CAGE EFFECTS IN THE THERMAL DECOMPOSITION OF 1,1'-AZOCYANOCYCLOHEXANE AND THE RELATED KETENIMINE

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ABSTRACT

The thermal decompositions of 1,1'-azocyanocyclohexane and the related N-(1-cyanocyclohexyl)-pentamethyleneketenimine were carried out in chlorobenzene solutions containing varying amounts of scavengers. Bromine and iodine were used to scavenge cyanocyclohexyl radicals from the decomposition of the azo compound and DPPH was similarly used in the case of the ketenimine. The stable 1,1'-dicyanobicyclohexyl is a main product in both decompositions and its formation is taken as a measure of the extent of geminate recombination. The decrease in its yield observed at high scavenger concentrations (> 0.1 M) is attributed to scavenging of caged radicals. The dependence of the decrease in yield on scavenger concentration indicates that secondary recombination is unimportant. Whereas theory predicts a dependence on the square root of the scavenger concentration, a linear relation is observed. It is concluded that interference, by scavenger, with primary recombination can occur only if the scavenger molecule is a nearest neighbor to the radical pair at the time of its formation.

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INTRODUCTION

INTRODUCTION

The concept of the cage reaction was introduced by Franck and Rabinowitch (1) in 1934 to describe the behavior of reactive radical fragments which are produced as nearest neighbors in solution. In 1945 Matheson (2) incorporated a cage reaction in his kinetic treatment of benzoyl peroxide initiated polymerizations and in 1951 Hammond (3) suggested that cage reactions might account for some of the anomalous behavior of benzoyloxy radicals. However, important evidence for the existence of the cage effect was not obtained until 1954-55 when it was generally realized that cage effects play an important role in thermal decomposition reactions (4-7). In 1960 Hammond (8,9) reported results for the thermal decomposition of two azonitriles which demonstrated that geminate radical recombination is an important path for formation of products.

The cage effect is a consequence of the large interaction between two particles in solution. Due to the slowness of diffusion in liquid systems, a pair of molecules exist as nearest neighbors for a time which is long compared to molecular vibration frequencies. Therefore, collisions between two particles in solution occur in sets, with each set corresponding to an encounter between the two particles. In addition, the probability for re-encounter between two particles which have been separated by one or two molecular diameters should be such that encounters between two particles in solution should also show a tendency to occur in sets (10,11,12). These considerations have led Noyes (13) to postulate the existence of at least three kinetically distinct radical-radical recombination processes: (1) "primary recombination" in which the fragments from a specific dissociation recombine in the cage in which they are formed; (2) "secondary recombination" in which the fragments from a specific dissociation recombine after being separated through diffusion; (3) recombination of radical fragments which escape both primary and secondary recombination with fragments from other dissociations. The recombination of original partners by primary and secondary recombination is referred to as geminate radical recombination or cage effect.

Recombination of Iodine Atoms

When molecules of iodine are dissociated photochemically in solution, the effect of geminate recombination is the reduction of the quantum yield of free iodine atoms. Any variation in size of the cage effect under different conditions of temperature, wavelength and viscosity of solvent produces an inverse variation in the quantum yield of iodine dissociation. To measure quantum yields, Noyes employed the allyl iodide scavenging technique (14) which involves measuring the additional iodine formed in the presence of oxygen and allyl iodide. Iodine atoms which escape their original partners react with allyl iodide to form iodine molecules and allyl radicals. The allyl radicals are scavenged by oxygen and ultimately yield products containing no iodine. Allyl iodide is also photochemically dissociated but it is possible to separate the contribution of free iodine atoms from allyl iodide by measuring rates of iodine formation at different concentrations of iodine and allyl iodide.

Noyes found that the quantum yield of iodine dissociation increased with increasing temperature and with light of decreasing wavelength (14,15). The latter result is consistent with the idea that the excess energy of a quantum containing more energy than necessary for bond breakage appears as kinetic energy of the separating atoms. The root-mean-square displacement distance for diffusion of iodine atoms was calculated by application of equations developed by Noyes. The results were 0.76 Å in hexane and 0.13 Å in hexachlorobutadiene (15). Noyes believes that the value for hexachlorobutadiene is too small even if diffusive displacements are opposed by no potential barrier.

The dependence of the quantum yield on viscosity was obtained with a series of hydrocarbon solvents and is represented graphically in Figure 1 (16). A six-fold increase in viscosity reduces the value from 0.66 in hexane to 0.18. At higher viscosities the quantum yield approaches a limiting value greater than zero. Noyes suggests that the limiting quantum yield is consistent with the Rabinowitch cage in which the separating atoms are pushing against only a few segments of molecules rather than against whole molecules.

Azonitriles

Aliphatic azonitriles have proved to be useful systems for the study of cage effects. These compounds are easily prepared using ketones, hydrazine and sodium cyanide as starting materials. The stabilizing effect of the cyano group on the radicals produced allows for rapid decomposition at temperatures below 100° C. Decomposition follows clean first-order kinetics with no evidence of induced decomposition and is independent of solvent. A variety of reaction rates are obtained by making suitable structural changes (17).

Thermal decomposition of azonitriles probably proceeds with simultaneous cleavage of the two carbon-nitrogen bonds and not by a process involving stepwise cleavage of these bonds. No direct evidence for simultaneous cleavage is available for azonitriles.

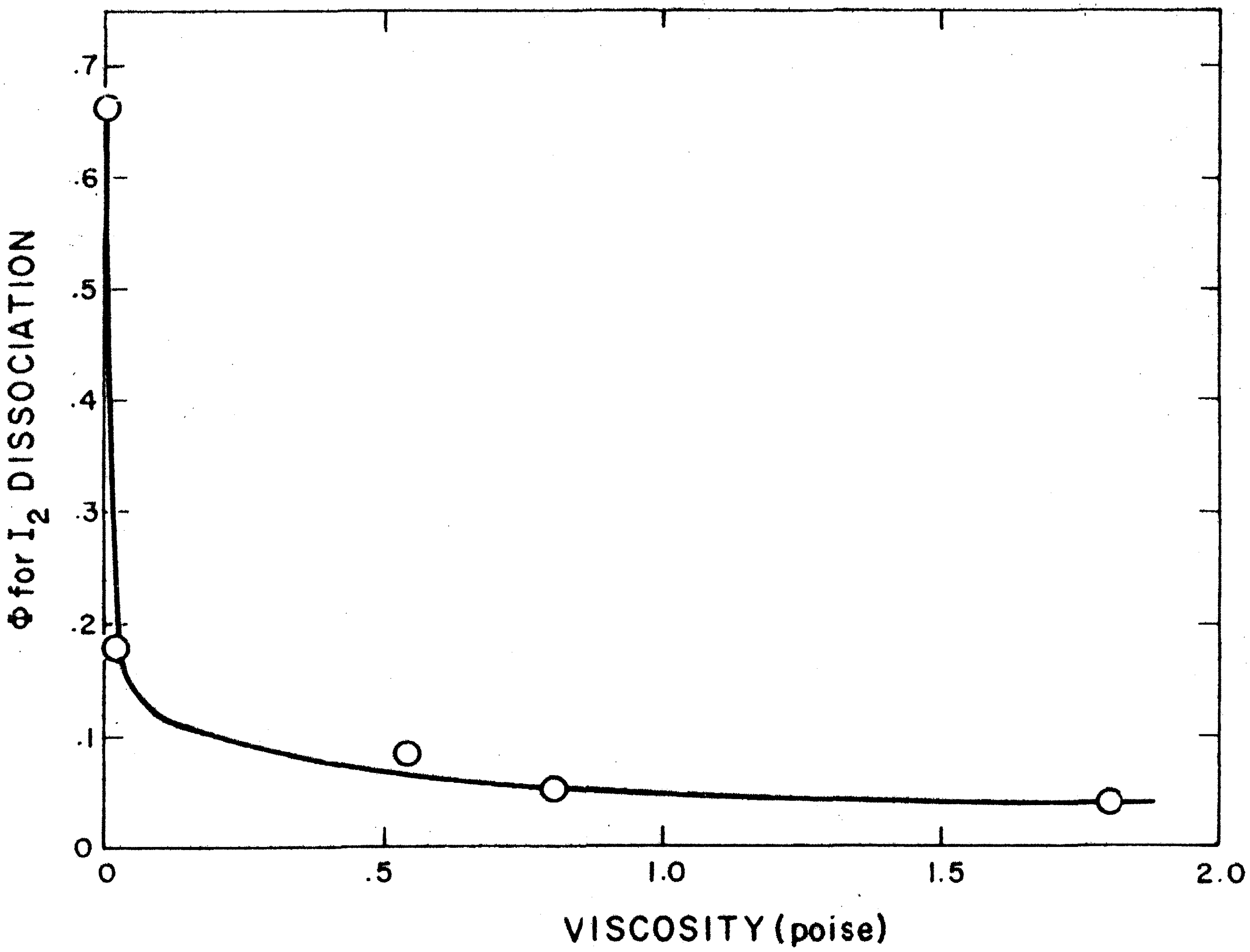
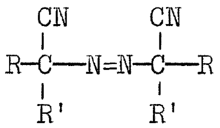


Fig. 1. Dependence of quantum yields for iodine dissociation on viscosity (16).

However, by comparing activation energies of several symmetrical and unsymmetrical azoalkanes, several authors (18-20) concluded that aliphatic azo compounds decompose with simultaneous cleavage of the two carbon-nitrogen bonds in the rate determining step. Seltzer (21,22) reached the same conclusion from his study of the secondary *α*-deuterium isotope effect in the thermal decomposition of azo-bis-*α*-phenylethane-*α*,*α*'-d_2, *α*-phenylethyl-*α*-d-azo-2-propane and *α*-phenylethylazo-2-propane-2-d. His interpretation of the observed isotope effect rested upon the comparison of its magnitude with those encountered in reactions approaching S_N1 character. Further indirect evidence for a one step process is the fact that no azo compounds are detected as products from reaction mixtures of two azonitriles (17). Also, the large heat of formation of the nitrogen molecule is probably required to account for the low activation energy (approximately 25-35 kcal/mole) of azonitrile decomposition (17).

Overberger (20,23-29) investigated the effect of structure on the reactivity of symmetrical aliphatic azonitriles of the general form



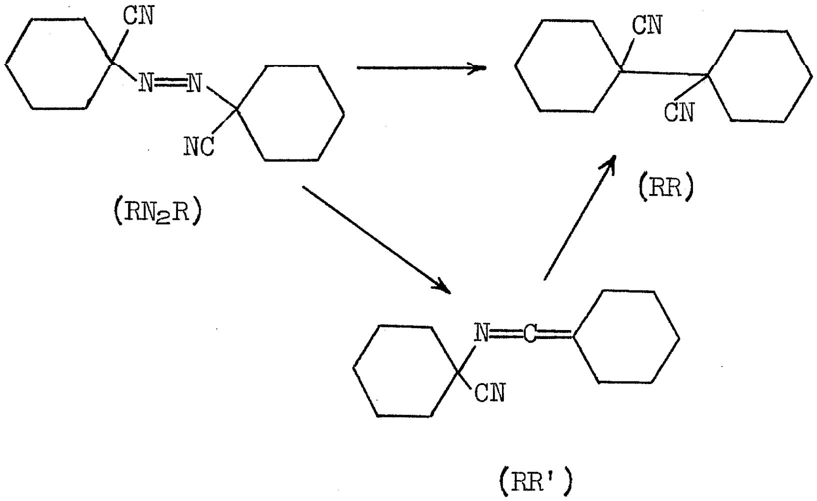
$$\mathrm{R-\underset{R'}{\overset{CN}{C}}-N=N-\underset{R'}{\overset{CN}{C}}-R}$$

He interpreted the variation in reactivity in terms of steric interactions between the alkyl groups on the same half of the azo linkage and, in some instances, between alkyl groups on different halves of the azo linkage. He found that symmetrical cycloalkylazonitriles are more stable than their open chain analogues and attributed this to ring strain which decreases resonance stabilization of the radicals (27).

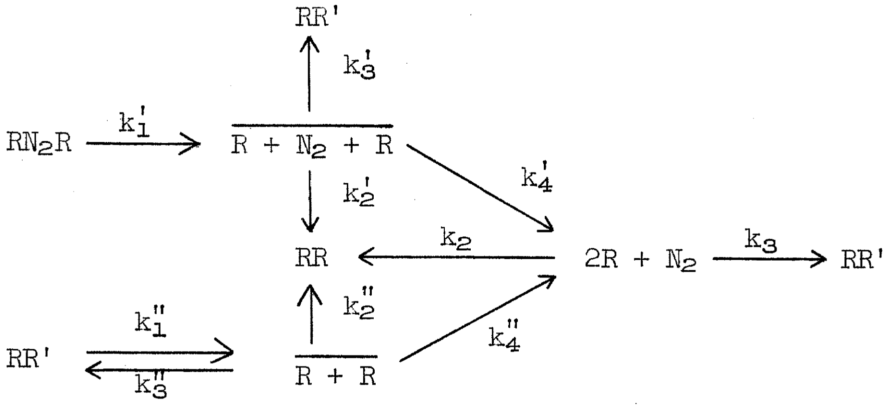
Cyanoalkyl radicals are relatively inactive species which disappear in inert solvents by reaction with other cyanoalkyl radicals. They initiate vinyl polymerization (23) and react with a large number of compounds such as mercaptans (4,30), quinones (31), iodine (32), bromine (8) and 1,1-diphenyl-2-picrylhydrazyl (4).

1,1'-Azocyanocyclohexane

The main products of 1,1'-azocyanocyclohexane (RN_2R) decomposition are the stable compound 1,1'-dicyanobicyclohexyl (RR) (23) and the intermediate N-(1-cyanocyclohexyl)-pentamethyleneketenimine (RR'). The intermediate RR' is unstable and slowly isomerizes to RR (8). Appreciable amounts of disproportionation products are formed since the yield of RR is only 72.4% under conditions where RR' would have reacted completely (27). The advantage of the cyanocyclohexyl system for kinetic studies is that RR' is an easily purified crystalline material at room temperature whose reactivity relative to RN_2R permits easy kinetic measurements (8).



Hammond, <u>et al</u>. (8), showed that the decomposition of RN$_2$R and RR' is a radical process involving two paths for the formation of products. These two paths are geminate radical (re)combination and the coupling of radicals separated from their original partners by diffusion into the bulk of the solution. The decompositions were described by the following kinetic scheme in which geminate radical pairs are indicated by placing a bar over the formulas. Disproportionation products were assumed to be stable and were counted as RR. No attempt was made to distinguish between stages of diffusive separation of geminate radicals.



Hammond distinguished between radical pairs arising from RN_2R and those arising from RR' since the effect of the nitrogen molecule is to separate, at least initially, the radicals by a molecular diameter. In addition, RN_2R and RR' may yield radical pairs which have different thermal energies at the time of their formation (8,9). Radicals which have diffused into the bulk of the solution should have achieved thermal equilibrium so no distinction was made between the "free" radicals produced from RR' and those produced from RN_2R.

Several of the kinetic results obtained by Hammond will be briefly presented. The following quantities relating to geminate radicals from RN_2R occur repeatedly in kinetic expressions and are defined here for simplicity.

a' = efficiency factor

$= k_4'/(k_2' + k_3' + k_4')$

z' = fraction of geminate radicals which form RR'

$= k_3'/(k_2' + k_3' + k_4')$

w' = fraction of geminate radicals which form RR

$= k_2'/(k_2' + k_3' + k_4')$

Analogous expressions relating to geminate radicals arising from RR' are represented by a'', z'' and w''. Only those experiments carried out at 80° C in chlorobenzene will be discussed.

The first-order rate constants for RN_2R and RR' decomposition were measured with and without added scavenger. Whereas the experimental rate constant for RN_2R corresponds to k_1' and is not appreciably affected by dilute scavenger, that for RR' is related to k_1'' by

$$k''_{exp} = k_1''(1 - z'' - a''k_3/(k_2 + k_3)) \qquad (\underline{1})$$

in the absence of scavenger and by

$$k''_{exp} = k_1''(1 - z'') \qquad (\underline{2})$$

in the presence of scavenger. The scavenger prevents formation of RR' by coupling of radicals which have escaped from their cage and was found to accelerate RR' decomposition by a factor of 1.5.

Two techniques were used to measure efficiency factors. The iodine-lifetime method (4) was applicable only to RN_2R and the value of a' was calculated with the equation

$$a' = (I_2)_0/k'_1 t_1 (RN_2R)_0 \qquad (\underline{3})$$

The oxidation-inhibition method (33) was used to measure rates of radical production from both RN_2R and RR'. However, measurements for RR' yielded a"/(1 - z") and not a". Calculations were made with the equations

$$a' = (DBPC)_0/k'_1 t_1 (RN_2R)_0 \qquad (\underline{4})$$

and

$$a''/(1 - z'') = (DBPC)_0/k''_{exp} t_1 (RR')_0 \qquad (\underline{5})$$

where DBPC is the inhibitor 2,4-di-*t*-butyl-*p*-cresol which should react with two cyanoalkylperoxy radicals (33).

