

functional chromophores of the nucleic acid bases in physical terms. Here, in particular, we show that a close relationship of the out-of-plane transitions with the structure of the nonbonding orbitals exists, *i.e.*, with a property of the electronic structure of the ground state. The transition densities of the  $n\pi^*$  states suggest that configuration interaction in general tends to increase the localization of these transitions on certain atoms or groups of atoms, as compared to the nonbonding orbitals themselves or results obtained without configuration interaction.<sup>20</sup> The structure of the transition density on such fragments often closely resembles that of small, well-known chromophores. The first  $n\pi^*$  transition of the molecules of the carbonyl class is an example of this, having a transition density qualitatively identical with that of the  $n\pi^*$  transition in acetone or formaldehyde. This means that the expectation values of many operators will be similar;<sup>10</sup> *i.e.*, the first  $n\pi^*$  transition in uracil or guanine will be essentially electric dipole forbidden but will have a large magnetic moment along the C=O axis. Due to the fact that the out-of-plane transitions of nucleic acid bases cannot be observed in the absorp-

(20) Similar observations on the localizing effect of CI on the hole left by an electron upon excitation from a nonbonding orbital have been made for thymine; see L. C. Snyder, R. G. Shulman, and D. B. Neuman, *J. Chem. Phys.*, **53**, 256 (1970).

tion spectra, many of our results cannot be checked directly against experimental data. In a paper<sup>21</sup> on the CD and MCD spectra of the mononucleosides, it will be shown, however, that the calculations are in good agreement with the indirect evidence provided by these spectra on out-of-plane transitions and that they provide a basis for their correct interpretation.

Many of the conclusions reached in this work are not limited to nucleic acid bases themselves. These chromophores represent model systems for and contain structural elements of a variety of compounds of chemical and biological interest, like pterins, flavins, or urobilins, and some of our results are useful in understanding the electronic structure and spectra of such compounds as well. The approach itself in dealing with complex low-symmetry chromophores in particular is also suited to rationalize data on excited states obtained by other than the CNDO-CI method, including as simple models as the Hückel method up to elaborate *ab initio* calculations.

**Acknowledgment.** This work was supported in part by Research Grant GM 10840 from the National Institute of Health and by the U. S. Atomic Energy Commission.

(21) W. Hug and I. Tinoco, Jr., manuscript in preparation.

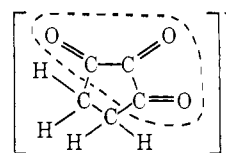
## Electron Spin Resonance Spectra of Radicals Related to the Intermediates in the Oxidation of Ascorbic Acid. Substituted 2,3,4-Trioxopyrrolidine Radical Anions<sup>1</sup>

Yutaka Kirino, Philip L. Southwick, and Robert H. Schuler\*

*Contribution from the Radiation Research Laboratories, Center for Special Studies, and Department of Chemistry, Mellon Institute of Science, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. Received September 7, 1973*

**Abstract:** Four substituted 2,3,4-trioxopyrrolidine radical anions have been prepared by the oxidative debromination and denitration of the corresponding 4-bromo- and 4-nitro-3-hydroxy-3-pyrrolin-2-ones. *In situ* radiolysis-*esr* methods were used to observe the radicals from the nitro derivatives whereas the bromo derivatives readily give the radicals chemically either in aqueous solution or in basic DMSO. The radicals substituted on the nitrogen are extremely unreactive and are observable for a period of at least 24 hr after sample preparation. All four radicals are very similar in that they have nitrogen hyperfine constants of  $\sim 2$  G. A methyl proton hyperfine constant of 3.35 G is observed for the *N*-methyl derivative showing that there is an electron spin density of  $\sim 0.11$  on the nitrogen atom. The very small hyperfine constants for the protons at the C<sub>3</sub> position (0.2–0.5 G) are explained as the result of almost complete cancelation of the effects of spin density on the nitrogen and C<sub>4</sub> carbon atoms. Comparison of the parameters observed in water and in DMSO shows that in the latter case an appreciably greater amount of spin density has been transferred to the carbonyl oxygen atoms. These present results substantiate the previous suggestion that in the similar radicals derived from  $\alpha$ -hydroxytetronic and ascorbic acids there is a spin density of 0.03 on the heterocyclic oxygen atom.

