# Photolysis of Formamides and Acetamides Studied by Electron Spin Resonance[1a]

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**Abstract:** The primary free-radical producing step in the photolysis of formamide is shown to be the formation of H atoms and $CONH_2$ radicals. Photolysis of acetamide produces $CH_3$ and $CONH_2$. Substitution of a methyl group on the nitrogen atom in these compounds does not change the primary step in that C–H and C–C bond scission is observed for N-methylformamide and N-methylacetamide, respectively. The free radicals produced at −196° were identified from their esr absorption spectra. The use of deuterium-labeled samples and generation of free radicals by OH radical attack on the parent molecules were used to help identify the free radicals produced in the photochemical decompositions.

The use of esr spectroscopy to identify the free radicals produced in photochemical decompositions has been employed in a number of reactions. Recently Volman and coworkers have used this technique in elucidating the photochemistry of aliphatic amines,[2a] as well as with some sulfur-containing compounds.[2b] This method was shown to be very useful in solving problems associated with the photodecomposition of nitro and nitroso compounds.[3] In this type of work, photolyses are carried out in rigid matrices, usually at −196°. Under these conditions the resulting esr absorption lines are quite broad; however, the resolution has been sufficiently good to provide unequivocal evidence for the primary steps in the above-mentioned photodecompositions. In this paper we report the results of our esr study of the free radicals produced in the photolysis of formamide, acetamide, and their N-methyl derivatives.

The photolysis of acetamide has been the subject of several studies. In aqueous solution, the photolysis was suggested to lead to $CH_3CO$ and $NH_2$ formation, followed by subsequent decomposition of the acetyl radical.[4] However, in dioxane or hexane solution the primary decomposition has been reported to be nonfree radical in nature but occurs *via* direct formation of $CH_3NH_2$ and CO.[5] Gas-phase photolysis of acetamide has been shown to produce $CH_3$, CO, and $NH_2$.[6] However, at the temperatures required for the gas-phase work any initially formed radicals such as $CONH_2$ and $CH_3CO$ would undergo unimolecular decomposition, and it was not possible to distinguish among the following primary steps.

$$\begin{aligned} CH_3CONH_2 + h\nu &\longrightarrow CH_3CO + NH_2 \\ &\longrightarrow CH_3 + CONH_2 \\ &\longrightarrow CH_3 + CO + NH_2 \end{aligned}$$

In addition to these reactions, direct molecular formation of $CH_3CN$ and $H_2O$ was reported.[6]

In view of the above results, we felt that definitive information on the photochemistry of acetamide might be obtained from the esr absorptions of free radicals produced in these reactions. Acetamide is a particularly interesting molecule to study because at the wavelengths employed ($\lambda < 2500$ Å) a number of reactions are energetically feasible including C–C, C–N, N–H, and C–H bond breakage.

In addition, almost no information is available on the photochemistry of formamide or the N-methyl derivatives of formamide or acetamide. Accordingly, the study was extended to include these molecules. We feel that our results provide direct evidence of the primary steps leading to free-radical production in the photolysis of these compounds.

## Experimental Section

The amides employed were Fisher spectroscopic grade quality Aqueous samples of the amides were prepared of various concentrations ranging from 5 to 30% by weight of the amides. A change in amide concentration caused no observable changes in the esr spectra of the free radicals produced by the photolysis. Dissolved oxygen was removed from the samples by a repeated freezing and pumping technique. Deuterated samples were prepared by simply allowing the amide hydrogens to exchange in $D_2O$ solution for a few hours, then pumping off the $D_2O$–$H_2O$ mixture.[7] This process was repeated three times, resulting in amides which had exchanged essentially all their N–H hydrogens. This was shown to be true *via* nmr analysis. No exchange of the hydrogen bonded to carbon could be observed in any of these compounds in agreement with previous reports.[8]

Samples were frozen to −196° in "Suprasil" quartz sample tubes and irradiated at that temperature. Irradiation of the samples was carried out using a General Electric UA-2 medium pressure mercury lamp. In view of the absorption coefficients of the amides and the experimental technique used, it is estimated that most of the effective radiation was in the wavelength range from 2000 to 2500 Å. After photolysis, the sample was transferred to the esr cavity which was precooled to approximately −185°. Absorptions were recorded using a Varian V-4503 esr spectrometer plus variable-temperature accessory. In many cases, samples were annealed at higher temperatures (up to −100°) and variations in the spectra were noted.

