Paramagnetic Resonance Study of Liquids during Photolysis. VI. Aliphatic Nitroanions[1,2]

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Abstract: Epr spectra of aliphatic nitroanion radicals were studied during photolysis of basic aqueous solutions containing an aliphatic compound and NO_2^-. The radicals were formed by replacement of a hydrogen atom of the compound by NO_2^-. Nitroanions were produced in this way from the formate, acetate, and propionate ions, acetone, methyl alcohol, 2-butanone, acetamide, ethylamine, and trimethylamine. Nitroanions were also produced by photolysis of basic aqueous or alcoholic solutions containing the corresponding nitroalkane.

Aliphatic nitroanion radicals were studied by electron paramagnetic resonance (epr) for the first time by Piette, Ludwig, and Adams.[3a] They reported[3] spectra of many simple aliphatic nitroanions generated directly in the microwave cavity by electrolytic reduction of aqueous solutions of the nitro compounds. We wish to report epr spectra of aliphatic nitroanions formed by photolysis of two kinds of solutions. In most of the work nitroanions were produced by photolysis of the nitrite ion in basic aqueous solutions containing an aliphatic compound. Nitroanions were also produced by photolysis of aliphatic nitro compounds in basic solutions.

Experimental Section

The microwave spectrometer operated at about 9.5 GHz and used 100-kHz field modulation. The experimental arrangement was described[4] earlier, and the same methods were used for making measurements and calculating g values and hyperfine couplings. The estimated error limits are ±0.00004 for g and ±0.03 G for the couplings unless otherwise indicated.

The sample-handling system has also been described.[4b] The solutions were freed of molecular oxygen by purging with gaseous helium. Photolysis then took place in a flat silica cell in the microwave cavity as the solution flowed through it usually at about 2 ml/min. The inside cross section of the cell was 0.4 mm thick (optical path length) by 9 mm wide. The temperature was measured as the liquid left the cavity.

All chemicals were reagent quality except those indicated below and were used as purchased. The nitromethane (Spectroquality Reagent) and nitroethane (practical grade) were from Matheson Coleman and Bell. The ethylamine and trimethylamine were Eastman Organic Chemicals No. 506 and 551, respectively.

Results

Solutions Containing Nitrite Ion. Many basic aqueous solutions containing nitrite ion and an aliphatic compound gave strong aliphatic nitroanion epr spectra during photolysis. Figure 1 is the spectrum due to $CH_3COCH_2NO_2\cdot^-$ in a basic aqueous solution at 37° containing KNO_2 and acetone. The 1–2–1 sequences split by 7.61 G arise from the equivalent CH_2 protons, and these repeat three times due to the nitrogen hyperfine coupling of 24.36 G. As indicated in the figure, the splittings due to nitrogen are not of equal value, and this is because of second-order effects. The measured spacings indicated in Figure 1 differ by 0.18 G which agrees excellently with the computed value from second-order theory[5] of 0.17 G. Spectra practically identical with Figure 1 showing structure due to a single nitrogen and two equivalent protons were seen for solutions containing methyl alcohol, potassium acetate, and 2-butanone. The compositions of the solutions photolyzed, the identity of the radicals, and computed parameters are given in Table I. In these cases, as well as in those that follow, second-order corrections were made as mentioned above for acetone. Unless otherwise indicated flow rates of about 2 ml/min were used. Faster flow rates gave weaker spectra (lower steady-state concentrations) presumably due to the relatively long lifetimes of the radicals estimated to be an appreciable fraction of a second.

Two nitroanions were formed from a solution containing propionate ion as shown in Figure 2. The stick spectrum identifies lines due to $CH_3CH(NO_2\cdot^-)COO^-$ while the remaining lines are due to $^-OOCCH_2CH_2NO_2\cdot^-$. The spectra for both radicals show hyperfine structure from all magnetic nuclei present in the radicals.

