Mechanism of Carbon–Carbon Bond Fission by Electron Transfer Leading to Dianions

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Abstract: The reduction of 1,2-di(α-naphthyl)ethane (NN) leads to radical ions ($NN\cdot^-,Alk^+$) which decompose by the fission of the CH_2–CH_2 bond into the salts of α-naphthylmethyl carbanions ($N\cdot^-,Alk^+$). The solution of free $NN\cdot^-$ ions in hexamethylphosphortriamide (HMPA) is stable, while the ion pairs (Li^+, Na^+, or Cs^+) dissolved in ethers (THF, THP, and DME) undergo decomposition. The reaction obeys a second-order rate law with respect to $NN\cdot^-$, Alk^+, and its rate is inversely proportional to the concentration of the nonreduced NN. The following mechanism accounts for these findings: $2NN\cdot^-,Alk^+ \rightleftarrows NN^{2-},2Alk^+ + NN$, K_1; $NN^{2-},2Alk^+ \rightarrow 2N^-,Alk^+$, k_2. The values of k_2K_1 were determined for several cations and solvents. $\Delta H_1 + E_2$ was found for the $NN\cdot^-,Na^+$–THF system.

Some radical anions derived from hydrocarbons such as $ArCH_2\cdot CH_2Ar$ or $Ar_2CH\cdot CHAr_2$ readily undergo decomposition.[1] The reaction produces carbanions, *viz.*, $ArCH_2^-$ or Ar_2CH^-, resulting from the fission of the central C–C bond.

To determine the mechanism of this dissociation, we investigated the kinetics of decomposition of radical anions derived from di(α-naphthyl)ethane, denoted here by NN (N represents the α-$C_{10}H_7\cdot CH_2$ moiety). The results proved that the dianion, $^-NN^- = NN^{2-}$, and not the radical ion $NN\cdot^-$, undergoes fission of the C–C bond, *i.e.*, the reaction is as follows.

$$2NN\cdot^- \rightleftarrows NN^{2-} + NN$$

$$NN^{2-} \longrightarrow 2N^-$$

For the sake of brevity, the counterions are omitted in these equations. However, their role is important, as will be shown later.

The disproportionation equilibrium (or stationary state) is rapidly established and the dissociation of NN^{2-} is the rate-determining step. Direct decomposition of $NN\cdot^-$ into $N^- + N\cdot$ followed by the electron transfer $NN\cdot^- + N\cdot \rightarrow NN + N^-$ is apparently too slow to be observed.

Experimental Section

1,2-Di(α-naphthyl)ethane (NN) was prepared according to the method of Copeland, Dean, and McNeil.[2] The final product was crystallized from ethanol and then sublimed under high vacuum. Its identity was confirmed by melting point (164.5–165.5°), nmr spectrum [τ 6.47 (4 H) and $\tau \sim 2.5$ (multiplet, 14 H)], and by the mass spectrum, showing the parent peak at *m/e* 282 and a ^{13}C satellite (283) having ~25% intensity of the parent peak. The purity was checked by vpc, which showed the absence of other components.

The solvents (THF, THP, DME, and HMPA) were purified by the conventional techniques used in the kinetic studies of carbanions and radical ions.[3,4]

The radical anions of NN, denoted by $NN\cdot^-$, were prepared by electron transfer from a suitable salt of biphenylide ($B\cdot^-$) to the parent hydrocarbon. This instantaneous reaction was performed in all-glass apparatus equipped with break-seals and an optical cell. The whole unit could be thermostated by keeping it in a Dewar equipped with optically flat windows, which fitted the cell compartment of a Cary-14 spectrophotometer.

To ascertain a quantitative electron transfer from $B\cdot^-$ to NN, an excess of the latter hydrocarbon was used. Therefore, always less than 25% of naphthyl moieties was converted into the respective radical ions. Alternatively, $NN\cdot^-$ could be formed by allowing contact, for a short time, between a solution of NN and the required alkali metal. The metal was formed by decomposing its azide—a procedure which prevents the contamination of the resulting mirror by other alkalis. Although the heterogeneity of the reduction makes this method of $NN\cdot^-$ formation inferior to the other, it had to be used for the preparation of THP solutions of $NN\cdot^-,Na^+$ because it is impractical to reduce biphenyl with sodium in that solvent (the conversion is much too low).