The radical intermediate in the oxidation of reductic acid has long been known from its *esr* spectrum to be a tricarbonyl anion (radical I) related to the intermediate present in the oxidation of ascorbic acid.<sup>2</sup>

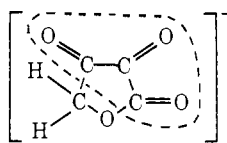


radical I

More recently the *esr* spectrum of the isoelectronic radical produced in the oxidation of  $\alpha$ -hydroxytetronic

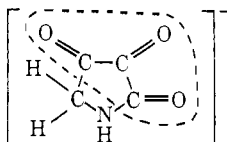
(1) Supported in part by the U. S. Atomic Energy Commission.  
(2) L. H. Piette, I. Yamazaki, and H. S. Mason, "Free Radicals in Biological Systems," M. S. Blois, Jr., H. W. Brown, R. W. Lemmon, R. O. Hindblom, and M. Weissbluth, Ed., Academic Press, New York, N. Y., 1961, Chapter 14, p 195.

acid (radical II) has been observed.<sup>3</sup> The <sup>13</sup>C esr



radical II

spectra of radicals I and II<sup>4</sup> show that the electronic structures of the two radicals are quite similar in that the unpaired electron is delocalized in the tricarbonyl system. The purpose of this work is to present information related to a third isoelectronic species, the 2,3,4-trioxopyrrolidine radical anion (radical III), which



radical III

is the nitrogen heterocyclic radical analogous to II. These observations have been carried out not on radical III itself but rather on radicals with hydrocarbon substituents at both the nitrogen and methylene positions. These radicals were prepared by the oxidative denitration and debromination of the 4-nitro and 4-bromo derivatives of the appropriately substituted 3-hydroxy-3-pyrrolin-2-one. The initial studies were carried out by the *in situ* radiolysis-esr method developed by Eiben and Fessenden<sup>5</sup> using OH as the oxidant. It was, however, soon found that the radicals substituted on the nitrogen position are quite unreactive and that those produced from the bromo derivatives can be readily observed even without irradiation. Auxiliary studies on the spectra of these radicals in dimethyl sulfoxide (DMSO) are also reported. A comparison of the esr parameters allows some insight to be obtained on the influence of the heterocyclic atom on the electron distribution in these three radicals.

### Experimental Section

**1-Methyl-3-hydroxy-4-bromo-3-pyrrolin-2-one.** The synthesis of 1-methyl-3-hydroxy-4-bromo-3-pyrrolin-2-one has not previously been reported. It was synthesized by a slight modification of the methods described by Southwick, *et al.*<sup>6</sup> A 37.1-g (0.20 mol) sample of 1-methyl-4-carbomethoxy-2,3-dioxopyrrolidine prepared from ethyl acrylate, methylamine, and diethyl oxalate<sup>6</sup> was hydrolyzed and decarboxylated by refluxing in 600 ml of 10% hydrochloric acid for 100 min. The solution was then cooled and evaporated under reduced pressure. No attempt was made to isolate the product 1-methyl-2,3-dioxopyrrolidine which appeared to have a relatively low-melting point (the oily appearing residue did, however, solidify to some extent). Bromine was added to the residue in chloroform until the bromine color persisted. After standing for 30 min at room temperature the precipitate was collected by filtration, washed with water, and dried to give 5.7 g (0.030 mol) of 1-methyl-3-hydroxy-4-bromo-3-pyrrolin-2-one. After recrystallization from toluene it had a melting point of 131–132° (with decomposition). The nmr spectrum in DMSO-*d*<sub>6</sub> consisted of single lines at  $\tau$  6.07 (ring methylene protons) and at  $\tau$  7.10 (*N*-methyl protons). The absorption of the remaining proton (the enolic OH proton) was too broad to be identified.

(3) Y. Kirino and T. Kwan, *Chem. Pharm. Bull.*, **19**, 718 (1971).

