119. *The Electron Spin Resonance Spectra of Some Hydroxylamine Free Radicals.*

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Hydroxylamine and *N*-substituted hydroxylamines can be oxidised to short-lived free radicals by use of one-electron-abstracting oxidants. The electron spin resonance spectra, and therefore the structures, of these radicals depend on the acidity of the reaction mixture. It is suggested that, in aqueous carbonate solutions, the radicals obtained from hydroxylamine and *N*-methylhydroxylamine are actually derived from hydroxy-carbamates, $HO{\cdot}NR{\cdot}CO_2^-$.

ELECTRON SPIN RESONANCE (e.s.r.) spectra of short-lived free radicals are obtained when hydroxylamine and a number of its simple derivatives are oxidised in the flow apparatus previously used in this laboratory.[1] Spectra of the hydroxylamine and *N*-methyl hydroxylamine radicals have been independantly observed by J. R. Thomas and his co-workers[2] in the Richmond Laboratory of the California Research Corporation and, by mutual agreement, we indicate in this Paper the extent of duplication of experimental work. These radicals are complementary to the *N*-phenylhydroxylamine radical observed by Buchachenko.[3] Our results are summarised in the Table.

The dominant features of the spectra are as follows.

(1) The hydroxylamine and *N*-methylhydroxylamine radicals were obtained by oxidation of the free base in methanol, or of the hydrochloride in 75% aqueous methanol, with ceric ammonium nitrate. No spectra were obtained on oxidation with ceric sulphate

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[1] Stone and Waters, *Proc. Chem. Soc.*, 1962, 253; Dixon and Norman, *J.*, 1963, 3122.

[2] Adams, Thomas, and Nicksic, unpublished results.

[3] Buchachenko, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1963, 1120.

Preparation and details of spectra of hydroxylamine radicals.

Hydroxylamine deriv. and buffer	Oxidant and buffer	Sol-vent *	In-tensity †	Coupling constants (œrsteds) ‡				Radical
				α_N	α_{N-H}	α_{N-CH_3}	α_{C-H} §	
NH_2OH	Ceric ammonium nitrate ‖	M	w	11·9	11·9			$\cdot O{-}NH_2$
NH_2OH,HCl	Ceric ammonium nitrate	aq. M	w	,,	,,			
NH_2OH,HCl in M/10-K_2CO_3	Ferricyanide in M/10-K_2CO_3	W	s	9·2	12·7			$\cdot O{-}NM{-}CO_2^-$
	or ceric ammonium nitrate, no buffer	W	s	,,	,,			
NH_2OH,HCl in M/10-$NaHCO_3$	Ferricyanide in M/10-$NaHCO_3$	W	w	,,	,,			
MeNHOH	Ceric ammonium nitrate ‖	M	w	13·8	13·8	13·8		$\cdot O{-}NH{-}Me$
MeNHOH,HCl	Ceric ammonium nitrate	aq. M	w	,,	,,	,,		
MeNHOH,HCl in N/10-NaOH (carbonate-free)	Ferricyanide in N/10-NaOH (carbonate-free)	W	vw	14·5 $\pm$1·0	14·5 $\pm$1·0	14·5 $\pm$1·0		
MeNHOH,HCl in M/10-K_2CO_3	Ferricyanide in M/10-K_2CO_3 or ceric ammonium nitrate, no buffer	W	s	10·8		11·3		$\cdot O{-}NMe{-}CO_2^-$
Slightly acid $HO{\cdot}NH{\cdot}SO_3H$	Ceric sulphate in M-H_2SO_4	W	s	10·8	10·8			$(\cdot O{-}NM{-}SO_3)_-$
,,	Ferricyanide in N/10-NaOH	W	w	9·7				$(\cdot O{-}\underset{\cdot\cdot}{\dot{N}}{-}SO_3)^{2-}$
$HO{\cdot}NH{\cdot}CO_2Et$ in M-H_2SO_4	Ceric sulphate in M-H_2SO_4	W	s	7·0	11·1		1·0	$\cdot O{-}NH{-}CO_2Et$
$HO{\cdot}NH{\cdot}CO_2Et$, pH 11—14	Ferricyanide, pH 11—14	W	s	7·3			1·2	$(\cdot O{-}\underset{\cdot\cdot}{\dot{N}}{-}CO_2Et)^-$
$HO{\cdot}NH{\cdot}CO_2Me$ in M-H_2SO_4	Ceric sulphate in M-H_2SO_4	W	s	7·0	11·1		1·1	$\cdot O{-}NH{-}CO_2Me$
$HO{\cdot}NH{\cdot}CO_2Me$, pH 11—14	Ferricyanide, pH 11—14	W	s	7·4			1·3	$(\cdot O{-}\underset{\cdot\cdot}{\dot{N}}{-}CO_2Me)^-$
$HO{\cdot}N(Me){\cdot}CO_2Et$ in M-H_2SO_4	Ceric sulphate in M-H_2SO_4	W	vs	9·1	10·1		1·0	$\cdot O{-}NMe{-}CO_2Et$
$HO{\cdot}N(Me){\cdot}CO_2Et$, pH 11—14	Ferricyanide, pH 11—14	W			**			
$HO{\cdot}NH{\cdot}COPh$ in M-H_2SO_4	Ceric sulphate in M-H_2SO_4	W	s	6·0	10·3			$\cdot O{-}NM{-}CO{-}Ph$
$HO{\cdot}NH{\cdot}COPh$, pH 11—14	Ferricyanide, pH 11—14	W	s	5·7				$(\cdot O{-}\underset{\cdot\cdot}{\dot{N}}{-}CO{-}Ph)^-$