The prepared solutions of $NN\cdot^-$ were poured into the optical cell and the decomposition was followed spectrophotometrically seconds after the formation of the radical anion. The optical density at 530 nm (λ_{max} of the product $C_{10}H_7\cdot CH_2^-$, ϵ 6500) was continually recorded. This procedure permitted us to measure the initial rate of the process and to check the spectrum of the solution at later stages of the decomposition. Alternatively, the progress of the reaction was followed by the esr technique. Changes in line width were negligible during the reaction. Therefore, the relative radical concentration was given by the peak-to-peak height of the first-derivative esr spectrum, which was quickly scanned. Before mixing a slowly scanned overmodulated spectrum of the known donor solution $B\cdot^-$ was taken, and the same was done for $NN\cdot^-$ at a stage of the reaction when the change in concentration was small during the scan time. Double integration[5] then gave the absolute concentration of $NN\cdot^-$. This procedure permitted us to keep the geometry constant. Of course, instrument settings such as modulation amplitude, microwave power, and scan rate were not changed during either the absolute or relative concentration measurements. The microwave power was kept low to reduce errors due to possible differences in saturation of the two radicals. The rate constants determined by this technique agreed with those determined spectrophotometrically.

Results

The solution of $NN\cdot^-$ in HMPA (hexamethylphosphortriamide) was found to be stable for many hours. Its optical spectrum is nearly identical with that of naphthalenide radical anion (λ_{max} 380 nm, $\lambda_{min} \sim 520$ nm, with other peaks in the 700–900-nm region). Although the esr signal could be observed, we never succeeded in resolving it.

When alkali metal (sodium or potassium) was used as the reducing agent, radical anions of α-methylnaphtha-

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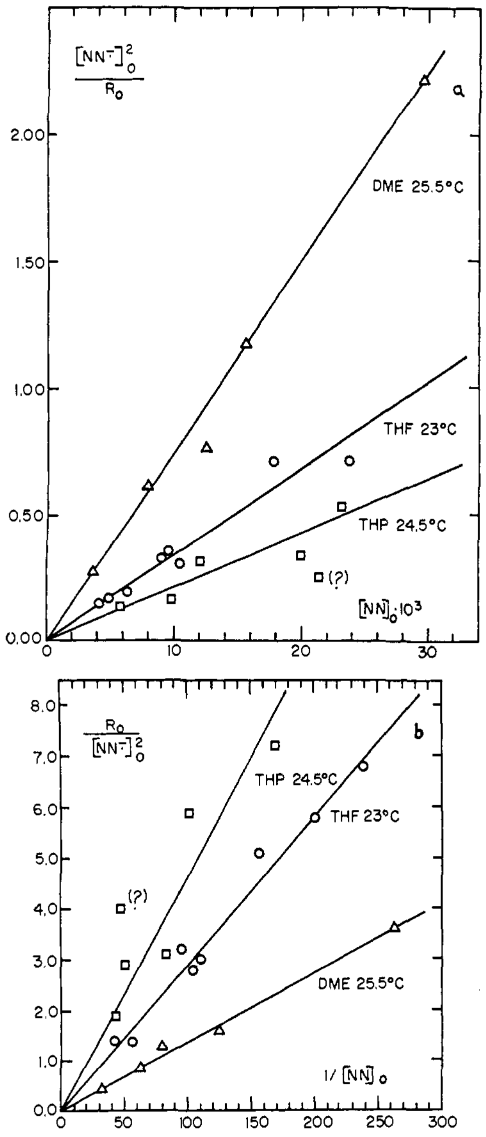

Figure 1. (a) Plot of $[NN^{\cdot-}]_0^2/R_0$ *vs.* $[NN]_0$, (b) plot of $R_0/[NN^{\cdot-}]_0^2$ *vs.* $1/[NN]_0$ for the sodium salt in THP, THF, and DME at ~25°.

