tive stability of the $ArNO_2H\cdot$ type complex is a function of the charge density on the nitro group so that the stability of the complex would be expected to decrease for larger aromatic systems. The proposed kinetic model is in excellent agreement with the observed dependence of the esr signal amplitude on acid concentration, light intensity, and time. The photochemical changes induced in the system account for the observed changes in conductivity assuming that the mobile hole $D^+$ is the charge carrier. This result is discussed at some length in the paper describing our electrical measurements.[11] The correspondence between the time dependence and thermal behavior of the esr signal and conductivity lend further support to this analysis. The concept of acid–base reactions with the photoexcited state species of a weak charge transfer complex is a new and useful concept and can lead to materials with novel electrical properties.

# Electron Spin Resonance Study of Pyrolysis and Photolysis of 2-Iodoacetic Acid and 2-Iodoacetamide

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**Abstract:** Using rare-gas matrix isolation techniques, esr spectra of the pyrolyzates and photolyzates of 2-iodoacetic acid and 2-iodoacetamide were examined. The results can be summarized as follows. The primary radicals

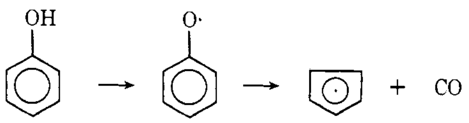
$$\mathrm{ICH_2COOH} \xrightarrow{\Delta} \mathrm{H_2\dot{C}COOH} \xrightarrow{\Delta} \mathrm{CH_3} + \mathrm{CO_2}$$

$$\mathrm{H_2\dot{C}COOH} \xrightarrow{h\nu} 2\mathrm{H\dot{C}O} + \dot{\mathrm{H}}$$

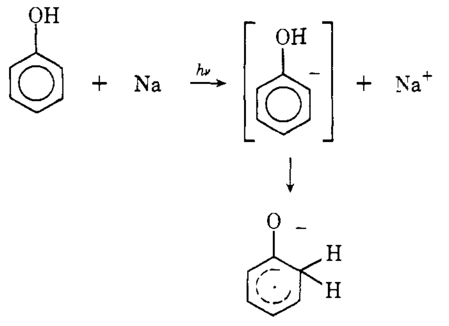
$$\mathrm{ICH_2CONH_2} \xrightarrow{\Delta} \mathrm{H_2\dot{C}CONH_2} \xrightarrow[\text{or } h\nu]{\Delta} \mathrm{H_2C{=}C{=}O} + \dot{\mathrm{N}}\mathrm{H_2}$$

(the carboxymethyl and the carbamylmethyl radicals) were detected only in low-temperature (300–400°) pyrolysis. The direct photolysis of the iodides produced only the final products.

During the course of our study of substituted phenyl radicals, it became apparent that the 1–3 intramolecular hydrogen transfer occurs quite readily in the case of 2-hydroxyphenyl radicals.[1] The rearrangement which occurs when the precursor *o*-iodophenol is pyrolyzed at ~500°, eventually yields the cyclopentadienyl radicals as shown below.



Almost an identical hydrogen transfer was observed when the phenol anion radical was generated within an argon matrix by the photoelectron transfer technique.[2]



The acidity of the phenolic hydrogen must be the major driving force toward such rearrangements.

In order to examine the generality of the process we studied the pyrolysis and photolysis of 2-iodoacetic acid and 2-iodoacetamide using the esr matrix isolation technique. The carboxymethyl radical $\mathrm{H_2\dot{C}{-}COOH}$ should represent the simplest 1–3 system containing an acidic hydrogen. The result confirmed our expectation that the 1–3 hydrogen occurs readily with $\mathrm{H_2\dot{C}{-}COOH}$ but to a much lesser extent with $\mathrm{H_2\dot{C}{-}CONH_2}$. The experiment also revealed an unexpected photolysis of $\mathrm{H_2\dot{C}{-}COOH}$ which results in the formation of the formyl radicals and atomic hydrogen. This report presents and discusses the spectral evidence obtained from these molecules supporting such rearrangement and decomposition processes.

## Experimental Section

The description of the liquid-helium cryostat and X-band esr spectrometer system which allows the trapping of transient radicals in an inert gas matrix and the observation of their esr spectra has been reported previously.[3] In the case of pyrolysis the precursors (2-iodoacetic acid and 2-iodoacetamide) were passed through a resistively heated quartz tube and then trapped in an argon or neon matrix being formed upon the cold finger, a flat spatula shaped sapphire rod in contact with the liquid helium reservoir. In the case of photolysis an argon matrix containing the precursor was first prepared and then irradiated with uv light through the side quartz window. A high-pressure mercury arc (GE, AH-6) equipped with a Corning 7-54 uv filter was used for this purpose. The

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(1) P. H. Kasai and D. McLeod, Jr., unpublished results.

(2) P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **94**, 6872 (1972).

(3) P. H. Kasai, E. Hedaya, and E. B. Whipple, *ibid.*, **91**, 4364 (1969).