In some experiments free radicals were produced *via* OH radical attack on the parent compounds. In these experiments 2% $H_2O_2$ solutions of the amides were photolyzed with a Pyrex window employed to filter out short-wavelength radiation. Warming of the samples after photolysis produced spectra which we can attribute to OH radical attack on the amides. With the Pyrex window in

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[1] (a) This research was supported by the Public Health Service, Grant No. GM-14110; (b) National Science Foundation Undergraduate Research Participant, Summer 1968.

[2] (a) S. G. Hadley and D. H. Volman, *J. Amer. Chem. Soc.*, **89**, 1053 (1967); (b) D. H. Volman, J. Wolstenholme, and S. G. Hadley, *J. Phys. Chem.*, **71**, 1798 (1967).

[3] B. H. J. Bielski and R. B. Timmons, *ibid.*, **68**, 347 (1964).

[4] D. H. Volman, *J. Amer. Chem. Soc.*, **63**, 2000 (1941).

[5] G. H. Booth and R. G. W. Norrish, *J. Chem. Soc.*, 188 (1952).

[6] B. C. Spall and E. W. R. Steacie, *Proc. Roy. Soc.* (London), **A239**, 1 (1957).

[7] L. H. Piette, J. D. Ray, and R. A. Ogg, *J. Mol. Spectry.*, **2**, 66, (1958).

[8] R. Livingston and H. Zeldes, *J. Chem. Phys.*, **47**, 4173 (1967).

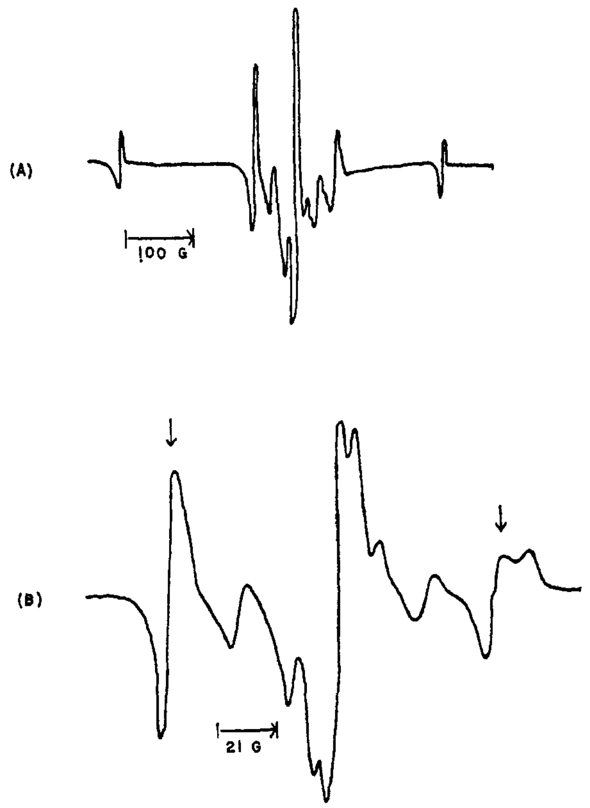

Figure 1. Esr spectra of $HCONH_2$ irradiated at −196° for 1 hr: (A) part of a 1000-G scan showing H atom absorptions; (B) 250-G scan of the central portion, the arrows indicating the CHO radical.

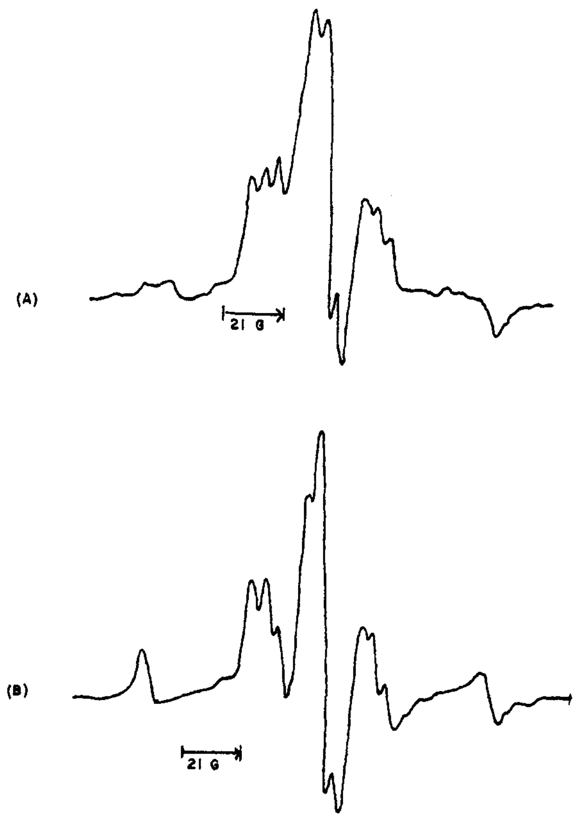

Figure 2. Esr spectra of $HCOND_2$ irradiated at −196°: (A) spectrum obtained after 3-min photolysis; (B) spectrum after 8-min photolysis.

