

Reaction Intermediates in the Radiolysis of Alkyl Halides at 77°K¹

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Abstract: For the purpose of investigating reaction intermediates in the radiolysis of alkyl halides, the spectra of C₂H₅I, n-C₄H₉I, i-C₄H₉I, n-C₅H₁₁I, n-C₄H₉Br, and n-C₄H₉Cl in the glassy state at 80°K have been determined in the 3000–8000-Å region immediately after exposure to γ-ray irradiation. The iodides all show essentially the same four absorption peaks. The growth and decay characteristics of the peaks indicate that they represent four different species and that there are short-lived precursors which are not seen. The fact that the bromide and chloride show different spectra than the iodides indicates that the absorption peaks are due to halogen-containing species. The 4050-Å peak, which grows with a first-order half-life following irradiation, is tentatively assigned to I₂⁻, and the 7500-Å peak to (RI)_n⁺. Other growth and decay patterns occurring as a function of time, bleaching, and temperature are discussed and compared with information on trapped radicals obtained from esr measurements.

The work reported below has been done to determine what trapped metastable intermediates can be identified by their optical spectra in a series of γ-irradiated alkyl halides, and to compare the thermal and photoannealing properties of these intermediates with those of the free radicals observable by esr spectra.^{2,3}

Experimental Section

Alkyl halides (Eastman White Label) were further purified by shaking with alumina and by preparative gas chromatography. Samples for irradiation and spectral examination were distilled through P₂O₅ into round, 5-mm i.d., high-purity silica (Suprasil) tubes, after degassing under vacuum. After rapid cooling in liquid nitrogen to convert the sample to the glassy form, the sample tube was placed in a brass holder with 1-mm slit apertures, by means of which it was placed in a cryostat fitted to a Cary 14 recording spectrophotometer. The cryostat⁴ allowed temperature control down to 80°K. For lower temperatures a Pyrex dewar with square faces in the optical path was used. Passing helium gas through the liquid nitrogen lowered its boiling temperature, thus avoiding "noise" from N₂ bubbles in the light beam and allowing the cell to be maintained at 69°K.

Round sample tubes were used because we were not able to prepare uncracked alkyl halide glasses in square tubes. To ensure that the narrow analyzing beam passed through the maximum path length of the round sample tubes, the cryostat was adjusted laterally across the path of the analyzing beam to obtain the position of minimum scattering each time a new tube was inserted for measurement. Reproducibility of ±10% was obtained for identical samples when examined in different tubes.

γ Irradiations were made under liquid nitrogen at 77°K with a Co⁶⁰ source giving a dose rate of 2 × 10¹⁸ ev g⁻¹ min⁻¹ to the samples.

Photobleaching experiments were done using the infrared source of the Cary 14 spectrophotometer and glass filteres. To avoid heating the samples, exposures were made in 15-sec increments with at least 60 sec between successive exposures.

(1) This work has been supported in part by U. S. Atomic Energy Commission Contract AT(11-1)-32 and by the W. F. Vilas Trust of the University of Wisconsin.

(2) Earlier investigations using esr to study the identity and reactions of free radicals produced from alkyl halides in solid matrices by radiolysis or photolysis include: (a) P. B. Ayscough and C. Thompson, *Trans. Faraday Soc.*, **59**, 1477 (1962); (b) H. Fenrick, S. V. Filseth, A. O. Hanson, and J. E. Willard, *J. Am. Chem. Soc.*, **85**, 3731 (1963); (c) R. F. C. Claridge and J. E. Willard, *ibid.*, **87**, 4992 (1965); (d) H. W. Fenrick and J. E. Willard, *ibid.*, **88**, 412 (1966).

(3) Hamill and co-workers have pioneered the use of optical absorption spectra to study trapped intermediates in solutions of alkyl iodides in alkane glasses: (a) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussion Faraday Soc.*, **36**, 169 (1963); (b) E. P. Bertin and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 1301 (1964).

(4) T. O. Jones and J. E. Willard, *Rev. Sci. Instr.*, **27**, 1037 (1956).

Samples for esr measurements were sealed in 3-mm i.d. Suprasil tubes and examined with a Varian spectrometer.

Negligible optical absorption was induced in the Suprasil absorption cells by the γ-doses used. Condensation of moisture on the faces of the cells was avoided by use of a drybox for transfers from the irradiation dewar to the spectrophotometer cryostat.