(4) G. P. Laroff, R. W. Fessenden, and R. H. Schuler, *J. Amer. Chem. Soc.*, **94**, 9062 (1972).

(5) K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, **75**, 1186 (1971).

(6) P. L. Southwick, E. P. Previc, J. Casanova, Jr., and E. H. Carlson, *J. Org. Chem.*, **21**, 1087 (1956); P. L. Southwick and J. A. Vida, *ibid.*, **27**, 3075 (1962).

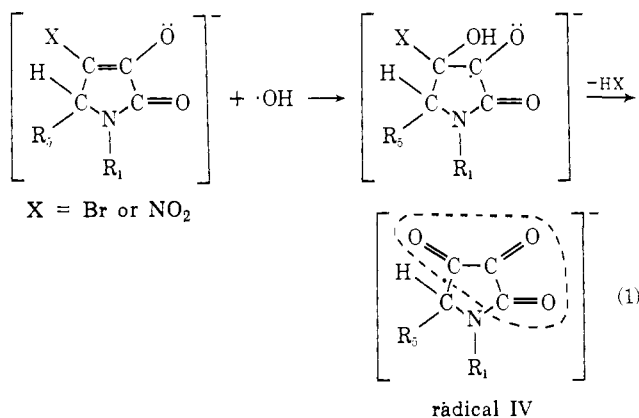
*Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>BrNO<sub>2</sub>: C, 31.27; H, 3.15; N, 7.30; Br, 41.62. Found: C, 31.12; H, 3.17; N, 7.29; Br, 41.59.

**Other Materials.** The syntheses of the three other substances examined (1-benzyl-3-hydroxy-4-bromo-3-pyrrolin-2-one,<sup>6</sup> 3-hydroxy-4-nitro-5-phenyl-3-pyrrolin-2-one,<sup>7a</sup> and 1-cyclohexyl-3-hydroxy-4-nitro-3-pyrrolin-2-one<sup>7b</sup>) are described elsewhere. Dimethyl sulfoxide was "Baker Analyzed" reagent and dried over molecular sieves. Potassium *tert*-butoxide was from Alfa Inorganics. Water and deuterium oxide were distilled and freed from organic impurities by passing the vapor with oxygen through a silica tube at ~600°. The deuterium content of the latter was >99%. All other chemicals were of the purest grade commercially available.

**Esr Observations.** The *in situ* radiolysis-esr experiments were carried out by the methods described by Eiben and Fessenden.<sup>5</sup> Field modulation and phase detection were at both 100 kHz and 200 Hz to give second-derivative spectra. Solutions at pH ~10.5 (adjusted with KOH) were saturated with N<sub>2</sub>O which served both to remove oxygen and to convert e<sub>aq</sub><sup>-</sup> formed in the radiolysis to OH. A flow system was used but because of the relatively long life of the radicals the experiments were carried out at both low flow rates and low electron beam currents. Experiments on chemically produced radicals were carried out with a second spectrometer employing 10 kHz field modulation and 20 kHz phase detection which also gives second-derivative spectra.<sup>8</sup> Both flow and static methods were used on aqueous solutions (pH ~10.5) and on solutions in dimethyl sulfoxide. In the latter case ~20 mM potassium *tert*-butoxide and ~1% water was added to the solution at the time of initiation of the experiment. These solutions were bubbled with N<sub>2</sub> in order to remove O<sub>2</sub> which otherwise broadened the spectral lines.

### Results and Discussion

In general the approach used here was to convert the 4-bromo or 4-nitro derivative of the appropriate 3-hydroxy-3-pyrrolin-2-one (this is the enol of 2,3-dioxopyrrolidine; various studies indicate that the compound exists essentially completely in the enolic form)<sup>6</sup> to the radical of interest by oxidative debromination or denitration as suggested by various other studies in these laboratories.<sup>4,9–11</sup> This reaction is expected to occur *via* OH addition at the bromo or nitro position followed by loss of HBr or HNO<sub>2</sub>, *i.e.*



**(IVa) The 5-Phenyl-2,3,4-trioxopyrrolidine Radical Anion.** A 0.083 mM alkaline nitrous oxide saturated solution of 3-hydroxy-4-nitro-5-phenyl-3-pyrrolin-2-one (sodium salt) gave the esr spectrum of Figure 1a during irradiation. No spectrum was observed in the absence