The initial rate of formation of RR' from RN_2R in the presence of scavenger was zero order with respect to RR'. Therefore, z' was calculated with the expression

$$z' = (d(RR')/dt)_{t \rightarrow 0}/k'_1 (RN_2R)_0 \qquad (\underline{6})$$

Table I contains the numerical values of the quantities determined by Hammond. The values for z", w" and w' were not determined although numerous other measurements were made with and without the presence of scavenger. In all their experiments the concentration of scavenger was so low that scavenging of caged radicals was of no significance.

TABLE I

Values of Distribution Factors Determined by Hammond (8)

a' (iodine-lifetime method) = 0.67
a' (oxidation-inhibition method) = 0.61
z' = 0.21
a"/(1 - z") = 0.43

Theory of Diffusion Controlled Reactions

Samuels (34), Monchick (35) and Kupperman (36,37) have presented theories of diffusion controlled reactions for radiation chemistry where large numbers of reactive species are produced in small regions of a solution. Roy, et al. (38-46), have treated the results of numerous experiments where radical pairs are produced by thermal, photochemical and radiation-chemical processes with a modification of the theory developed by Samuels and Magee (34). Noyes (12,13,47-49) and Monchick (50) have developed theories of diffusion controlled reactions which are specifically applicable to radicals produced in pairs. The theory developed by Noyes is based on the Rabinowitch cage (1) and is mathematically more simple than that developed by Monchick.

Noyes considered the reaction of an isolated pair of molecules in a liquid of infinite volume and used probability concepts to describe the relative reactivity of the two molecules. The theory is applicable to a geminate molecular pair if the initial configuration of the system is taken as that for two molecules which have just separated from a non-reactive encounter at time zero. The fundamental parameters in the theory are

α = probability two molecules will react during an encounter

β = probability two molecules separating from a non-reactive encounter will ultimately encounter each other at least once more

β_o = probability two molecules whose centers were initially separated by a distance r_o will ultimately encounter each other at least once more

β' = probability two molecules separating from a non-reactive encounter will ultimately react with each other

β'_o = probability two molecules whose centers were initially separated by a distance r_o will ultimately react with each other

$h(t)dt$ = time dependent probability two molecules separating from a non-reactive encounter at time zero will react with each other between t and t + dt

$h_o(t)dt$ = time dependent probability two molecules whose centers were initially separated by a distance r_o at time zero will react with each other between t and t + dt

The relationships between the fundamental parameters are given by the following equations which are essentially a result of the above definitions.

$$\beta' = \int_0^\infty h(t)dt \qquad (\underline{7})$$

$$\beta_o' = \int_0^\infty h_o(t)dt \qquad (\underline{8})$$

$$\beta' = \alpha\beta/(1 - \beta + \alpha\beta) \qquad (\underline{9})$$

$$\beta_o' = \alpha\beta_o/(1 - \beta + \alpha\beta) \qquad (\underline{10})$$

The "true" rate constant for radical-radical reaction, k^o, is the product of the rate constant for encounters and the probability of reaction during an encounter. It is the value of the rate constant at the instant of formation of the radicals. The instantaneous rate constant, k_t, is related to k^o by

$$k_t = k^o(1 - \int_0^t h(t)dt) \qquad (\underline{11})$$

At long times k_t falls to a "long time" rate constant, k', where

$$k' = k^o(1 - \beta') \qquad (\underline{12})$$

If the molecular pair is assumed to be inert and to have relative displacements which are randomly directed at all molecular separations, the frequency of reencounters at time t is given by the theory of random flights (51) and takes the form $pt^{-3/2}e^{-q/t}$, where p and q are constants. Noyes assumed that h(t) obeys this form and satisfies equation (7). Then h(t) is given by

$$h(t) = at^{-3/2}e^{-\pi a^2/\beta'^2 t} \tag{13}$$

where a is a constant having dimension sec.$^{1/2}$. If the initial separation is r_o, $h_o(t)$ is given by

$$h_o(t) = at^{-3/2}e^{-\pi a^2/\beta_o'^2 t} \tag{14}$$

Noyes further assumed that at relatively long times h(t) could be approximated by

$$\begin{aligned} h(t) &= 0 & 0 < t < 4a^2/\beta'^2 \\ &= at^{-3/2} & 4a^2/\beta'^2 < t < \infty \end{aligned} \tag{15}$$

or if the initial separation is r_o

$$\begin{aligned} h_o(t) &= 0 & 0 < t < 4a^2/\beta_o'^2 \\ &= at^{-3/2} & 4a^2/\beta_o'^2 < t < \infty \end{aligned} \tag{16}$$

The probability that two molecules which are inert to recombination will have reacted with added scavenger by time t is $(1 - e^{-2k_s(S)t})$. Then the probability, ϕ, that the molecular pair, which otherwise would have recombined, reacts with scavenger is given by

$$\phi = \int_0^\infty (1 - e^{-2k_s(S)t})h(t)dt \qquad (\underline{17})$$

where k_s is the "long time" scavenging rate constant. Noyes assumed h(t) to be given by equation (<u>15</u>) and determined that

$$\phi = 2a(2\pi k_s(S))^{1/2} + 8k_s a^2(S)/\beta' + \cdots \qquad (\underline{18})$$

$$\cong 2a(2\pi k_s(S))^{1/2} \qquad (\underline{19})$$

To a first approximation, ϕ is independent of the initial separation and is a linear function of the square root of the scavenger concentration. The square root dependence on scavenger concentration was also predicted by Monchick (35) and Roy (41).

Jortner, <u>et al</u>. (52,53), investigated the photochemistry of aqueous iodide solutions and proposed the following mechanism involving two cages.

$$\begin{array}{lll}
I^- & \xrightarrow{h\nu} & \overline{I + e^-} \\
\overline{I + e^-} & \longrightarrow & I^- \\
 & \longrightarrow & I + e^- \\
 & \xrightarrow{H^+} & \overline{I + H} \\
\overline{I + H} & \longrightarrow & I^- + H^+ \\
 & \longrightarrow & I + H \\
 & \xrightarrow{H^+} & I + H^+ + H \\
 & \xrightarrow{R_2CHOH} & I + R_2\dot{C}OH + H_2
\end{array}$$

Electrons which diffuse into the bulk of the solution are oxidized by hydrogen ion. Iodine and hydrogen are formed from reactions of kinetically free iodine and hydrogen atoms.

$$\begin{array}{rcl}
2H & \longrightarrow & H_2 \\
2I & \longrightarrow & I_2 \\
I + I^- & \longrightarrow & I_2^- \\
I + I_2^- & \longrightarrow & I_3^- \\
2I_2^- & \longrightarrow & I_3^- + I^-
\end{array}$$

They derived a more general expression for ϕ by letting $h(t)$ in equation (<u>17</u>) take the form given by equation (<u>14</u>). The more general expression for ϕ approximated equation (19) for scavenger concentrations less than one molar.

They observed equivalent quantum yields of iodine and hydrogen formation in the absence of alcohol over a pH range of -1 to +6. A good fit to the square root law was obtained. Also, the same limiting quantum yields at high and low pH were observed in the presence of 1 M alcohol. However, the quantum yield of hydrogen formation had increased to its limiting value at a pH (~ 3) where the quantum yields in the absence of alcohol were unaffected by hydrogen ions. No dependence of the quantum yields on the alcohol concentration was found when it was present at levels greater than 0.2 M. These results were interpreted in terms of consecutive scavenging by H^+; the scavenging of H atoms from $\overline{I + H}$ by H^+ ions takes place in the pH region where complete scavenging of $\overline{I + e^-}$ has already occurred.

Noyes chose a microscopic model which involves randomly directed diffusive displacements and used the theory of random flights to obtain explicit functions for the fundamental parameters in terms of the microscopic parameters. The use of equations from the theory of random flights rested upon the assumption that the encounter diameter was sufficiently small compared to the root-mean-square displacement distance for relative diffusive motion. This assumption is also implicit in equations (13) and (14).

RESULTS AND DISCUSSION

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The yields of RR for the thermal decomposition of RN_2R at 80° in chlorobenzene solutions containing varying amounts of bromine or iodine were determined by isotope dilution analysis. A low initial concentration (10^{-5} M) of 1,1'-azo-(cyano-C^{14})-cyclohexane was employed so that the scavenger remained in excess throughout decomposition, even at very low scavenger concentrations. Decomposition was carried to at least 99.6% completion. Since bromine and iodine efficiently scavenge R and rapidly destroy RR' (8), the only path open for the formation of RR is by combination of geminate radicals from RN_2R.

The data are presented graphically in Figure 2 and tabulated in Table II. They show that iodine and bromine give essentially identical results. The constancy of the RR yield for scavenger concentrations lower than 0.1 M indicates that below this concentration only those R which escape geminate combination are scavenged. Table VI shows that the constancy of the RR yield is not due to reaction of R with an impurity which might preclude detection of any variation in RR yield. The fact that the yield of RR becomes dependent on scavenger concentration when the latter is present at levels greater than 0.1 M demonstratesthat scavenging of paired radicals becomes fast enough to compete with geminate combination.

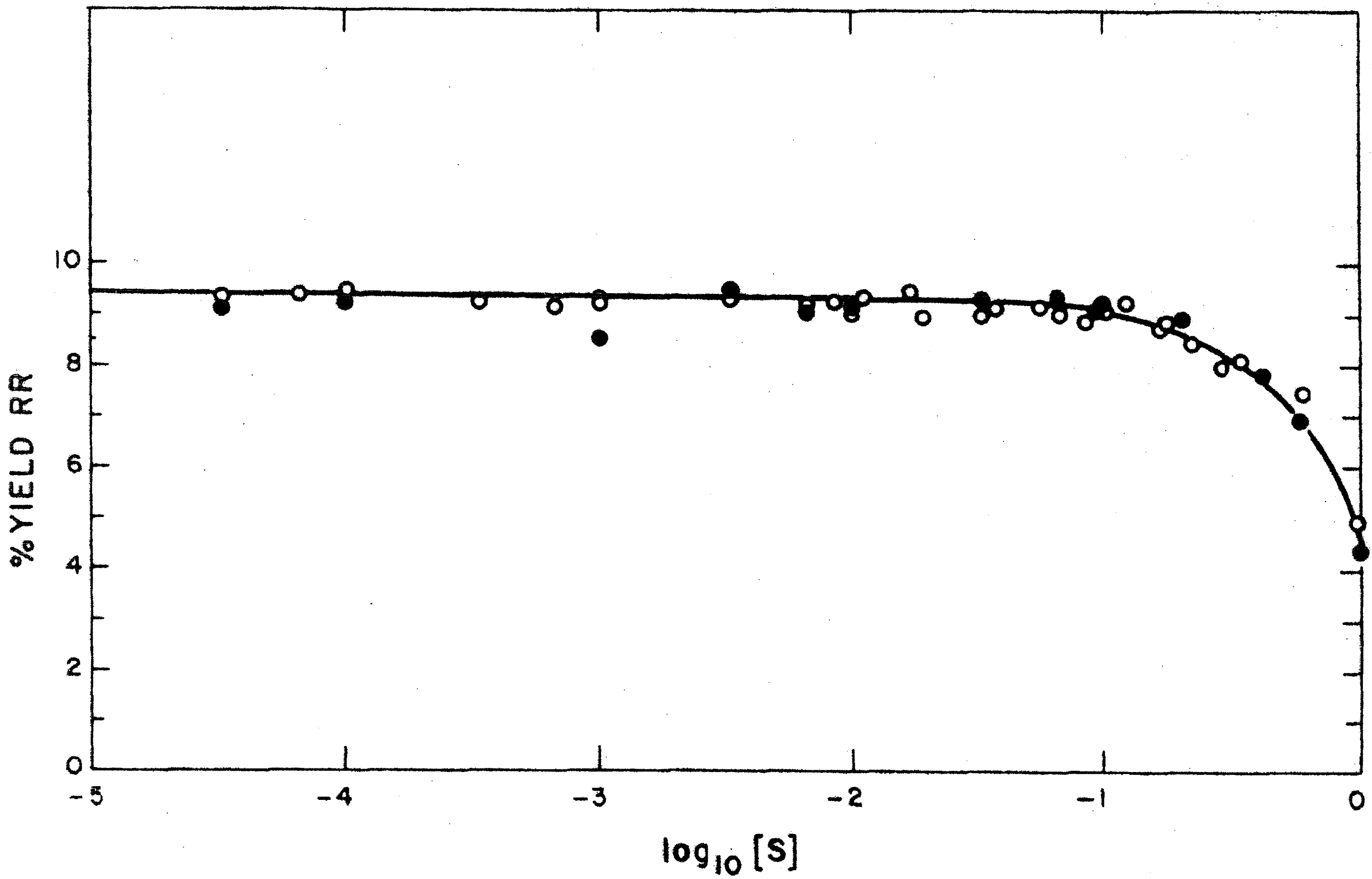

Fig. 2. Yield of RR produced by decomposition of RN_2R at 80.0° C in chlorobenzene containing varying amounts of scavenger: ○ , bromine; ● , iodine.

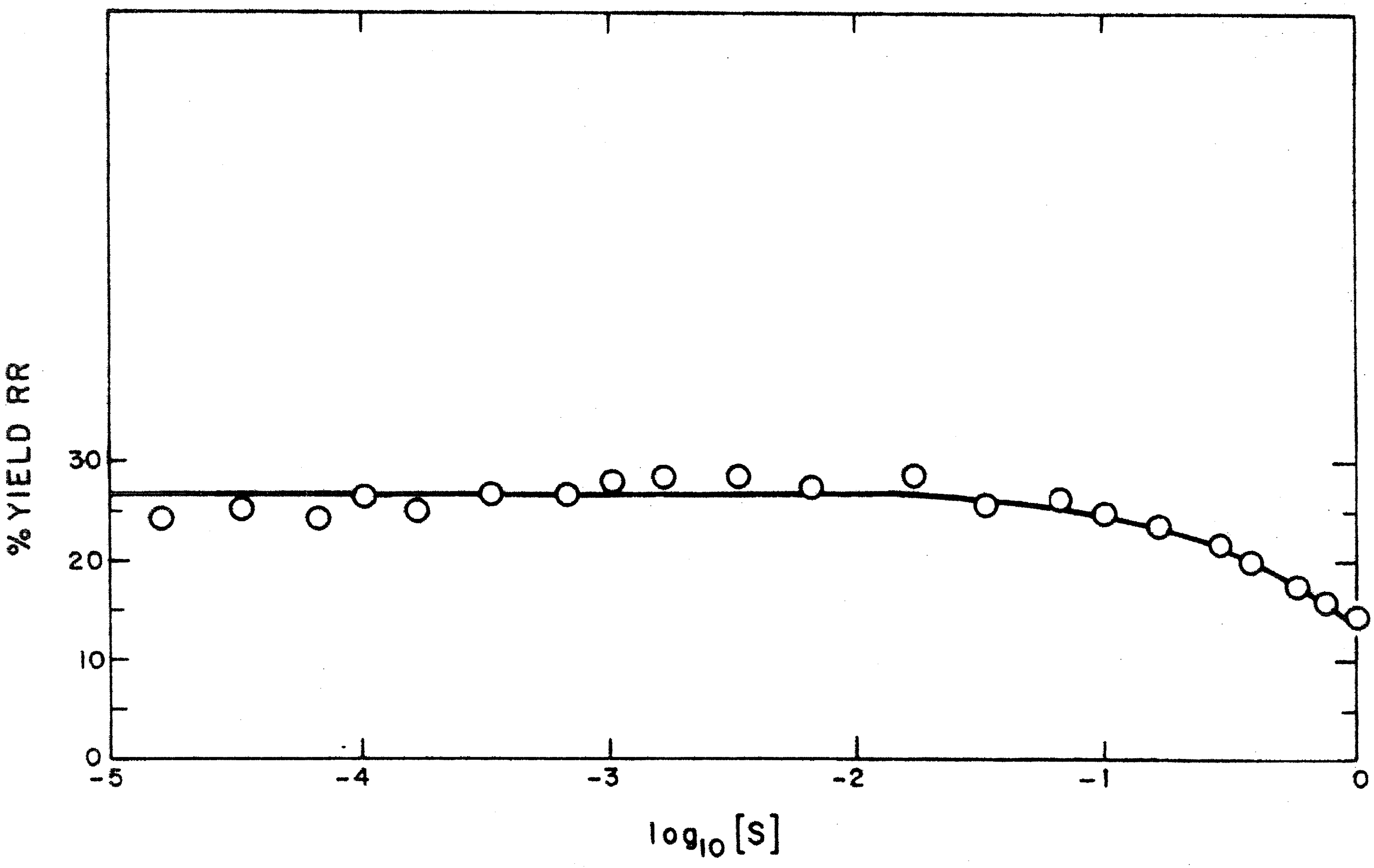

Fig. 3. Yield of RR produced by decomposition of RR' at 80.0° C in chlorobenzene containing varying amounts of DPPH.

