0.002
	5	.092	.004
	6	.108	.006
	8	.139	.010
0.040	4	.142	.009
	5	.170	.015
	6	.196	.022
	8	.240	.038
0.060	4	.199	.020
	5	.234	.032
	6	.264	.046
	8	.311	.079
0.080	4	.249	.034
	5	.287	.054
	6	.316	.077
	8	.357	.130

Inherent in our results is at least one indication that some relative motion of radicals must be taken into account. The azo compound undoubtedly has the *trans* configuration, so decomposition should produce a radical pair separated by a nitrogen molecule. Since there is extensive geminate recombination, albeit less than when the radicals are produced as nearest neighbors from RR', exchange of positions between R· and N_2 must be fairly efficient in comparison with the rate of permanent separation. Whether or not this process is similar to diffusive displacements of radicals into the bulk solvent is not at all certain. If the two movements are similar in frequency and path length, all geminate recombination after decomposition of RN_2R is secondary recombination. Since the cage effect with the azo compound is larger than the amount of scavenging that we want to attribute to diffusive processes, we are inclined to believe the relative motion of R· and N_2 may be more rapid than excursions of R· into the solvent.

Comparison with Other Results.—There are a number of reports of scavenging experiments in the literature[3,11,15] which give results that appear to fit the half-order relationship between ϕ and the scavenger concentration. However, in most instances the effects of scavengers are observed at much lower concentration levels than would be predicted even by Noyes' theory. One can see why sensitivity to scavenger effects might be rather different in high energy radiation experiments since radicals are produced in clusters rather than pairs and all subsequent chemical behavior is strongly influenced by the number of radicals in a spur.[16] The same is not true of photolytic experiments in which radicals are produced in pairs. Perhaps the details of photolyses which show high sensitivity to low concentrations of scavengers should be reviewed carefully. In some cases the observed effects may be due to interaction of scavengers with undissociated excited states of the molecules undergoing photolysis. There is at least one example of apparently sharply divergent results in the thermolysis and photolysis of a single compound. Roy, Nash, Williams, and Hamill[17] studied both thermal and photochemical decomposition of ABN in the presence of iodine. They measured the extent of incorporation of iodine in the organic products as a function of the iodine concentration. In the photochemical experiments, the amount of organic iodide increased monotonously as the iodine concentration was increased from levels below 10^{-3} M; in the thermal decompositions the yield of organic iodide was not increased by an increase of the initial iodine concentration from 0.02 to 0.15 M. The authors concluded that the effects of iodine in the photochemical decomposition should be attributed to interference with secondary recombination. We believe that they failed to face adequately the real dilemma of the results which seem to imply that radicals produced photochemically in a given medium undergo recombination after numerous diffusive excursions whereas those produced in the thermal process do not. Assignment of the inefficient part of the thermal process to decomposition by way of a concerted mechanism does not resolve the dilemma presented by the apparent fact that radicals produced in thermal process do not undergo diffusive recombination. Since the results of the present study, with a closely related azonitrile, are in good agreement with the results of Roy, *et al.*, in thermal decomposition of ABN, we suggest that the "anomalies" are to be found in the details of the photochemical experiments.

We can find no serious fault with the mathematical analyses[2-4] of the problem of secondary recombination, although we have done some work with modest modifications of the methods. None change the results in such a way as to lead to the expectation that primary and secondary recombination will be separable *in view of our experimental results.*

Experimental

Chlorobenzene.—Matheson Coleman and Bell reagent grade chlorobenzene was extracted repeatedly with small portions of concentrated sulfuric acid, washed successively with water and 5% aqueous sodium bicarbonate solution, dried with calcium chloride, and, finally, distilled from phosphorus pentoxide through a Vigreux column at atmospheric pressure. The middle fraction was collected, made 0.1 M in RN_2R, and heated under a nitrogen atmosphere for 3 days at 80°. The chlorobenzene was filtered, distilled at reduced pressure, extracted repeatedly with small portions of concentrated sulfuric acid, washed successively with water and 10% aqueous potassium hydroxide solution, dried with calcium chloride, and distilled from phosphorus pentoxide

(14) Furthermore, as has been stated by Noyes,[2b,d] the half-order relationship is obtained as the result of approximating a double integral as a series expansion with retention of only the first term.