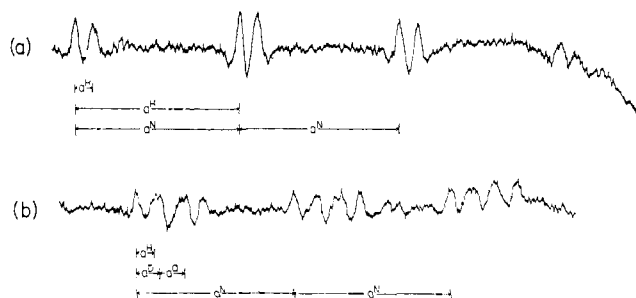
(7) (a) P. L. Southwick, J. A. Fitzgerald, R. Madhav, and D. A. Welsh, *J. Org. Chem.*, **34**, 3279 (1969); (b) J. J. Lindsey, Ph.D. Dissertation, Carnegie-Mellon University, 1973.

(8) Described by R. W. Fessenden, *J. Chem. Phys.*, **48**, 3725 (1968).

(9) K. M. Bansal, L. K. Patterson, and R. H. Schuler, *J. Phys. Chem.*, **76**, 2386 (1972); P. Neta, *ibid.*, **76**, 2399 (1972).

(10) P. Neta and C. L. Greenstock, *Chem. Commun.*, 309 (1973).

(11) C. L. Greenstock, I. Dunlop, and P. Neta, *J. Phys. Chem.*, **77**, 1187 (1973).

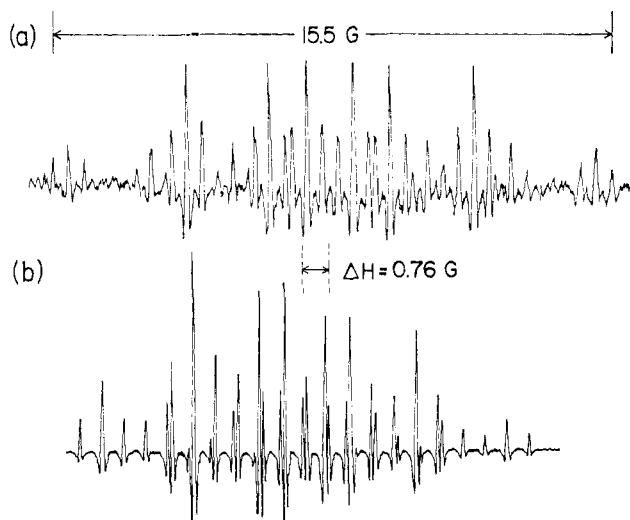


**Figure 1.** (a) Second-derivative esr spectrum observed during the irradiation of a 0.083 mM nitrous oxide saturated alkaline aqueous solution of 3-hydroxy-4-nitro-5-phenyl-3-pyrrolin-2-one. Hyperfine coupling constants are determined as  $a^H = 0.20$ ,  $a^H = 1.89$ , and  $a^N = 1.89$  G. The base line is distorted at high field because of interference by the signal from quartz. (b) Second-derivative esr spectrum observed under the same conditions as in (a) except using  $D_2O$  as the solvent. Coupling constants are  $a^H = 0.21$ ,  $a^D = 0.29$ , and  $a^N = 1.86$  G.

