sion spectrum is shown in Figure 2 (as determined with 400-mμ stimulating light, using an Aminco emission spectrometer). In the presence of the complex, however, the phosphorescent or triplet-state emission is quenched, but not that of the first singlet state. The implication is that it is the triplet state that is active in the sensitization.

In addition, a series of measurements was carried out using benzophenone as sensitizer and various concentrations of complex. An oxygen effect is present at least in this particular system, since the yield for Co(II) production rose from 0.064 to 0.36 on thorough degassing of the solution. Further, the quantum yield of the nondeaerated solutions decreases with decreasing complex concentration, presumably as a result of competition between deactivation of the sensitizer by the complex and by other processes. The following reaction scheme is thus suggested

$$\mathrm{S} \xrightarrow{h\nu} \mathrm{S}^* \longrightarrow \mathrm{T} \qquad (1)$$

$$\mathrm{T} \xrightarrow{k_1} \mathrm{S} \qquad (2)$$

$$\mathrm{T} + \mathrm{C} \xrightarrow{k_2} \mathrm{S} + \mathrm{Co(II)} \qquad (3)$$

where S denotes sensitizer and T its triplet state, produced *via* an excited singlet state S*, T being produced in over-all quantum yield ϕ. It is assumed that the complex, C, may reactively deactivate T. In the present case C diminishes with time; assuming $d[\mathrm{T}]/dt = 0$, *i.e.*, stationary-state kinetics, one obtains

$$1/\phi_{\mathrm{obsd}} = 1/\phi + (k_1/k_2\phi)(\beta/C_0) \qquad (4)$$

where ϕ_{obsd} is the observed quantum yield for Co(II) formation, C_0 is the initial complex concentration, and β is given by

$$\beta = [C_0/(C_0 - C)] \ln (C_0/C) \qquad (5)$$

with C now denoting the final complex concentration.

The results are plotted according to eq 4 in Figure 3, and the intercept and slope give about unity and 0.013 for ϕ and k_1/k_2, respectively. If reaction 3 is diffusion controlled, k_2 should be about $6 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$,[9] which would then make k_1 about $8 \times 10^7\ \mathrm{sec}^{-1}$. This last value is similar to those reported for other systems involving benzophenone.[10]

Our investigations are continuing, but some preliminary discussion is appropriate here. The wavelengths of the stimulating light used, as well as those corresponding to the triplet-state energies of the various sensitizers, are much longer than the threshold wavelengths for direct photodecomposition of these complexes. This situation plus the lack of any appreciable photosensitivity of the d–d bands themselves make it seem unlikely that energy transfer has occurred into the d–d or ligand field system. On the other hand, the first CT bands of these complexes lie at much higher energies than available here. The remaining possibility seems to be that the sensitizers are interacting with CT triplet states of the complexes. Such triplet states must exist in principle, and their theoretical description has been discussed to some extent.[11] The actual singlet–triplet CT transitions are not evident in the absorption spectra of Co(III) complexes, presumably because of being hidden by more intense d–d ones. Our suggestion is then that the sensitized decompositions reported here are those of low-lying CT triplet states which happen not to be easily populated by direct absorption of light.

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Studies of Free Radicals. II. Chemical Properties of Nitronylnitroxides. A Unique Radical Anion

Sir:

In an earlier communication the preparation of the highly stable aromatic nitronylnitroxide radicals III (R = Ar) was described.[1] We now report on some unusual chemical properties of the nitronylnitroxide grouping.

The alkylnitronylnitroxides III (R = alkyl) are prepared like their aromatic analogs by treatment of the bishydroxylamine I with aldehydes to give tetrahydroimidazoles II, which are subsequently oxidized with aqueous sodium periodate or lead dioxide. The resulting radicals are deep red solids which display esr spectra in solution having basic five-line patterns caused by coupling with two equivalent nitrogen nuclei. Further splitting of each line by the α-alkyl hydrogens usually is also observed together with occasionally resolved very weak coupling with the twelve methyl hydrogens (Table I).

Table I. Coupling Constants (in gauss)[a] of Nitronylnitroxides III in Benzene

R	a_{N}	$a_{\alpha\text{-H}}$	$a_{4,5\text{-CH}_3}$
CH_3	7.42	3.3	0.21
CH_2CH_3	7.42	2.0	
$(CH_2)_{12}CH_3$	7.45	2.1	
CH_2OH	7.48	2.2	0.2
$CH(CH_3)_2$	7.5	~0.9	
$CH(OC_2H_5)_2$	7.25	<0.5	0.24

[a] ±0.03 gauss.

Although many of these radicals can be stored at room temperature for several weeks without decomposition, the radicals bearing α hydrogens are somewhat less stable than their aromatic analogs. By comparison, however, the hydroxymethylnitronylnitroxide III (R = CH_2OH)[2] was exceptionally labile and was found to undergo a gradual change on standing that could be greatly accelerated in alcoholic sodium hydroxide. The almost exclusive product of this reaction was a new red water-soluble radical, identified as III, R = H,[2] from its esr pattern of five doublets [$a_{\mathrm{N}} = 7.26$,

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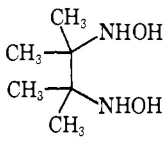
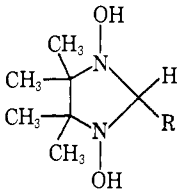
[1] J. H. Osiecki and E. F. Ullman, *J. Am. Chem. Soc.*, 90, 1078 (1968).