lene were formed. The latter were revealed then by their sharp, well-resolved spectrum, virtually identical with that reported by Fraenkel and his coworkers.[6] Apparently the metal solutions are stronger reducing agents than biphenylide, and their local excess, arising from a noninstantaneous mixing, may lead to the formation of NN^{2-} and, subsequently, of N^-. The latter is unstable in HMPA (see later), and eventually its direct or indirect protonation leads to the radical anion of α-methylnaphthalene. We do not intend to unravel the mechanism of this complicated side reaction. It should be stressed, however, that in any solvent N^-, left in contact with alkali metal, ultimately produces the radical anions of α-methylnaphthalene. A possible route might involve the sequence of steps such as

$$\text{alkali metal} + C_{10}H_7CH_2^- \longrightarrow C_{10}H_7\cdot CH_2\cdot^{2-}$$

$$C_{10}H_7\cdot CH_2\cdot^{2-} + \text{solvent} \longrightarrow C_{10}H_7\cdot CH_3\cdot^{-} + \ldots$$

Formation of radical anions of α-methylnaphthalene observed in HMPA-Na solution raises the question of whether indeed the solution of $NN\cdot^-$ in that solvent is stable when the latter is formed by electron transfer from biphenylide. Positive evidence was obtained by the following experiment.

A solution of biphenylide was prepared in HMPA and the concentration of these radical anions was determined spectrophotometrically. Thereafter, double integration of their overmodulated esr spectrum at low microwave power provided an alternative measure of the concentration. On addition of a large excess of NN, the optical spectrum of biphenylide disappeared and that of $NN\cdot^-$ appeared, indicating that at least 80% of the former was converted into the latter. Nevertheless, the overmodulated esr signal retained its original intensity which then remained constant for many hours. This demonstrated that the solution contained at least 90% of the original amount of odd electrons. Obviously, the formation of 1 mol of radical ions of α-methylnaphthalene requires the destruction of twice as many odd electrons and, hence, such a process should reduce at least by a factor of 2 their total concentration as determined by esr.

In ethereal solvents $NN\cdot^-$ decomposes, producing $C_{10}H_7\cdot CH_2^-$ carbanions. Their identity was established by protonation of the products of decomposition, which yielded α-methylnaphthalene, and through examination of their spectrum. The latter shows an absorption band at λ_{max} 530 nm. A closely similar optical spectrum of $C_{10}H_7\cdot CH_2^-$, Na^+ in THF was reported;[7] it resembles the spectrum of living poly(vinyl-α-naphthalene)[7] which has a maximum at λ 558 nm.

The $C_{10}H_7\cdot CH_2^-$, Na^+ is indefinitely stable in dioxane and in THP. However, some slow, not yet investigated, reactions occur in THF, DME, and THF–HMPA mixtures. These reactions result in eventual decrease of OD at 530 nm and in the appearance of some new species absorbing at 420–430 nm as well as at longer wavelengths (>700 nm). The "aging" process interferes with kinetic studies at later stages of the decomposition, although the initial rates could be determined reliably.

The kinetic results showed that in each experiment the initial rate of the product formation was proportional to the square of $NN\cdot^-$ concentration. The plot of $1/\{OD(530)_\infty - OD(530)_t\}$ should therefore be linear with time, and from its slope the apparent second-order rate constant could be calculated. However, since in many experiments the exact value of OD_∞ could not be determined, the following procedure was adopted in evaluating the data.

A computer program was developed to calculate the least-squares lines for the reciprocal relation for a set of values of OD_∞. That value of OD_∞ which led to the smallest standard deviation of the experimental points from the linear relation was chosen as the "correct" OD_∞. Subsequently, the initial rates, R_0's, and the apparent second-order rate constants were computed for each experiment by the standard procedure. The relevant data are summarized in Tables I–IV.