Acetamide gave the spectrum from $H_2NCOCH_2NO_2\cdot^-$ shown in Figure 3. Splittings from both nitrogens are present; the small triplet splitting (0.50 G) obviously comes from the NH_2 nitrogen while the large splitting comes from hyperfine coupling (25.18 G) of the nitro nitrogen. An 8.07-G coupling from a pair of equivalent hydrogens is assigned to the CH_2 group.

Nitroanions were also made from amines. A solution containing ethylamine gave the radical $CH_3CH(NO_2\cdot^-)NH_2$. A portion of the spectrum is shown in Figure 4a. The entire spectrum consists of three groups of lines like the group illustrated spaced by about 26 G due to the nitrogen hyperfine coupling (26.30 G) of the nitro group. The group of lines (Figure 4a) shows splittings of 4.42 G due to CH hydrogen, 0.96 G due to NH_2 nitrogen, and 0.38 G due to the pair of equivalent NH_2 hydrogens. A deuterated form of the same radical was obtained by photolyzing a solution prepared by adding 2.2 vol of D_2O to 1 vol of the original solution. The spectrum of one of the three groups of lines is illustrated in Figure 4b. When comparing with Figure 4a note that the scale for field is considerably compressed. The structure due to the exchangeable NH_2 hydrogens is now absent. The

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] The preceding paper of this series is by R. Livingston and H. Zeldes, *J. Chem. Phys.*, 47, 4173 (1967).

[3] (a) L. H. Piette, P. Ludwig, and R. N. Adams, *J. Am. Chem. Soc.*, **83**, 3909 (1961); (b) *ibid.*, **84**, 4212 (1962).

[4] (a) R. Livingston and H. Zeldes, *ibid.*, **88**, 4333 (1966); (b) *J. Chem. Phys.*, 44, 1245 (1966).

[5] See, for instance, G. K. Fraenkel, *J. Phys. Chem.*, 71, 139 (1967).

Table I. Parameters for Aliphatic Nitroanions and Other Radicals[a]

Solution Photolyzed	Radical	g	a_N	a_H
Nitroanions				
35 ml of CH_3NO_2, 250 ml of H_2O, and 2.4 ml of 1 *N* NaOH per liter of ethanol solution at 37°	$CH_3NO_2\cdot^-$	2.00508	25.88	11.67 (CH_3)
25 ml of nitroethane (practical grade), 190 ml of isopropyl alcohol, and 10.5 g of KOH per liter of aqueous solution at 42°	$CH_3NO_2\cdot^-$ $CH_3CH_2NO_2\cdot^-$	2.00501 2.00503	25.87 25.90	12.00 (CH_3) 9.89 (CH_2) 0.44 (CH_3)
82 ml of CH_3OH, 82 g of KNO_2, and 15 ml of 1 *N* NaOH per liter of aqueous solution at 38°	$HOCH_2NO_2\cdot^-$	2.00511	25.17	8.95 (CH_2)
167 g of HCOONa and 83 g of KNO_2 per liter of aqueous solution at 33°	$^-O_2CNO_2\cdot^-$ [b]	2.00505	14.38	
125 g of CH_3COOK, 83 g of KNO_2, and 50 ml of 50% NaOH per liter of aqueous solution at 32°	$^-O_2CCH_2NO_2\cdot^-$	2.00500	24.52	8.10 (CH_2)
133 ml of propionic acid, 100 g of KNO_2, and 120 ml of 50% NaOH per liter of aqueous solution at 41°	$^-O_2CCH_2CH_2NO_2\cdot^-$	2.00504	25.91	10.40 (CH_2) 0.66 (CH_2)
	$^-O_2C\underset{\mid\atop NO_2\cdot^-}{C}HCH_3$	2.00501	25.38	7.82 (CH) 0.34 (CH_3) 0.34 (CH_3)
125 ml of acetone, 83 g of KNO_2, and 6 ml of 1 *N* NaOH per liter of aqueous solution at 37°	$CH_3COCH_2NO_2\cdot^-$	2.00504	24.36	7.61 (CH_2)
117 ml of 2-butanone, 78 g of KNO_2, and 68 ml of 1 *N* NaOH per liter of aqueous solution at 37°	$CH_3CH_2COCH_2$-$NO_2\cdot^-$	2.00503	24.43	7.69 (CH_2)
107 g of acetamide, 107 g of KNO_2, and 21 ml of 50% NaOH per liter of aqueous solution at 40°	$H_2NCOCH_2NO_2\cdot^-$	2.00508	25.18 0.50	8.07 (CH_2)
100 g of ethylamine and 70 g of KNO_2 per liter of aqueous solution at 34°	$CH_3\underset{\mid\atop NH_2}{C}HNO_2\cdot^-$	2.00513	26.30 0.96	4.42 (CH) 0.38 (NH_2)
125 g of $(CH_3)_3N$ and 75 g of KNO_2 per liter of aqueous solution at 40°	$(CH_3)_2NCH_2NO_2\cdot^-$	2.00505	23.49 2.21	7.33 (CH_2) 0.26 $(CH_3)_2$
Other Radicals				
17 g of KNO_2 and 83 ml of H_2O per liter of methanol solution at 33°	$(HOCH_2)_2\dot{N}O$ [c]	2.00602	14.07	7.08 $(CH_2)_2$
20 g of KNO_2 and 167 ml of H_2O per liter of acetone solution at 32°	$CH_3COCH{=}\dot{N}O$ [c]	2.00461	28.90	6.08 (CH)
83 g of KNO_2 and 167 ml of *t*-butyl alcohol per liter of aqueous solution at 37°	Unidentified	2.00576	11.46 6.42	2.81 (H)