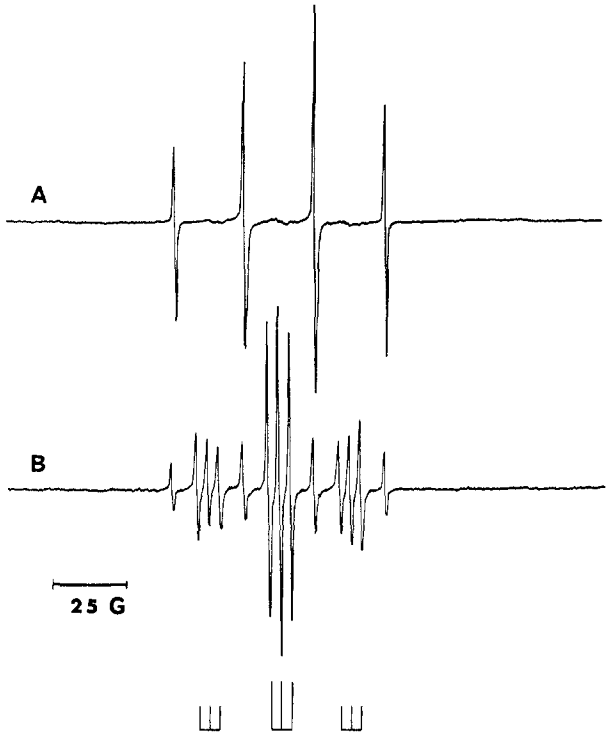


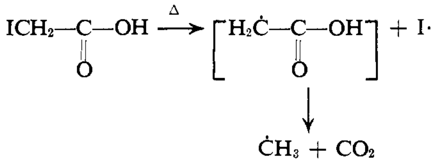
Figure 1. Esr spectra of argon matrices containing the pyrolyzates at 500° of $ICH_2COOH$ (A) and $ICH_2COOD$ (B). The quartet and the triplet of triplets are due to $CH_3$ and $CH_2D$, respectively.

spectrometer frequency locked to the loaded sample cavity was 9.436 GHz.

Both 2-iodoacetic acid and 2-iodoacetamide were obtained from Aldrich Chemical Co., and purified by sublimation prior to usage. Deuterated samples $ICH_2$–COOD and $ICH_2$–$COND_2$ were prepared by refluxing the materials in $D_2O$ followed by evaporation of the solvent.

## Results and Discussions

**Pyrolysis of 2-Iodoacetic Acid.** The esr spectrum of an argon matrix obtained when the pyrolysis was carried out at 500° is shown in Figure 1A. The sharp strong quartet with the spacing between the successive lines of 23.1 G is that of the methyl radicals. These signals are extremely sharp ($\Delta H_{\text{peak-to-peak}} = 0.7$ G) owing to the rotational motion of the radicals within the matrix which averages out the anisotropy of the hyperfine coupling tensors as well as that of the $g$ tensor. The pyrolysis of the deuterated material $ICH_2$–COOD at 500° resulted in the spectrum shown in Figure 1B. The triplet-of-triplet pattern can be readily recognized as that of $\dot{C}H_2D$. The primary process which occurs in the pyrolysis of 2-iodoacetic acid must be the cleavage of the C–I bond. The 1–3 transfer of the hydroxy hydrogen to the $\alpha$-carbon in the carboxymethyl radical must therefore be the mechanism leading to the formation of the methyl radicals.



$$\mathrm{ICH_2{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}OH} \xrightarrow{\Delta} \left[\mathrm{H_2\dot{C}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}OH}\right] + \mathrm{I\cdot}$$
$$\downarrow$$
$$\mathrm{\dot{C}H_3 + CO_2}$$

In order to confirm the formation of the carboxymethyl radical in the primary step of the pyrolysis sequence, we repeated the experiment at 300°. The result obtained from the normal species is shown in Figure 2A. In addition to the quartet due to the methyl radicals, one can recognize the broad triplet pattern spread between the methyl signals. This pattern is assigned to the primary radicals $H_2\dot{C}$–COOH. The isotropic (liquid state) spectrum of $H_2\dot{C}$–COOH has been observed by Smith, *et al.*[4] They reported the isotropic coupling constant to the $\alpha$ proton of 21.3 G. The coupling constant to the hydroxy proton was too small to be resolved. Thus the radical can be viewed essentially as a substituted methyl radical with very little delocalization of the spin density into the carboxyl group. The complexity and the broadness of the signal observed here are primarily due to the anisotropy of the hyperfine coupling tensors to the $\alpha$ protons, and to the partially resolved hyperfine interaction with the hydroxy proton. The lack of prominence in the central component of the triplet is a consequence of the fact that the principal axes of the hyperfine coupling tensors to the $\alpha$ protons are not coincident. That the triplet indeed possesses the expected intensity ratio of 1:2:1 was revealed when the spectrum was recorded in the integrated form (Figure 2B). The magnitudes and the orientations of these hyperfine coupling tensors were assessed approximately from the observed spectrum. The results are given in Table I.[5] Figure

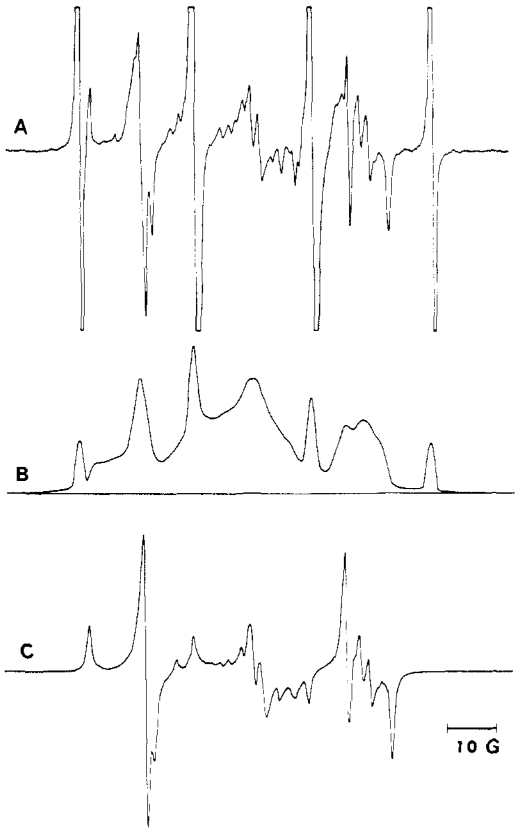


Figure 2. (A) Esr spectrum of an argon matrix containing the pyrolyzate at 300° of $ICH_2COOH$. (B) Its integral. (C) The spectrum of $H_2\dot{C}$–COOH simulated by a computer program based upon the assignment given in Table I.