(15) (a) W. H. Hamill, *et al.*, *J. Phys. Chem.*, **60**, 823 (1956); (b) **67**, 292 (1963); (c) W. H. Hamill, *et al.*, *J. Am. Chem. Soc.*, **77**, 2953 (1955); (d) **78**, 6228 (1956); (e) **80**, 4224 (1958); (f) **82**, 5974 (1960); (g) **83**, 17 (1961).

(16) A. Kuppermann and G. G. Belford, *J. Chem. Phys.*, **36**, 1427 (1962).

(17) J. C. Roy, J. R. Nash, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, **78**, 519 (1956).

through a spinning band column at atmospheric pressure. The middle fraction was collected for experimental use.

Bromine.—Mallinckrodt analytical reagent grade bromine was used without further purification.

Iodine.—Baker and Adamson reagent grade iodine was used without further purification.

1,1-Diphenyl-2-picrylhydrazine (HDPPH).—The method of Poirier, Kahler, and Benington[18] was followed. Three recrystallizations of the crude compound from a chloroform–ethanol solution gave material melting at 172.3–173.9°, reported[18] m.p. 174–176°.

1,1-Diphenyl-2-picrylhydrazyl (DPPH).—The method of Goldschmidt and Renn[19] was followed. Two recrystallizations of the crude compound from a chloroform–ligroin solution gave material melting at 134–136°. After heating under vacuum at 100° for 8 hr., the compound melted at 134–136°, reported[20] m.p. 137°.

1,1'-Azo(cyano-C^{14})cyclohexane (RN$_2$R-C^{14}).[7c]—The method of preparation of RN$_2$R has already been described. The preparation of the radioactive azo compound consisted in adding a small amount of NaCN-C^{14} to the reaction mixture in the preparation of the hydrazine compound. RN$_2$R-C^{14} of high specific activity ($\sim$0.5 mc./mmole) was obtained by adding 8.3 mg. (1.69 mmoles) of NaCN-C^{14} (Tracerlab), specific activity = 5.9 mc./mmoles, to an initial reaction mixture containing 100 mg. (20.4 mmoles) of NaCN. The RN$_2$R-C^{14} compound was purified by column chromatography in benzene on neutral alumina (Merck reagent grade) followed by two recrystallizations from methanol; m.p. 113.5–114.5° dec., reported[21] m.p. 114–115° dec.

N-(1-Cyano-C^{14}-cyclohexyl)pentamethyleneketenimine (RR'-C^{14}).—RR'-C^{14} of high specific activity was prepared from RN$_2$R-C^{14} by the procedure of Wu, Hammond, and Wright.[7o] The crude RR'-C^{14} was purified by sublimation; m.p. 68.3–70.2°, reported m.p. 68–69°.

1,1'-Dicyanobicyclohexyl (RR).—A solution of 38 g. of RN$_2$R in 2 l. of reagent grade n-heptane was refluxed under a nitrogen atmosphere for 3 days. Half the solvent was removed by evaporation on a hot plate and the solution was allowed to cool to room temperature. The crystals were filtered, dried under vacuum at 100° for 2 days, and sublimed under vacuum at 120°; m.p. 221–222°, reported[21] m.p. 224–225°. RR-C^{14} was obtained from the kinetic runs with RN$_2$R-C^{14}.

Counting Procedure.—Radiocarbon analyses were performed with a Packard Tri-Carb liquid scintillation spectrometer, Model 314-EX, using 20 ml. potassium-free, no-vit glass liquid scintillation spectrometer vials with tinfoil-lined, toluene-resistant caps. Packard Instruments Co. scintillation grades 2,5-diphenyloxazole, PPO, and p-bis[2-(5-phenyloxazoyl)]benzene, POPOP, were used as primary and secondary scintillators, respectively. The scintillation solution consisted of 3.50 g. of PPO and 0.100 g. of POPOP dissolved in 1 l. of Baker and Adamson reagent grade toluene. A sample was prepared for counting by pipetting 20.0 ml. of scintillation solution into a vial containing a known amount of active compound.