[a] Couplings are in gauss. [b] $a(^{13}C) = 3.74 \pm 0.2$ G for a similar solution to which NaOH had been added. [c] Provisional assignment.

coupling is too small to show resolved structure from the ND_2 deuterium atoms. With trimethylamine the spectrum of Figure 5 was obtained which arises from the radical $(CH_3)_2NCH_2NO_2\cdot^-$. Each line is resolvable into components as indicated for one of the lines by a high-resolution recording. These components arise from the six equivalent CH_3 protons which give seven components of relative intensities 1:6:15:20:15:6:1, but those of strength 1 are too weak to be seen. Structure due to all magnetic nuclei of this radical is present.

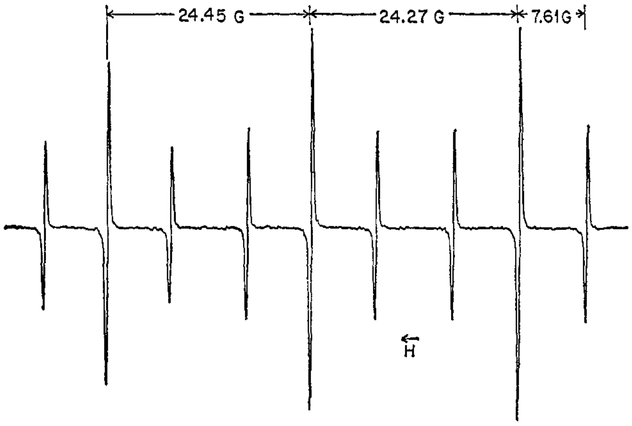

Figure 1. Spectrum due to $CH_3COCH_2NO_2^-$ during photolysis of an aqueous solution at 37° containing 83 g of KNO_2, 125 ml of acetone, and 17 ml of 1 *N* NaOH per liter.

A solution containing formate ion gave a spectrum of three intense lines coming from a single nitrogen with a hyperfine coupling of 14.38 G rather than about 25 G. With high sensitivity, weak lines due to ^{13}C and ^{15}N in natural abundance were observed as indicated in Figure 6. The relative intensities are as expected, and the ^{15}N splitting is also just that expected by comparison with ^{14}N. The radical contains C and N and is believed to be $^-O_2CNO_2\cdot^-$.