TABLE II

Yield of RR Produced by Decomposition of RN_2R in Chlorobenzene Containing Varying Amounts of Scavenger:

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

$(Br_2)_o$ mole $l.^{-1}$	% Yield RR	$(I_2)_o$ mole $l.^{-1}$	% Yield RR
3.30×10^{-5}	9.36	3.31×10^{-5}	9.20
6.61	9.45	9.94	9.23
9.91	9.36;9.45	9.94×10^{-4}	8.58
3.30×10^{-4}	9.27	3.31×10^{-3}	9.47
6.61	9.18	6.63	9.09
9.91	9.27;9.36	9.94	9.13
3.30×10^{-3}	9.36	3.31×10^{-2}	9.23
6.61	9.18	6.63	9.33
8.48	9.27	9.52	9.04
9.91	9.00	9.94	9.20
1.13×10^{-2}	9.36	2.00×10^{-1}	8.91
1.70	9.45	4.17	7.81
1.90	8.96	5.75	6.89
3.30	9.00	1.03×10^{0}	4.36
3.80	9.18		
5.65	9.18		
6.61	9.00		
8.48	8.88		
9.91	9.09		
1.23×10^{-1}	9.23		
1.70	8.80		
1.73	8.88		
2.24	8.45		
2.87	7.97		
3.56	8.11		
5.89	7.47		
1.02×10^{0}	4.91		

TABLE III

Yield of RR Produced by Decomposition of RR' in Chlorobenzene Containing Varying Amounts of DPPH:

[RR']$_o$ = 1.72 x 10^{-5} mole l.$^{-1}$ at 80.0° C for 14 Days

(DPPH)$_o$ mole l.$^{-1}$	% Yield RR
1.67x10^{-5}	24.3
3.33	25.3
6.67	24.3
1.00x10^{-4}	26.5
1.67	25.1
3.33	26.8
6.67	26.8
1.00x10^{-3}	28.1
1.67	28.5
3.33	28.6
6.67	27.3
1.67x10^{-2}	28.6
3.33	25.7
6.67	26.4
1.00x10^{-1}	24.8
1.62	23.6
2.90	21.7
3.85	20.0
5.70	17.4
7.52	15.8
1.02x10^{0}	14.3
1.24	13.2
	24.9

It is unlikely that the observed decrease in RR yield at high scavenger concentration arises from destruction of RN_2R or RR in the reaction mixture. This conclusion is supported by the equivalent decreases in RR yield when bromine and iodine are used as scavengers (Fig. 2). The two halogens would not be expected to have equivalent reactivity in any bimolecular reactions with RN_2R or RR. Furthermore, Figure 4 shows that RR survives in the reaction mixture when the bromine concentration is less than one molar. Also, the first-order rate constant for the decomposition of RN_2R at 80° in chlorobenzene containing 0.819 <u>M</u> bromine was determined by isotope dilution analysis (Fig. 5) and calculated to be 1.33×10^{-5} sec.$^{-1}$. The value (8) in neat chlorobenzene is 8.42×10^{-6} sec.$^{-1}$ so that RN_2R decomposition is 1.58 times faster in chlorobenzene containing 0.819 <u>M</u> bromine than in pure chlorobenzene. This small rate difference is best ascribed to a solvent effect and not to reaction of RN_2R by any path other than spontaneous decomposition. Trapp and Hammond (54) found that the decomposition of azobisisobutyronitrile, ABN, in liquid bromine at 80° was no more than a factor of two faster than in other media.

That RR does not survive in chlorobenzene solutions when the bromine concentration is greater than one molar is surprising, because 80% of the RR was recovered when it was heated in liquid bromine

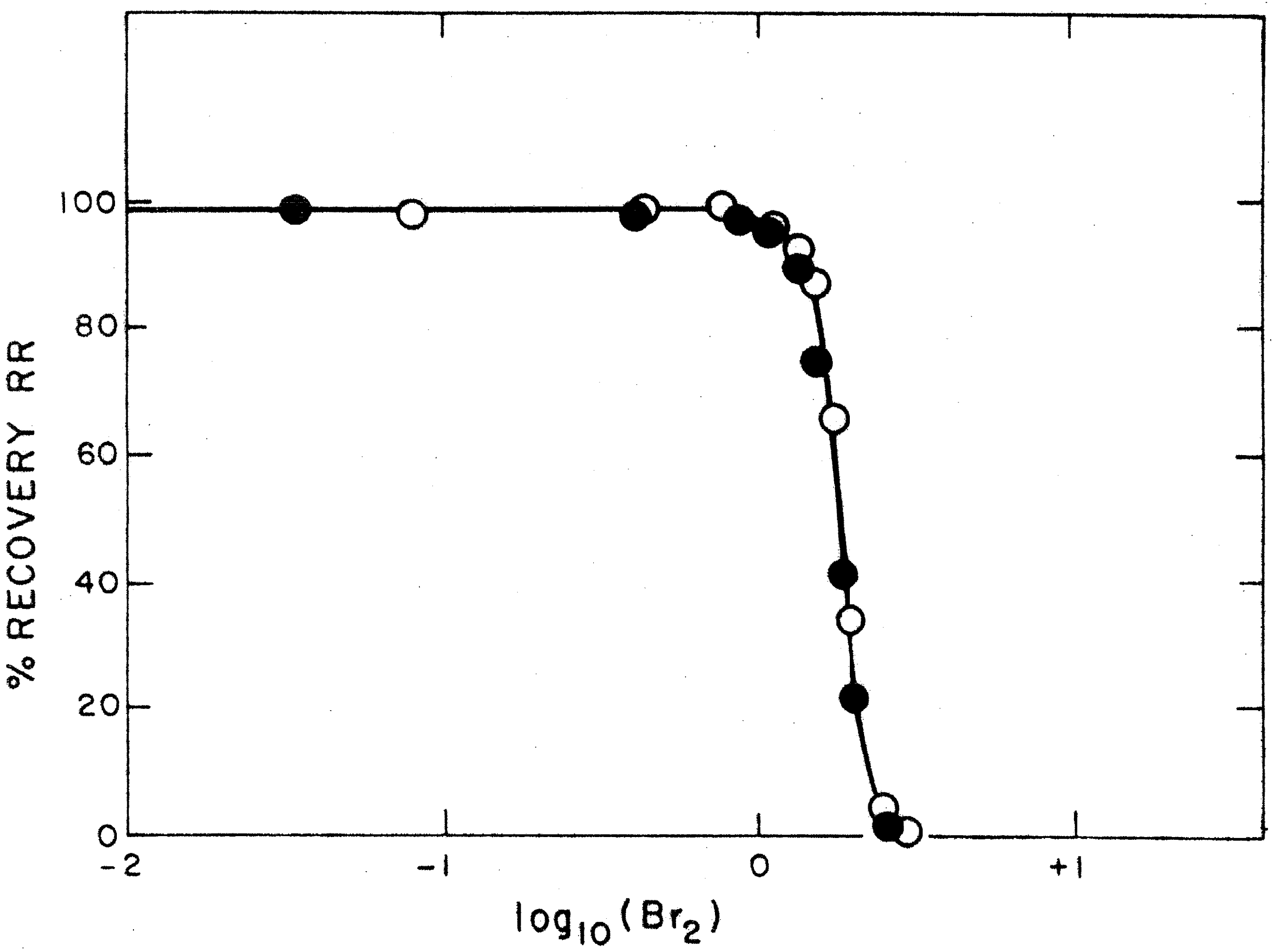

Fig. 4. Recovery of RR after heating at 80.0° C in chlorobenzene solutions containing varying amounts of bromine: ○ , RN_2R absent; ● , RN_2R present.

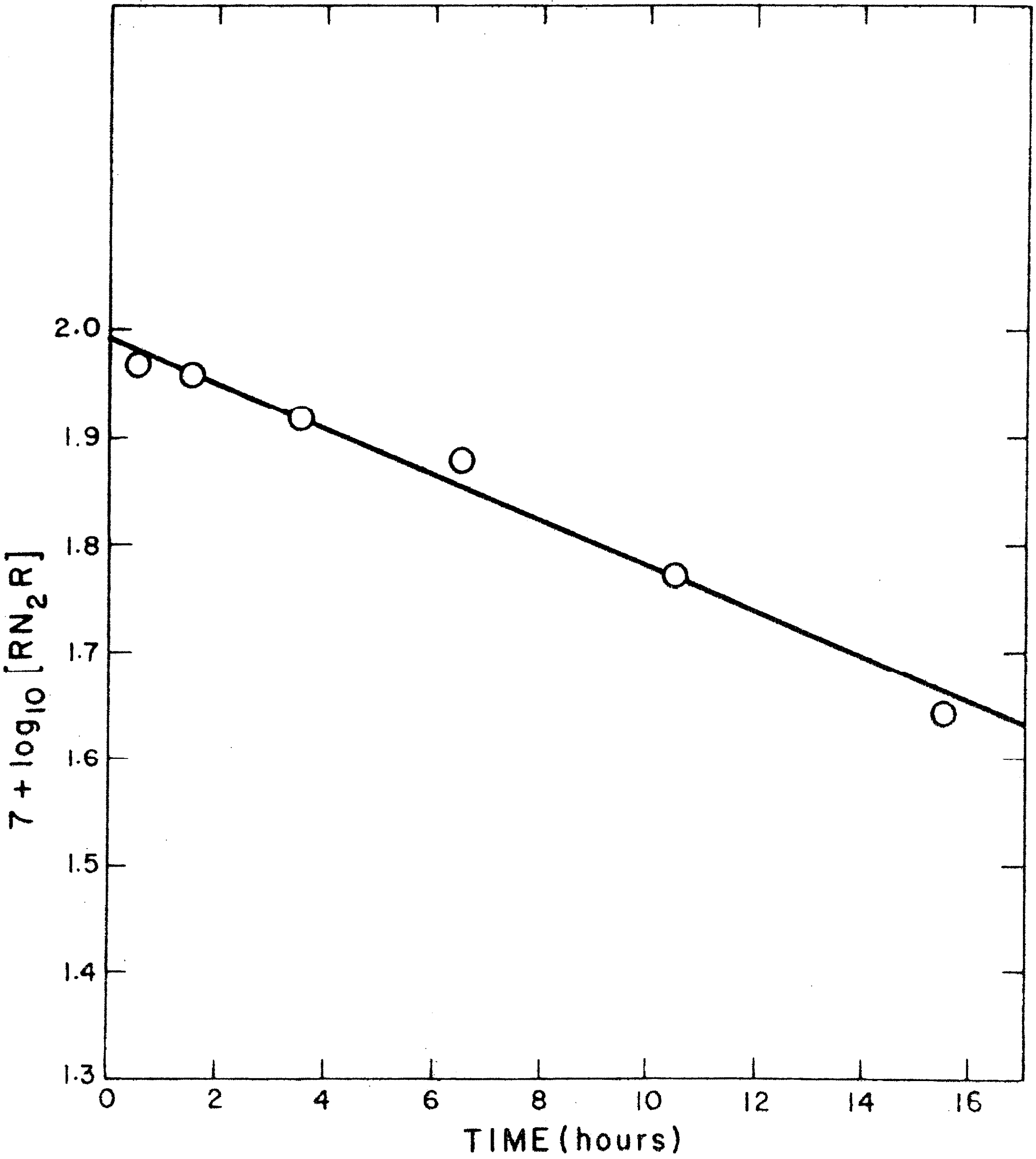

Fig. 5. Rate of decomposition of RN_2R at 80.0° C in chlorobenzene containing 0.819 M bromine.

at 80° for eight days. However, the results in Table VII indicate that both ionic and radical bromination of chlorobenzene occur at high bromine concentrations and it may be that some intermediate or by-product in the formation of p-bromochlorobenzene destroys RR. It is possible that HBr destroys RR or catalyzes its reaction with bromine.

RN_2R was also decomposed in the presence and absence of 1,1-diphenyl-2-picrylhydrazyl, DPPH, and the yields of RR determined by isotope dilution analysis. The formation of RR in solutions containing DPPH occurs by combination of geminate radicals from RN_2R and RR', since DPPH does not react with RR' (8). Table VI shows that larger yields of RR were obtained without the presence of DPPH so that at least some of the radicals which diffused from their cage coupled to form RR. In the absence of DPPH, progressively smaller RR yields were obtained with decreasing initial RN_2R concentrations. Apparently the reaction between R and some scavenger became fast enough to compete with radical-radical reactions between free R. Since the solvent was carefully purified in these experiments (the purification procedure included heating chlorobenzene solutions of 0.1 M RN_2R at 80° for three days to eliminate very small amounts of active impurities), the free R were probably scavenged by chlorobenzene. Table VI shows that surface effects played no significant role in the destruction of free R except, possibly, when the initial RN_2R concentration was 10^{-5} M.

TABLE IV

Recovery of RR after Heating in Chlorobenzene Solutions Containing Varying Amounts of Bromine at 80.0° C for 8 Days: $[RR]_o = 1.01 \times 10^{-2}$ mole $l.^{-1}$

Without RN_2R		With $(RN_2R)_o = 1.00 \times 10^{-2}$ mole $l.^{-1}$	
$(Br_2)_o$ mole $l.^{-1}$	% Recovery RR	$(Br_2)_o$ mole $l.^{-1}$	% Recovery RR
0.0787	98.3	0.0341	98.6
0.450	98.6	0.408	97.3
0.800	99.9	0.850	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

TABLE V

Rate of Decomposition of RN_2R at 80.0° C in Chlorobenzene Containing 0.819 M Bromine: $[RN_2R]_o = 1.00 \times 10^{-5}$ mole $l.^{-1}$

Time (hours)	$7 + \log_{10} [RN_2R]$
0.5	1.97
1.5	1.96
3.5	1.92
6.5	1.88
10.5	1.77
15.5	1.64

TABLE VI

Yield of RR Produced by Decomposition of RN_2R in Chlorobenzene Solutions at 80.0° C for 8 Days

$(RN_2R)_0$ mole $l.^{-1}$	$(DPPH)_0$ mole $l.^{-1}$	% 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	---

TABLE VII

Production of Bromochlorobenzenes from Chlorobenzene Solutions Heated at 80.0° C for 8 Days

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

*Based on bromine

The experiments reported in Table VI were not carried to completion. Although the reaction time of eight days was sufficient to achieve at least 99.6% conversion of RN_2R, it was not long enough for complete reaction of the intermediate RR' (the undecomposed RR' was destroyed with bromine at the end of the reaction period). The yield of undecomposed RR' would be approximately 12% if no scavenger were present in the reaction mixture. The yield of RR would, therefore, fall between 68% and 80% in the complete conversion of RN_2R at initial concentration of 10^{-1} M. The value reported in the literature is 72% (27).

Roy, et al. (41), studied the thermal decomposition of ABN at 80° in toluene solutions containing varying amounts of iodine. They found no dependence of the amount of iodide incorporated in the reaction products as organoiodides on the iodine concentration. However, since the maximum iodine concentration in their experiments was 0.151 M and since ABN and RN_2R are thought to decompose by the same mechanism (8,9), these results are in agreement with the data in Figure 2.

The yields of RR for the thermal decomposition of RR' at 80° in chlorobenzene solutions containing varying amounts of DPPH were also determined by isotope dilution analysis. A low initial concentration (1.72×10^{-5} M) of N-(1-cyano-C^{14}-cyclohexyl)-pentamethyleneketenimine was used and the decomposition was carried to at least 99.6% completion. Under these conditions the only path for RR formation is coupling of geminate radicals. Results are reported graphically in Figure 3 and tabulated in Table III. The decrease in RR yield at high DPPH concentration indicates that scavenging of paired radicals can be made fast enough to compete with geminate recombination.

The RR yield without DPPH was only 24.9% so that a significant amount of reactive impurity was present in the reaction solutions. However, the chlorobenzene used in the RR' and RN_2R experiments was purified by the same procedure so that the concentration of impurity should not have been exceptionally large.

Table VIII shows that RR survived in reaction mixtures containing DPPH. Although the exact solubility of DPPH in chlorobenzene at 80° was not determined, its saturation point was less than 1.5 M. This concentration is the highest value listed in Table VIII.