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[4] P. Smith, J. J. Pearson, P. B. Wood, and T. C. Smith, *J. Chem. Phys.*, 43, 1535 (1965).

[5] These tensors are quite similar to those reported for $H_2CCOOH$ radicals detected in a $\gamma$-irradiated single crystal of malonic acid. For these radicals, however, the plane of the $\dot{C}H_2$ group was found to be perpendicular to the plane of the COOH group, due probably to the crystal field effect: A. Horsfield, J. R. Morton, and P. H. Whiffen, *Mol. Phys.*, 4, 327 (1961).

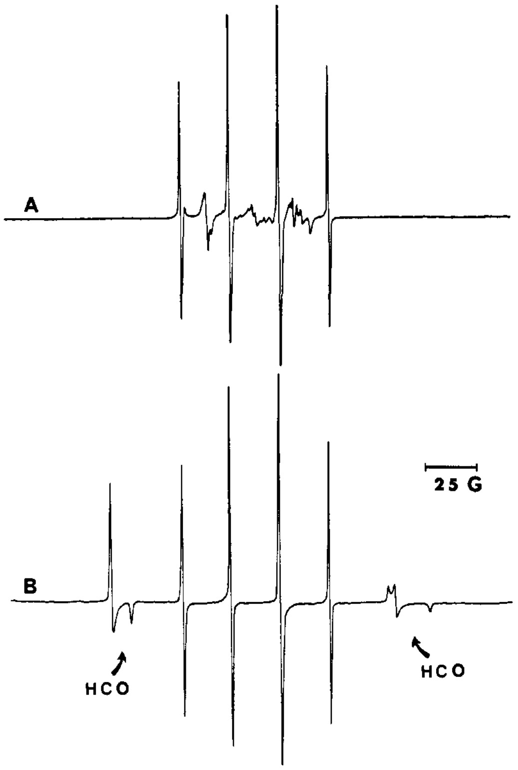

Figure 3. Esr spectra of an argon matrix containing the pyrolyzate at 300° of $ICH_2COOH$ before (A) and after (B) the irradiation of the matrix with uv light (~3650 Å). Note the disappearance of the carboxymethyl radicals and the appearance of the formyl radicals.

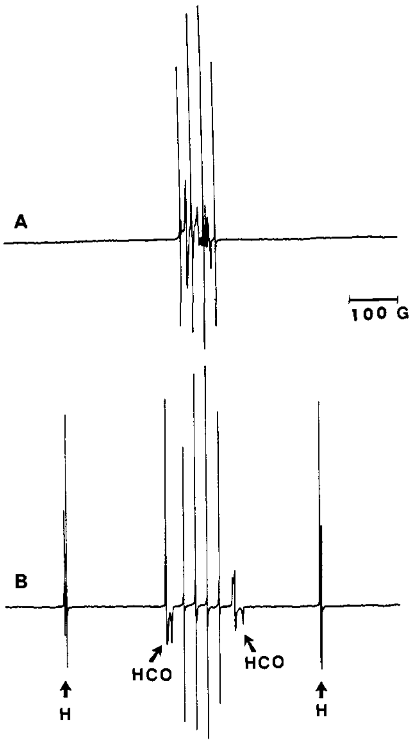

Figure 4. Same as Figure 3 except scanned over 1000 G. Note the appearance of the signals due to hydrogen atoms after the photo-irradiation.

Table I. The $g$ and the Hyperfine Coupling Tensors of $H_2\dot{C}$–COOH Approximately Assessed from the Observed Pattern (Figure 2A)

| | $X$ | $Y$ | $Z$ | $\phi$,[a] deg |
|---|---|---|---|---|
| $g$ | 2.0034 | 2.0041 | 2.0020 | |
| H($\alpha$) | −34.3 | −9.4 | −21.5 | 120 |
| H($\alpha$) | −34.3 | −9.4 | −21.5 | 240 |
| (OH) | 0.0 | 0.0 | 1.7 | 0 |

[a] The $z$ axes are perpendicular to the molecular plane, hence collinear among all the tensors. $\phi$ denotes the angle between the $x$ axes of the $g$ and the principal hyperfine coupling tensors.

2C is a computer simulated spectrum based upon these parameters.[6] The agreement between the observed and computed spectra is reasonable. Both the magnitudes and the orientations of these tensors are exactly those expected for the carboxymethyl radical, the spin density of which is mostly localized at the $\alpha$ carbon.