Discussion

The decomposition of $NN\cdot^-$ into $2N^-$ is second order in radical anions. This observation excludes the unimolecular mechanism governed by $NN\cdot^- \rightarrow N^- + N\cdot$,

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Table I. Kinetics of C–C Fission in THF; Counterion Na$^+$

Run	Temp, °C	[NN·$^-$] × 10^3, *M*	[NN] × 10^3, *M*	R_0 × 10^6, *M*/sec	Aparent second-order rate constant, M^{-1} sec^{-1}	$2k_2K_1$ × 10^3, sec^{-1}
1	23	0.45	9.1	0.6	3.0	27^a
2	23	0.75	9.6	1.6	2.8	27
3	23	1.03	4.2	7.2	6.8	29
4	24	1.2	10.5	4.6	3.2	33
5	23	1.7	6.4	14.4	5.1	33
6	23	2.0	17.8	5.4	1.4	25
7	23	2.3	5.0	30.5	5.8	29^a
8	23	4.6	23.8	28.6	1.4	33
						Av 29.5
9	1	1.4	1.85	1.60	0.82	1.5
10	1	1.5	8.2	0.48	0.21	1.7
11	1	1.9	7.8	0.85	0.23	1.8^a
12	1	2.3	4.4	2.3	0.42	1.8^a
						Av 1.7
13	−10	2.0	5.0	0.35	0.089	0.45
14	−18	2.8	9.6	0.095	0.012	0.115
15	−18	2.8	18.3	0.048	0.0062	0.113
						Av 0.114

[a] Experiments performed in the presence of sodium tetraphenylboride.

Table II. Kinetics of C–C Fission in THF

Run	Temp, °C	[NN·$^-$] × 10^3, *M*	[NN] × 10^3, *M*	R_0 × 10^6, *M*/sec	Apparent second-order rate constant, M^{-1} sec^{-1}	$2k_2K_1$ × 10^3, sec^{-1}
			Counterion Li$^{+\,b}$			
16	24	0.8	23.0	0.3	0.5	12
17	24	0.94	4.3	3.3	3.8	16
			Counterion K$^{+\,b}$			
24	22.5	1.2	3.4	16.3	11.3	39
25	22.5	1.3	9.5	7.0	4.2	40
			Counterion Cs$^{+\,b}$			
18	24.5	1.8	2.35	41.3	12.6	*a*
19	24.5	1.6	17.6	8.3	3.3	*a*
20	24	1.7	4.9	22.9	7.7	*a*
21	25	2.1	29.8	9.2	2.1	*a*

[a] $2k_2K_1 = 70 \times 10^{-3}$ sec^{-1} as determined from Figure 3. [b] Salts of N$^-$ carbanions show a shift in the absorption spectrum which depends on the counterion. Thus, λ_{max} is 500, 530, 545, and 555 nm for the Li$^+$, Na$^+$, K$^+$, and Cs$^+$ salts, respectively.

Table III. Kinetics of C–C Fission; Counterion Na$^+$

Run	Temp, °C	[NN·$^-$] × 10^3, *M*	[NN] × 10^3, *M*	R_0 × 10^6, *M*/sec	Apparent second-order rate constant, M^{-1} sec^{-1}	$2k_2K_1$ × 10^3, sec^{-1}
			Solvent THP			
31	25	0.74	21.4	2.2	4.0	85?
32	24.5	1.38	5.9	13.8	7.2	42
33	24.5	1.44	9.9	12.2	5.9	53
34	24	1.47	20.0	6.2	2.9	58
35	25	1.6	23.3	4.7	1.9	44
36	25	1.6	12.1	7.9	3.1	38
						Av 47
			Solvent DME			
41	25	0.57	8.0	0.50	1.6	13
42	24	0.64	12.5	0.53	1.3	16^a
43	25	0.65	29.6	0.19	0.45	12
44	27	1.34	3.8	6.4	3.6	14^a
45	26	2.6	15.7	5.9	0.85	13
						Av 13.5

[a] Experiments performed in the presence of sodium tetraphenylboride.

this rate-determining step being followed by a rapid reaction, N· + NN·$^-$ → N$^-$ + NN.