Results and Discussion

Nature of Optical Absorption Spectra. Table I shows the absorption maxima found in alkyl halide samples at 80°K 5 min after a 1-min exposure to a dose of 2 × 10¹⁸ ev g⁻¹ min⁻¹.

Table I. Absorption Maxima in γ-Irradiated Alkyl Halide Glasses at 80°K

	Absorption		maxima, Å	
Ethyl iodide	7500	5250	4050	<3500
n-Butyl iodide	7500	5200	4050	<3500
Isobutyl iodide	7600	5175	4050	<3500
n-Amyl iodide	7600	5200	4050	<3500
n-Butyl bromide		6000	3750	
n-Butyl chloride			None	

The similarity of the maxima for the four iodides, the different spectrum for butyl bromide, and the absence of absorption by the butyl chloride indicate that the nature of the halogen rather than the nature of the alkyl group determines the character of these spectra. These absorption peaks are all unstable at room temperature. The only remaining absorption after melting the irradiated alkyl iodide glasses is a small peak at 4400 Å corresponding to the RI·I₂ complex.

Figure 1 shows the spectrum of n-C₄H₉I glass before irradiation, immediately following γ irradiation, after successive 20-min periods of standing in the dark at 80°K, and after photobleaching. The facts that the 4050-Å peak grows on standing while the 5200- and 7500-Å peaks do not change, and that the 7500-Å peak is photobleached while the 4050- 5200-Å peaks are apparently unchanged,⁵ indicate that these three

(5) The decrease in height of the 4050- and 5200-Å peaks on photobleaching appears to be due to a disappearance of the low wavelength tail of the 7500-Å absorption. The photobleaching shown in curve 5 of Figure 1 was caused by a total of 5-min exposure to light from the Cary infrared source through Corning filters 1-69 and 2-64 (6800-10,000 Å) with incident dose on the cell of approximately 5 × 10¹⁶ photons sec⁻¹.

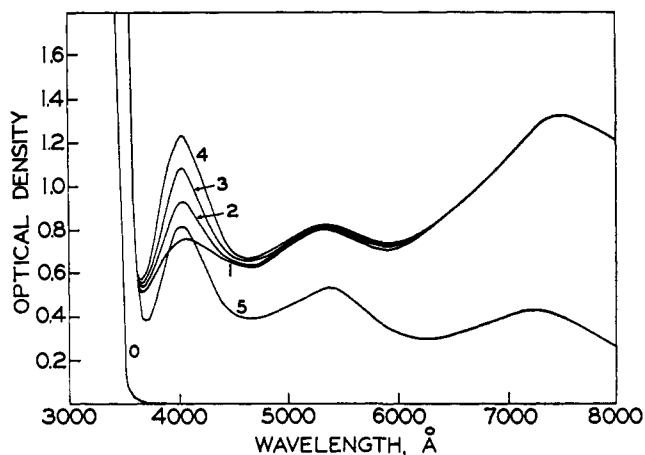


Figure 1. Spectra of $n\text{-C}_4\text{H}_9\text{I}$ glass: (0) before irradiation; (1) at 80°K immediately after 1-min irradiation at 77°K ; (2-4) after 20, 40, and 66 min, respectively, at 80°K ; (5) after bleaching with visible light.

peaks represent three different species. The sharp rise in absorption at 3500 \AA , which does not change with standing or illumination, represents a fourth species.

Esr examination of the γ -irradiated glassy $n\text{-C}_4\text{H}_9\text{I}$ in this and previous work^{2a,b} shows a signal attributable to the n -butyl radical. These radicals are not readily removed by illumination with visible light (a few per cent decay was caused by illumination which removed 50% of the 7500-\AA peak). They do not grow in concentration on standing following irradiation, as do the 4050 and 5200 optical peaks. They must, therefore, be different species from those represented by the optical peaks.

The behavior of the ethyl iodide spectrum differed from that of n -butyl iodide in that the 5250-\AA peak grew with time of standing at 80°K after irradiation (Figure 2).

Changes in the spectrum of irradiated $i\text{-C}_4\text{H}_9\text{I}$ glass on warming from 80°K through several stages to 143°K , above which it crystallized, are shown in Figure 3. The most notable differences between these changes with increasing temperature and those shown in Figure 2 and Figure 3 (lines 1 and 2) for standing for 40 min at 80°K are the growth of the broad peak at 3750 \AA and the appearance of a weak peak at 5800 \AA , following decay of the 5200- and 7600-\AA peaks at 138°K .