Toluene-C^{14} was used to determine the effects of RN$_2$R, RR, and RR' on the scintillation processes; RR was the only compound which did not change the counting rate. For convenience, RR-C^{14} was used in place of toluene-C^{14} as a radiation source in the calibration vials needed to correct for the scintillation effects of RN$_2$R and RR'.

Specific activities of the very active RN$_2$R-C^{14} and RR'-C^{14} compounds were determined by measuring counting rates for 1 ml. of their dilute ($\sim$10^{-5} M) chlorobenzene solutions. Corrections were made for the scintillation effect of chlorobenzene.

All counting rates necessary for the calculation of yields were determined at the same time and were corrected for background radiation. Yields were calculated with the expression

$$\text{yield} = \left(\frac{\text{mmoles carrier}}{\text{mmoles starting material}}\right) \times$$

$$\left(\frac{\text{s.a. enriched carrier}}{\text{s.a. starting material} - \text{s.a. enriched carrier}}\right)$$

(18) R. H. Poirier, E. J. Kahler, and H. Benington, *J. Org. Chem.*, **17**, 1437 (1952).

(19) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

(20) J. A. Lyons and W. F. Waters, *J. Polymer Sci.*, **18**, 141 (1955).

(21) C. G. Overberger, *et al.*, *J. Am. Chem. Soc.*, **75**, 2078 (1953).

Degassing Procedure.—Ampoules were prepared by constricting 100 × 13 mm. or 150 × 18 mm. culture tubes. Solutions (1–5 ml.) were pipetted into the tubes which were then degassed by four freeze–pump–thaw cycles with freezing at liquid nitrogen temperatures and thawing at room temperature. The ampoules were sealed under vacuum while immersed in the cooling bath.

Isotope Dilution Procedure.—Ampoules were removed from the constant temperature bath, cleaned, and immersed in a liquid nitrogen bath. After its contents had solidified, a tube was opened by carefully removing its top. Both parts of the tube were then immediately placed in an erlenmeyer flask containing a known amount of RR, $\sim$0.2 g., dissolved in 50 ml. of benzene. In the bromine experiments, the carrier solution also contained a few drops of acetone which destroyed the scavenger. Complete mixing was achieved by swirling the flask.

The benzene solutions were added to alumina (Merck reagent grade) columns (300 × 20 mm., dry packed) which were then eluted with an additional 200 ml. of benzene. In the bromine experiments, the benzene solutions were diluted with 450 ml. of ligroin, added to alumina columns, and eluted with 500 ml. of ligroin and, finally, 200 ml. of benzene.

The benzene eluents were evaporated to a few milliliters on a steam bath and diluted with twice as many milliliters of ligroin. The crystals of RR-C^{14} were collected by filtration, dried under vacuum for at least 2 hr., and weighed into scintillation vials.

Decomposition of RN$_2$R and RR'.—Reaction solutions containing scavengers were made from prepared stock solutions of RN$_2$R-C^{14} and RR'-C^{14} in chlorobenzene. For concentrations of iodine or DPPH greater than 0.1 M, the stock chlorobenzene solutions were added to ampoules containing known amounts of these scavengers. The concentration of bromine present at levels greater than 0.1 M was determined by weighing the ampoules when they contained only stock solutions and again after addition of bromine and sealing. At smaller scavenger concentrations the reaction solutions were prepared by repeated dilutions of $\sim$0.1 M scavenger solutions.

The sealed tubes were kept in a constant temperature bath at 80.0° for a period long enough to effect at least 99.6% decomposition. Solutions containing RN$_2$R-C^{14} were heated for 8 days, whereas those containing RR'-C^{14} and DPPH required 14 days of heating.