In all RN_2R and RR' experiments where scavenger is listed as present in amounts greater than 0.1 M, the units of concentration are actually moles per milliliter of solvent and not moles per milliliter of solution. However, calibration experiments with bromine showed that below one molar the two concentration values differ at room temperature by only a few per cent. A similar result would also be expected for iodine and DPPH.

1,1-Diphenyl-2-picrylhydrazine, HDPPH, gave anomalous behavior when it was used as a scavenger for RR' decomposition (Table XII). The RR yields were always lower than those obtained with DPPH and were not reproducible. Hammond (8) observed analogous scavenging behavior for HDPPH and suggested that induced decomposition of RR' occurs.

TABLE VIII

Recovery of RR after Heating in Chlorobenzene Solutions Containing Varying Amounts of DPPH at 80.0° C for 14 Days:

$[RR]_o = 5.03 \times 10^{-2}$ mole l.$^{-1}$

Without RN_2R		With $(RN_2R)_o = 5.10 \times 10^{-2}$ mole l.$^{-1}$	
$(DPPH)_o$ mole l.$^{-1}$	% Recovery RR	$(DPPH)_o$ mole l.$^{-1}$	% Recovery RR
0.0255	97.2	0.0446	95.6
0.149	96.0	0.157	93.1
0.306	97.7	0.611	94.6
0.637	98.7	1.15	96.6
1.06	97.4	1.51	96.2
1.59	98.1		

Distribution Factors for RN_2R and RR'

The distribution factors for geminate radicals as defined earlier are not exactly correct in that disproportionation products were counted as RR. Since more than 20% of the materials from decomposition of RN_2R are disproportionation products and since a significant part of this amount might be due to geminate disproportionation, the distribution factors are redefined. The following terms are for geminate radicals from RN_2R, where k_d' is the rate constant for geminate radical disproportionation:

a' = efficiency factor

$= k_4'/(k_2' + k_3' + k_4' + k_d')$

z' = fraction of geminate radicals which form RR'

$= k_3'/(k_2' + k_3' + k_4' + k_d')$

w' = fraction of geminate radicals which form RR

$= k_2'/(k_2' + k_3' + k_4' + k_d')$

x' = fraction of geminate radicals which disproportionate

$= k_d'/(k_2' + k_3' + k_4' + k_d')$

Analogous expressions relating to geminate radicals from RR' are represented by a", z", w" and x". The quantities a', z' and a"/(1 - z") as defined here have the same experimental values (Table I) as the corresponding quantities defined by Hammond (8).

A complete analysis of the distribution of geminate radicals produced by RN_2R can be made and used to determine which measurement of the efficiency factor, a', gives the more accurate value. The efficiency factor determined by the iodine-lifetime method (a' = 0.67) yields a value of 2.6% for x' whereas that determined by the oxidation-inhibition method (a' = 0.61) yields x' equal to 8.6%. It seems unlikely that only 2.6% of the disproportionation products arise from geminate radicals. Therefore, the value of a' determined by the oxidation-inhibition method is arbitrarily chosen and listed in Table IX.

TABLE IX

Distribution Factors for Geminate Radicals

Produced by RN_2R and RR'

RN_2R	RR'
a' = 0.61	a" = 0.26
z' = 0.21	z" = 0.40
w' = 0.094	w" = 0.16
x' = 0.086	x" = 0.18

The ketenimine distribution factors are calculated with the following four linear algebraic equations.

$$a'' + z'' + w'' + x'' = 1 \qquad (\underline{20})$$

$$w''/(1 - z'') = 0.27 \qquad (\underline{21})$$

$$a''/(1 - z'') = 0.43 \qquad (\underline{22})$$

$$z''/(z'' + w'' + x'') = 0.54 \qquad (\underline{23})$$

Equation (21) relates the experimental yield of RR (Fig. 3) to w'' and z''. The factor $(1 - z'')^{-1}$ arises because geminate radicals produced by RR' may recombine to regenerate RR'. The yield of RR is then given by

$$\%RR/100 = w'' + w''z'' + \cdots + w''(z'')^n + \cdots \qquad (\underline{24})$$
$$= w''/(1 - z'')$$

Similarly, the $(1 - z'')^{-1}$ factor occurs in equation (22). Enough independent experiments have not been carried out with RR' so that some assumption about the relative reaction rates of geminate radicals from RR' is necessary. The least restrictive assumption is that the geminate reactivity ratio, equation (23), is identical to that found for RN_2R decomposition. It is not necessarily accurate but it should give a good estimate of a''. The very high value of a' relative to a'' is not surprising since the radicals produced from the azo compound are separated initially by a nitrogen molecule.

The yield of RR produced by decomposition of RN_2R in the presence of DPPH is 15.4% (average of four values listed in Table VI) and is given by

$$.154 = w' + z'w'' + z'w''z'' + \cdots + z'w''(z'')^n + \cdots \qquad (\underline{25})$$
$$= w' + z'w''/(1 - z'')$$

Equation (25) can be rearranged to give the yield of RR produced by decomposition of RR' in the presence of DPPH. Equation (26) then relates four quantities which were determined by independent experiments.

$$\%RR/100 = w''/(1 - z'') = (.154 - w')/z' \qquad (\underline{26})$$
$$= (.154 - .094)/.21$$
$$= .286$$

The results accord very well since the experimental value of %RR is 27.0% (Fig. 3).

Dependence of RR Yield on Scavenger Concentration

The data for decomposition of RN_2R and RR' at 80° in chlorobenzene demonstrate that reactions of scavenger (bromine, iodine and DPPH) with geminate cyanocyclohexyl radicals occur at scavenger concentrations above 0.1 M. The efficiency of scavenging of paired radicals is predicted by three independent theories (13,35,41) to vary with the square root of the scavenger concentration. The theory developed by Noyes (13) predicts a linear relationship, equation (19), between ϕ and the square root of the scavenger concentration. The variable ϕ can be related to the RR yields for RN_2R and RR' decomposition. The expression for the azo compound is

$$\%RR/100 = w'(1 - \phi) \qquad (\underline{27})$$

and that for the ketenimine is

$$\begin{aligned}\%RR/100 &= w''(1 - \phi) + z''(1 - \phi)w''(1 - \phi) + \cdots \\ &\cdots + w''(z'')^n(1 - \phi)^{n+1} + \cdots \\ &= w''(1 - \phi)/(1 - z''(1 - \phi)) \qquad (\underline{28})\end{aligned}$$

Equation (<u>28</u>) rearranges to

$$\%RR/(100w'' + \%RRz'') = (1 - \phi) \qquad (\underline{29})$$

Therefore, the theories predict that

$$\%RR/100w' = 1 - m(S)^{1/2} \qquad (\underline{30})$$

for RN_2R and

$$\%RR/(100w'' + \%RRz'') = 1 - m'(S)^{1/2} \qquad (\underline{31})$$

for RR', where m and m' are constants.

The functions given by equations (<u>30</u>) and (<u>31</u>) are plotted in Figures 6 and 7. It is clear that these plots do not define a straight line <u>with an intercept of one</u> and, consequently, that the square root law is not obeyed by either system. Also, Figures 8 and 9 show that ϕ is a linear function of the <u>first power</u> of the scavenger concentration.

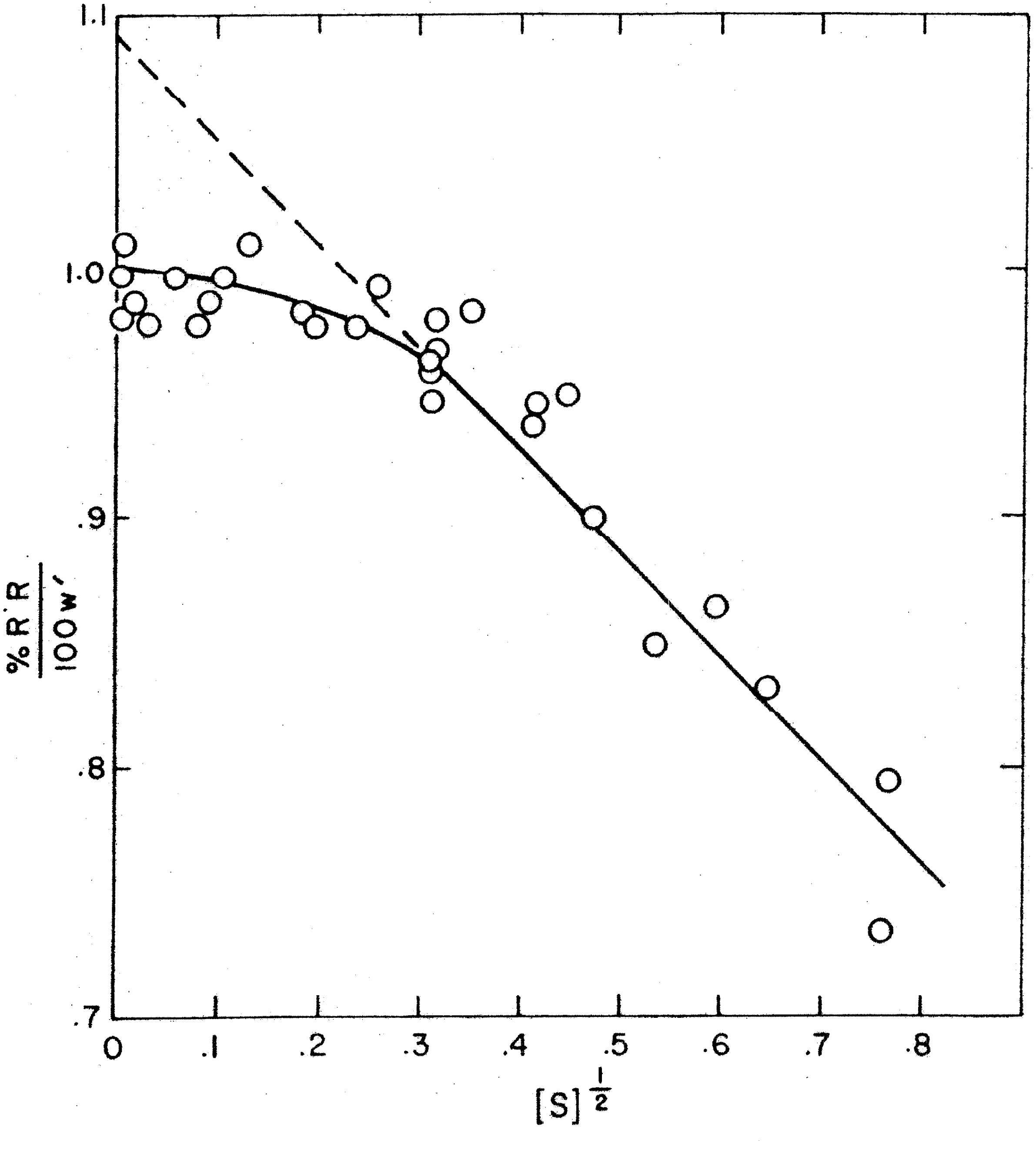

Fig. 6. Dependence of RR yield on the square root of the scavenger concentration for RN_2R decomposition.

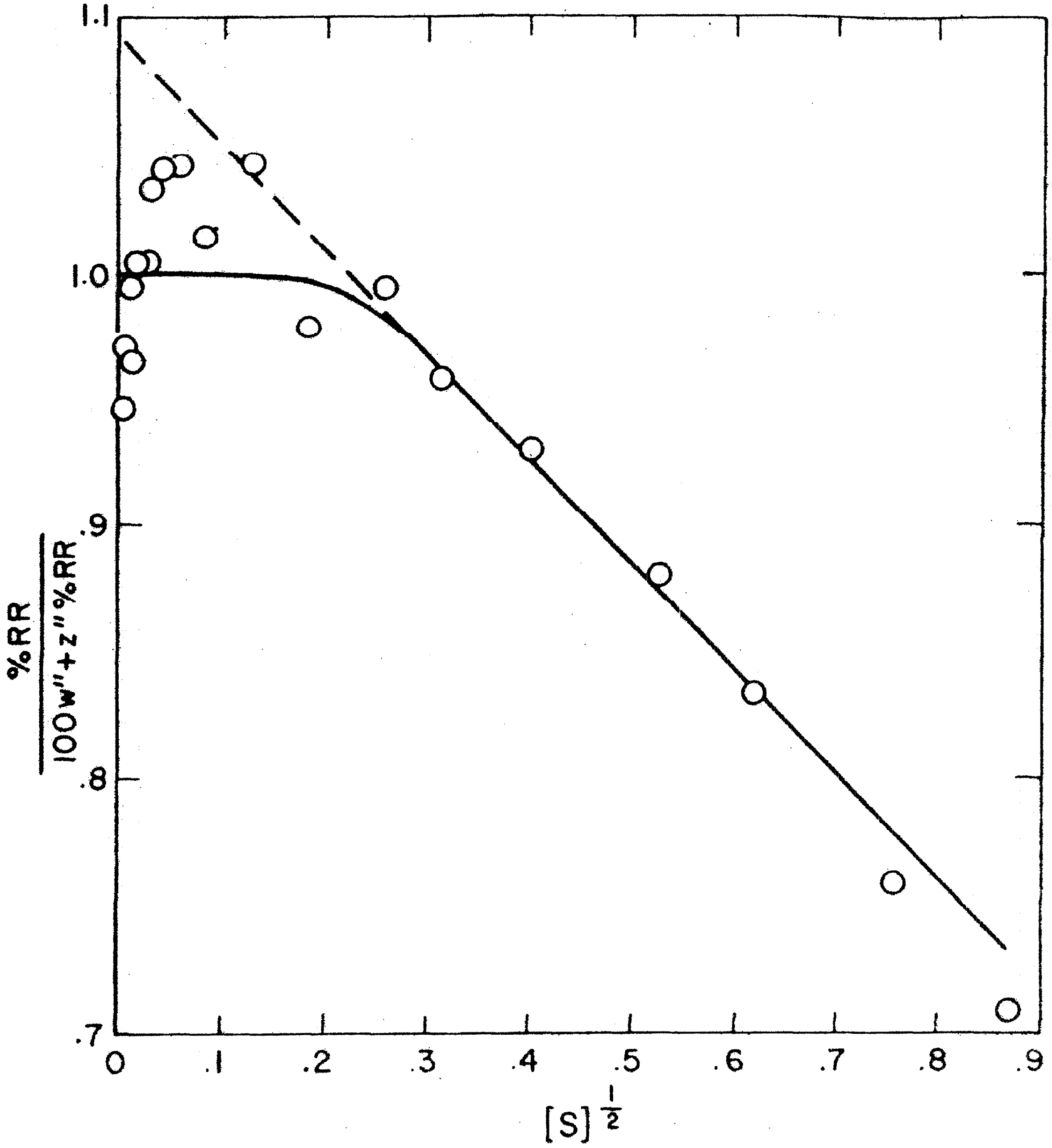

Fig. 7. Dependence of RR yield on the square root of the scavenger concentration for RR' decomposition.