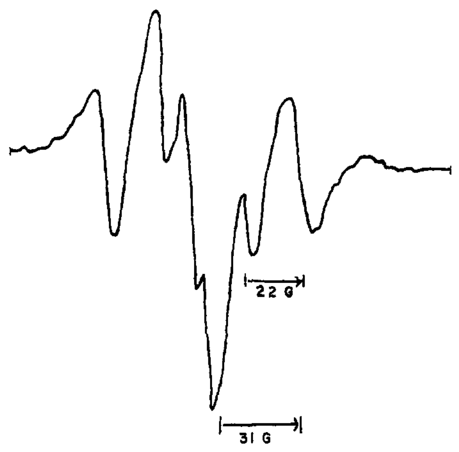

Figure 3. Esr spectrum of the free radical produced by OH radical attack on $HCONH_2$.

place, photolysis of the amide solution alone produced no observable free-radical absorption spectra.

In general, photolysis times were limited to 3 min or less in order to avoid complications from secondary photolysis of free radicals initially produced. However, in some cases, particularly for formamide, much longer times were employed as noted in the next section.

## Results and Discussion

**Formamide.** The esr spectra obtained in the photolysis of formamide in a water matrix is shown in Figure 1A for a 1000-G scan, and the central portion of this spectrum is shown in higher resolution with a 250-G scan in Figure 1B. Both spectra were recorded at −180°. In Figure 1A, the absorption lines separated by 510 G can be attributed only to H-atom absorption. In Figure 1B, the central portion of the esr signal from formamide photolysis reveals a number of interesting factors. The strong signals labeled with the arrows on either end of the spectrum are undoubtedly from the CHO radical. The coupling constant for these lines is 135 G in agreement with that reported by a number of workers.[9] In addition the spectrum is identical with that of the CHO radical reported by Sullivan and Koski[10] including the asymmetry of the high-field line.

In our work we have found that the formyl radical signals are strongly time dependent, increasing in intensity with increasing time of photolysis much faster than the central region of the spectrum. In Figure 1B, it is seen that after 1 hr of photolysis, the formyl radical signals are very prominent. In contrast to this, Figure 2 demonstrates that in the photolysis of $HCOND_2$ the HCO absorption after 3 min of photolysis is very weak, increasing significantly after a total photolysis time of 8 min, while the central absorption remains relatively constant. From these observations we conclude that the HCO radical is being produced by secondary processes and not *via* direct photolysis of formamide.

In order to establish the identity of the central spectra, it was necessary to compare the esr absorption spectra obtained from $HCONH_2$ with that from $HCOND_2$ (Figure 2) as well as the free radical obtained from the attack of OH radicals on $HCONH_2$ (Figure 3). In this analysis we rely heavily on the work of Livingston and Zeldes[8] who obtained high-resolution spectra in solu-

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

[10] P. J. Sullivan and W. S. Koski, *J. Amer. Chem. Soc.*, 85, 384 (1963).