Figure 2. Spectrum taken during photolysis of an aqueous solution at 41° containing 100 g of KNO_2, 133 ml of propionic acid, and 120 ml of 50% NaOH per liter. Lines labeled by the stick spectrum are due to $CH_3CH(NO_2^-)COO^-$. The remaining lines are due to $^-OOCCH_2CH_2NO_2^-$.

Not all aliphatic compounds in basic aqueous solutions containing nitrite ion gave satisfactory results. Compounds that gave either no or poor quality spectra of the nitroanion included 3-pentanone, ethyl alcohol, isopropyl alcohol, *t*-butyl alcohol, propionitrile, isobutyronitrile, and formamide. With 3-pentanone and propionitrile very weak spectra having a nitrogen splitting of approximately 25 G and presumably coming from nitroanions were seen. With 3-pentanone there was a further splitting due to a single hydrogen of roughly 5.6 G. A small amount of the radical C_2H_5-

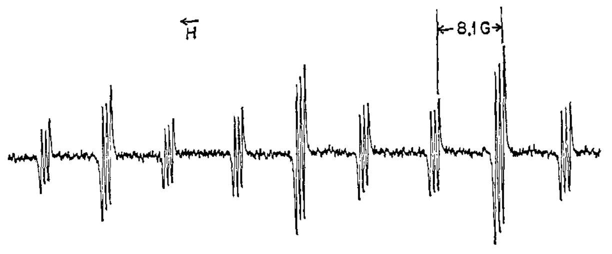

Figure 3. Spectrum due to $H_2NCOCH_2NO_2^-$ during photolysis of an aqueous solution at 40° containing 107 g of KNO_2, 107 g of acetamide, and 21 ml of 50% NaOH per liter.

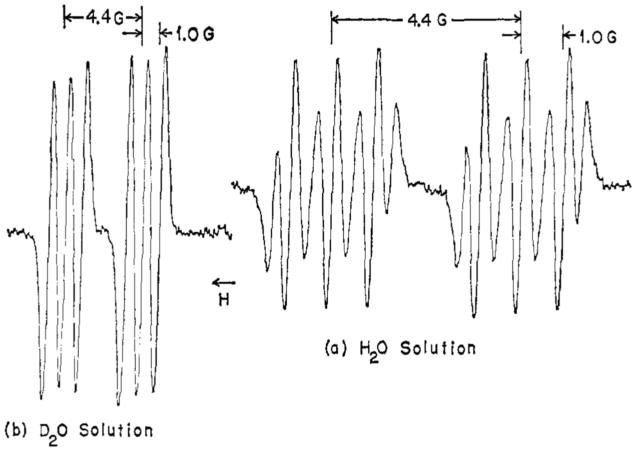

Figure 4. (a) One of the three equivalent equally spaced groups of lines due to $CH_3CH(NO_2^-)NH_2$ during photolysis of an aqueous solution at 34° containing 70 g of KNO_2 and 100 g of ethylamine per liter. (b) The same group of lines after adding 2.2 vol of D_2O to 1 vol of the above solution. Note that the scale for field is compressed compared to (a).

$COCH(NO_2\cdot^-)CH_3$ was presumably present. With propionitrile there was a further splitting due to two equivalent hydrogens of roughly 9.7 G, and the lines were complex and seemed to be split by another pair of equivalent hydrogens with spacings of 0.5 G. This corresponds to a small yield of $CH_2(NO_2\cdot^-)CH_2CN$. Aqueous solutions containing nitrite ion did not give nitroanions in the absence of base except for those containing formate ion and acetone. In these cases the spectra were very weak compared to those obtained after adding base.