* M, methanol; aq. M, 75% aq. methanol; W, water. † w, Weak; s, strong; v, very. ‡ The coupling constants are estimated to be accurate to within 0·2 œrsted. § a_{C-H} due to ester protons in $O{\cdot}CH_3$ or $O{\cdot}CH_2{\cdot}$ groups. ‖ Thomas *et al.*[2] ** As above, but no secondary radical was observed (see text).

in aqueous sulphuric acid, or with aqueous alkaline ferricyanide buffered with sodium silicate, sodium borate, or trisodium phosphate. However, in carbonate-free sodium hydroxide, *N*-methylhydroxylamine gave a very weak signal of a similar type on oxidation with potassium ferricyanide. The hydroxylamine radical shows a 1 : 3 : 4 : 3 : 1 grouping, attributable to the $-NH_2$ group, with $a_N \sim a_H$ (Fig. 1). The *N*-methylhydroxylamine radical shows a 1 : 5 : 11 : 14 : 11 : 5 : 1 grouping, attributable to the $CH_3{-}NH{-}$ grouping, with $a_N \sim a_H \sim a_{CH_3}$. We therefore ascribe the spectra to the radicals $\cdot O{-}NH_2$ and $\cdot O{-}NH{-}CH_3$, respectively.

(2) Oxidation of hydroxylamine with ferricyanide in alkaline carbonate solution gave a radical showing an N–H grouping (Fig. 2), while the radical from *N*-methylhydroxylamine, formed under the same conditions, shows an $N{-}CH_3$ grouping (Fig. 3). The spectra may also be obtained in a static system when hydroxylamine and *N*-methylhydroxylamine are oxidised with ferricyanide in hydrogen carbonate solution. Since these spectra were not

obtained in carbonate-free solutions of the same pH, we ascribe them to radicals derived from the *N*-hydroxy-carbamates $HO{\cdot}NH{\cdot}CO_2^-$ and $HO{\cdot}NMe{\cdot}CO_2^-$. Additional evidence for this assignment is provided by the fact that when a solution of hydroxylamine in sodium carbonate is treated with a little ferric chloride, a deep orange-red solution results, the colour being similar to that of the ferric complex of an aliphatic hydroxamic acid. When ferric chloride is added to a solution of the hydroxylamine in sodium hydroxide or in aqueous ammonia, there is immediate precipitation of ferric hydroxide and no sign of formation of a soluble iron complex. We therefore conclude that the reversible reaction

Electron spin resonance spectra.

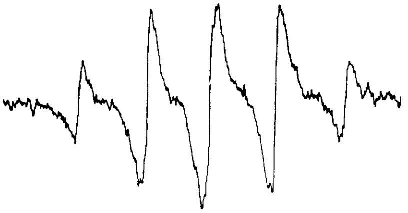


FIG. 1. The hydroxylamine radical, $\cdot O{-}NH_2$.

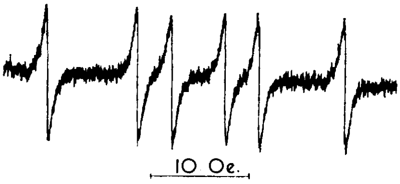


FIG. 2. Radical from hydroxylamine in carbonate solution, $\cdot O{-}NH{-}CO_2^-$.

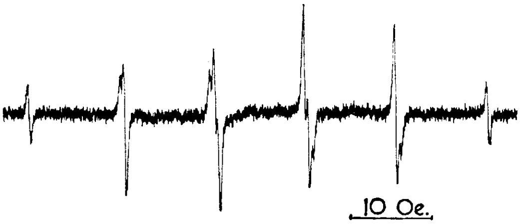


FIG. 3. Radical from *N*-methylhydroxylamine in carbonate solution, $\cdot O{-}NMe{-}CO_2^-$.