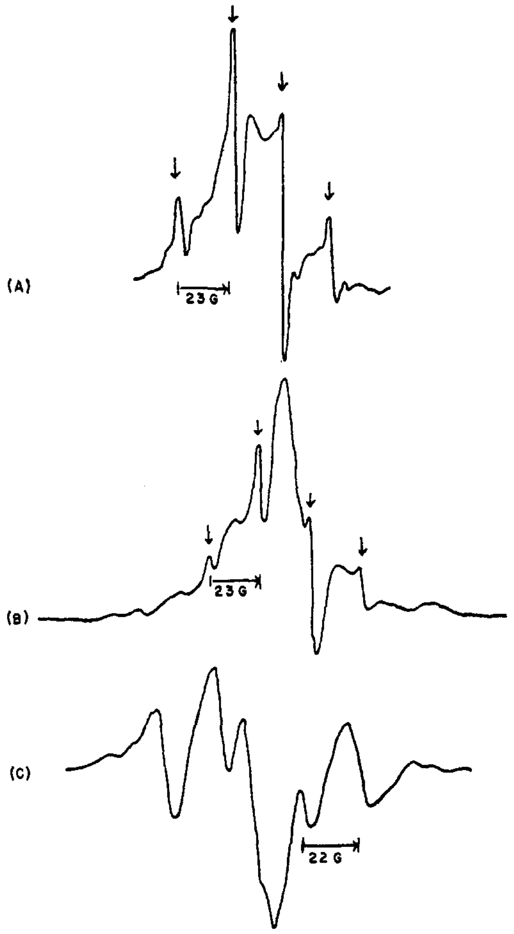


Figure 4. Esr spectra obtained in the photolysis of acetamide irradiated at −196°: (A) spectrum recorded at −180°, (B) spectrum recorded at −140°, (C) spectrum recorded after the sample was warmed to −120° for several minutes and then cooled to −180°. Spectrum was recorded at −180°. In spectra A and B, arrows indicate the positions of $CH_3$ absorption.

tion of the free radicals produced by photolysis of formamide mixed with $H_2O_2$ or $CH_3COCH_3$. In both of these cases, they observed esr absorptions which could be attributed to the $CONH_2$ radical. Unusual spin parameters were observed for this radical in that it was shown that the two hydrogens are not equivalent. The coupling constants observed for this radical at 32° were $a^N = 21.69$ G, $a_1^H = 1.27$ G, and $a_2^H = 30.41$ G. The inequivalence of the two hydrogens and their vastly different coupling constants was reasonably explained in terms of the formation of a "non-$\pi$" radical having hindered rotation about the C–N bond.

The spectrum we obtain in the photolysis of aqueous mixtures of formamide and $H_2O_2$ is shown in Figure 3. Quite clearly the spectrum consists of six lines, all of approximately equal intensity. It has been shown[8] that the OH radical produced by the decomposition of $H_2O_2$ will preferentially abstract an H atom from the CHO group of formamide to form $CONH_2$. The coupling constant between the lines shown of 22 and 31 G are in excellent agreement with that shown by Livingston and Zeldes for $CONH_2$. In the solid matrix the absorption lines are too broad to be able to resolve the hyperfine structure from the weakly coupled hydrogen and thus we observe only six lines. This assignment is further confirmed in the photolysis of $HCOND_2$ where it is seen that the six lines have been replaced by three sets of triplets (Figure 2). The coupling constants of 5 G between each line in the triplet and 21 G between central lines of adjacent triplets is in excellent agreement with the values for the $COND_2$ radical observed by Livingston and Zeldes.[8]

In view of the observation of H-atom signals, the $CONH_2$ and $COND_2$ spectra and the much stronger time dependence of the CHO signal relative to the $CONH_2$ absorption, we conclude that the only major free-radical producing step in this photolysis is

$$HCONH_2 + h\nu \longrightarrow H + CONH_2 \qquad (1)$$

We feel that the HCO we observe might arise from a disproportionation reaction between H atoms and $CONH_2$, or possibly by H-atom addition to CO formed by the subsequent photolysis of $CONH_2$. It has been demonstrated previously that at low temperatures H atoms do indeed add to CO to form HCO.[9] If either of these processes are occurring, then we should also observe absorption by $NH_2$ radicals. Unfortunately these signals would be masked somewhat by the $CONH_2$ radical. In addition, the $NH_2$ radical concentration would probably be a good deal less than that of the CHO radical in view of its greater reactivity and perhaps greater mobility in the solid matrix.

**Acetamide.** The results of the photolysis of acetamide are shown in Figure 4. The spectra consist of a quartet of lines in an intensity ratio of 1:3:3:1 plus a remaining six-line spectrum. The decrease in intensity of these lines with increasing temperature is also shown in Figure 4. The quartet disappears rapidly with increasing temperature whereas the remaining lines show relatively little change up to temperatures of −120°. The coupling constants of 23 G for the quartet, their intensity ratio, and their rapid disappearance at higher temperatures are consistent with the behavior of $CH_3$ radicals. The spectrum remaining after the $CH_3$ radicals have disappeared is identical with the $CONH_2$ radical as shown in Figure 3. On the basis of this result we feel the primary step in the photolysis of acetamide is

$$CH_3CONH_2 + h\nu \longrightarrow CH_3 + CONH_2 \qquad (2)$$

This assignment was confirmed by the photolysis of $CH_3COND_2$. The spectrum of the remaining radical obtained after annealing out the $CH_3$ is identical with that obtained from the photolysis of $HCOND_2$.