Table II summarizes the approximate temperatures at which reactions affecting the different metastable species occur rapidly enough to be observable over a 5-min period. Another type of indication as to the relative stability of the species responsible for the 7500-\AA peak in ethyl iodide and the C_2H_5 radicals observable by esr is that the intense blue color of γ -irradiated $\text{C}_2\text{H}_5\text{I}$ glass fades very little during a year of standing at 77°K , while the esr signal decreases to 10^{-3} of its initial value.

Bleaching in the wavelength range of $4900\text{--}5300\text{ \AA}$ (Baird Atomic interference filter I. F. 41998 and Corning filter 1-69, $\sim 2 \times 10^{16}$ photons sec^{-1}) and in the wavelength range $4000\text{--}4250\text{ \AA}$ (Baird Atomic interference filter I. F. 71913B and Corning filter 1-69, $\sim 1 \times 10^{16}$ photons sec^{-1}) for 30 min caused a decrease of the 7500-\AA absorption. This is believed to be due to absorption by the species with λ_{max} of 7500 \AA , in the region of its low wavelength tail, since the optical density ascribable to the species with λ_{max} at 4050 and 5200 \AA did not appear to be appreciably changed.

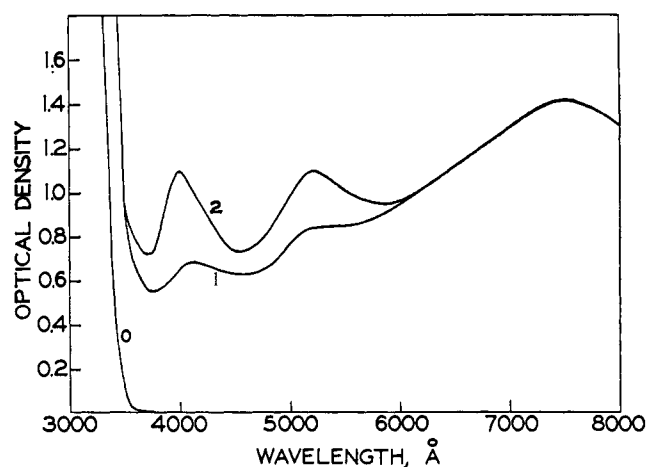


Figure 2. Spectra of $\text{C}_2\text{H}_5\text{I}$ glass: (0) at 77°K before irradiation; (1) at 80°K immediately after 1-min γ irradiation at 77°K ; (2) after 40 min at 80°K .

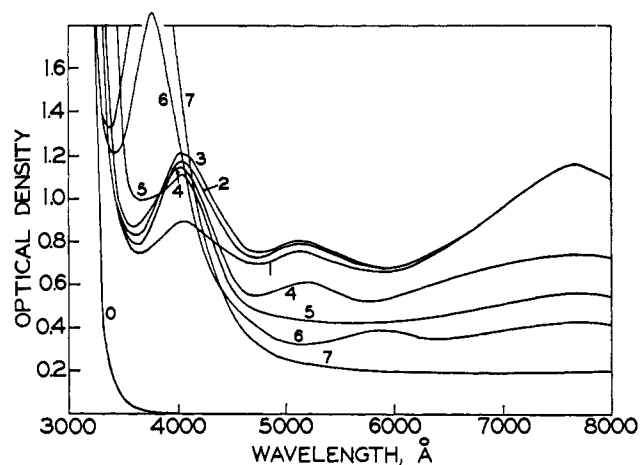


Figure 3. Spectra of $i\text{-C}_4\text{H}_9\text{I}$ glass: (0) at 77°K before irradiation; (1) at 80°K immediately after 1-min γ irradiation at 77°K ; (2) after 40 min at 80°K ; (3-7) immediately after successive warmings to 120 , 132 , 135 , 138 , and 143°K , respectively.

Identification of Species. Convincing evidence^{2c} for the occurrence of the reaction $e^- + \text{RX} \rightarrow \text{R} + \text{X}^-$ (and presumably also $e^- + \text{RX} \rightarrow \text{RX}^-$) in organic glasses containing alkyl halides leads to the

Table II. Approximate Temperatures of Rapid Change of Spectra Produced in Alkyl Iodide Glasses by γ Irradiation at 77°K