of irradiation nor in the DMSO–potassium *tert*-butoxide system. The spectrum appears to consist of eight lines with a doublet splitting of 0.20 G being readily apparent. The four doublets form a 1:2:2:1 pattern (with a separation of 1.89 G) which can be accounted for if a proton and a nitrogen nucleus have experimentally indistinguishable hyperfine interactions. The  $g$  factor is 2.00497 and the experimental line width is 0.11 G, which is similar to that for other narrow lined radicals under identical spectrometer conditions. The high  $g$  factor and small hyperfine constants are as expected for radical IV from the similar properties of the radicals from reductic and  $\alpha$ -hydroxytetronic acid so that the assignment to IV with  $R_1 = H$  and  $R_5 = \text{phenyl}$  seems quite certain. Two assignments of the proton hyperfine constants are possible. At first the similarity between the 1.89 G proton hyperfine constant and the 2.3 G observed for the  $CH_2$  protons in the  $\alpha$ -hydroxytetronic acid system would seem to indicate that this constant should be assigned to the proton at the  $C_5$  position. This assignment is, however, at variance with the general rule that protons attached to a heterocyclic nitrogen atom have hyperfine constants similar to that of the nitrogen atom<sup>12</sup> and also with the results in  $D_2O$  described below. The 1.89 G constant is, therefore, assigned to the proton on the nitrogen and the 0.20 G constant to the proton at the  $C_5$  position. The hyperfine interaction with the phenyl protons is clearly very small. Comparison of the line shape with that of synthetic multiplets assuming two equivalent ortho protons shows that any contribution must be less than 0.03 G, a fact which is not surprising in view of the small  $C_5$  proton constant.

Because of the ambiguity indicated above, the experiment was repeated in  $D_2O$  where the proton on the nitrogen is replaced by deuterium. The spectrum of Figure 1b shows that the proton doublet of 1.89 G is replaced by a deuterium pattern having a spacing of  $\sim 1.89/6.514 = 0.290$  G as expected from the above assignment for the protonated radical. In this case the hydrogen and deuterium hyperfine constants are similar so that the lines of the central pairs of the six-line subpatterns almost overlap, but the difference  $a^D - a^H$  can be accurately determined to be 0.08 G from the

(12) R. W. Fessenden and P. Neta, *Chem. Phys. Lett.*, **18**, 14 (1973).



**Figure 2.** Second-derivative esr spectrum derived from 1 mM 1-methyl-3-hydroxy-4-bromo-3-pyrrolin-2-one (a) in  $H_2O$  (pH 10.5) and (b) in DMSO containing  $\sim 20$  mM potassium *tert*-butoxide and 1% water. Because of the  $g$  factor difference of 0.00045 the center of the spectrum in DMSO is 0.76 G lower than in water as indicated. In each case the spectrum consists of three equally spaced triplets of quartets which can be assigned to a  $CH_2$  group with equivalent protons, a methyl group, and a nitrogen atom. The field is scanned from low to high field. In DMSO insufficient averaging of the  $g$  factor and hyperfine anisotropies results in appreciably smaller peak heights of the lines on the high-field side of the spectrum.

degree of overlap. The outermost lines give  $2a^D + a^H = 0.80$  G. The individual hyperfine constants are, therefore,  $a^H = 0.21$  and  $a^D = 0.29$  G.

**(IVb) The 1-Cyclohexyl-2,3,4-trioxopyrrolidine Radical Anion.** Irradiation of a 0.5 mM nitrous oxide saturated solution of 1-cyclohexyl-3-hydroxy-4-nitro-3-pyrrolin-2-one gave a weak spectrum of three groups of lines separated by 2.3 G. Each of these groups consisted of 12–14 lines separated by  $\sim 0.2$  G but which could not, however, be analyzed further. Since the center of the spectrum is at  $g = 2.00491$  and the presence of a nitrogen atom is evident by the tripling of the pattern, it is obvious that the radical present is related to the other radicals described here. Presumably, it is radical IV with  $R_1 = \text{cyclohexyl}$  and  $R_5 = H$  with the complicated fine structure resulting from hyperfine interactions of  $\sim 0.2$  G by nonequivalent  $\beta$  protons of the cyclohexyl groups. If the  $\beta$  protons are equivalent in pairs, one would expect the individual groups to consist of patterns of 18 lines.

**(IVc) The 1-Benzyl-2,3,4-trioxopyrrolidine Radical Anion.** Aqueous solutions of 1-benzyl-3-hydroxy-4-bromo-3-pyrrolin-2-one showed a reasonably intense spectrum of radical IV with  $R_1 = \text{benzyl}$  and  $R_5 = H$  even without irradiation. This spectrum consists of 27 lines resulting from hyperfine interaction by one nitrogen ( $a^N = 2.19$  G), two equivalent protons ( $a^H = 2.01$  G), and a second group of two equivalent protons ( $a^H = 0.49$  G). The center of the spectrum is at  $g = 2.00493$ .