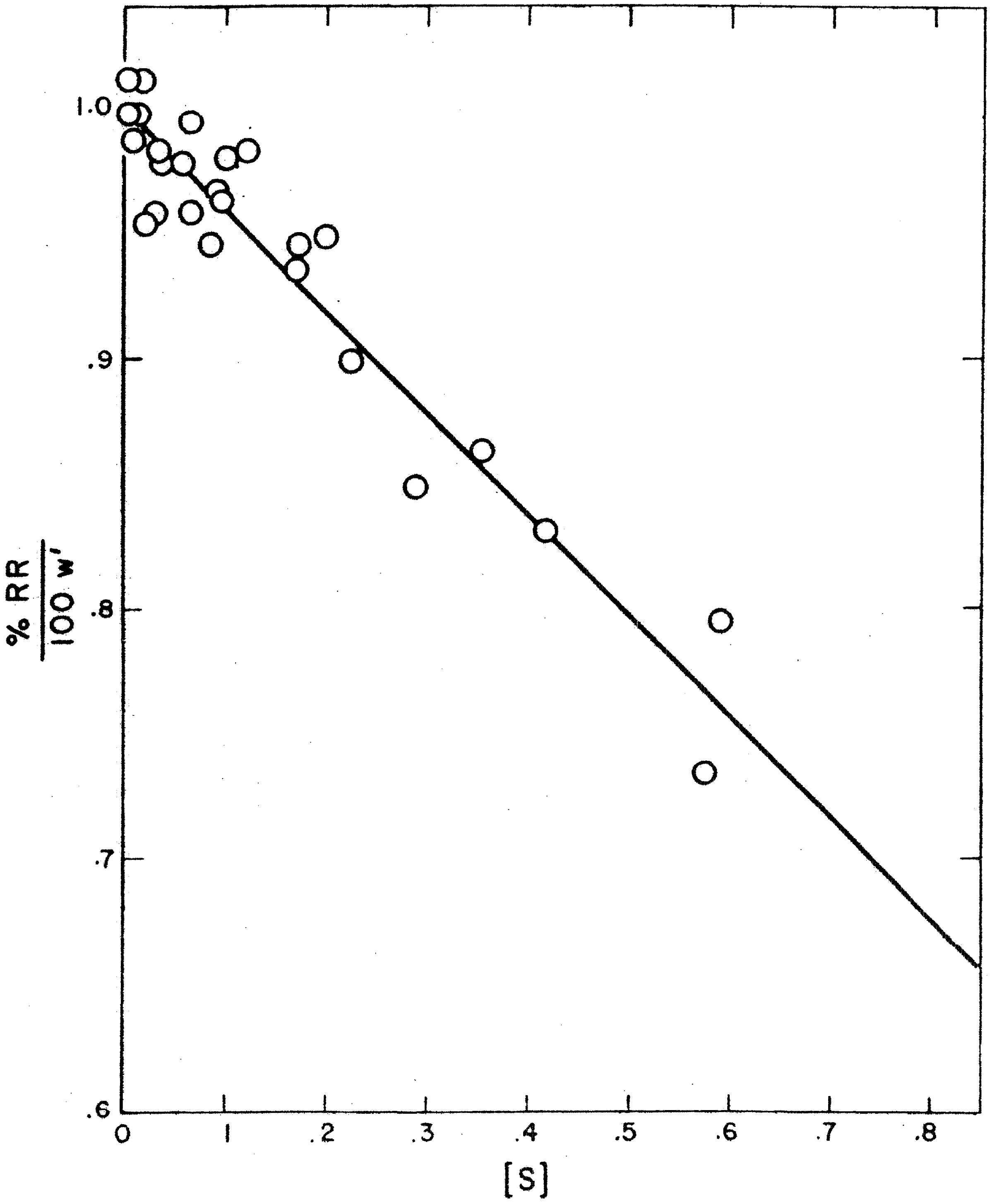

Fig. 8. Dependence of RR yield on the first power of the scavenger concentration for RN_2R decomposition.

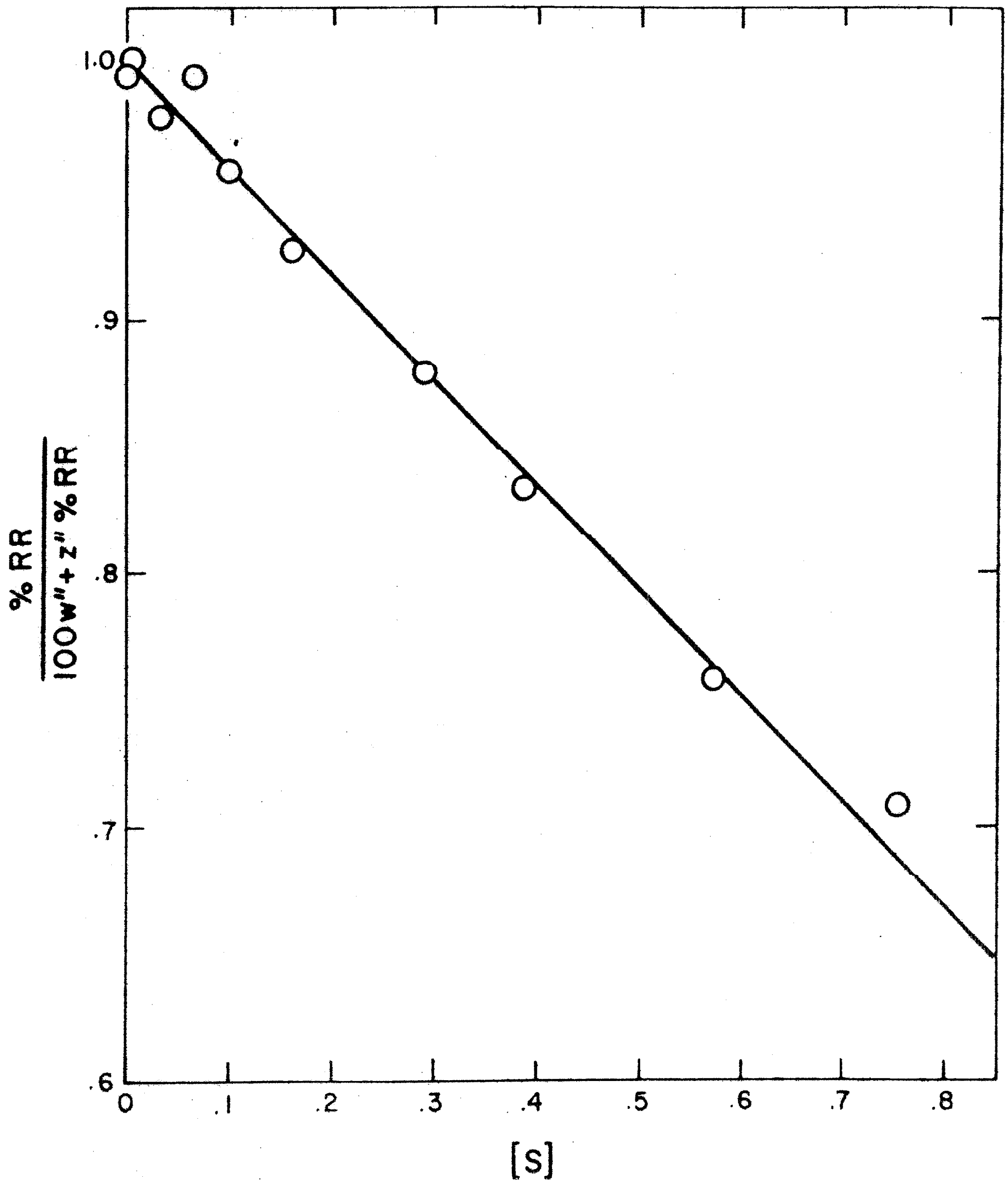

Fig. 9. Dependence of RR yield on the first power of the scavenger concentration for RR' decomposition.

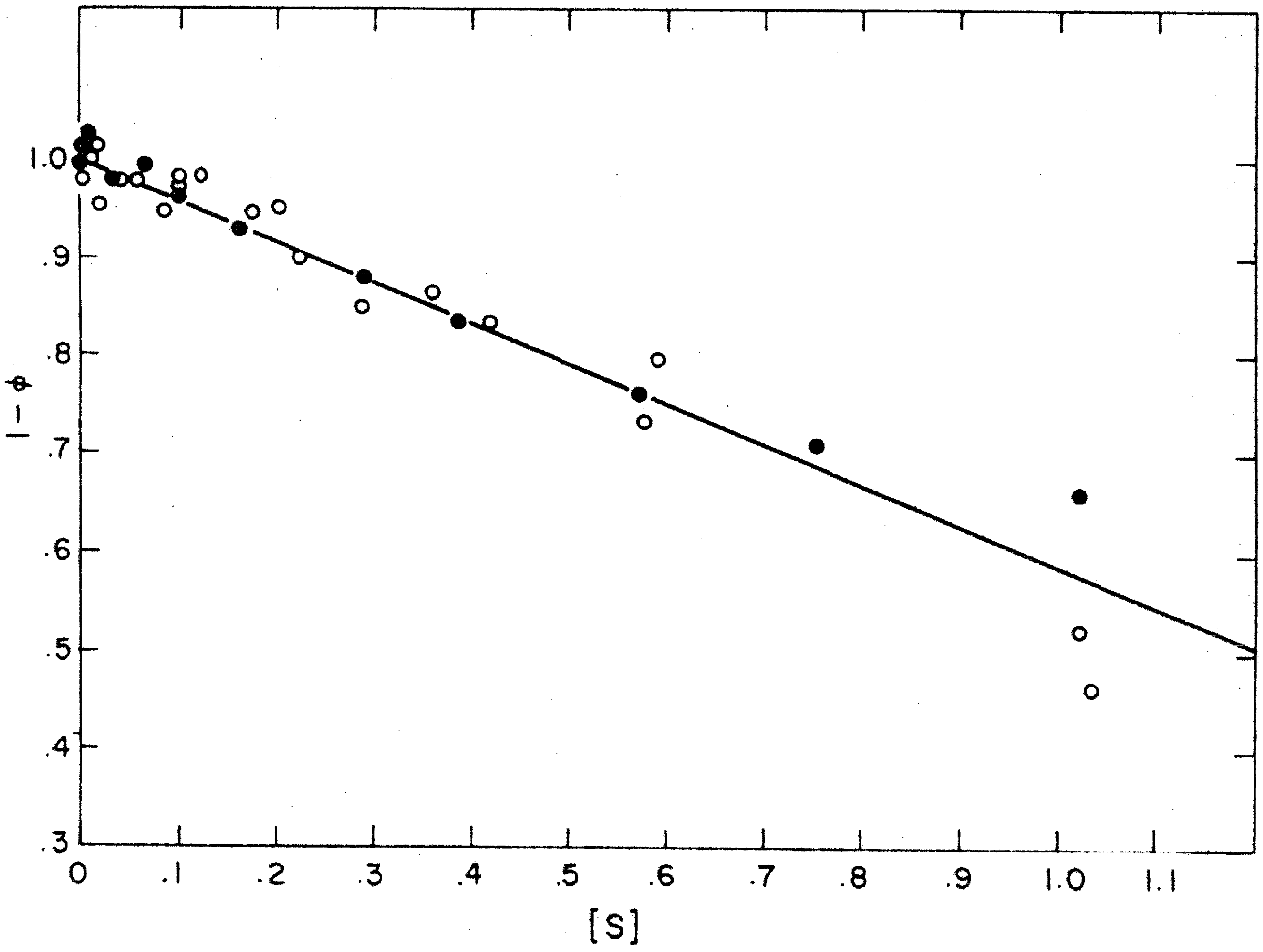

Fig. 10. Dependence of 1-ϕ on scavenger concentration for RN_2R and RR' decomposition: ○ , RN_2R; ● , RR'.

Although these results might be considered to indicate that the rates of the reactions of the scavengers with the radicals are less than diffusion controlled, this does not appear to be the case because iodine and bromine give essentially identical results. Also, Figure 10 shows that within the precision of the determination of the yields of RR and within the accuracy of the estimation of w" and z", bromine, iodine and DPPH scavenge the radicals at almost equivalent rates. It would appear, therefore, that the theoretical treatments of diffusion controlled reactions of radicals produced in pairs are in error.

A basic assumption inherent in the theory developed by Noyes and, presumably, inherent as well in the other two theories is that the encounter diameter for radicals be sufficiently small compared to the displacement distance for relative diffusive motion. This is the condition that real molecules of finite size behave as point particles or that their diffusive motion be truly random in three dimensions. The mathematical treatments employed do not account for any influence of molecular size or geometry on the relative motion of two particles at close proximity.

Another assumption made by Noyes is that the probability at time t of reaction between a particular molecular pair is equivalent to that calculated for a pair of inert molecules. However, for a real system the probability of reaction at time t is dependent on the event that the specific molecular pair has not reacted by time t. Therefore, the probability used by Noyes for reaction at time t should be multiplied by the time dependent probability that the two molecules have not already reacted with each other. The theory can be extended to describe the reactions of real molecules by introducing the variable $\tau(t)$ to represent the probability that the molecular pair has not reacted by time t. The following treatment is similar to that of Noyes (12,13,47-49) and requires the definitions of the following quantities:

α = probability that two molecules will react with each other during an encounter

$h_o(t)$ = time dependent rate constant for encounters in the absence of scavenger between two inert molecules whose centers were initially separated by r_c

$\tau(t)$ = time dependent probability that in the absence of scavenger the two molecules have not reacted with each other by time t

$\delta(t)$ = time dependent probability that two inert molecules have not "reacted" with scavenger by time t

$\theta(t)$ = time dependent probability that the two molecules have not reacted with each other or with scavenger by time t.

It is assumed that α is time independent.

When a molecular pair is formed at time zero in the absence of scavenger, the time rate of change of $\tau(t)$ is given by

$$-d\tau(t)/dt = \alpha h_o(t)\tau(t) \qquad (32)$$

so that

$$\tau(t) = \exp-\int_0^t \alpha h_o(t)dt \qquad (33)$$

In the presence of scavenger the time rate of change of $\delta(t)$ is given by

$$-d\delta(t)/dt = 2k_s(S)\delta(t) \qquad (34)$$

and

$$\delta(t) = \exp-2k_s(S)t \qquad (35)$$

where k_s, the rate constant for scavenging, is assumed to be time independent. The variable $\theta(t)$ describes the situation encountered in real systems. Its time rate of change is

$$-d\theta(t)/dt = \alpha h_o(t)\theta(t) + 2k_s(S)\theta(t) \qquad (36)$$

It follows that

$$\theta(t) = \tau(t)\delta(t) \qquad (37)$$

The last expression states that the probability that a molecular pair has not reacted by time t is the product of the probability that the two molecules have not combined by time t and the probability that they have not reacted with scavenger by time t. Integration of equation (36) over all times gives

$$-\int_1^0 d\theta(t) = 1 = \int_0^\infty \alpha h_0(t)\tau(t)\delta(t)dt + \int_0^\infty 2k_s(S)\tau(t)\delta(t)dt \qquad (\underline{38})$$

Equation (38) states that the sum probability of eventual recombination and of eventual reaction with scavenger is one.

If τ_∞ is the probability that in the absence of scavenger the radical pair never reacts (τ_∞ is the efficiency factor), then

$$(1 - \tau_\infty) = \int_0^\infty \alpha h_0(t)\tau(t)dt \qquad (\underline{39})$$

Equation (39) is a boundary condition and differs by the factor $\tau(t)$ from that used by Noyes. Noyes assumed $\tau(t)$ to be one at all times.

The probability, ϕ, is given by the integral over all times of the product of the probability, $(1 - \delta(t))$, that the molecular pair has reacted with scavenger by time t and the probability, $\alpha h_0(t)\tau(t)dt$, that the molecular pair would otherwise have recombined at time t.

$$\phi = \int_0^\infty (1 - \delta(t))\alpha h_0(t)\tau(t)dt \qquad (\underline{40})$$

$$= (1 - \tau_\infty) - \int_0^\infty \alpha h_0(t)\tau(t)\delta(t)dt \qquad (\underline{41})$$

$$= -\tau_\infty + \int_0^\infty 2k_s(S)\tau(t)\delta(t)dt \qquad (\underline{42})$$

If the expression for $h_o(t)$ is taken to be that given by the theory of random flights (51),

$$h_o(t) = at^{-3/2}e^{-b/t} \tag{43}$$

then $\tau(t)$ takes the form

$$(t) = \tau_\infty \exp(\ln\tau_\infty^{-1})(\text{erf } x) \tag{44}$$

where

$$x = \alpha a\,(\pi/t)^{1/2}/\ln\tau_\infty^{-1}$$

If $\tau(t)$ is given by equation (44), the integrals in equations (40), (41) and (42) apparently do not have analytic solutions and would require analysis by numerical methods. Also, there appear to be no "obvious" approximate solutions of the integrals valid at dilute scavenger concentrations. Since ϕ must be simply proportional to the first power of the scavenger concentration when it is present in small amounts (Fig. 10), the use of equation (43) to represent $h_o(t)$ is suspect. Equation (43) actually is an approximation valid only for a relatively large number of successive diffusive displacements (51). If the recombination process for a molecular pair should be over after a few diffusive steps, the description of their relative motion by the random flights method is not valid.

Monchick (50) used the Smoluchowski or diffusion equation to describe the behavior of a geminate radical pair. Chandresekhar (51) showed that the Smoluchowski partial differential equation can be derived from the theory of random flights by a limiting process which is valid only for a large number of successive flights. However, the treatment based on the differential equation assumes that diffusive motion is continuous, i.e., the molecules undergo very small diffusive displacements at a very high frequency. It is argued, therefore, that the differential equation should apply for time intervals greater than ca. 10^{-13} sec. (50). The theory predicts a linear relationship between ϕ and the square root of the scavenger concentration. The model chosen is that of two inert particles which can "react" with each other. As with the theory of Noyes, no account is taken of the fact that real molecules can react only once.

The theoretical treatments consider recombination of a molecular pair to be very probable after the occurrence of a fairly large number of diffusive jumps. Consequently, they predict that scavenging of radicals should be competitive with secondary recombination at low scavenger concentrations (10^{-3} - 10^{-2} M) (13). The mathematical equations are complex and, if they are applicable, do not appear to "easily" yield a linear dependence between ϕ and the square root of the scavenger concentration. The theories contain the necessary simplifying assumption that the effect of solvent on the reactivity of a molecule is negligible so that α is time independent.