Interestingly, when an argon matrix containing carboxymethyl radicals was irradiated with uv light (for 10 min), its esr spectrum changed drastically (Figures 3 and 4). The change is characterized by the disappearance of the carboxymethyl radicals, the appearances of a sharp doublet due to H atoms ($A$ = 508 G), and an asymmetric doublet with a separation of about 130 G. The latter doublet was readily identified as that of the formyl radical, $H\dot{C}O$, generated and examined earlier in an argon matrix by Adrian, *et al.*[7]

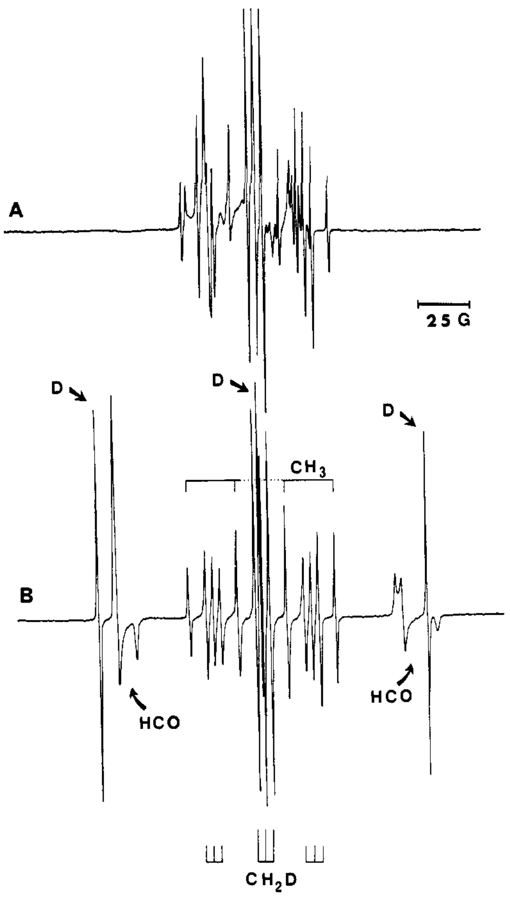

Figure 5. Esr spectra of an argon matrix containing the pyrolysate at 300° of $ICH_2COOD$ before (A) and after (B) the irradiation of the matrix with uv light.

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[6] The simulation was done allowing the forbidden transitions for the two $\alpha$ protons; see P. H. Kasai, *J. Amer. Chem. Soc.*, **94**, 5950 (1972).

[7] F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962).

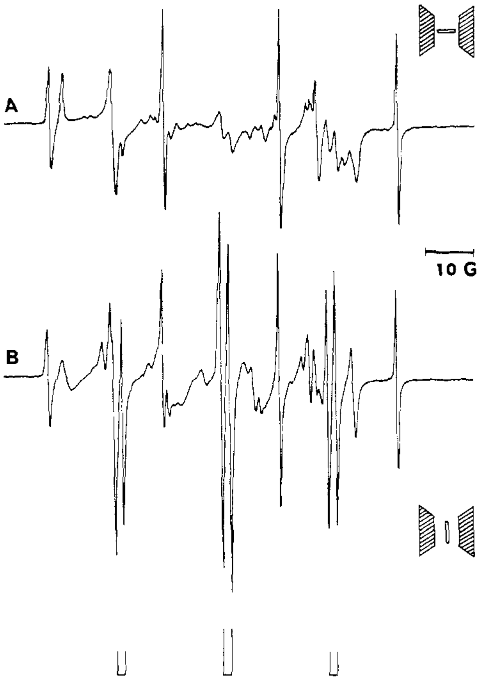
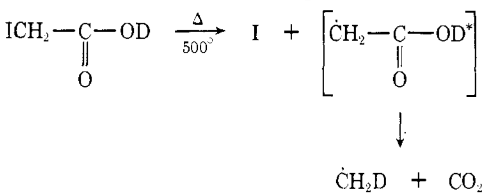


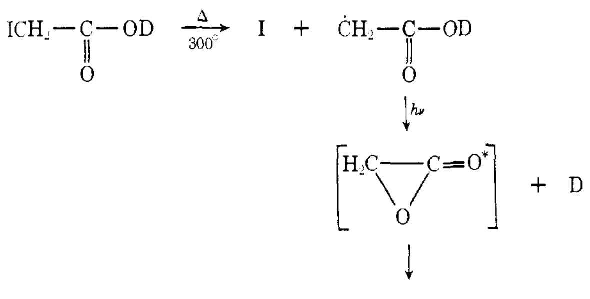
Figure 6. Esr spectra of the carboxymethyl radicals partially oriented in a neon matrix observed with the magnetic field parallel to (A) and perpendicular to (B) the plane of the sapphire rod.

Only a trace amount of signals due to HCO and H atoms appeared when the matrix containing the pyrolyzates at 500° was irradiated with the uv light. Figures 5A and 5B are the spectra obtained, respectively, when the monodeuterated species $ICH_2{-}COOD$ was pyrolyzed at 300°, and when the resulting matrix was subsequently irradiated with the uv light. Because of the overlap with the sharp signals due to $CH_2D$, the signals due to $\dot{C}H_2{-}COOD$ are difficult to recognize (Figure 5A). The spectrum obtained after the photolysis, however, is well resolved, and, as indicated in Figure 5B, the signals can be assigned unambiguously to $\dot{C}H_2D$, $\dot{C}H_3$, $H\dot{C}O$, and D atoms, respectively. The $CH_3$ radicals formed presumably as the result of the back-exchange reactions with the surface adsorbed water of the system. The most intriguing aspect of this trace is the complete absence of the signal attributable to DCO.