**(IVd) The 1-Methyl-2,3,4-trioxopyrrolidine Radical Anion.** A more extensive series of studies was carried out on aqueous solutions of 1-methyl-3-hydroxy-4-bromo-3-pyrrolin-2-one which gave the spectrum of Figure 2a in the absence of irradiation. The 36-line pattern exhibited by this radical shows  $a^H(CH_3) = 3.35$

Table I. ESR Spectral Parameters of Radical IV

	Radical		Parent molecule X	Solvent	g factor <sup>a</sup>	Hyperfine constants <sup>a</sup>		
	R <sub>1</sub>	R <sub>5</sub>				a <sup>N</sup>	a <sup>H</sup> (C <sub>5</sub> proton)	a <sup>H</sup> (others)
IVa	H	Phenyl	NO <sub>2</sub>	H <sub>2</sub> O	2.00497	1.89	0.20	1.89 (nitrogen proton)
	D	Phenyl	NO <sub>2</sub>	D <sub>2</sub> O	2.00497	1.86	0.21	0.29 (nitrogen deuteron) <sup>b</sup>
IVb	Cyclohexyl	H	NO <sub>2</sub>	H <sub>2</sub> O	2.00491	~2.3	<sup>c</sup>	<sup>c</sup>
IVc	Benzyl	H	Br	H <sub>2</sub> O	2.00493	2.19	0.49 (2)	2.01 (2)(benzyl CH <sub>2</sub> protons)
				DMSO	2.00537	1.84	0.67 (2)	1.54 (2)(benzyl CH <sub>2</sub> protons)
IVd	Methyl	H	Br	H <sub>2</sub> O	2.00492	2.31	0.42 (2)	3.35 (3)(methyl protons)
				DMSO	2.00537	1.92	0.63 (2)	2.68 (3)(methyl protons)

<sup>a</sup> The g factors are accurate to  $\pm 0.00003$  and hyperfine constants to  $\pm 0.02$  G. The number of equivalent nuclei are given parenthetically. <sup>b</sup> Deuterium hyperfine constant. A value of  $1.89/6.514 = 0.290$  is expected from the corresponding proton hyperfine constant. <sup>c</sup> Pattern too complex for detailed analysis at the observed intensity.

G,  $a^{\text{H}}(\text{CH}_2) = 0.42$  G, and  $a^{\text{N}} = 2.31$  G and clearly allows one to assign the spectrum to radical IV with  $R_1 = \text{CH}_3$  and  $R_5 = \text{H}$ . The g factor is 2.00492. The intensity of the spectrum reaches the level of Figure 2a ~20 min after preparation of the solution (1 mM, pH 10.5). The radical present is very stable and while it decays slowly it has been observed for at least 24 hr after sample preparation. From this fact one can estimate the second-order rate for reaction with itself as  $< 10^2 \text{ M}^{-1} \text{ sec}^{-1}$ . Irradiation of the solution with ultraviolet light or with an electron beam at the currents normally used in the *in situ* radiolysis studies brings about an immediate decrease in spectral intensity, apparently because the radical is removed by other more abundant radicals produced in the photolysis or radiolysis. Irradiation at very low electron beam currents does, however, produce an increase in intensity so that reaction sequence I appears to be at least one source of radical IV in this case. Saturation of the solution with oxygen causes the spectrum to disappear because of paramagnetic broadening, but the radicals are apparently unaffected since the spectrum reappears in its original intensity upon purging of the oxygen by bubbling with nitrogen. Attempts to observe spectra in acidic solutions were unsuccessful.