An alternate viewpoint is to assume that recombination occurs only before diffusion takes place or, at the latest, after one or two small diffusive steps. The assumption is that geminate radicals lose their identity immediately after diffusion or that the probability for secondary recombination is very small. The quantity ϕ is then directly proportional to the statistical distribution of scavenger about the molecular pair at the time of its birth.

Nearest neighbor scavenging can be included in the kinetic scheme.

$$\begin{aligned}\overline{2R + N_2 + S} &\xrightarrow{k_g'''} RR,\ RR',\ \text{etc.}\\ &\xrightarrow{k_s'''} RS + R + N_2\\ &\xrightarrow{k_4'''} R + S + R + N_2\end{aligned}$$

k_g''' = sum of the rate constants for geminate destruction of radicals

$= k_2''' + k_3''' + k_d'''$

g = fraction of geminate radicals which react with each other when formed beside a scavenger

$$= \frac{k_g'''}{k_g''' + k_s''' + k_4'''} = w''' + z''' + x'''$$

v = fraction of geminate radicals which react with a scavenger when formed as nearest neighbor to it

$$= \frac{k_s'''}{k_g''' + k_s''' + k_4'''}$$

γ_1 = probability that RN_2R has one scavenger molecule as nearest neighbor.

At dilute scavenger concentrations ϕ is given by

$$\phi = \gamma_1 v \qquad (\underline{45})$$

If X_s is the mole fraction of scavenger present and if n is the average number of nearest neighbor molecules around a radical pair at the instant of its formation, then

$$\gamma_1 = nX_s(1 - X_s)^{n-1} \qquad (\underline{46})$$

At high concentrations of scavenger the probability of having two or more nearest neighbor scavenger molecules must be considered:

$$\gamma = \gamma_1 + \gamma_2 + \cdots + \gamma_n = [1 - (1 - X_s)^n] \qquad (\underline{47})$$

$$\gamma - \gamma_1 = [1 - (1 - X_s)^n] - nX_s\,(1 - X_s)^{n-1}$$

γ = probability that RN_2R has one or more scavenger molecules as nearest neighbors

Table X shows that $\gamma - \gamma_1$ is significantly large in the concentration range of interest (in chlorobenzene solutions X_s is

TABLE X

	n	γ_1	$\gamma - \gamma_1$
$X_s = 0.020$	4	0.075	0.002
	5	.092	.004
	6	.108	.006
	8	.139	.010
$X_s = 0.040$	4	.142	.009
	5	.170	.015
	6	.196	.022
	8	.240	.038
$X_s = 0.060$	4	.199	.020
	5	.234	.032
	6	.264	.046
	8	.311	.079
$X_s = 0.080$	4	.249	.034
	5	.287	.054
	6	.316	.077
	8	.357	.130

one-tenth the molarity at concentrations less than one molar). Unless $v \cong 1$ even when $\gamma - \gamma_1$ is negligible, any variation of v with X_s should be important.

Figure 11 contains a plot of $1 - \gamma$ against X_s for four values of n. The plots show that the probability function has more curvature at higher values of n. However, within the precision of the determination of RR yields (Fig. 10), all four curves approximate a straight line.

$$\phi \cong \text{constant} \times (X_s) \qquad (\underline{48})$$

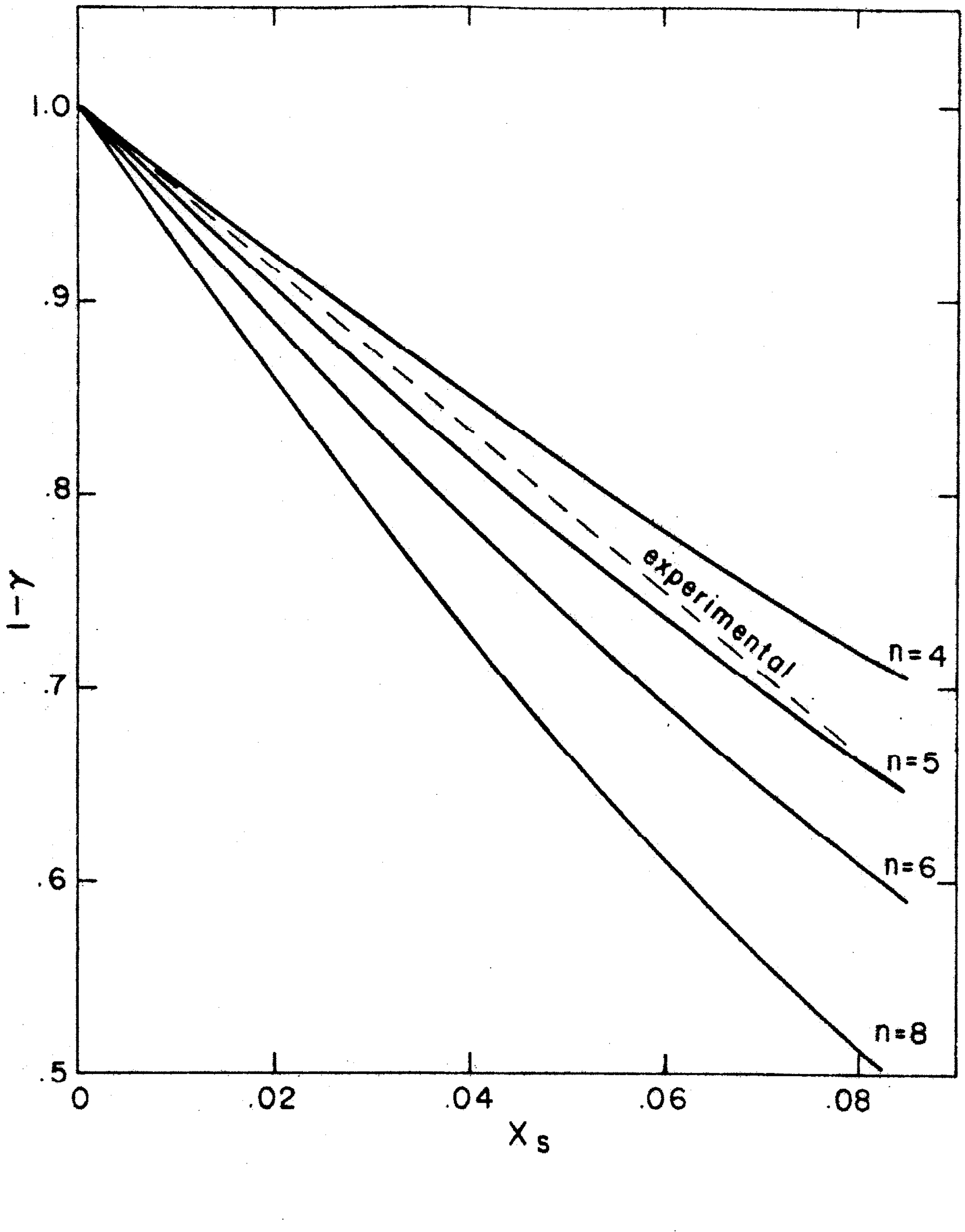

Fig. 11. Plots of 1-γ against X_s.

The fact that bromine, iodine and DPPH give identical results (Fig. 10) suggests that v should be essentially unity for all values of X_s. When $v \cong 1$, the ordinate in Figure 11 is equivalent to $(1 - \phi)$ and excellent agreement between the experimental line and the curve for $n = 5$ is obtained. This value of n is reasonable and, on the average, is the smallest possible number of nearest neighbors.

The experimental data for RN_2R and RR' decomposition are consistent with the assertion that geminate recombination is almost entirely primary recombination with little or no contribution from secondary recombination. Radicals which are produced in pairs may react in their natal cage or they may separate by diffusion. Once the imprisoned radicals escape from their cage, their pairing identity is lost and they have little chance of reacting with their original partners. The decrease in the probability of reaction immediately after the diffusion process has started may be caused by a "collapsing cage" effect in which the radicals are pushed apart by the solvent molecules. Alternatively, the solvent molecules may complex with the radicals and decrease α to such an extent that no reaction results from reencounters of "geminate radicals." It is probable in either case that the initial diffusion process is not a completely random one.

The absence of secondary recombination might be a result of the fact that diffusive displacement distances of cyanocyclohexyl radicals are larger than their encounter diameters. Calculations show that secondary recombination is unimportant under these conditions (12). A diffusion model which involves large diffusive jumps occurring at a low frequency would also account for extensive primary recombination of the relatively inert cyanocyclohexyl radicals.

Most of the earlier work in the literature which supported the notion of secondary recombination involved experiments concerned with energy transfer processes (38-46). The effects of scavengers and of reaction products on these energy transfer processes were not clearly determined. It is possible, therefore, that data attributed to interference by scavenger with secondary recombination was actually a result of the destruction of excited states in the radiolysis and photolysis experiments. The results of Jortner (52,53) are not understood and no explanation is offered.

The z' Factor

The fraction of geminate radicals which form RR' in the thermal decomposition of RN_2R was previously measured in chlorobenzene (8). The study has been extended and the values of z' determined for three additional solvents: n-heptane, sym-tetrachloroethane and N,N-dimethylaniline. Initial rates of formation of RR' in the presence of DPPH were measured and the distribution factors calculated with equation (6). The data are reported in Table XI and show that, within experimental accuracy, the z' factor is independent of a threefold change in viscosity. Noyes found that the amount of geminate recombination of iodine atoms was markedly reduced by a sixfold change in the viscosity of the hydrocarbon solvents (Fig. 1).

The higher value of z' obtained with N,N-dimethylaniline is probably not a result of coupling of kinetically free radicals. The initial rate of formation of RR' measured in the absence of DPPH corresponds to that measured in the presence of the scavenger (the fraction of RN_2R which forms RR' in the absence of DPPH was calculated to be 0.31). It appears, therefore, that this solvent is an efficient scavenger of cyanocyclohexyl radicals.

The larger cage effect observed with N,N-dimethylaniline can be rationalized by assuming that this electron rich solvent complexes strongly with cyanocyclohexyl radicals. If the reactivity of the complexed radicals is such that α is essentially unchanged, the geminate radicals would be in an encounter position and could react even after being separated by two solvent molecules. Therefore, scavenging of the cage by solvent molecules which complex with the radicals could decrease radical mobility more than reactivity and produce a larger cage effect. This result would be best realized if the diffusion process involves rather large diffusive jumps which occur at a low frequency.

TABLE XI

The Fraction of Geminate Radicals which Form RR' in the Decomposition of RN_2R at 80.0° C

Solvent	Viscosity at 80.0° C millipoise	$k_1' \times 10^6$ sec.$^{-1}$	$(RN_2R)_o$ mole l.$^{-1}$	$(DPPH)_o \times 10^2$ mole l.$^{-1}$	z'
n-C_7H_{16}	2.43 (55)	5.95	0.182	3.32	0.21
$CHCl_2CHCl_2$	7.63 (56)	9.64	.179	4.60	.20
C_6H_5-Cl (8)	4.31 (57)	8.25	.0781	3.92	.21
C_6H_5-N-$(CH_3)_2$	6.42 (56)	8.74	.152	7.17	.31
			.188	–	.31

EXPERIMENTAL

EXPERIMENTAL

All melting and boiling points are uncorrected.

n-Heptane.—Matheson, Coleman and Bell reagent grade n-heptane was distilled through a Vigreux column and the fraction boiling at 64.0° C, 242 mm. Hg, was collected for experimental use.

sym-Tetrachloroethane.—Matheson, Coleman and Bell reagent grade sym-tetrachloroethane was used without further purification.

N,N-Dimethylaniline.—Following the procedure of Meltzer and Tobolsky (58), one kilogram of Matheson, Coleman and Bell mono-free grade, N,N-dimethylaniline was refluxed with 100 g. of acetic anhydride for four hours. The cooled solution was added slowly to 1.5 l. of 6 M hydrochloric acid using an ice bath to keep the aqueous solution below 25° C. After repeated extractions with small portions of ether, the aqueous solution was neutralized by slow addition of a concentrated aqueous sodium hydroxide solution. An ice bath was used to keep the temperature below 25° C. The organic layer was separated from the water layer and washed successively with 0.5 M aqueous sodium hydroxide solution and water; dried with sodium hydroxide pellets; and distilled twice at reduced pressure. Approximately 500 ml. of colorless material boiling at 72.5° C, 10 mm. Hg, was collected for experimental use from the second distillation.

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 three days at 80° C. 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 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 (59) was followed. Three recrystallizations of the crude compound from a chloroform-ethanol solution gave material melting at 172.3-173.9° C; reported (59) m.p. is 174-176° C.

<u>1,1-Diphenyl-2-picrylhydrazyl (DPPH)</u>.—The method of Goldschmidt and Renn (60) was followed. Two recrystallizations of the crude compound from a chloroform-ligroin solution gave material melting at 134-136° C. After heating under vacuum at 100° C for eight hours, the compound melted at 134-136° C; reported (61) m.p. is 137° C.

<u>1,1'-Azo-(cyano-C^{14})-cyclohexane (RN_2R-C^{14})</u>.—The method of preparation of RN_2R has already been described (8). 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_2R-C^{14} of high specific activity (~ 0.5 mc./mmoles.) 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_2R-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° C, dec.; reported (27) m.p. is 114-115° C, dec.

<u>N-(1-Cyano-C^{14}-cyclohexyl)-pentamethyleneketenimine (RR'-C^{14})</u>.—RR'C^{14} of high specific activity was prepared from RN_2R-C^{14} by the procedure of Wu, Hammond, and Wright (8). A solution of 485 mg.

(1.99 mmoles.) of RN_2R-C^{14} in 10 ml. of n-heptane was refluxed under a nitrogen atmosphere for 7.5 hours. The solution was cooled to room temperature and the crystals which separated were filtered. The yellow, oily residue obtained by allowing the filtrate to evaporate to dryness at room temperature was dissolved in 5 ml. of benzene and diluted with 104 mg. (0.482 mmoles.) of inactive RR'. The benzene solution was added to an alumina (Merck reagent grade) column and developed with a 1:1 mixture of pentane and benzene. Evaporation at room temperature of the chromatograms gave a small amount of light yellow solid. This material was sublimed under vacuum at 30° C to give 16.4 mg. (3.07% yield) of white $RR'-C^{14}$ melting at 68.3-70.2° C; reported (8) m.p. is 68-69° C.

1,1'-Dicyanobicyclohexyl (RR).--A solution of 38 g. RN_2R in 2 l. of reagent grade n-heptane was refluxed under a nitrogen atmosphere for three 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° C for two days and sublimed under vacuum at 120° C; m.p. 221-222° C; reported (27) m.p. is 224-225° C. $RR-C^{14}$ was obtained from the kinetic runs with RN_2R-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 tin foil 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 one liter 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_2R, RR and RR' on the scintillation processes. The results are shown graphically in Figures 12, 13 and 14. RR was the only compound which did not change the counting rate. Relatively poor precision was obtained since only a few milligrams of very active toluene was employed. 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_2R and RR'.