Another kind of radical was formed in an acetone-rich solution containing nitrite ion, but there were indications that the solution underwent chemical change before it was photolyzed. A typical solution containing 20 g of KNO_2 and 167 ml of H_2O per liter of acetone solution gave this new spectrum showing a nitrogen hyperfine coupling of 28.90 G and a single hydrogen coupling of 6.08 G. Repeating the experiment gave a spectrum of greatly different strength, and it appeared that these solutions were unstable. A series of experiments was carried out in which the solution was slightly acidified (several milliliters of 1 *N* HCl per liter), a spectrum recorded, made slightly basic with NaOH, a new spectrum recorded, and then again acidified. When the solution was basic the strong nitroanion spectrum reported above (Figure 1) was obtained. When the solution was acid the nitroanion spectrum was absent and the new spectrum was present becoming progressively stronger during the few hours required for the experiment. This spectrum is shown in Figure 7 and is tentatively identified as the iminoxy radical, $CH_3COCH{=}\dot{N}O$.

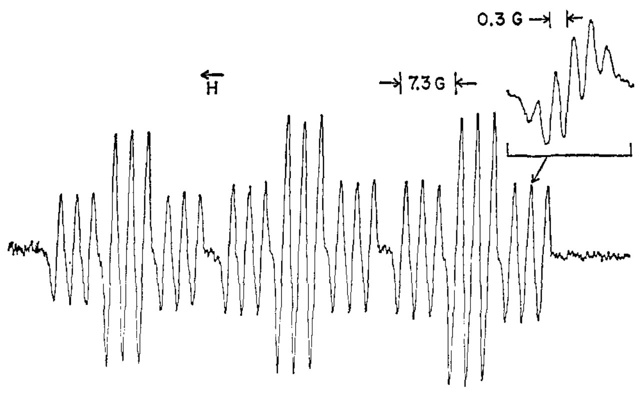

Figure 5. Spectrum due to $(CH_3)_2NCH_2NO_2^-$ during photolysis of an aqueous solution at 40° containing 100 g of KNO_2 and 95 g of $(CH_3)_3N$ per liter. One line is shown at higher resolution.

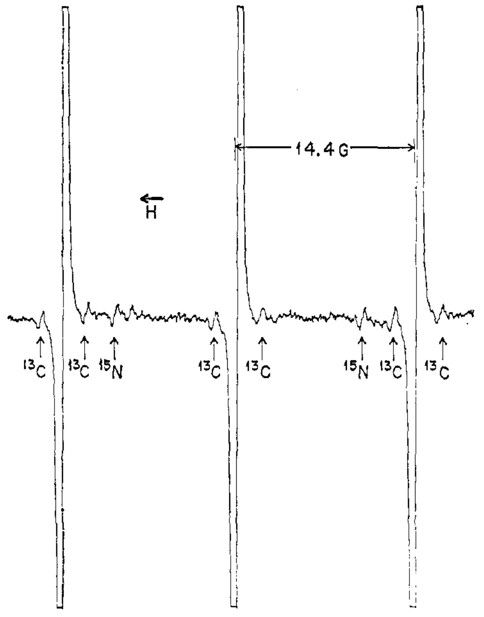

Figure 6. Spectrum due to $^-O_2CNO_2^-$ during photolysis of an aqueous solution at 44° containing 82 g of KNO_2, 156 g of sodium formate, and 24 ml of 50% NaOH per liter. Hyperfine lines due to ^{13}C and ^{15}N present in natural abundances are identified.

A solution of methyl alcohol containing KNO_2 and water gave the nine-line spectrum shown in Figure 8. The lines are approximately equally spaced and have intensities very nearly in the ratio 1:4:7:8:8:8:7:4:1 which would result from four equivalently coupled hydrogens and one nitrogen with a hyperfine coupling twice that of the hydrogens. With this interpretation the measurements give the values 14.07 and 7.08 G for the nitrogen and hydrogen hyperfine couplings. The radical is provisionally identified as the nitroxide, $(HOCH_2)_2\dot{N}O$.