We are thus led to summarize the pyrolysis of 2-iodoacetic acid as shown in eq 1 and 2. Here the

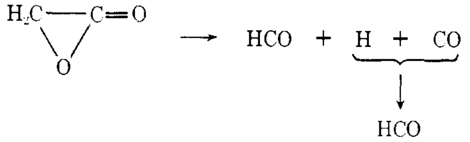


$$\mathrm{ICH_2{-}\underset{\underset{O}{\parallel}}{C}{-}OD} \xrightarrow[500^\circ]{\Delta} \mathrm{I} + \left[\mathrm{\dot{C}H_2{-}\underset{\underset{O}{\parallel}}{C}{-}OD}\right]^{*} \longrightarrow \mathrm{\dot{C}H_2D + CO_2} \qquad (1)$$



$$\mathrm{ICH_2{-}\underset{\underset{O}{\parallel}}{C}{-}OD} \xrightarrow[300^\circ]{\Delta} \mathrm{I} + \mathrm{\dot{C}H_2{-}\underset{\underset{O}{\parallel}}{C}{-}OD} \xrightarrow{h\nu} [\text{H}_2\text{C—C=O}]^{*} + \mathrm{D} \longrightarrow \mathrm{2HC{=}O} \qquad (2)$$

asterisks are used to indicate "hot species." For the lower temperature pyrolysis sequence the one-step intramolecular rearrangement of α-lactone yielding two formyl radicals was proposed instead of the two-step reaction sequence (eq 3).



$$\longrightarrow \mathrm{HCO} + \underbrace{\mathrm{H + CO}}_{\downarrow\ \mathrm{HCO}} \qquad (3)$$

Hydrogen atoms are known to react with CO to produce the formyl radicals.[7] However, if CO was formed, owing to its proximity to the D atom, one would expect the formation of some DCO as well as HCO. As stated earlier, no DCO was detected.

**Carboxymethyl Radicals Oriented in Neon Matrix.** It has been shown that, when the molecules being trapped possess a proper amount of thermal energy relative to the hardness (or softness) of the matrix surface being formed, a matrix can be produced in which the trapped molecules exhibit a strong preference toward a certain orientation.[8] For molecules possessing a well-defined molecular plane, the preferred orientation is the one in which the molecular plane lies parallel to the surface of the sapphire rod. Argon matrices containing the pyrolyzates of 2-iodoacetic acid at 300° showed little indication of such orientation.

Figures 6A and 6B are the esr spectra of a neon matrix containing the pyrolyzates at 300° of 2-iodoacetic acid observed with the magnetic field applied parallel to and perpendicular to the plane of the sapphire rod, respectively. The effect of the preferred orientation is quite conspicuous. Particularly noticeable is the single-crystal-like triplet-of-doublet pattern obtained with the magnetic field perpendicular to the plane of the sapphire rod. These results can be understood easily if we assume (1) that the carboxymethyl radical possesses a well-defined molecular plane and (2) that, in a neon matrix, it preferentially orients itself in the manner described above. Thus the sharp single-crystal-like pattern seen in Figure 6B represents the resonance spectrum of the carboxymethyl radicals when the magnetic field is applied perpendicular to their molecular planes. The triplet pattern with the spacing of 21.1 ± 0.1 G is attributed to the two α protons, and the narrow doublet pattern with the spacing of 1.8 ± 0.1 G is assigned to the hydroxy proton. We should note that the coupling constants to the two α protons need not be identical in magnitude. The simple pattern resolved here indicates, however, that the difference between the spin densities at these protons is indeed very small.

Shown in Figure 7 is the HCO region of the esr spectra obtained after the neon matrix containing the oriented carboxymethyl radicals had been irradiated with uv light. The figure shows that the resulting formyl radicals are also partially oriented. According to the analysis given by Adrian, *et al.*,[7] the portions of the spectrum which become singularly strong when the magnetic field is applied perpendicular to the plane of the sapphire rod correspond to the resonance positions

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(8) P. H. Kasai, W. Weltner, Jr., and E. B. Whipple, *J. Chem. Phys.* 42, 1120 (1965); 44, 2581 (1966).

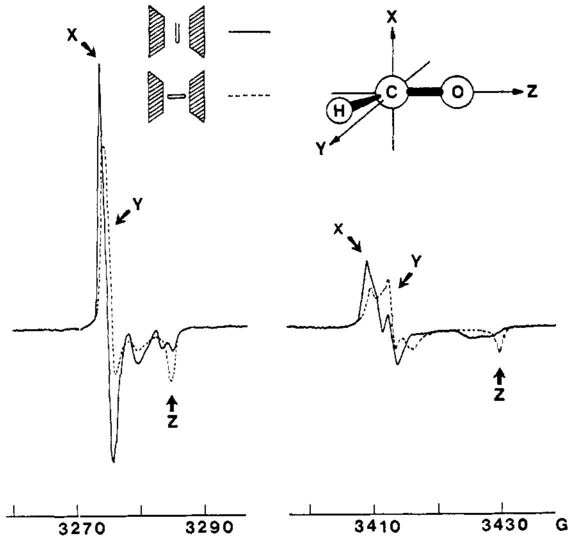


Figure 7. Esr spectra of HCO radicals obtained after the photoirradiation of the neon matrix containing partially oriented carboxymethyl radicals.