Specific activities of the very active RN_2R-C^{14} and RR'-C^{14} compounds were determined by measuring counting rates for one milli-

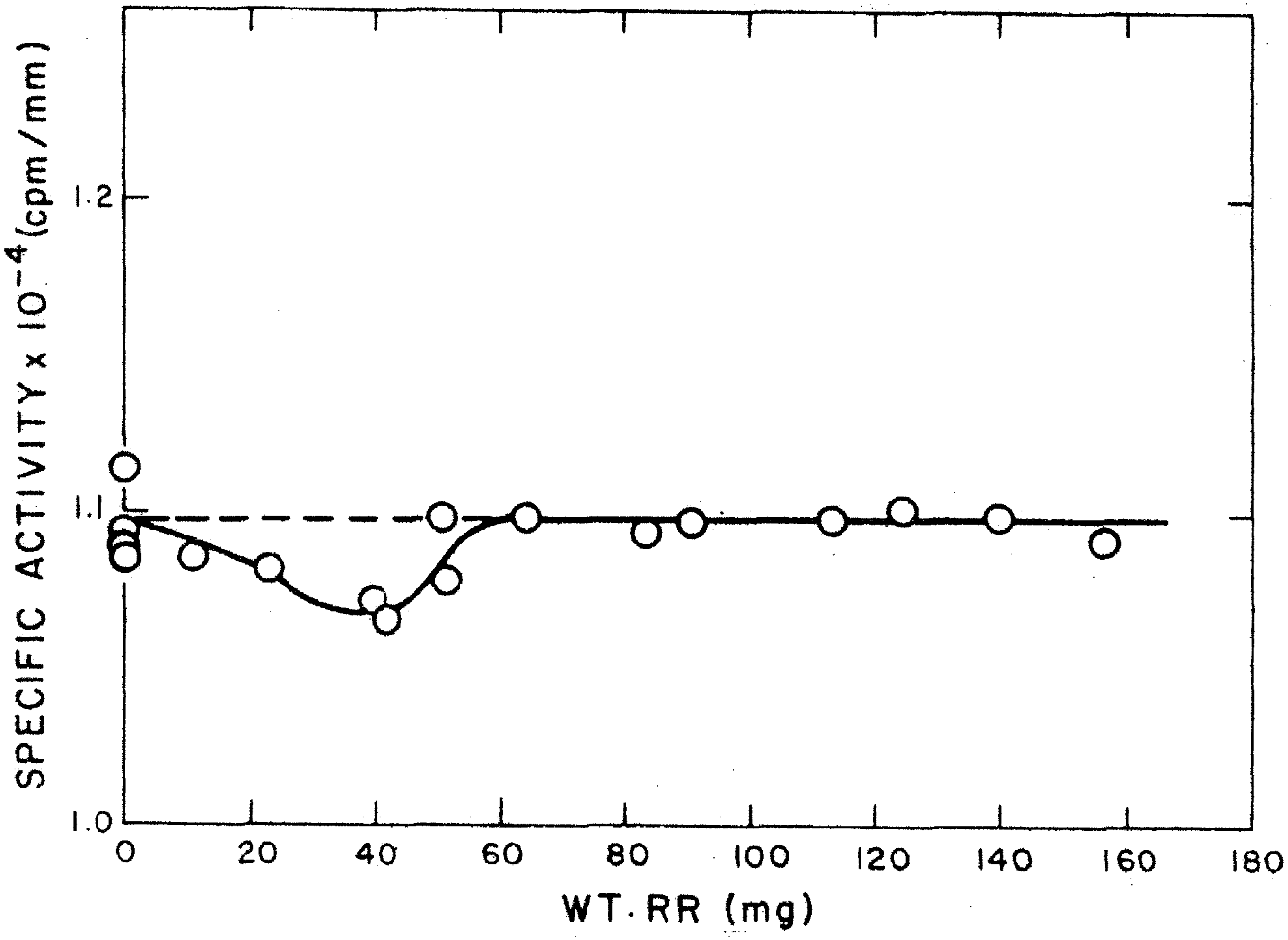

Fig. 12. Scintillation effect of RR.

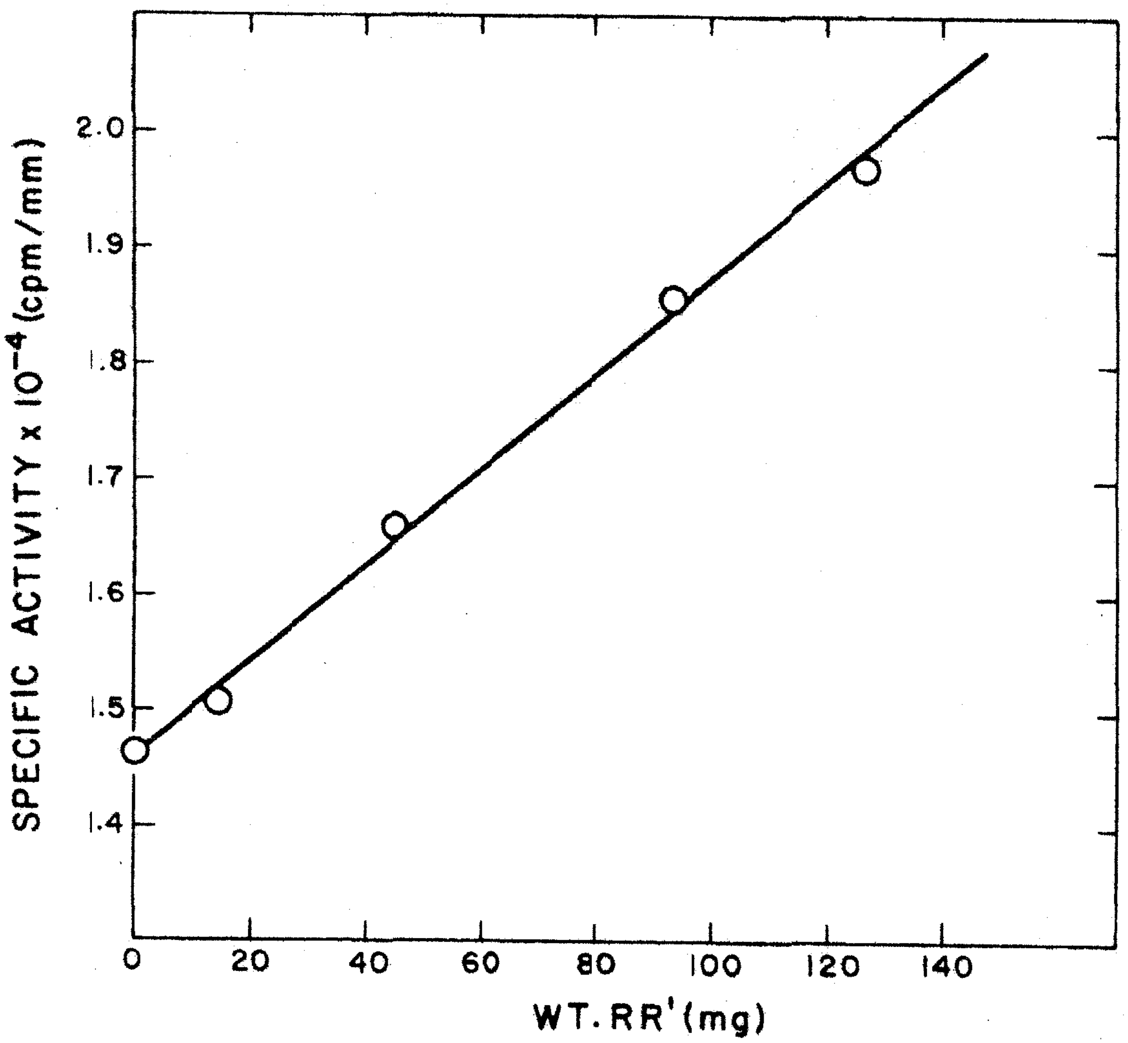

Fig. 13. Scintillation effect of RR'.

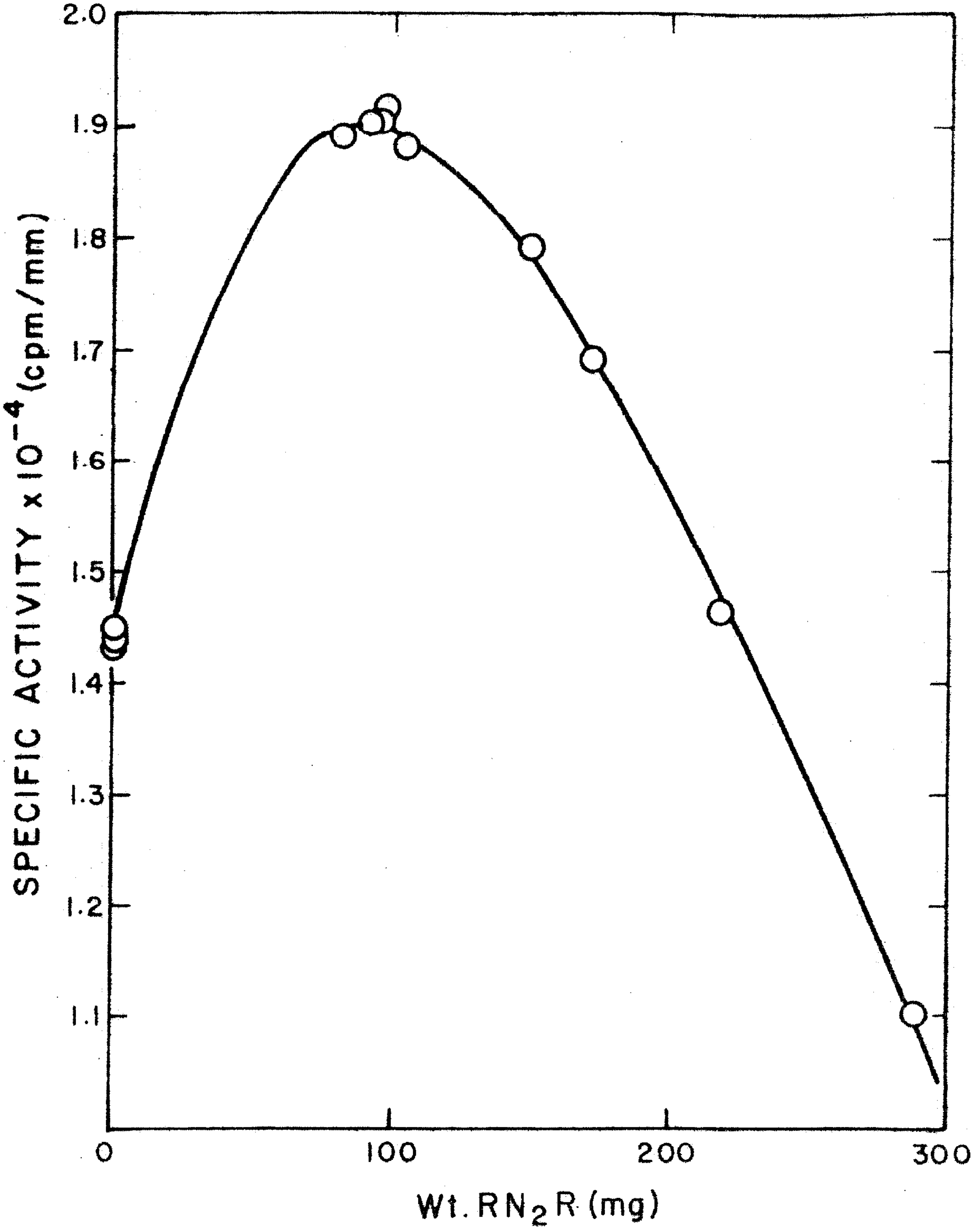

Fig. 14. Scintillation effect of RN_2R.

liter of their dilute ($\sim 10^{-5}$ $\underline{M}$) 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 following expression.

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

<u>Degassing Procedure</u>.—Ampoules were prepared by constricting 100 x 13 mm. or 150 x 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.

<u>Isotope Dilution Procedure</u>.—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 (~ 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 x 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 $RR\text{-}C^{14}$ were collected by filtration, dried under vacuum at room temperature for at least two hours and weighed into scintillation vials.

Decomposition of RN_2R and RR'.—Reaction solutions containing scavengers were made from prepared stock solutions of $RN_2R\text{-}C^{14}$ and $RR'\text{-}C^{14}$ 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 ~ 0.1 M scavenger solutions.

The sealed tubes were kept in a constant temperature bath at 80.0° C for a period long enough to effect at least 99.6% decomposition. Solutions containing RN_2R-C^{14} were heated for 8 days whereas those containing $RR'-C^{14}$ and DPPH required 14 days of heating.

Chlorobenzene solutions of RR' and HDPPH were similarly prepared and heated at 80.0° C for 14 days. The results are reported in Table XII.

When RN_2R-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 workup process.

Survival of RR in the Reaction Mixtures.—Stock solutions of $RR-C^{14}$ and $RR-C^{14}$ plus RN_2R in chlorobenzene were prepared and used to make up reaction solutions containing bromine and DPPH. The preparation of ampoules and the workup procedures were identical to those used in the decomposition experiments. Sealed tubes containing bromine were heated at 80.0° C for 8 days; those containing DPPH were heated at 80.0° C for 14 days.

In one experiment a solution of 119 mg. (0.552 mmoles.) of RR in 3 ml. of bromine was heated in a sealed tube at 80.0° C 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° C and recovery was calculated to be 79.8%.

TABLE XII

Yield of RR Produced by Decomposition of RR' in Chlorobenzene Containing Varying Amounts of HDPPH:

$[RR']_o$ = 1.72 x 10^{-5} mole $l.^{-1}$ at 80.0° C for 14 Days

$(HDPPH)_o$ mole $l.^{-1}$	% Yield RR
$1.67x10^{-5}$	24.3
3.33	5.4
6.67	11.1
$1.00x10^{-4}$	26.5
1.67	16.0
3.33	26.7
6.67	21.5
$1.00x10^{-3}$	21.0
1.67	22.8
3.33	10.2
6.67	9.4
$1.00x10^{-2}$	21.2
1.67	8.7
3.33	15.0
6.67	21.3
$1.00x10^{-1}$	16.9
1.05	14.5
1.49	13.0
2.77	11.0
3.87	10.3
5.54	11.5
7.90	10.4
$1.00x10^{0}$	10.4
–	22.4

Rate of Decomposition of RN_2R in the Presence of Bromine.—A 1.00×10^{-5} M solution of $RN_2R\text{-}C^{14}$ in chlorobenzene was made 0.819 M in bromine. Ampoules containing one ml. of this solution were degassed and heated at 80.0° C in a constant temperature bath for periods of one to seventy hours. The carrier solutions consisted of known amounts of RN_2R (~ 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 grade) columns (300 x 20 mm., dry packed) followed by elution with 200 ml. of benzene. The eluents were allowed to evaporate to dryness at room temperature. The $RN_2R\text{-}C^{14}$ was recrystallized twice from methanol, dried under vacuum at room temperature for two hours and weighed into scintillation vials for analysis.

A good fit to first order kinetics was obtained (Fig. 5) 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 RN_2R were heated in sealed ampoules for eight days at 80.0° C. Aliquots from the reaction mixtures were subjected to vapor phase chromatography on a silicone column at 172° C. 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.

Infrared Analyses.—Measurements were made with a Beckmann model IR7 recording infrared spectrometer using a single pair of matched, 1-mm., sodium chloride cells. The absorption band of the ketenimine at 2020 cm.^{-1} was followed. Empirical calibration curves of optical density versus concentration were determined for each solvent. The concentrations of RR' were obtained from these curves.

Initial Rates of RR' Formation.—The initial rates of formation of RR' from RN_2R were determined in n-heptane, sym-tetrachloroethane and N,N-dimethylaniline using DPPH as a scavenger in each solvent. The batch-sampling technique of Wu, Hammond and Wright (8) was used for kinetic measurements. The amount of ketenimine formed was determined by infrared analysis and the data were fitted to the integrated form of the first-order law by the method of least squares.

The first-order rate constants for decomposition of RN_2R in n-heptane, sym-tetrachloroethane and N,N-dimethylaniline were determined by manometric monitoring of the rate of nitrogen evolution. The apparatus and procedure were those described by Hammond, et al. (33).

The z' factors were calculated with equation (6).

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PROPOSITIONS

PROPOSITION I

Molecular Clustering in Binary Liquid Mixtures

Most explanations of critical phenomena which occur in the region of the critical solution temperature of binary liquid systems have in common the assumption of microheterogeneity or molecular clustering in the liquid mixture. It is proposed that measurements of the cage effect near the critical solution temperature of certain binary liquid mixtures might provide further evidence of molecular clustering.

Critical Phenomena of Binary Liquid Systems

Within a temperature range of one or two degrees above the critical solution temperature, binary liquid mixtures exhibit the phenomenon of critical opalescence (an abnormally strong scattering of light which increases with decreasing wavelength). Since a continuous and homogeneous medium would have a constant index of refraction from one volume element to another, this phenomenon is generally attributed (1-5) to concentration fluctuations so that the refractive index of the medium varies throughout the volume elements. A large number of binary liquid systems of organic compounds have been investigated. By studying the anomalous depolarization of scattered light, Krishnan (6) claims to have detected the presence of molecular clusters in the system aniline-cyclohexane over a temperature range extending 20° above the critical solution temperature.

Chynoweth and Schneider (7) first studied ultrasonic (about 600 k.c.) absorption in binary liquid systems near the critical solution temperature. They investigated the systems aniline-n-hexane and triethylamine-water and found a large anomalous absorption of sound energy in the region extending approximately 2° on either side of the critical solution temperature and increasing rapidly as the transition temperature was approached. This critical phenomenon has since been observed (8-12) in a variety of binary liquid systems. Explanations of this anomalous effect include a molecular mechanism which depends upon the microheterogeneity of the single phase (7,8,13, 14).

Numerous other physical properties such as viscosity, heat capacity and flow birefrigence show anomalous behavior in the region of the critical solution temperature. As with the two examples discussed, the notion of molecular clustering is usually invoked in their explanation.