An aqueous solution containing 83 g of KNO_2 and 167 ml of *t*-butyl alcohol per liter was investigated at flow rates which were very low compared to the typically used flow rate of about 2 ml/min. At very slow flow there was a strong spectrum of 18 lines with equal intensities. Flow rates as low as 0.08 ml/min were

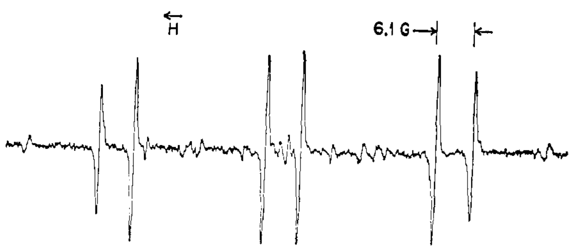

Figure 7. Spectrum probably due to $CH_3COCH{=}NO$ during photolysis of an acetone solution at about 35° containing 19.6 g of KNO_2, 164 ml of H_2O, and 0.4 ml of 1 *N* HCl per liter. Weak lines due to other radicals are present.

Figure 8. Spectrum probably due to $(HOCH_2)_2NO$ during photolysis of a methanol solution at 33° containing 16.6 g of KNO_2 and 83 ml of H_2O per liter.

tried, and the absorption signal increased each time the flow rate was decreased. The light shining on the sample was then interrupted with the magnetic field fixed on one of the absorption lines. It was seen that the absorption signal decayed or grew with the 1-sec response time of the spectrometer as the light was turned off or on. On the other hand, the absorption signal was still responsive to flow rate, and the rate was so slow that it would take about 10 sec for photolyzed liquid to flow out of the active region of the cavity after turning off the light. Clearly production of the radical required the presence of a photolytically produced precursor with a fairly long lifetime (approximately 10 sec or longer). We have not identified this radical but are reporting it with the others since the spectrum was measured and analyzed. The hyperfine structure is due to two differently coupled nitrogens and one hydrogen with coupling values of 11.46, 6.42, and 2.81 G, respectively.

Solutions Containing Aliphatic Nitro Compounds. Only solutions containing nitromethane and nitroethane were investigated. Aqueous solutions gave strong anion-radical spectra during photolysis, but only after base was added. The spectra were even stronger if some of the water was replaced by an alcohol. Figure 9 shows the spectrum for an aqueous solution containing practical grade nitroethane, isopropyl alcohol, and base. The strongest radical spectrum is due to $CH_3CH_2NO_2\cdot^-$, and there are well-resolved splittings from all magnetic nuclei. The stick spectrum identifies lines from $CH_3NO_2\cdot^-$, and the arrows point to broad unresolved lines which probably are from one or more radicals of the type $RR'CHNO_2\cdot^-$. These may very well arise from CH_3NO_2 and $RR'CHNO_2$ impurities. The spectra for both $CH_3CH_2NO_2\cdot^-$ and $CH_3NO_2\cdot^-$ were measured for this solution. Then a small amount of CH_3NO_2 was added to the solution, and it was verified that the spectrum attributed to $CH_3NO_2\cdot^-$ became stronger. The spectrum for $CH_3NO_2\cdot^-$ was also measured in an ethyl alcohol solution containing CH_3NO_2, H_2O, and base.

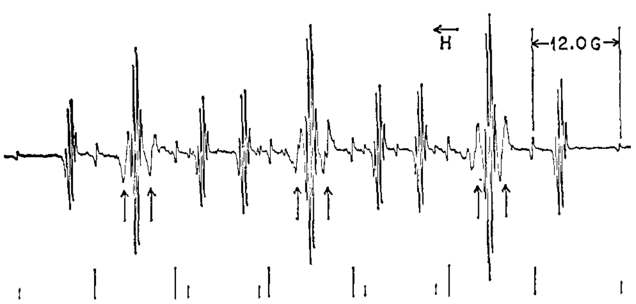

Figure 9. Spectrum during photolysis of an aqueous solution at 41° containing 25 ml of nitroethane (practical grade), 190 ml of isopropyl alcohol, and 10.5 g of KOH per liter. The stick spectrum identifies line due to $CH_3NO_2^-$. The strong radical spectrum is due to $CH_3CH_2NO_2.^-$ The arrows point to broad unresolved lines probably due to one or more radicals of the type $RR'CHNO_2^-$.