	Temp, $^\circ\text{K}$			
	$\text{C}_2\text{H}_5\text{I}$	$n\text{-C}_4\text{H}_9\text{I}$	$i\text{-C}_4\text{H}_9\text{I}$	$n\text{-C}_8\text{H}_{17}\text{I}$
Decay at 7500 \AA	103	110	130	132
Decay of esr radical spectra ^{2b}	100	106	...	118
Decay at 5200 \AA	107	115	132	135
Decay at 4050 \AA	108	...	132	135
Growth at 3700 \AA	104	...	132	135
Growth at 5800 \AA	108	...	130	135
Decay at 5800 \AA	114	...	143	140
Crystallization	123	...	145	154
Melting point	165	170	179	187

conclusion that one or more of the absorption peaks from the alkyl iodide glass must be due to I^- , RI^- , or complexes of these species. A peak at 3950 \AA

in γ -irradiated solutions of methyl iodide in 3-methylpentane glass, which corresponds to the 4050-A peak in the present work, has been attributed by Hamill and co-workers³ to I^- , because the photon energy corresponds to the ionization potential of gaseous I^- ,⁶ and because the peak is enhanced by additives which stabilize positive charge and decreased by those which readily capture electrons. Investigations of the radiolysis of alkyl halides in 3-methylpentane and 2-methylpentane glasses at 77°K in our laboratory⁷ confirm the fact that the peak must be due to a species with negative charge but show that, as in the present work, it is produced by growth from a precursor following irradiation. There does not appear to be any way in which I^- could grow in the system following irradiation unless it were by the reaction $e^- + RI \rightarrow R + I^-$, and esr examination has failed to show either the presence of e^- ⁸ or the growth of radicals following irradiation. It is probable that those electrons produced by the ionizing radiation which do not immediately return to the parent positive ion all form either I^- or RI^- and that one of these is the precursor of the species which absorbs at 4050 A.

The growth of the 4050-A peak in glassy C_2H_5I was examined at a series of temperatures from 69 to 102°K by plotting $\log(OD_{max} - OD_t)$ vs. time. These plots gave straight lines indicating a first-order mechanism with half-lives (Table III) ranging from 25 to 113 min and an apparent activation energy of 0.6 kcal mole⁻¹. Consistent with the first-order plots, the half-life was not significantly changed by a threefold change in radiation dose. The first-order growth implies that the species responsible for the absorption is formed by reaction of the precursor with the solvent or with an intermediate or stable product born in the same spur as the precursor. The low activation energy argues against diffusion being required, unless diffusion within the disorganized region of the spur is relatively easy. Reactions to be considered include: (1) rearrangement of the solvent to allow I^- or RI^- to form an absorbing complex with an RI molecule; (2) reaction of I^- or RI^- with an I atom, I_2 molecule, or HI molecule formed in very close proximity.

Table III. Half-Lives for Growth of the 4050-A Peak in γ -Irradiated Ethyl Iodide as a Function of Temperature and Dose

Dose, ev g ⁻¹ × 10 ⁻¹⁸	Temp, °K	Half-life, min	OD _{max} 4050 A
2	102	25	0.43
2	98	25	0.48
2	92	36	0.45
2	91	48	0.48
2	89	48	0.43
2	83	55	0.46
1	81	70	0.22
3	81	65	0.73
2	69	113	0.48

(6) R. S. Berry, C. W. Reimann, and G. N. Spokes, *J. Chem. Phys.*, **37**, 2278 (1962).

(7) R. F. C. Claridge and J. E. Willard, unpublished.

(8) (a) The single esr line at the free-electron g value^{20,8b} and attributable to a physically trapped electron or a negative ion without spin such as CO_2^{8d} is never observed in systems with even very small amounts of alkyl halide present: (b) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **42**, 2209 (1964); (c) D. W. Skelly, R. G. Hayes, and W. H. Hamill, *J. Chem. Phys.*, **43**, 2795 (1965); (d) P. M. Johnson and A. C. Albrecht, *ibid.*, **44**, 1845 (1966).

With the present information the most probable product to account for the 4050-A peak seems to be I_2^- formed by the reaction $I^- + I \rightarrow I_2^-$, with the absorption being due to the ${}^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ transition. This absorption is accompanied by the absorption in the 7000–7400-A region which remains after photo- or thermal bleaching of the 7500-A band, as seen in Figure 1 and many other experiments, and which can be attributed to the ${}^2\Sigma_u^+ \rightarrow {}^2\Pi_{g1/2}$ transition. The ratio of the absorbancies at the two wavelengths is in plausible agreement with observations on I_2^- in other systems. Flash photolysis of I^- in aqueous,^{9,10} alcoholic,^{9,11} and methyl cyanide⁹ solutions yields absorption bands with maxima at 3700 A ascribed to I_2^- . The action of ionizing radiation on KI crystals at 77°K produces four bands of the V center of the form I_2^- established by electron spin resonance analysis.¹² The strongest bands at 4000 and 8000 A are attributed to the ${}^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ and ${}^2\Sigma_u^+ \rightarrow {}^2\Pi_{g1/2}$ transitions. The absorbancy of the second band is one-half that of the first. Photolysis of I^- in boric acid^{13,14} glasses at room temperature also yields I_2^- with maxima at 3650 and at 6800 A with an absorbancy ratio of 2.5. Although the positions of the maxima are shifted for the different media and different temperatures, the energy separation remains nearly constant and a little greater than that observed in the present work for the separation of the 4050- and 7200-A bands in the alkyl iodide glasses.