Molecular Clustering

Suppose the molecular structure of a solution of two liquids, A and B, consists of molecular aggregates of A mixed with molecular aggregates of B. Also, suppose that a solid solute C is very soluble in liquid A and insoluble in liquid B. If the aggregates of A are relatively large, then we might expect the molecules of C to distribute themselves almost exclusively in the clusters of liquid A. If C can cleave thermally to yield radical fragments, the amount of geminate recombination in the liquid mixture should be nearly identical to that for pure liquid A. This result could be observed experimentally by further restricting the choice of liquids A and B so that the amount of geminate recombination is significantly different in the two liquids.

Figure 1 illustrates a typical phase diagram at constant pressure for two partially miscible liquids whose coexistence curve possesses an upper consolute temperature. The region outside the coexistence curve corresponds to one-phase systems, whereas the region within the curve represents two-phase systems. Addition to a mixture of two partially miscible liquids of a solute which is soluble in one of the liquid components and insoluble in the other would probably cause the critical solution temperature to increase (15). If we restrict the choice of two partially miscible liquids, A and B, so that a solute C is very soluble in A and relatively insoluble in B, then Figure 1 should also illustrate the general shape of the coexistence curve for mixtures of A and B containing a small amount of solute C.

Evidence for molecular association might be obtained by measuring the amount of geminate recombination associated with the thermal decomposition of C along the constant composition line OX_T. Figure 2 illustrates a possible variation with temperature of the amount of geminate recombination for liquid A, α_A, and that for liquid B, α_B. Liquids A and B are chosen so that α_B is significantly smaller than α_A. We would expect α_A and α_B to decrease with increasing temperature.

If large molecular clusters do indeed exist in the region of the critical solution temperature, the variation with temperature along the line OX_T of the amount of geminate radical recombination, α, for the liquid mixture of composition X_T should be approximately equal to α_A in this region. As long as relatively large clusters of A exist, α should be almost identical with α_A. If at temperatures somewhat above the critical solution temperature molecular association disappears and we have completely random mixing on the molecular level, α should deviate from α_A and might behave as indicated by the broken curve in Figure 2.

Further evidence for molecular clustering could be obtained by observing the behavior of α as the mole fraction of liquid A is changed at constant temperature. Thus, if α is measured along the constant temperature line OT_X in Figure 1, its variation might be similar to the broken curve in Figure 3.

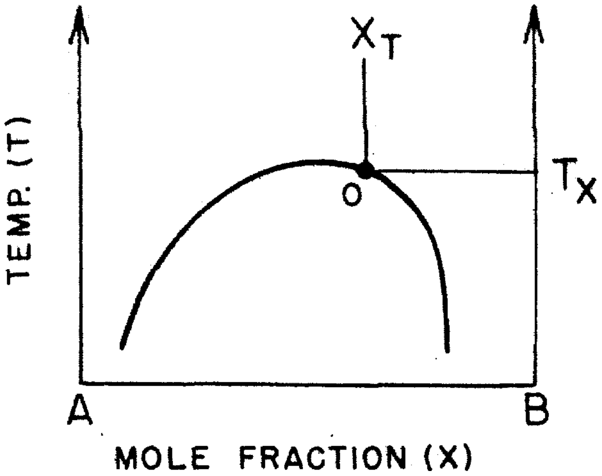

Fig. 1

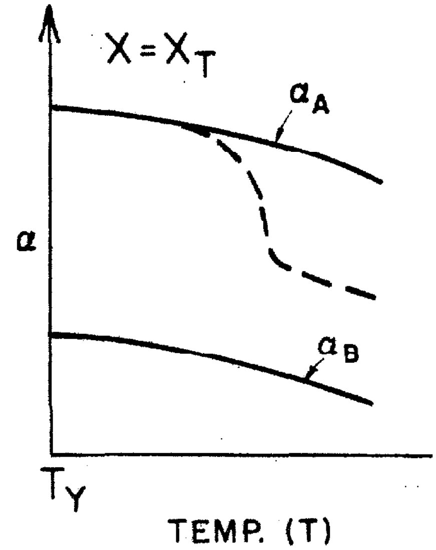

Fig. 2

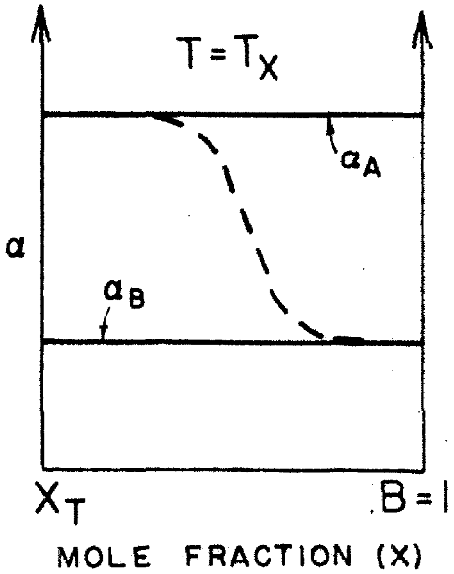

Fig. 3

By measuring α as a function of temperature at constant composition of the liquid mixture and as a function of the composition of the liquid mixture at constant temperature, a qualitative picture of the structure of a liquid mixture might be constructed in terms of molecular association over the one-phase domain.

Measurement of Geminate Recombination

A system which permits easy measurement of the amount of geminate recombination is 1,1'-azocyanocyclohexane (RN_2R). The yield of either RR or RR' produced by its thermal decomposition in the presence of scavenger could be used as a measure of the extent of geminate recombination.

Choice of a Binary Liquid System

The two liquid components of the binary liquid system must have the following properties: (1) the two partially miscible liquids should have an upper consolute temperature around 80°, the temperature region for relatively rapid decomposition of RN_2R; (2) the solubility near 80° of RN_2R should be significantly different in the two liquids; (3) the amount of geminate recombination should be significantly different in the two liquids; and, (4) the scavenger must be efficient in the liquid mixture. The last condition can be tested by varying the scavenger concentration.

A high molecular weight hydrocarbon (n-hexadecane) and a low molecular weight polar compound (benzene) will probably have these properties. Since critical solution temperature data for systems of this kind are presently unavailable, preliminary tests would have to be performed in order to find the right liquid system.

The choice of benzene and a hydrocarbon is reasonable since X-ray studies by Bell and Davey (16) support the notion of molecular association in the benzene-cyclohexane system. Nosworthy, et al. (17) have also hypothesized molecular clustering for the benzene-cyclohexane system in order to explain energy transfer phenomena in scintillation measurements.

If the initial experiments for the thermal decomposition of RN_2R prove fruitful, the measurement of geminate recombination in the photolysis of this compound is desirable since the temperature restriction on the binary liquid system is removed.

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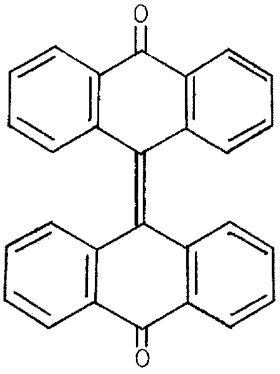
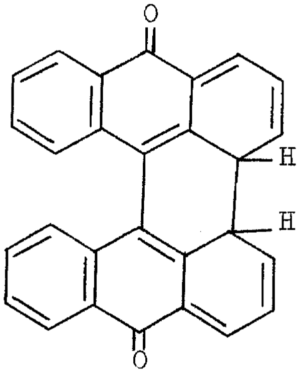
PROPOSITION II

The Photochromic State of Dianthrone

Recent studies of the photochemistry of *cis*-stilbene indicate that 12,13-dihydrophenanthrene is an unstable photoproduct which either regenerates *cis*-stilbene by thermal isomerization or reacts with a suitable hydrogen acceptor to form phenanthrene (1-3). It is proposed that an analogous process, the formation of 1,1'-dihydrohelianthrone, II, is responsible for the photochromism exhibited by dianthrone, I.



I

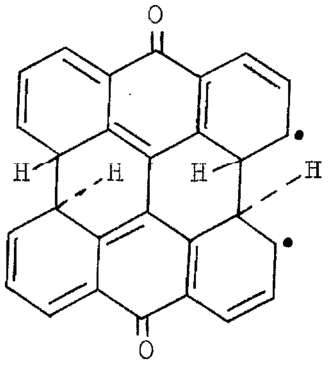


II

The phenomenon of photochromism is closely related to that of thermochromism, the two having been frequently interpreted as triplet-triplet transitions (4). Kistiakowsky (5) studied the thermochromism of I and concluded that the colored species is the lowest triplet of I in which the two aromatic ring systems are in planes perpendicular to each other. Electron paramagnetic resonance measurements on thermochromic solutions demonstrate the presence of paramagnetic species (6), although these are thought to be decomposition products of I (7). Magnetic susceptibility measurements by Kortum (8) on a thermochromic derivative of I showed that it was diamagnetic at all temperatures. He proposed that the thermochromic state is a geometric isomer of I with a singlet ground state. Harnik (9,10) reached a similar conclusion from X-ray crystallographic studies of I.

Hirshberg (11) claims that the thermochromic and photochromic spectra are identical and that the colored species is a geometrical isomer of I. Kortum has questioned this conclusion and offered spectroscopic evidence that the two states are different. He proposes that the photochromic state is a triplet similar to that proposed by Kistiakowsky for the thermochromic state. However, no electron paramagnetic resonance was observed with photochromic solutions of I (12).

Woodward (13) proposed the diradical III to represent the colored species formed from I.



III

The evidence for structure III is that pyridine solutions of I at 25° display an e.p.r. which increases with temperature (14). However, the enolic form of II is produced upon low temperature irradiation of pyridine solutions of I.

The rate of disappearance of the colored species in ethanol is greater than that in isooctane by only a factor of two (13). This result indicates the absence of a betaine structure.

Evidence which supports a photochromic state represented by II is the formation of helianthrone upon irradiation of solutions of I containing oxygen (15). In addition, II might be expected to enolize in pyridine and the e.p.r. observed in this solvent could be due to decomposition products of the enolic form. Oxidation experiments with photochromic solutions of I would determine if the colored species is the precursor of helianthrone.

A series of energy transfer experiments are proposed to determine the spin state of the photochromic species. Sensitization and quenching experiments with compounds possessing known triplet energies should show whether the colored species is a long lived biradical such as III. Results from these experiments, coupled with those from the oxidation experiments, should determine whether II is the best representation of the photochromic species.

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PROPOSITION III

Cage Effects in the Decomposition of Cyclic Azonitriles

Recent experiments (1) indicate that radical pairs produced thermally from acyclic azonitriles undergo little or no secondary recombination. However, such a process might occur if the geminate radicals are so constrained that they are physically unable to diffuse into the bulk of the solution. In order to investigate this possibility, it is proposed that cage effects in the pyrolysis and photolysis of cyclic azonitriles be measured over a wide range of scavenger concentrations.

Evidence that supports a secondary recombination process already exists. The inefficiency of diradicals in initiating polymerizations has been attributed to chemical reactions between the ends of the growing polymer chains (2). For example, Overberger (3) found that cyclic azo compounds are very poor initiators compared with their open chain analogues. Also, statistical calculations predict self-termination reactions to be more probable than biradical chain propagation reactions (4). Since the calculations ignore the influence of ring strain, the probability of the latter reactions figures to be vanishingly small.

The only attempt (5) to prepare a cyclic azonitrile failed, apparently because of thermal instability. However, the synthesis involved a six-membered ring where the azo bonds would necessarily be of the cis-configuration. A stable cyclic azonitrile will probably require a large ring where the azo group can assume the more stable trans-configuration. Cyclic phenyl azo compounds of small, medium and large ring sizes have been prepared and their decompositions studied (6). However, a complicating side reaction, isomerization to a hydrazone, makes their use as model compounds unattractive. Nevertheless, they can be used in this study should the preparation of the azonitriles be unsuccessful.

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PROPOSITION IV

Energy Transfer in Scintillator Solutions

Since the phenomenon of liquid scintillation was studied by Kallmann (1), the luminescence of a large number of organic scintillators in various solvents has been investigated (1-12). However, most studies have been more concerned with the discovery of new scintillators and more efficient scintillation solvents than with a detailed investigation of the excitation transfer processes. For example, nearly all scintillation data have been obtained with aerated solutions even though it is known (13,14) that the presence of dissolved gases markedly affects counting rates. It is proposed that excitation transfer processes in scintillation solutions containing carbon-14 be studied. The initial experiments can be carried out with commercial liquid scintillation spectrometers but later work may require modifications of the photomultiplier, light reflecting and electronic components of these instruments.

It is known (15,16) that, at the low scintillator concentrations ordinarily employed, excitation energy from the ionizing particle is transferred through the solvent to the scintillator molecule. Under these conditions, added solutes present at higher concentrations quench excited solvent molecules and catch the energy before it can reach the scintillator. Some preliminary experiments involving ketones as quenchers have been carried out. The data are reported in Table I and show a correlation between the quenching effects of the ketones and their triplet energies. It is proposed that this study be continued in order to determine the effects of concentration variation, of any luminescence of the ketones and, possibly, phosphorescence of POPOP on the counting rates. We may then be able to understand some of the energy transfer processes occurring in these solutions.

It would be of great interest to investigate the possibility of detecting phosphorescence with a scintillation spectrometer since phosphorescent counting rates would prove invaluable in the study of triplet-triplet energy transfer. This technique could provide a convenient method for determining whether molecules in the triplet state can escape the local region of a disintegration and diffuse into the bulk of the solution.

TABLE I

Quenching Effects of Carbonyl Compounds on the Scintillation of POPOP[†]
in Benzene Solutions* Containing ACC-C^{14} as a Radiation Source:
[ACC-C^{14}] = 10^{-5} mole $1.^{-1}$; [POPOP] = 10^{-4} $1.^{-1}$

	Molarity x10^2	cpm/10ml.[a, b]	E_T(kcal.)[c]
——	—	33,000	—
propiophenone	0.82	17,000	74.7
xanthone	0.99	6,734	74.2
acetophenone	1.05	13,800	73.6
benzophenone	1.03	9,380	68.5
4-acetylbiphenyl	1.03	9,320	64.1
β-acetonaphthone	1.03	8,260	59.3
α-acetonaphthone	1.02	6,240	56.4
biacetyl	0.98	4,350	54.9
fluorenone	1.01	6,690	53.0
benzanthrone	1.00	64	51.0
3-acetylpyrene	1.00	2,150	~ 47

*All solutions were degassed before counting.

[a] Activity of benzene solutions > 10^5 dpm/10 ml.

[b] Counting rate of benzene without POPOP = 2,760 cpm/10 ml.

[c] The fluorescent maximum of POPOP is ~ 73 kcal.

[†] p-bis-[2-(5-phenyloxazoyl)]-benzene.

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PROPOSITION V

A Test of the Dual Ion Pair Hypothesis

Winstein, et al. (1), have carried out detailed studies of salt effects in the solvolysis of arylsulfonates and related compounds. They observed a special salt effect superimposed on the normal salt effect and attributed the former to interference by added salt with ion pair return. They found that lithium perchlorate salt effects on the polarimetric rate constant in the acetolysis of *threo*-3-anisyl-2-butyl bromobenzenesulfonate showed only the normal linear effect. In addition, the salt effects on the titrimetric rate constant showed a combination of the initial special non-linear effect and the normal linear effect. However, the special salt effect only partly closed the gap between the polarimetric and titrimetric rate constants. Winstein (2) concluded that the best interpretation of these results is that two ion pairs, intimate and solvent separated, are discrete intermediates in the acetolysis.

$$RX \rightleftharpoons R^{+}X^{-} \rightleftharpoons R^{+}\|X^{-} \rightleftharpoons R^{+} + X^{-}$$

intimate ion pair	solvent-separated ion pair	dissociated ions

It was concluded that return from dissociated ions is unimportant in the *threo*-3-anisyl-2-butyl system since it showed no common ion rate depression of acetolysis (3). However, the occurrence of induced common ion rate depression of acetolysis (4) showed that the scavenging reaction of lithium perchlorate is reversible.

$$R^+ \| X^- + Li^+ClO_4 \rightleftharpoons R^+ \| ClO_4^- + Li^+X^-$$

Swain (5) has pointed out an alternate interpretation of these results which does not require the dual ion pair hypothesis. The gap between the polarimetric and titrimetric rate constants can be due to reaction of $R^+ \| ClO_4^-$ with Li^+X^- to regenerate $R^+ \| X^-$.

In order to test Swain's suggestion, it is proposed that concentration variation studies of the acetolysis of the *threo*-3-anisyl-2-butyl system be carried out. Lower initial substrate concentrations would give smaller steady-state concentrations of Li^+X^- which, if made small enough, could decrease the regeneration of $R^+ \| X^-$. If the gap between the polarimetric and titrimetric rate constants is decreased at lower substrate concentrations, the dual ion pair hypothesis will be questionable. Very low initial substrate concentrations can be investigated using radiocarbon techniques.

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