Discussion

Table I summarizes the measurements of hyperfine couplings and *g* values. Couplings have previously been reported[3,6] for $CH_3CH_2NO_2\cdot^-$ and $CH_3NO_2\cdot^-$ in aqueous solution. Our spectrum for $CH_3CH_2NO_2\cdot^-$ showed small resolved splittings for the methyl group protons which were not reported[3] in the spectrum produced by electrolysis. Our values for a_N and $a_H(CH_2)$ are higher than those reported[3] previously by 0.4 and 0.14 G, respectively. However, the solution compositions were different, and the temperatures may have been significantly different. Our values of a_N for $CH_3NO_2\cdot^-$ in the two solutions measured, one mostly water and the other mostly ethyl alcohol, were almost the same. However, they were larger than the values reported[6] in aqueous 10% methyl alcohol and in aqueous 10% isopropyl alcohol by the surprisingly large amounts of 1.6 and 0.9 G, respectively.

With the exception of $^-O_2CNO_2\cdot^-$ the values of $a_N(NO_2^-)$ are in the neighborhood of 25 G which is typical of aliphatic nitroanions. The smaller value of 14.38 G for $^-O_2CNO_2\cdot^-$ is like that of aromatic nitroanions in aqueous solution.[3b] Geske and Ragle[7] have shown that the value of a_N for aromatic nitroanions approaches that for aliphatics when the nitro group is strongly hindered by benzene ring substituents. They attributed the increase largely to a decoupling of the nitro group π-electron system from the aromatic π-electron system caused by the twisting of the nitro group out of the plane of the benzene ring. Similarly, the low value for $^-O_2CNO_2\cdot^-$ indicates that the nitro group π-electron system is strongly coupled to the π-electron system of the rest of the molecule; the molecule is probably planar. The very small ^{13}C coupling (3.74 G) is reasonable for an unpaired electron occupying a π orbital of the planar molecule.

All of the nitroanion radicals formed by photolysis of basic aqueous solutions containing nitrite ion and an organic compound are ones which result from replacing a hydrogen atom of the compound by NO_2^-. It is quite possible that the radical R· was produced from RH after excitation of the nitrite ion and that R· then

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[6] W. E. Griffiths, G. F. Longster, J. Myatt, and P. F. Todd, *J. Chem. Soc.*, *B*, 533 (1967).

[7] D. H. Geske and J. L. Ragle, *J. Am. Chem. Soc.*, **83**, 3532 (1961).

combined with NO_2^-, which was present in high concentration, to form $RNO_2\cdot^-$.

$$NO_2^- + RH \xrightarrow{h\nu} R\cdot + HNO_2\cdot^- \qquad (1)$$

$$R\cdot + NO_2^- \longrightarrow RNO_2\cdot^- \qquad (2)$$

Step 2 has previously been proposed by Kornblum.[8]