When RN$_2$R-C^{14} was decomposed in the absence of scavenger, the carrier solution contained a few drops of bromine to destroy any undecomposed RR'-C^{14} which might otherwise have produced additional RR-C^{14} in the subsequent work-up process.

Survival of RR in the Reaction Mixtures.—Stock solutions of RR-C^{14} and RR-C^{14} plus RN$_2$R in chlorobenzene were prepared and used to make up reaction solutions containing bromine and DPPH. The preparation of ampoules and the work-up procedures were identical with those used in the decomposition experiments. Sealed tubes containing bromine were heated at 80.0° for 8 days; those containing DPPH were heated at 80.0° for 14 days. There was complete recovery of RR-C^{14} from reaction solutions containing DPPH.

In one experiment a solution of 119 mg. (0.552 mmole) of RR in 3 ml. of bromine was heated in a sealed tube at 80.0° for 8 days. The reaction mixture was diluted with 239 mg. (1.11 mmoles) of RR-C^{14} followed by removal of bromine at room temperature with an aspirator. The white residue was dissolved in 50 ml. of benzene and recrystallized twice from the same solvent. The RR-C^{14} melted at 220–221.5° and recovery was calculated to be 79.8%.

Rate of Decomposition of RN$_2$R in the Presence of Bromine.—A 1.00 × 10^{-5} M solution of RN$_2$R-C^{14} in chlorobenzene was made 0.819 M in bromine. Ampoules containing 1 ml. of this solution were degassed and heated at 80.0° in a constant temperature bath for periods of 1 to 70 hr. The carrier solutions consisted of known amounts of RN$_2$R, $\sim$0.3 g., in 25 ml. of benzene. They also contained enough acetone to destroy the scavenger. After isotopic mixing, the solutions were added to alumina (Merck reagent) columns (300 × 20 mm., dry packed) followed by elution with 200 ml. of benzene. The eluents were allowed to evaporate to dryness at room temperature. The RN$_2$R-C^{14} was recrystallized twice from methanol, dried under vacuum at room temperature for 2 hr., and weighed into scintillation vials for analysis.

A good fit to first-order kinetics was obtained and the value of k_1 was calculated to be 1.33 × 10^{-5} sec.$^{-1}$.

Formation of Bromochlorobenzenes.—Solutions of bromine in chlorobenzene and of bromine in chlorobenzene also 0.1 M in

TABLE VIII

PRODUCTION OF BROMOCHLOROBENZENES

$(RN_2R)_0$, mole l.$^{-1}$	$(Br_2)_0$, mole l.$^{-1}$	Yield, %^{a} Bromochlorobenzenes
...	1.44	10
0.100	1.35	27
...	2.66	16
0.100	2.70	40

^{a} Based on bromine.

RN_2R were heated in sealed ampoules for 8 days at 80.0°. Aliquots from the reaction mixtures were subjected to vapor phase chromatography on a silicone column at 172°. Symmetrical peaks were obtained at the retention time characteristic of p-bromochlorobenzene. Aliquots from samples of the reaction mixtures in which bromine had been destroyed with acetone showed identical peak areas. No peaks characteristic of m- and o-bromochlorobenzene were observed since their retention times under these conditions were almost identical with the retention time for the para-compound. Yields were determined by comparison of the peak areas with those obtained from chromatograms of solutions containing known amounts of p-bromochlorobenzene. The results are shown in Table VIII.

Cage Effects in Thermal and Photochemical Decomposition of an Azo Compound
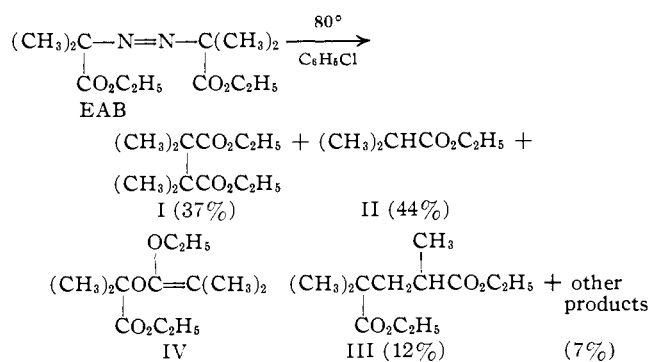
BY GEORGE S. HAMMOND AND JOHN R. FOX

Ethyl 2,2'-azobisisobutyrate has been decomposed both thermally and photochemically. In the presence of low concentrations of radical scavengers both reactions are measurably inefficient in the production of kinetically free radicals. Small differences in the efficiency factors are attributed to differences in the temperatures of the two kinds of experiments and we conclude that the fundamental processes in thermolysis and photolysis are essentially identical.