**Experiments in DMSO.** Solutions of the two bromo compounds in DMSO containing potassium *tert*-butoxide gave spectra with patterns similar to those found in the aqueous solutions but approximately 10 times more intense. Addition of a small concentration of water (1%) was necessary in order to fully develop the spectra. The spectrum obtained with 1-methyl-3-hydroxy-4-bromo-3-pyrrolin-2-one is indicated in Figure 2b. During the course of a single scan there was little change in the concentration of radicals so that the asymmetry in line intensity is quite real. Apparently, there is insufficient averaging of the anisotropies in the relatively viscous DMSO solutions. Russell<sup>13</sup> has described generation of semidiones from  $\alpha$ -bromo ketones in basic DMSO solutions, and the chemistry here is presumably similar, *i.e.*, replacement of the halogen by OH and subsequent oxidation to the radical. No spectrum was observed from the 3-hydroxy-4-nitro-5-phenyl-3-pyrrolin-2-one in the DMSO-potassium *tert*-butoxide system. It is readily seen in Figure 2 that a considerable difference exists between the esr parameters in aqueous and in DMSO solution.

The spectral data for all of the above radicals are summarized in Table I.

(13) G. A. Russell, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, p 95.

**Comments on the Radical Chemistry.** Considering the relative unreactivity of these radicals, the intensities of their esr spectra, as observed in the radiolysis experiments, are very weak relative to those found for radicals I and II under similar conditions where it was possible to observe the <sup>13</sup>C spectra at the natural abundance level.<sup>4</sup> In the present cases the large number of lines does, of course, result in reduction of the relative intensity of the individual lines. For example, in the *N*-methyl substituted radical the unit lines represent a fraction of the total intensity of the spectrum smaller by a factor of 24 than those of radical II. However, even after this reduction is taken into account, the observed intensities are still very much lower than expected. The various radiolysis experiments on the radicals from the bromo derivatives show that the radicals are consumed very rapidly by other radiation-produced radicals as in the case of the radiation-induced oxidation of  $\alpha$ -bromotetronic acid by OH radicals where the esr spectra are also less intense than expected.<sup>4,14</sup> In order to explain the low intensities observed here similarly one must assume that the production of the radicals by reaction sequence I is relatively inefficient (accounting for perhaps only 10% of the OH). For the bromo derivatives it was possible, as indicated above, to demonstrate that an increase in radical concentration can be produced by irradiation at an appropriately low-beam current so that reaction sequence I seems to be a likely source. Other oxidation mechanisms are obviously readily operative and very probably involve hydrolysis of the bromide and subsequent oxidation of the 4-hydroxy derivative. In the cases of the nitro derivatives no radicals were observed in the absence of irradiation so that sequence I seems to be the sole source in these experiments, presumably because in these cases the nitro derivatives do not hydrolyze readily.

**Electronic Structure of the Radicals.** In no case is there any evidence for magnetic nonequivalence of the two protons at the C<sub>5</sub> position either in DMSO or in water. The equivalence of these protons indicates that the three CO groups, the C<sub>5</sub> carbon atom, and the nitrogen atom occupy a plane which also contains the remaining bonding orbital of the nitrogen. The g factors (2.00491–2.00497) are high and very similar to those found for radical I (2.00519)<sup>4</sup> and radical II (2.00519).<sup>3,4</sup> These high g factors imply the existence of considerable spin density of the oxygen atoms and there seems to be little question but that the electron is for the most part delocalized in the tricarbonyl system. The 3.35 G

(14) M. A. Schuler, K. Bhatia, and R. H. Schuler, submitted for publication.

hyperfine constant for the methyl protons in the *N*-methyl radical indicates, however, that there is also considerable spin density on the ring nitrogen. Observations on various simple radicals with CH<sub>3</sub> attached to a nitrogen ( $a^{\text{H}}(\text{CH}_3) = 33.61$  G for (CH<sub>3</sub>)<sub>2</sub>-NH<sup>+</sup>,<sup>15,16</sup> 28.56 G for (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>,<sup>15</sup> and 28.48 G for (CH<sub>3</sub>)<sub>2</sub>N<sup>·</sup>,<sup>15,16</sup>) suggest a value for  $Q^{\text{H}}(\text{CH}_3)$  slightly higher than the value of 29.3 G derived for a CH<sub>3</sub> group attached to carbon.<sup>17</sup> Using a value of 30 G we calculate a spin density of 0.11 on the ring nitrogen. Since  $Q^{\text{N}}$  is  $\sim 20$  G,<sup>15</sup> a spin density of this magnitude completely explains the relatively high nitrogen hyperfine constants observed for the *N*-substituted radicals (2.2–2.3 G), in spite of the fact that one expects some contribution from spin density on the adjacent C<sub>2</sub> carbon. The 1.89 G proton and nitrogen hyperfine constants of the first entry in Table I indicate that where a proton is attached to the nitrogen the spin density on the nitrogen is slightly ( $\sim 20\%$ ) lower.