We feel that any photolysis to produce $CH_3CO$ and $NH_2$ must represent a relatively insignificant primary step. The formation of $CH_3CO$ would have produced a quartet of lines, 17 G apart and in an intensity ratio of 1:3:3:1.[11] We do not observe any such lines and thus conclude that reaction 2 adequately represents the primary step in acetamide photolysis. In this sense we do not agree with the work of Booth and Norrish who concluded that acetamide photolysis proceeds *via* an entirely nonfree radical process.

**N-Methyl Derivatives.** A typical spectrum obtained from N-methylformamide is shown in Figure 5A. In addition H-atom signals were again observed. Identical spectra were obtained in the case of N-methylacetamide, Figure 5B, with the exception that the spec-

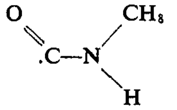
(11) J. R. Morton and W. E. Falconer, *Nature*, 197, 1103 (1963).

tra showed the presence of $CH_3$ radicals and the absence of H atoms. The photolysis of the deuterated N-methylformamide or N-methylacetamide produced no change in the esr spectra. On the basis of these observations we feel that the primary steps in the photolysis of these substituted compounds are comparable to those obtained in the photolysis of formamide and acetamide, namely

$$HCONH(CH_3) + h\nu \longrightarrow H + CONH(CH_3)$$

$$CH_3CONH(CH_3) + h\nu \longrightarrow CH_3 + CONH(CH_3)$$

In this way we can account for the similarity of the spectra shown in Figure 5. Both the nmr spectra of N-methylformamide and N-methylacetamide reveal the presence of only one isomer, believed to be the isomer with the N–H *trans* to the C=O group.[7] Thus we believe that the esr signal shown in Figure 5 is caused by the radical



where free rotation about the C–N bond is not observed. However, it is impossible to assign any coupling constants for the various nuclei as the resolution is not sufficiently good under our experimental conditions. In addition from the work of Livingston and Zeldes[8] with comparable radicals, it would appear likely that the C–H hydrogens are not equivalent, and thus one needs much better resolution than can be obtained in a solid matrix to make any definitive assignments.

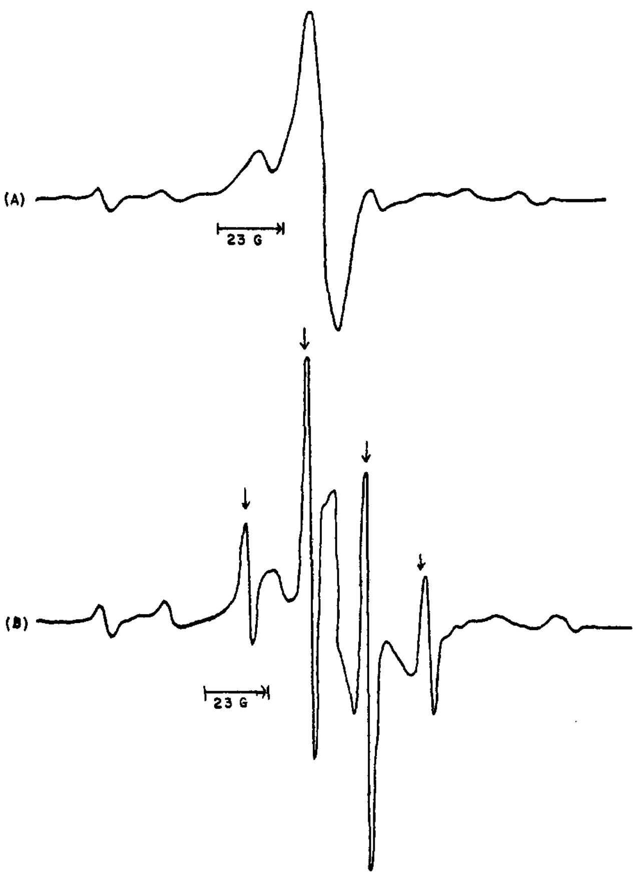


Figure 5. Esr spectra obtained in the photolysis of N-methyl derivatives of formamide and acetamide: (A) N-methylformamide, (B) N-methylacetamide. In spectrum B, the arrows indicate the positions of $CH_3$ absorption.

## Conclusions

We feel that this esr study provides unequivocal evidence that the main free-radical producing step in the photolysis of formamide and N-methylformamide is scission of the C–H bonds. Contrary to some previous reports, the photolysis of acetamide and N-methylacetamide is shown to produce free radicals, in both cases decomposition taking place at the C–C bond. From our results we conclude that these reactions are the only major free-radical producing reactions. However, we must emphasize that these free-radical producing steps were observed at −196°. The primary mechanism might be different in the gas phase or in liquids at much higher temperatures.