The data given in Tables I–III show that the apparent second-order rate constants of the decomposition are not affected by the addition of the salts of tetraphenyl boride sharing with NN·$^-$ salts a common counterion (compare, *e.g.*, experiments 1 and 2, 5 and 7, or 10 and 11, all listed in Table I). Evidently the reaction involves ion pairs and the small fraction of the free NN·$^-$ ions, present in equilibrium with NN·$^-$,Na$^+$ pairs, negligibly contributes to the decomposition, apparently because of their low reactivity.

Further inspection of the data shows that the apparent second-order rate constants decrease with increasing concentration of the nonreduced NN. Plots of $[\mathrm{NN}\cdot^-]_0^2/R_0$ *vs.* $[\mathrm{NN}]_0$ or of $R_0/[\mathrm{NN}\cdot^-]_0^2$ *vs.* $1/[\mathrm{NN}]_0$ (where R_0 is the initial rate of decomposition) are linear (see Figure 1). Note that the first plot overemphasizes the significance of the data obtained for the highest values of $[\mathrm{NN}]_0$ while the second weighs heavily those corresponding to the lowest $[\mathrm{NN}]_0$. The facts that both plots are linear and the product of their slopes is unity provide evidence for the reliability of the experimental data. For example, the lines shown in Figure 1 have the slopes 34 and 0.029 (product 0.98), 75 and 0.0135 (product 0.95), and 21 and 0.046 (product 0.96) for the reaction proceeding in THF, DME, and THP, respectively.

The retardation of decomposition by unreduced NN implies that the overall reaction is not a simple bimolecular process, 2NN·$^-$,Alk$^+$ → NN + 2N$^-$,Alk$^+$. Instead, it must involve two steps; a rapidly established disproportionation equilibrium, *i.e.*

$$2\mathrm{NN}\cdot^-,\mathrm{Alk}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NN}^{2-},2\mathrm{Alk}^+ + \mathrm{NN} \qquad k_1/k_{-1} = K_1$$

followed by the rate-determining step

$$\mathrm{NN}^{2-},2\mathrm{Alk}^+ \xrightarrow{k_2} 2\mathrm{N}^-,\mathrm{Alk}^+$$

A rapid reaction, NN·$^-$ ⇄ N$^-$ + N·, followed by the improbable rate-determining step, NN·$^-$ + N· →

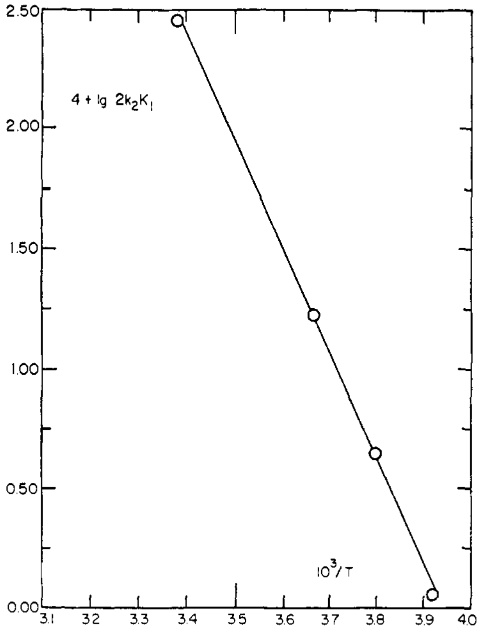

Figure 2. Plot of log $2k_2K_1$ *vs.* $1/T$ for the $NN\cdot^-,Na^+$-THF system.

$NN + N^-$, could account for the observed products, stoichiometry, and the second-order dependence of the rate on $[NN\cdot^-]$. However, its rate would not be affected by NN, but instead inhibited by the product, N^-, contrary to our findings.

In the most general case of a stationary state, the proposed mechanism leads to

$$d[N^-,Alk^+]/dt = 2k_2K_1[NN\cdot^-,Alk^+]^2/([NN] + k_2/k_{-1})$$

i.e., a plot of $[NN\cdot^-,Alk^+]^2/R_0$ should be linear with [NN], its slope giving $1/2k_2K_1$ and its intercept giving $1/2k_1$. For the system in which $[NN] \gg k_2/k_{-1}$ the above equation is reduced to the form

$$d[N^-,Alk^+]/dt = 2k_2K_1[NN\cdot^-,Alk^+]^2/[NN]$$

This relation applies to most of our systems.