We can now intercompare the very small hyperfine constants observed for the C<sub>5</sub> protons with values for the corresponding protons in the radicals from reductive acid (radical I; 6.00 G) and hydroxytetronic acid (radical II; 2.32 G). It previously was pointed out that the large difference between these latter values implied significant spin density on the heterocyclic oxygen atom of radical II.<sup>4</sup> Assuming that the signs of the molecular wave function at the positions of the two atoms adjacent to the CH<sub>2</sub> group are opposite, the effects of spin density at these two positions will partially cancel as was pointed out some time ago by Whiffen.<sup>18</sup> Assuming this to be the case, it was previously suggested that for radical II there is a spin density  $\sim 0.03$  on the heterocyclic oxygen atom. The <sup>13</sup>C spectra of radicals I and II show that the electronic configurations of these two radicals are quite similar and suggest a spin density on the carbon atom adjacent to the CH<sub>2</sub> group of  $\sim 0.16$ . The spin density cannot be significantly larger since the hyperfine interaction of the protons of a methyl group attached at

this position is only  $\sim 0.05$  G.<sup>19</sup> While the <sup>13</sup>C spectra are not available for the present examples, the similarity in *g* factors indicates that the spin distribution cannot be grossly different from that of radicals I and II. As indicated above, the present case is extremely important in that the spin density on the heterocyclic atom can be directly probed by the attached H atom or CH<sub>3</sub> group. One can test the arguments used in the discussion of radical II, since in the present case one expects from these arguments almost complete cancellation of the effects of spin density at the two positions<sup>20</sup> and as a result a very small coupling constant for the CH<sub>2</sub> protons, *i.e.*

$$a^{\text{H}}(\text{CH}_2) = 35.2[\sqrt{\rho(\text{CH}_4)} - \sqrt{\rho(\text{N})}]^2 \sim 0.2 \text{ G} \quad (2)$$

The value observed for the *N*-methyl radical is only slightly greater. The present study gives, therefore, substantial additional weight to the suggestion of a spin density  $\sim 0.03$  on the heterocyclic oxygen in the radicals produced by oxidation of  $\alpha$ -hydroxytetronic and ascorbic acids.

In the studies in DMSO a considerable increase in the *g* factors is observed indicating that an even greater amount of spin density has been transferred from the ring atoms to the carbonyl oxygen atoms. Such a transfer is corroborated by a decrease in the hyperfine constants of both the nitrogen and the protons on the groups attached to the nitrogen. For example, in the case of the *N*-methyl derivative  $a^{\text{N}}$  drops by a factor of 0.83 and  $a^{\text{H}}(\text{CH}_3)$  by a factor of 0.80. Accompanying this decrease there is also a substantial increase in the hyperfine constants of the protons at the C<sub>5</sub> position, as would be expected according to eq 2 as a result of the decrease in the spin density on the nitrogen.

**Acknowledgment.** The authors wish to thank Professor R. W. Fessenden for valuable discussions and J. J. Lindsey for kindly furnishing samples of the two nitro derivatives prepared during the course of his thesis researches.

- (15) R. W. Fessenden and P. Neta, *J. Phys. Chem.*, **76**, 2857 (1972).  
 (16) W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, **92**, 5235 (1970).  
 (17) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).  
 (18) D. H. Whiffen, *Mol. Phys.*, **6**, 223 (1963).

- (19) Y. Kirino and R. H. Schuler, *J. Amer. Chem. Soc.*, **95**, 6926 (1973).  
 (20) R. W. Fessenden and R. H. Schuler, "Advances in Radiation Chemistry," Vol. II, M. Burton and J. L. Magee, Ed., Wiley, New York, N. Y., 1970, p 103.