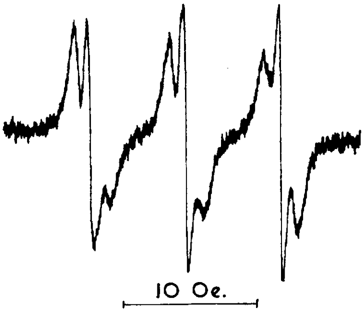
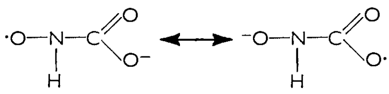


FIG. 4. Radical from ethyl *N*-hydroxycarbamate at pH 11—14 $(\cdot O{-}N{-}CO_2Et)^-$.

$$HO{\cdot}NH_2 + CO_3^{2-} \rightleftharpoons HO{\cdot}NH{\cdot}CO_2^- + OH^-$$

occurs, and that extended mesomerism involving the oxycarbonyl groups, *i.e.*,



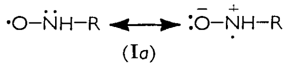
gives additional stability to the resulting radical.

(3) Oxidation of ethyl and methyl *N*-hydroxycarbamate gave spectra in accordance with radicals of the type $\cdot O{-}NH{-}CO_2R$, showing fine-structure due to interaction with the alkoxy-group. Similarly, oxidation of benzhydroxamic acid gave the radical $\cdot O{-}NH{-}CO{-}Ph$, but no fine-structure due to interaction with the phenyl group was observed. Oxidation of these compounds with alkaline ferricyanide gave spectra in which interaction with the N–H group was no longer apparent (Fig. 4). These we ascribe to radicals of the type $(\cdot O{-}N{-}CO_2R)^-$ and to $(\cdot O{-}N{-}COPh)^-$, respectively.

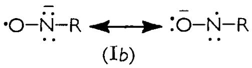
(4) Oxidation of ethyl *N*-hydroxy-*N*-methylcarbamate, either with ceric ions in aqueous acid or with alkaline ferricyanide, gave identical spectra, showing splitting due to N, CH_3, and $-CH_2CH_3$ groups, in accordance with the radical $\cdot O{-}NMe{-}CO_2Et$. In acid solution, extra lines due to a secondary radical, appeared when a low flow-rate was used.

(5) Oxidation of hydroxylaminemonosulphonate ion with ceric ion in aqueous acid gave a 1 : 2 : 2 : 1 quartet, which we assign to the radical $(\cdot\text{O–NH–SO}_3)^-$, with $a_\text{N} \sim a_\text{H}$. Oxidation of hydroxylaminemonosulphonate ion with ferricyanide in aqueous sodium hydroxide gave a triplet signal, which we ascribe to the radical $(\cdot\text{O–}\underset{\cdot\cdot}{\dot{\text{N}}}\text{–SO}_3)^{2-}$. When hydroxylaminedisulphonate ion was oxidised with an acidic solution of ceric ions, using the flow system, the a_N value was the same as that obtained from an alkaline solution of Frémy's salt.

We have formulated the radicals described above as being of the type $\cdot\text{O–}\ddot{\text{N}}\text{H–R}$ in acid solution and $(\cdot\text{O–}\underset{\cdot\cdot}{\ddot{\text{N}}}\text{–R})^-$ in alkali, since, for these, mesomeric structures involving favourable charge-separation, with the unpaired electron on nitrogen, may be written as (I*a*) and (I*b*), respectively:

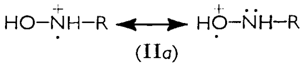

$\cdot\text{O}-\ddot{\text{N}}\text{H}-\text{R} \longleftrightarrow :\overset{-}{\text{O}}-\underset{\cdot}{\overset{+}{\text{N}}}\text{H}-\text{R}$

(I*a*)

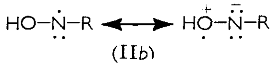

$\cdot\text{O}-\underset{\cdot\cdot}{\overset{-}{\text{N}}}-\text{R} \longleftrightarrow :\overset{-}{\text{O}}-\underset{\cdot\cdot}{\dot{\text{N}}}-\text{R}$

(I*b*)

This, however, is not the case for the protonated species (II*a*) and (II*b*):


$\text{HO}-\underset{\cdot}{\overset{+}{\text{N}}}\text{H}-\text{R} \longleftrightarrow \text{H}\underset{\cdot}{\overset{+}{\text{O}}}-\ddot{\text{N}}\text{H}-\text{R}$