The composite constants $2k_2K_1$ are given in the last columns of Tables I, II, and III. The plot of log $(2k_2K_1)$ *vs.* $1/T$ for the THF-Na^+,$NN\cdot^-$ system is shown in Figure 2, and leads to $\Delta H_1 + E_2 = 20 \pm 2$ kcal/mol.

In the system $NN\cdot^-Cs^+$ in THF at 24° the k_2/k_{-1} is apparently comparable to [NN]. Indeed, the plot of $[NN\cdot^-,Cs^+]^2/R_0$ *vs.* [NN], shown in Figure 3, yields a straight line with positive intercept of $\sim$0.05 and slope 14. Hence, in this system $k_1 \sim 10$ M^{-1} sec^{-1} and $2k_2K_1 \sim 70 \times 10^{-3}$ sec^{-1}.

Solvents and counterions greatly influence the rate of the decomposition. Unfortunately, our data do not allow us to decide to what extent the observed variations arise from changes in k_2 or K_1. In a somewhat analogous system, *i.e.*, tetraphenylethylene, the disproportionation constant increases with decreasing polarity of the solvent and increasing size of the counterion.[8] These trends parallel our present observations (see Tables I, II, and III), and suggest that also in our system K_1 increases with decreasing solvating power of the ether and increasing size of the cation. The variations of K_1 can be attributed to the different degree of dissociation of ion pairs into free ions. The behavior of $NN\cdot^-$ in HMPA confirms this conclusion. In the latter solvent virtually all the ion pairs are dissociated[9] and the solution contains essentially only the $NN\cdot^-$ free anions. The stability of the HMPA solutions of $NN\cdot^-$ proves, therefore, that the free $NN\cdot^-$ ions do not disproportionate.

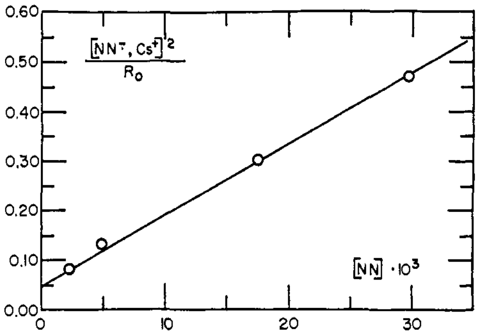

Figure 3. Plot of $[NN\cdot^-]^2/R_0$ *vs.* $[NN]_0$ for the $NN\cdot^-,Cs^+$-THF system. Intercept = $1/2k_1$, slope $1/2k_2K_1$.

It is probable that the dissociation constants of $NN\cdot^-$, alk^+ ion pairs in ethereal solvents are similar to those of the respective salts of naphthalenide radical ions[10] and, thence, the fraction of free ions in those systems should be well below 10%. The low proportion of the free ions and their low reactivity therefore make their contribution to the observed reaction negligible. The observed variations of the rates, arising from variations of the solvent or counterion, should probably be attributed to changes in the structure of ion pairs. Apparently the "tight" pairs disproportionate to a greater degree than the "loose" pairs.[11]

The relation between the reactivity (or disproportionation constant) and the structure of ion pairs is upheld by experiments in which small amounts of HMPA (a powerful solvating agent) are added to the solution of $NN\cdot^-,Na^+$ in THF. The results are summarized in Table IV. The addition of HMPA converts the tight $NN\cdot$,Na^+ ion pairs into the loose ones. The dissociation of ion pairs into free ions is still low, even after the addition of HMPA; nevertheless, the reactivity $(2k_2K_1)$

Table IV. Kinetics of C-C Fission in THF + HMPA; Counterion Na^+

Run	Temp, °C	$[NN\cdot^-] \times 10^3$, M	$[NN] \times 10^3$, M	$[HMPA] \times 10^3$, M	$R_0 \times 10^6$, M/sec
4	24.5	1.21	10.5	0.0	4.6
51	25	1.22	10.6	1.6	4.2
52	25	1.22	10.9	2.5	3.6
53	24.5	1.15	10.5	3.3	3.1
55	25	1.18	10.4	12.4	1.8

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is greatly reduced. The results support, therefore, the idea that the tight ion pairs are more reactive than the loose ones.