If it is assumed that the 4050-A peak is due to I_2^- , with an absorbancy index equal to that in aqueous solution (1.5×10^4 l. mole⁻¹ cm⁻¹),¹³ the estimated $G(I_2^-)$ for glassy C_2H_5I observed in the present work is 1.2, similar to $G(I_2)$ for glassy ethyl iodide as determined by chemical analysis following melting.¹⁵

The spectral peaks from n -butyl bromide have not been investigated in as much detail as those of the iodides. It has, however, been found that the peak at 3750 A grows with time of standing at 80°K as does the 4050-A peak of the iodides. It may, therefore, be tentatively assigned to Br_2^- . Prolonged bleaching of the 6000-A peak with visible light reduces the optical density and shifts the λ_{max} to 5700 A. The weak second absorption of Br_2^- at about 7500 A is probably obscured by the long wavelength tail of this absorption peak.

The fact that no absorption occurs in the 3600–3700-A range, where Cl_2^- might be expected to absorb, in the irradiated n - C_4H_9Cl system is probably accounted for by the fact that Cl atoms form HCl when alkyl chlorides are radiolyzed.¹⁶

There is reason to believe that the 7500-A peak is due to a positively charged species. In solutions of alkyl halides in 3-methylpentane glass at 77°K, the peak at this wavelength grows following irradiation,⁷ in parallel with the decay of a peak at 4400 A. The peak at 4400

(9) F. H. C. Edgecombe and R. W. G. Norrish, *Proc. Roy. Soc. (London)*, **A253**, 154 (1959).

(10) L. I. Grossweiner and M. S. Matheson, *J. Chem. Phys.*, **23**, 2443 (1955).

(11) G. Dobson and L. I. Grossweiner, *Radiation Res.*, **23**, 290 (1964).

(12) C. J. Delbecq, W. Hayes, and P. H. Yuster, *Phys. Rev.*, **121**, 1043 (1961).

(13) A. Zaliouk-Gitler and A. Treinin, *J. Chem. Phys.*, **42**, 2019 (1965).

(14) T. Feldmann and A. Treinin, *ibid.*, **39**, 1352 (1963).

(15) E. O. Hornig and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 2429 (1957).

(16) H. L. Benson, Jr., and J. E. Willard, *ibid.*, **83**, 4672 (1961).

A is enhanced by additives such as CCl_4 , which tend to stabilize electrons, and reduced by alkenes, which trap positive charges. It has been proposed^{3b,7} that the 4400-A peak may be due to RI^+ , and the 7500-A peak to $(\text{RI})_n^+$ resulting from solvation of the monomer, or to R_2I^+ resulting from an ion-molecule reaction of the type $\text{RI}^+ + \text{RI} \rightarrow \text{R}_2\text{I}^+ + \text{I}$, such as has been observed in the gas phase.¹⁷ If the latter species exist, it is plausible that in pure alkyl iodides they would be formed from the RI^+ so rapidly that the 4400-A peak would not be observed.

The 5200-A peak in $\text{C}_2\text{H}_5\text{I}$ glass grows following irradiation, in parallel with the growth of the 4050-A peak, whereas in $n\text{-C}_4\text{H}_9\text{I}$ it is present immediately after irradiation and remains constant while the 4050-A peak grows. It does not appear to be due to I_2 or an $\text{RI}\cdot\text{I}_2$ complex, since iodine dissolved in $\text{C}_2\text{H}_5\text{I}$ shows one absorption peak, with the maximum at 4800 Å at 298°K and at 4400 Å at 77°K. It is unlikely that an $\text{RI}\cdot\text{I}$ complex is responsible for the 5200-A absorption, since photolysis at 2500 Å of alkyl iodide glasses or of dilute alkyl iodides in hydrocarbon glasses does not