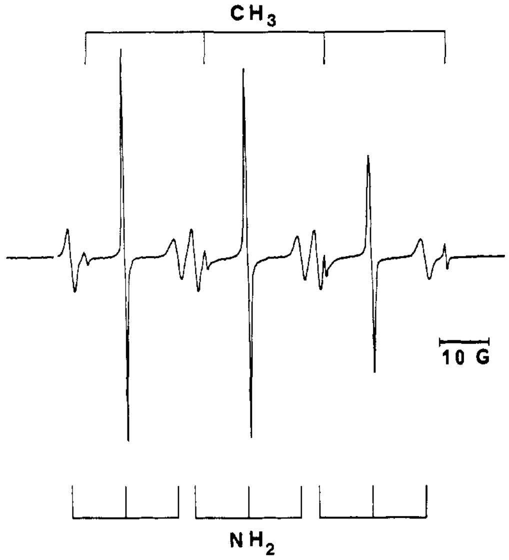


Figure 8. Esr spectrum of an argon matrix containing the pyrolyzate at 600° of $ICH_2CONH_2$.

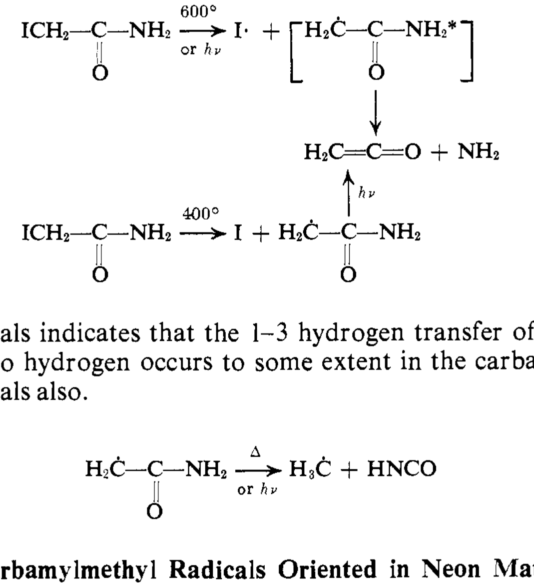
when the field is perpendicular to the molecular plane of HCO. This retention of the orientation effect in a consistent manner through the photolytic process provides an added support for the existence of the $\alpha$-lactone intermediate whose molecular plane would coincide with that of the primary radical $H_2\dot{C}{-}COOH$.

**Photolysis of 2-Iodoacetic Acid.** Irradiation with uv of an argon matrix containing 2-iodoacetic acid resulted in the formation of the methyl radicals, as well as the formyl radicals and hydrogen atoms. It thus appears that the photocleavage of the C–I bond produces a thermally excited primary radical $H_2\dot{C}{-}COOH$. It can then undergo either the spontaneous decomposition yielding $\dot{C}H_3$ and $CO_2$, or, after having been relaxed by the matrix, the second photolysis sequence which yields HCO and H.

**2-Iodoacetamide.** The esr spectrum of an argon matrix obtained when 2-iodoacetmide was pyrolyzed at 600° is shown in Figure 8. The sharp triplet-of-triplet pattern indicated in the figure arises from the amino radicals $NH_2$. The esr spectrum of $NH_2$ radicals isolated in an argon matrix has been reported by Foner, *et al.*[9] Also noted in Figure 8 are the signals due to the methyl radicals. The latter signals, however, are significantly weaker than those of the $NH_2$ radicals. Almost an identical spectrum was obtained when an argon matrix containing 2-iodoacetamide was irradiated with uv light. The spectrum obtained from an argon matrix containing the pyrolyzate of 2-iodoacetamide at 400° is shown in Figure 9A. Here, as the integrated spectrum (the insert) shows, the major fraction of the intensity belongs to the primary carbamylmethyl radical $H_2\dot{C}{-}CONH_2$. As expected, the overall envelop of its spectrum is almost identical with that of $H_2\dot{C}{-}COOH$. The detailed features, however, are more complex because of the more complex hyperfine structures expected from the amino group.

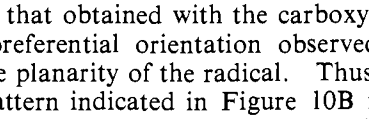
Irradiation with uv light of the matrix containing the carbamylmethyl radicals resulted in the disappearance of the original spectrum and the several-fold increase of the amino radical signals (Figure 9B). Although to a lesser extent, an increase of the methyl radical signal was also noted.

The dominant reaction for the pyrolysis and/or the photolysis of 2-iodoacetamide thus can be summarized as in eq 4. The formation of a small amount of methyl



$$\begin{array}{c} \mathrm{ICH_2{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}NH_2} \xrightarrow[\text{or } h\nu]{600^\circ} \mathrm{I\cdot} + \left[\mathrm{H_2\dot{C}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH_2{}^*}\right] \\ \downarrow \\ \mathrm{H_2C{=}C{=}O + NH_2} \qquad (4) \\ \uparrow h\nu \\ \mathrm{ICH_2{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH_2} \xrightarrow{400^\circ} \mathrm{I} + \mathrm{H_2\dot{C}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH_2} \end{array}$$

radicals indicates that the 1–3 hydrogen transfer of the amino hydrogen occurs to some extent in the carbamyl radicals also.



$$\mathrm{H_2\dot{C}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH_2} \xrightarrow[\text{or } h\nu]{\Delta} \mathrm{H_3\dot{C} + HNCO}$$

**Carbamylmethyl Radicals Oriented in Neon Matrix.** Figures 10A and 10B are the spectra of a neon matrix containing the pyrolyzate at 400° of deuterated 2-iodoacetamide $ICH_2{-}COND_2$ obtained, respectively, with the magnetic field applied parallel to and perpendicular to the plane of the sapphire rod. Although not as pronounced as that obtained with the carboxymethyl radicals, the preferential orientation observed here also supports the planarity of the radical. Thus the triplet-of-triplet pattern indicated in Figure 10B must correspond to the resonance positions when the magnetic field is applied perpendicular to the molecular plane. Only in this orientation the two $\alpha$ protons become truly equivalent, and the large triplet with a spacing of 22 G becomes discernible. The small triplet with a spacing of 1.5 G is ascribed to the $^{14}N$ nucleus in the

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[9] S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, *Phys. Rev. Lett.*, 1, 91 (1958).