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Paramagnetic Resonance Study of Liquids during Photolysis. XIII. Uracil and Derivatives[1,2]

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Abstract: Paramagnetic resonance spectra of short-lived free radicals made from uracil, uracil-6-carboxylic acid (orotic acid), uracil-5-carboxylic acid (isoorotic acid), and thymine have been studied upon photolysis with uv light of solutions near room temperature. When these pyrimidines are photolyzed in hydrogen-donating solvents (isopropyl alcohol, ethyl alcohol, and *p*-dioxane), they abstract a hydrogen from the solvent, and two different radicals are observed due to the addition of hydrogen to the pyrimidine and to the loss of hydrogen from the solvent molecule. When the pyrimidines are photolyzed in aqueous solutions containing hydrogen peroxide, $\cdot OH$ is formed which then produces radicals from the pyrimidines by addition. The spectra and chemical behavior of the radicals in many cases depend upon the pH, and dynamic exchange phenomena are observed. Hyperfine couplings and g values are given, and the structure of the radicals is discussed.

We have been studying the paramagnetic resonance spectra of short-lived free radicals made during the course of photolysis of liquids with uv light. In a preceding paper[2] we reported on radicals derived from heterocyclic compounds containing nitrogen including alloxan and parabanic acid. In this paper the work has been extended to solutions of the pyrimidine base uracil and certain derivatives including uracil-6-carboxylic acid (orotic acid), uracil-5-carboxylic acid (isoorotic acid), and thymine.

There have been many paramagnetic resonance studies of free radicals formed from pyrimidine bases and related compounds. Most of these studies have been on solids, where the radical life times are longer than in solution. While most have involved ionizing radiation, a few have used uv light to form the radicals. For example, Pershan and coworkers[4] have identified a radical from thymine obtained by uv irradiation of DNA at low temperatures. There have been essentially no paramagnetic resonance investigations of radicals formed from these substances in solution upon uv photolysis.[5] There has, however, been work on short-lived radicals formed in solutions of pyrimidines using the rapid mixing technique.[6]

In the present work, two general methods have been used to prepare radicals by photolysis; the substances of interest have been photolyzed in solvents that are good hydrogen donors, and the substances have been photolyzed in aqueous solutions containing hydrogen peroxide. In the former case the pyrimidine is excited by the uv light and then abstracts hydrogen from the solvent to form a pair of short-lived radicals. The behavior is parallel to the photoinduced reduction of ketones[7] and of formic acid and its esters[8] in hydrogen-donating solvents. We have used isopropyl alcohol, ethyl alcohol, and *p*-dioxane as solvents. The spectra of the radicals formed by abstraction of hydrogen from these substances are very well known.[7,9] Forming a pair of radicals sometimes has the disadvantage that lines in their spectra overlap, but there is a distinct advantage in seeing both spectra in that it confirms that a primary process is the transfer of a hydrogen from the solvent to the pyrimidine. Photolysis of solutions containing hydrogen peroxide gives $\cdot OH$, which in turn may react with the pyrimidine. This approach is similar to the rapid mixing method[6] where the $\cdot OH$ is generated chemically. This radical may abstract hydrogen or may add to a double bond. The selectivity of $\cdot OH$ formed photolytically may be different from that of $\cdot OH$ formed by rapid mixing. This may, in part, be due to the nature of the media. For example, photolytically generated $\cdot OH$ abstracts hydrogen from allyl alcohol,[9] while $\cdot OH$ generated in rapid mixing experiments adds to the double bond.[10]

In our earlier studies of photolytically generated radicals from simple organic substances, we have usually been able to easily and unambiguously identify the radicals. Members of a given class of compounds, say,

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(2) Part XII: J. K. Dohrmann, R. Livingston, and H. Zeldes, *J. Amer. Chem. Soc.*, **93**, 3343 (1971).

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