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THE PHOTOLYSIS OF ALKYL NITRITES IN ALCOHOLIC MEDIA

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Recently, Mackor et al. reported the formation of dialkyl nitroxides and alkoxy-alkyl-nitroxides during the photolysis of alkyl nitrites in hydrocarbon solvents. (1) These radicals, which were characterised by their electron spin resonance spectra, showed nitrogen hyperfine splitting constants of approximately 15 gauss and 25-30 gauss respectively. We here report and discuss the observation of the e.s.r. spectra of similar radicals generated in alcoholic solvents.

The radicals were produced by photolysis of solutions made by addition of ethyl nitrite or t-butyl nitrite to an alcohol. The solutions were initially 0.1 to 0.7 M in nitrite and were irradiated with light from a 200 watt mercury lamp as they were pumped, at speeds of 0.5 to 30 ml. per sec., through an aqueous sample cell positioned in the cavity of a Varian spectrometer. The solution temperature was controlled by passing the liquid through a heat-exchanger immersed in a suitable coolant or heating bath.

In general the spectra of the nitroxide radicals predominated over those of the alkoxy-alkyl-nitroxides at high temperatures and slow flow rates as would be expected from the results of Mackor et al. (1) However the radicals observed were derived from the photolysis of the solvolysis product of the original nitrite by the alcohol solvent. Thus, photolysis of RONO in R OH always gave rise inter alia. to the species $R'O{-}N(S){-}\dot{O}$ (where S is a fragment derived from the solvent) with no sign of the radical $RO{-}N(S){-}\dot{O}$, and the overall reaction scheme may be written as :

$$\begin{aligned}
\mathrm{RONO} + \mathrm{R'OH} &\rightleftharpoons \mathrm{R'ONO} + \mathrm{ROH} \\
\mathrm{R'ONO} &\xrightarrow{h\nu} \mathrm{R'\dot{O}} + \mathrm{N\dot{O}} \\
\mathrm{R'\dot{O}} + \mathrm{R'OH} &\longrightarrow \mathrm{R'OH} + \mathrm{\dot{S}} \\
\mathrm{\dot{S}} + \mathrm{N\dot{O}} &\longrightarrow \mathrm{S{-}N{=}O} \\
\mathrm{S{-}N{=}O} + \mathrm{\dot{S}} &\longrightarrow \mathrm{S_2N{-}\dot{O}} \quad (a_N \approx 15 \text{ gauss}) \\
\mathrm{S{-}N{=}O} + \mathrm{R'\dot{O}} &\longrightarrow \mathrm{R'O{-}N(S){-}\dot{O}} \; (a_N \approx 25\text{-}30 \text{ gauss})
\end{aligned}$$

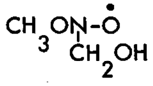
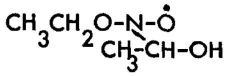
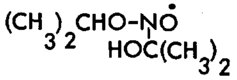
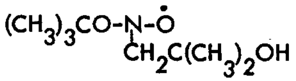
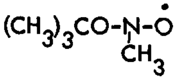
The fast alcoholysis of alkyl nitrites has been shown by Allen and Schonbaum to be an acid-catalysed reaction which follows the rate law (2) :-

$$-\frac{d}{dt}[\mathrm{RONO}] = k_2[\mathrm{H^+}][\mathrm{RONO}]$$

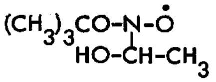
They suggested that the source of hydrogen ions in the so-called "neutral" alcoholysis of alkyl nitrites was nitric acid generated photochemically from the alkyl nitrite and their values for k_2 were typically of the order of $10\ \mathrm{sec.}^{-1}\ \mathrm{m.}^{-1}\ \mathrm{l.}$ In our systems, solvolysis must have proceeded largely to completion in thirty minutes, the time which elapsed between preparing the solutions and recording the first spectrum, which would imply the presence of a hydrogen ion concentration of about 10^{-4} moles per litre.