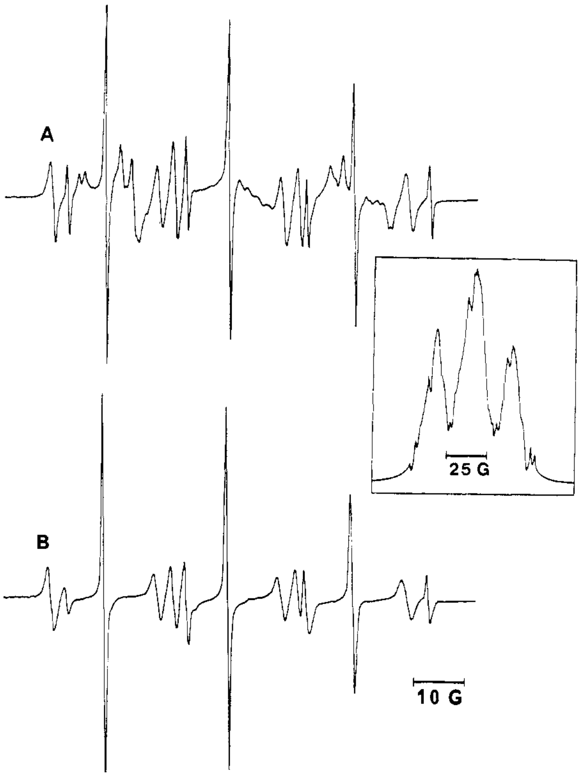


Figure 9. (A) Esr spectrum of an argon matrix containing the pyrolyzate at 400° of $ICH_2CONH_2$. Its integral is shown in the insert. (B) Esr spectrum of the same matrix observed after it had been irradiated with the uv light (spectrometer gain = $^1/_3$).

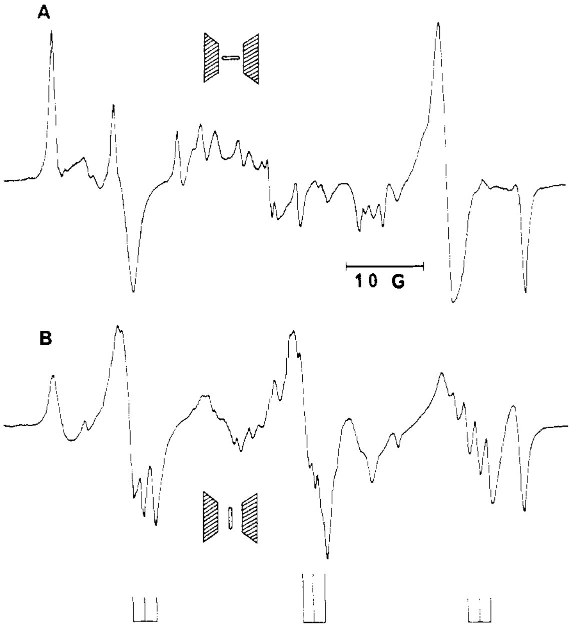


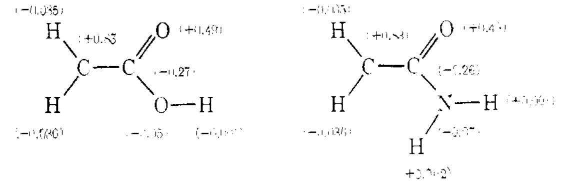
Figure 10. Esr spectra of the carbamylmethyl radicals partially oriented in a neon matrix observed with the magnetic field parallel to (A) and perpendicular to (B) the plane of the sapphire rod.

amino group.[10] It has been well established that, if a radical contains a nitrogen atom, and the LCAO description of its semifilled orbital involves a 2p orbital of the nitrogen but not its 2s orbital, the largest hyperfine interaction with the $^{14}N$ nucleus is observed along the direction parallel to the p orbital, and the coupling constants with the nitrogen nucleus along the two other principal axes are nearly zero.[11] Thus the fact that the hyperfine structure due to the $^{14}N$ nucleus is observed only in the direction indicated in Figure 9B, but not in the signals prominent in Figure 9A, is also consistent with the planar structure of the radical whose unpaired electron can be delocalized over a $\pi$ orbital. The small splitting of 1.5 G, however, indicates a very small spin density (~0.03) at the nitrogen nucleus.

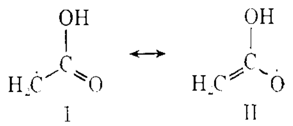
## Summary and Final Remarks

The present study clearly showed that the intramolecular 1-3 transfer of the acidic hydrogen occurs with the carboxymethyl radical. Also discovered in the study is a unique photolysis of the carboxymethyl radical which results in the formation of the formyl radical and the hydrogen atom. As expected, the 1-3 transfer of the amino group hydrogen occurs to a much lesser extent with the carbamylmethyl radical. With this radical the dominant process under pyrolysis or photolysis was found to be the cleavage of the C-N bond resulting in the formation of the amino radicals and presumably the ketene molecules. The much weaker acidity of the hydrogen in the amino group and a weaker strength of the C-N bond relative to the C-O bond would explain the different behavior of this radical.