(17) H. A. Gillis, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 17 (1961).

yield a peak in this region. A $\text{C}_2\text{H}_5\text{I}\cdot\text{I}$ complex in liquid ethyl iodide at 298°K has been reported to have λ_{max} at 4900 Å.¹⁸ By analogy to the $\text{RI}\cdot\text{I}_2$ peak, this peak may be shifted to a lower wavelength at 77°K. The fact that the 5200-A peak grows in some systems following irradiation, and its relatively high stability, are consistent with some type of complex formation. Since $\text{RI}\cdot\text{I}_2$ and $\text{RI}\cdot\text{I}$ appear to be eliminated, a charged complex (for example, $\text{C}_2\text{H}_5\text{I}\cdot\text{I}^-$) seems probable.

It is probable that a complex or complexes involving HI are responsible for the absorption in the 3500-A region which is induced in alkyl halide glasses by γ radiation, and which increases and spreads to higher wavelengths on warming. HI is known to be formed in the radiolysis of glassy $\text{C}_2\text{H}_5\text{I}$ and it has been shown that solutions of HI in $\text{C}_2\text{H}_5\text{I}$ in the liquid at 195°K and the glass at 80°K show intense absorption in the 3500–4000-A region,¹⁹ the position of the maxima depending on the relative amount of I_2 present.

(18) T. A. Gover and G. Porter, *Proc. Roy. Soc. (London)*, **A262**, 476 (1961).

(19) (a) T. O. Jones, R. H. Luebke, Jr., J. R. Wilson, and J. E. Willard, *J. Phys. Chem.*, **62**, 9 (1958); (b) H. J. Arnikaar and J. E. Willard, unpublished.

Spectroscopic Studies of Keto–Enol Equilibria.

IX. N^{15} -Substituted Anilides^{1,2}

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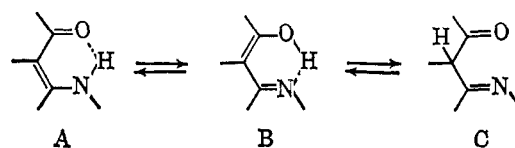
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Abstract: Proton magnetic resonance (pmr) spectroscopy was used to determine the keto–enol equilibria as a function of solvent and temperature in the Schiff bases derived from the N^{15} -substituted anilines and the following aldehydes and ketones: benzoylacetone, 2-acetyldimedone, salicylaldehyde, 2-hydroxyacetophenone, 2-hydroxy-1-naphthaldehyde, and 1-hydroxy-2-acetonaphthone. The ultraviolet spectra of a number of these Schiff bases were recorded and, with the aid of the pmr data, the ultraviolet extinction coefficients were computed for the tautomers of each base. The values of the extinction coefficients indicated that the pmr and ultraviolet spectra were measuring the same phenomenon.

In a previous report³ concerned with the keto–enol equilibria in Schiff bases derived from N^{15} -methylamine and several carbonyl compounds, it was shown that intramolecular proton exchange between the oxygen and nitrogen is rapid. The observed spin coupling therefore provides a good measure of the residence time of the proton on nitrogen. This technique has now been extended to Schiff bases derived from N^{15} -aniline to determine the effect of the N-phenyl group upon the keto–enol equilibria. Some studies on the basicities of aliphatic Schiff base anilides have appeared, but the results are ambiguous.⁴

- (1) Part VIII: G. O. Dudek, *J. Org. Chem.*, **30**, 548 (1965).
- (2) Part of the work on the phenols has appeared previously: G. Dudek and E. P. Dudek, *Chem. Comm.*, 464 (1965).
- (3) G. O. Dudek and E. P. Dudek, *J. Am. Chem. Soc.*, **86**, 4283 (1964).
- (4) D. F. Martin, G. A. Janusonis, and B. B. Martin, *ibid.*, **83**, 73 (1961).

The proton magnetic resonance (pmr) spectra of the N^{15} -anilide derivatives have been recorded in several solvents as a function of temperature. From the measured values of the N^{15} -H spin coupling, the relative amounts of the three possible tautomers have been



determined for each Schiff base.⁵ The ultraviolet spectra of the Schiff bases were obtained, and with the

- (5) Although C is a possible tautomer, there is no evidence for the presence of any detectable amount of this nonconjugated species in the pmr spectra of the N^{15} -aniline Schiff bases. Similarly, in all our previous studies of Schiff bases, this tautomer has not been observed.^{3,6}
- (6) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **84**, 2691 (1962).