The structures and splitting constants of the radicals which were detected are given in the table and show several noteworthy features. Although both ethanol and isopropanol contain two types of C-H bond the structures of the radicals generated in these solvents indicate that hydrogen atom abstraction by the photolytically-generated alkoxy radicals occurs predominately at those bonds adjacent to the alcoholic hydroxyl groups. This is consistent with the known electrophilic properties of alkoxy radicals (3) which are further illustrated by the observation of $t\text{-BuO-N(CH(OH)CH}_3)\text{-}\dot{\mathrm{O}}$ as the predominant radical during the photolysis of 0.7 M ethyl nitrite in t-butanol. Evidently the alkoxy radicals react preferentially with the ethanol formed in the solvolysis reaction rather than with t-butanol even though the concentration of the latter is 25 times greater. The slower rate of formation of alkyl radicals in the alkyl nitrite/t-butanol system as compared with the other systems investigated is presumably also responsible for the non-observation of dialkyl nitroxides in this system. Another feature of the reactions involving t-butanol as solvent is the

TABLE

Solvent		Radicals observed (h.f.s. at 25° C)
Methanol	$(HOCH_2)_2-N\dot{O}$ a_N = 13.6 gauss a_H (4) = 6.8 gauss	 $CH_3O\underset{CH_2OH}{N}-\dot{O}$ a_N = 27.5 gauss a_H (2) = 5.1 gauss a_H (3) = 1.4 gauss
Ethanol	$(CH_3CHOH)_2-N\dot{O}$ Two Isomers a) a_N = 14.0 gauss a_H(2) = 5.3 gauss b) a_N = 14.0 gauss a_H(2) = 4.0 gauss	 $CH_3CH_2O-\underset{CH_3-CH-OH}{N}-\dot{O}$ a_N = 27.3 gauss a_H (1) = 3.5 gauss a_H(2) = 1.2 gauss
Isopropanol	$[(CH_3)_2\ COH]_2-N\dot{O}$ a_N = 15.2 gauss	 $(CH_3)_2CHO-\underset{HOC(CH_3)_2}{N}\dot{O}$ a_N = 27.4 gauss a_H(1) $<$ 1.0 gauss
t-Butanol	No dialkyl nitroxide radicals were detected.  $(CH_3)_3CO-\underset{CH_2C(CH_3)_2OH}{N}-\dot{O}$ a_N = 25.0 gauss a_H(2) = 7.6 gauss	 $(CH_3)_3CO-\underset{CH_3}{N}-\dot{O}$ a_N = 26.2 gauss a_H(3) = 8.7 gauss

In addition, the photolysis of 0.6 M ethyl nitrite in t-butanol leads to the formation of :



$(CH_3)_3CO-\underset{HO-CH-CH_3}{N}-\dot{O}$

a_N = 26.7 gauss

a_H(1) = 4.0 gauss

formation of t-BuO-N(CH_3)-$\dot{O}$ which indicates the intermediacy of the methyl radical produced by the well-known fragmentation of t-butoxy radicals. (3)

Some of the radicals listed in the table show interesting conformational effects. Thus in the series of alkoxy alkyl-nitroxides formed in methanol, ethanol and isopropanol, the trend in the proton splittings of the CH_3O, CH_3CH_2O and $(CH_3)_2CHO$ groups is presumably explicable in terms of conformational weighting of the various alkyl group rotamers. (4) A similar explaination accounts for the decrease from 5.1 gauss to 3.5 gauss of the α-hydrogen splittings from the groups $-CH_2OH$ and $-CH(CH_3)OH$ in the first two of these radicals. During the photolysis of a nitrite in ethanol, the spectra of two nitroxide species are observed; they have virtually identical g-factors and nitrogen hyperfine splitting constants and are possibly due to conformational isomers of the radical $(CH_3CHOH)_2$-N$\dot{O}$. The relative amplitudes of these spectra are temperature dependent and this effect is being further investigated in order to obtain information about the possible interconversion of the two species.

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