The large coupling constants (~21-22 G) observed with the $\alpha$ protons of both the carboxymethyl radical and the carbamylmethyl radical suggest that these radicals may be viewed as monosubstituted methyl radicals with very little delocalization of the spin density into the substituent group. Shown below are the spin density distributions among the $2p_\pi$ orbitals of the second row atoms and the hydrogen 1s orbitals of these radicals predicted by INDO molecular orbital calculations.[12] The calculations predict, in an agreement



with the observed results, a large spin density at the $\alpha$ carbon of each radical. They also predict, however, a surprisingly large positive spin density at the oxygen atom of the carbonyl group and a comparatively large negative spin density at the carbon atom of the same



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[10] The isotropic (liquid state) spectrum of $H_2C\text{-}CONH_2$ has been observed by P. Smith and P. B. Wood, *Can. J. Chem.*, 44, 3085 (1966), and also by R. Livingston and H. Zeldes, *J. Chem. Phys.*, 47, 4173 (1967). These authors reported the isotropic coupling constants of 21.3 and 1.8 G for the methylene protons and the nitrogen nucleus, respectively.

[11] See, for example, the result obtained for $H_2C{=}N$ by E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **36**, 1938 (1962), or for $NF_2$ by P. H. Kasai and E. B. Whipple, *Mol. Phys.*, **9**, 497 (1965).

[12] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. Standard bond lengths and angles given in this reference were used for the calculations.

group, indicating the importance of the resonance structure II. The theory thus states that these radicals are more analogous to the allyl radicals than to the methyl radicals, and indicates a danger of conjecturing the electronic nature of this type of radicals in terms of the hyperfine coupling constants to the protons only.

# Extinction Coefficient and Recombination Rate of Benzyl Radicals. I.[1] Photolysis of Sodium Phenylacetate

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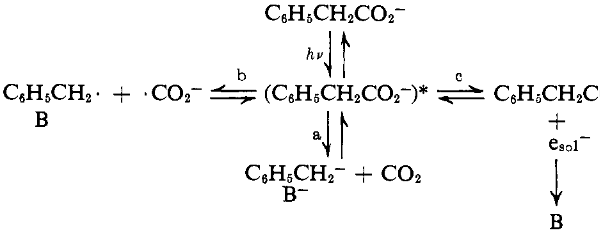
**Abstract:** The photolysis of sodium phenylacetate in methanol at 26° gives the following products ($\Phi$): in the absence of oxygen, $C_6H_5CH_3$ (0.03), $CO_2$ (0.031), $(C_6H_5CH_2)_2$ (0.0007), $C_6H_5CHO$ (<0.0001); in the presence of oxygen, $C_6H_5CH_3$ (<0.0001), $CO_2$ (~0.03), $(C_6H_5CH_2)_2$ (<0.0001), $C_6H_5CHO$ (~0.028). It is proposed that the primary process in methanol yields benzyl anion and carbon dioxide, and that the minor path (<5%) involves benzyl and carboxylate ($\cdot CO_2^-$) radicals. The photolysis of sodium phenylacetate in water yields mostly polymer and carbon dioxide, very little toluene, and some bibenzyl; in flash experiments, transient benzyl radicals and hydrated electrons are detectable; we therefore propose that a photoionization mechanism dominates here. By following the growth and decay of the transients in water, we have been able to compute the extinction coefficient ($\epsilon_B$) of the benzyl radical at 2000 ± 500 $M^{-1}$ cm$^{-1}$ and its recombination rate constant, $2k_R = 8 \times 10^9 M^{-1}$ sec$^{-1}$.

This is one of three studies on the photoproducts and -mechanisms of compounds related to phenylacetic acid.[2] Although the photoprocesses differ, they all involve, to some degree, the benzyl radical (B). Besides working out the details of the decomposition of sodium phenylacetate, we estimate the recombination rate constant $k_R$ as well as a value for the still controversial extinction coefficient, $\epsilon_B$ ($\lambda_{max}$ 318 nm), of B in this paper.



(1)

Of the numerous (>20) photocleavage steps open to a carboxylic acid derivative,[2a] only a few have been observed with the salts to date. Equation 1 outlines the overall photodecarboxylation mechanism for several arylacetates, *e.g.*, 1-naphthylacetate, thymine-1-acetate, or 2-pyridylacetate, although significant photodecomposition may be initiated at sites not involving carboxylate.[3] Concerning the steps of eq 1, the formation of the anion ($B^-$) appears to predominate among mono- and dinitrophenylacetates,[4] the ejection of the solvated electron (step 1b) was noted for the series $C_6H_5(CH_2)_nCOO^-$ ($n$ = 0 to 4),[5] and the homolysis to give B and carboxylate radical anion (step 1b) will be discussed presently. Missing from eq 1 are steps leading to carbon monoxide, which are important in the photolysis of phenylacetic acid and its esters,[2a] or benzyl ketones,[6] but which turn out not to be significant for our salt.

Benzyl is an important species which continues to evoke general interest.[7] This radical and its substituted analogs have been generated by a variety of techniques, among them $\gamma$-radiolysis,[8] pulse radiolysis,[9] electric discharge,[10a] electrolysis,[10b,c] thermolysis,[10d–i] and rad-

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(1) Taken from the Ph.D. thesis of T. O. M., Illinois Institute of Technology, 1970. Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract No. PHYS-13. Financial support from the Federal Water Pollution Control Administration in the form of a fellowship for T. O. M. and on Public Health Service Grants GM7021 and EY-516 is gratefully acknowledged.

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