The photochemistry of aliphatic nitro compounds resulting in nitroanions may be similar to that of the aromatic compounds. Ayscough and Sargent[9] produced aromatic nitroanion radicals by photolysis of aromatic nitro compounds in concentrated sodium ethoxide, methoxide, or hydroxide solutions. They presumed that electron transfer took place from the alkoxide or hydroxide ion to the electronically excited aromatic nitro compound. On the other hand, Russell and Geels[10] suggested that the mechanism involves abstraction of hydrogen by the photolytically excited aromatic nitro compound. Hydrogen abstraction has been proposed by Ward[11a] to explain epr results for photolyzed solutions of nitrobenzene in tetrahydrofuran. He observed a radical which he interpreted as containing a hydrogen taken from tetrahydrofuran; however, very recent work[11b] indicates that *this* radical rapidly disappears and that the observed radical was the adduct of nitrobenzene with the solvent radical. Evidence for hydrogen abstraction from isopropyl alcohol following excitation of nitrobenzene has been obtained[12] from a quantum yield study. It is quite possible that hydrogen abstraction is the important process leading to nitroanions for our solutions containing nitromethane and nitroethane. There was no evidence that adduct radicals formed in our cases. Not much base was needed to get the nitroanion spectra during photolysis, and its function may have been to neutralize the conjugate acid $R\dot{N}O_2H$ to form $RNO_2\cdot^-$.

The radical believed to be $(HOCH_2)_2\dot{N}O$ has parameters which are typical of dialkyl nitroxide radicals. The *g* value of 2.00602 may be compared with values of 2.0063 for di-*t*-butyl nitroxide[13] and 2.00585 for di-*sec*-butyl nitroxide.[14] The hyperfine couplings are also reasonable when compared[15] with other nitroxides. The proposed nitroxide may have been formed by a mechanism proposed by Hoffmann, Hodgson, and Jura[16]

$$R\cdot + RNO_2\cdot^- \longrightarrow R\text{—}N\text{=}O + RO^- \qquad (3)$$

$$R\cdot + R\text{—}N\text{=}O \longrightarrow R_2\dot{N}\text{—}O \qquad (4)$$

where $R\cdot$ is $\cdot CH_2OH$. Again we assume that $R\cdot$ is produced by photolysis of NO_2^- in the presence of RH, and that $R\cdot$ and NO_2^- combine to form $RNO_2\cdot^-$. In the absence of base and with not too much NO_2^- present, reactions 3 and 4 are assumed to become important. Reaction 4 is also supported by epr studies[17] of nitroxides produced from nitroso compounds.

The radical believed to be $CH_3COCH{=}\dot{N}O$ has parameters which are reasonable for iminoxy radicals.[18] The nitrogen coupling is somewhat low, but not outside the range of those studied. The *g* value (2.00461) is unusually low, but it is close to that (2.0047) of an iminoxy radical[18b] derived from benzil monoxime which is also of the form $R'COC(R){=}\dot{N}O$. We had evidence that the acetone solution giving this radical was unstable before uv irradiation, and it is well known[19] that acetone is easily nitrosated to give the oximino ketone $CH_3COCH{=}NOH$ in aqueous solution. Photolysis of NO_2^- may have led to the abstraction of a hydrogen atom of the oximino ketone (present before photolysis) to give the observed radical.

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[8] See footnote 16 of H. Feuer, *Tetrahedron Suppl.*, **1**, 107 (1964).

[9] P. B. Ayscough and F. P. Sargent, *Proc. Chem. Soc.*, 94 (1963).

[10] G. A. Russell and E. J. Geels, *Tetrahedron Letters*, 1333 (1963).

[11] (a) R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963); (b) D. J. Cowley and L. H. Sutcliffe, *Chem. Commun.*, 201 (1968).

[12] R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **88**, 4330 (1966).

[13] H. A. Lemaire, A. Rassat, P. Servoz-Gavin, and G. Berthier, *J. Chim. Phys.*, **59**, 1247 (1962).

[14] J. C. Baird, *J. Chem. Phys.*, **37**, 1879 (1962).

[15] See, for instance, J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *ibid.*, **45**, 654 (1966).

[16] A. K. Hoffmann, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **83**, 4675 (1961).

[17] A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 2115 (1966).

[18] (a) J. R. Thomas, *J. Am. Chem. Soc.*, **86**, (1964); (b) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., B*, 86 (1966).

[19] I. T. Millar and H. D. Springall, "Sidgwick's Organic Chemistry of Nitrogen," Clarendon Press, Oxford, England, 1966, p 341.