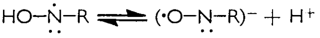
(II*a*)


$\text{HO}-\underset{\cdot\cdot}{\dot{\text{N}}}-\text{R} \longleftrightarrow \text{H}\underset{\cdot}{\overset{+}{\text{O}}}-\underset{\cdot\cdot}{\overset{-}{\dot{\text{N}}}}-\text{R}$

(II*b*)

This is equivalent to saying that the N–O bond in (I) is a three-electron bond.[4] Radical (II*a*) would be analogous to the hydrazine radical $(\text{NH}_2\text{–NH}_2)^+$ studied by Adams and Thomas.[5] Radicals of the type (I) and (II) may not be distinguishable by means of e.s.r. spectroscopy, since hyperfine splitting due to hydroxyl protons is usually small and is sometimes not observable.[6] Again, the fact that radicals of type (I) and (II) are related by the acid–base equilibria:


$(\text{HO}-\dot{\text{N}}\text{H}-\text{R})^+ \rightleftharpoons \cdot\text{O}-\text{NH}-\text{R} + \text{H}^+$


$\text{HO}-\underset{\cdot\cdot}{\dot{\text{N}}}-\text{R} \rightleftharpoons (\cdot\text{O}-\underset{\cdot\cdot}{\text{N}}-\text{R})^- + \text{H}^+$

may vitiate any attempts to distinguish experimentally between them. However, the fact that *O*-methylhydroxylamine is only slowly oxidised in aqueous acid containing ceric ion, in methanolic ceric ammonium nitrate, or in alkaline ferricyanide, and that no spectra could be observed either in a static system or by using the flow method, is strong support for our radicals being formulated as of type (I). The very unstable radical obtained from *N*-methylhydroxylamine in carbonate-free sodium hydroxide still appears to be of type (I*a*), containing an N–H group, but this is absent in the radicals formed when acylated compounds HO·NH·COR (R = Ph, OEt, or OMe) are oxidised with alkaline ferricyanide. We ascribe this stabilisation of structure (I*b*) to the electrophilic character of the acyl group.

EXPERIMENTAL

Materials.—*N*-Methylhydroxylamine hydrochloride was prepared by reducing nitromethane with zinc and ammonium chloride,[7] and was crystallised from ethanol. *O*-Methylhydroxylamine was supplied by Eastman Organic Chemicals. Ethyl *N*-hydroxycarbamate was prepared, in ether, from hydroxylamine hydrochloride and ethyl chloroformate in the presence of potassium carbonate; [8] the colourless oil obtained on evaporation of the ether was not purified further. Methyl *N*-hydroxycarbamate was similarly prepared, using methyl chloroformate. Ethyl *N*-hydroxy-*N*-methylcarbamate was prepared from *N*-methylhydroxylamine hydrochloride. The sodium salt of benzhydroxamic acid was made by treating hydroxylamine, in n-butyl alcohol, with ethyl benzoate and then with sodium ethoxide; [9] the precipitated salt was washed with ethanol and then with ether. An aqueous solution of hydroxylaminemonosulphonate was

[4] Linnett, *J. Amer. Chem. Soc.*, 1961, **83**, 2651.
[5] Adams and Thomas, *J. Chem. Phys.*, 1963, **39**, 1904.
[6] Symons, *Tetrahedron*, 1962, **18**, 333.
[7] Meisenheimer and Chou, *Annalen*, 1939, **539**, 84.
[8] Jones, *Amer. Chem. J.*, 1898, **20**, 39.
[9] DeWitt, Hurd, and Brownstein, *J. Amer. Chem. Soc.*, 1925, **47**, 67.

obtained by boiling an aqueous solution of dipotassium hydroxylaminedisulphonate[10] for 30 min., to effect the required degree of hydrolysis. Methanolic solutions of free hydroxylamine and of *N*-methylhydroxylamine were prepared by treating the hydrochlorides in methanol with sodium methoxide, the precipitated sodium chloride being filtered off.

Reactions.—2×10^{-2}M-solutions of the hydroxylamine derivatives were mixed with 10^{-2}M-solutions of the oxidants. The flow rates varied between 100 and 300 ml./min., and were adjusted to give the optimum resolution and signal-to-noise ratio. Signals described as "weak" in the Table required high microwave power and modulation amplitude for their detection, as well as high flow rates. The spectra were calibrated immediately after recording by reference to Frémy's salt.

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[10] Rollefson and Oldershaw, *J. Amer. Chem. Soc.*, 1932, **54**, 977.