[2] Mass spectral and analytical data were in accord with the assigned structure.

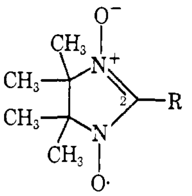
a_{H_2} = 3.44 gauss (benzene)] and by independent synthesis by condensation of I with either ethyl orthoformate with an acid catalyst or with formaldehyde followed by sodium periodate oxidation.



I



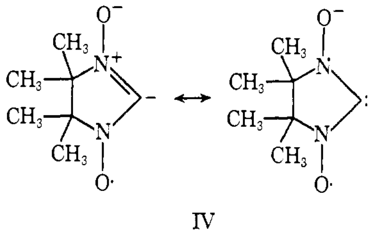
II



III

Among several possible mechanisms for the loss of the hydroxymethyl group from III, R = CH_2OH, is direct base-catalyzed elimination of formaldehyde to give an intermediate "carbenoid" radical anion IV. The possibility that the nitronylnitroxide grouping might have a sufficiently strong inductive effect to stabilize IV was suggested by the rapid alkaline hydrolysis of the ester III, R = $COOCH_3$[2] [prepared from I, methyl oxalic anhydride, and alcoholic sodium acetate; λ_{max}^{KBr} 1745 cm^{-1}, a_N = 7.12 gauss (benzene)] which proceeded roughly 2000 times faster than methyl benzoate ($k_{23°}{}^{H_2O}$ = 20 l./mole sec).[3] Moreover, an alkaline solution of the resulting carboxylate radical III (R = COO^-) [a_N = 8.1 gauss (H_2O)], while relatively stable at 0°, decarboxylated smoothly at 68.5° to give III, R = H ($k = 3.4 \times 10^{-4}$ sec^{-1}). Although more rapid formation of III, R = H, occurred upon acidification of solutions of III, R = COO^-, in basic solutions acid-catalyzed decarboxylation was unimportant since the rate was insensitive to pH. Thus decarboxylation of III, R = COO^-, appears to be unimolecular and very likely proceeds through the radical anion IV.

More direct evidence for the formation of IV was found by observation of rapid exchange at the 2 position in III, R = H, in deuterium oxide in the range pD 7–8 ($k_{23°} \sim 3.6 \times 10^4$[OD] sec^{-1}). Above pD 8 the rate was too fast to follow and below pD 7 the rate of exchange was nearly independent of pD ($k_{23°} \sim 3.3 \times 10^{-3}$ sec^{-1}). By contrast, exchange of the α hydrogens in III, R = CH_3, was also observed, but the rate was 10^7–10^8 times slower which suggests that this compound may be significantly less acidic than III, R = H.



IV

The above exchange data for III, R = H, suggest two independent exchange mechanisms. One is an uncatalyzed exchange with D_2O below pD 7 which may involve a concerted process. The second, which is dominant above pD 7, is hydroxide ion catalyzed abstraction of the 2-hydrogen to give the radical anion IV. Assuming that IV is reprotonated in basic solutions at a diffusion-controlled rate (5×10^{10} l./mole sec),[4] the pK_a of III, R = H, is estimated from the above rate constant to be ~21.9. In accord with this estimate III, R = H, was not ionized by potassium *t*-butoxide in *t*-butyl alcohol (p$K_a \approx 19$),[5] but, in the more basic medium, DMSO–potassium *t*-butoxide, the five-doublet esr spectrum of III, R = H, collapsed to five single lines (a_N = 8.49 gauss) with additional weak coupling of 0.2 gauss due to the twelve methyl hydrogens. This new radical decomposed within 30 min at room temperature, but, on rapid reacidification of the solution, 80% of the starting radical III, R = H, could be regenerated. Convincing evidence that the new radical species must be IV was obtained by quenching the anion with chloromethyl ether to give a 24% yield of the methoxymethyl radical III (R = CH_2OCH_3) (a_N = 7.32, a_H = 1.5 gauss; benzene).

The behavior of III, R = H, toward base is reminiscent of the ready exchange of the 2-hydrogens in thiazolium and related heterocyclic cations.[6] Surprisingly, the rate of base-catalyzed deuterium exchange in the uncharged radical is comparable to all but the highest observed rates of exchange even in these positively charged compounds.[7] This exceptional acidity of the nitronylnitroxide radical III, R = H, is possibly due to the effect of the two nitrogens adjacent to the acidic site which are estimated from the nitrogen coupling constants to bear a total positive charge of nearly 1.6. However, despite this strong inductive influence at the 2-carbon, the effect seems to be greatly attenuated at the α position in the substituted radicals. This is manifest by the relatively low kinetic acidity of III, R = CH_3, and by the rather modest ester hydrolysis rate enhancement in III, R = $COOCH_3$. This rapid drop off in the inductive effect at the α position appears consistent with the expected field effect of the negatively charged oxygens which flank this position.

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[7] Based on the present results in acid solution, the reported very high rates of base-catalyzed exchange of several heterocyclic cations that have been calculated from exchange measurements in acidic solution must be considered suspect.[6]

[8] Synvar Postdoctoral Fellow, 1967–1969.

[9] Synvar Postdoctoral Fellow, 1967–1968.