Thermal decomposition of azonitriles[1] and azoamidines[2] is measurably inefficient in the production of radicals that become available for reaction with small concentrations of scavengers and for the initiation of chain reactions such as vinyl polymerization[3] and hydrocarbon oxidation.[4] The inefficiency has usually been attributed to geminate recombination of radical pairs, although nonradical mechanisms for thermal decomposition can be formulated. Evidence against the radical mechanism of the inefficient reaction was presented by Roy, Nash, Williams, and Hamill[5] who studied iodine scavenging in both the thermal and photochemical decomposition of azobisisobutyronitrile (ABN). They found that variation of the iodine concentration up to 0.1 M did not increase the amount of iodine incorporated into organic reaction products whereas iodine incorporation in photochemical experiments increased monotonously as the iodine concentration was raised from 10^{-3} to 0.3 M. Variation in the latter case was attributed to competition by the scavenger with secondary recombination of geminate radicals; consequently they also concluded that there was no geminate recombination in the thermal reaction. We have presented evidence that in the thermal decomposition of another azonitrile, iodine scavenging, attributed to reaction with geminate radicals pairs, only becomes important at scavenger concentrations above 0.1 M[6] and it has been pointed out[1,6] that alternative explanations of the photochemical results are possible. However, further detailed comparison of the efficiencies of radical production by thermal and photochemical decomposition of the same compound seems to be of considerable interest. Since decomposition of azonitriles by either photochemical[7] or thermal reactions is complicated by intermediate formation of unstable ketenimines, we chose to make the comparison using an azo ester, ethyl 2,2'-azobisisobutyrate (EAB).

Results and Discussion

Thermal decomposition of EAB in chlorobenzene solution and in the absence of oxygen gives products as indicated in the equation. The structure of a possible isomeric coupling product (IV) is also shown.

$$(CH_3)_2C-N\!=\!N-C(CH_3)_2 \xrightarrow[C_6H_5Cl]{80°}$$
$$\underset{CO_2C_2H_5}{|} \quad \underset{CO_2C_2H_5}{|}$$
$$EAB$$

$$(CH_3)_2CCO_2C_2H_5 + (CH_3)_2CHCO_2C_2H_5 +$$
$$\underset{(CH_3)_2CCO_2C_2H_5}{|}$$
$$I\ (37\%) \qquad\qquad II\ (44\%)$$

$$\underset{(CH_3)_2COC\!=\!C(CH_3)_2}{\overset{OC_2H_5}{|}} \quad \underset{(CH_3)_2CCH_2CHCO_2C_2H_5}{\overset{CH_3}{|}} + other$$
$$\underset{CO_2C_2H_5}{|} \qquad\qquad \underset{CO_2C_2H_5}{|} \qquad products$$
$$IV \qquad\qquad III\ (12\%) \qquad (7\%)$$

The results are comparable to those reported for the corresponding methyl ester by Bickel and Waters[8] except that they reported a 4% yield of methyl methacrylate. We find that no detectable amount of ethyl methacrylate is formed. The apparent minor discrepancy is probably not real since Bickel and Waters estimated the product by catalytic hydrogenation of a solution containing all the reaction products. The 7% products of unknown structure may include some un-

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

(4) G. S. Hammond, J. N. Sen, and C. E. Boozer, ibid., **77**, 3244 (1955).

(5) J. C. Roy, J. R. Nash, R. R. Williams, and W. H. Hamill, ibid., **78**, 519 (1956).

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