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ALKYLPEROXYNITROXIDES IN THE PHOTO-OXIDATION OF C-NITROSOALKANES AND THE 'SPIN TRAPPING' OF PEROXY RADICALS BY C-NITROSO-COMPOUNDS

Josef Pfab
Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, Scotland.

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The difficulties inherent in characterising reactive free radicals by electron spin resonance can often be avoided by the use of a 'spin trapping' technique. The method is based on the conversion of transient radicals to long-lived paramagnetic species by their addition to a diamagnetic scavenger, for example a monomeric C-nitroso-compound[1,2]. An impressive variety of carbon- and heteroradicals have been trapped successfully in this way. Surprisingly the application of the technique to the identification of peroxy radicals has not hitherto been studied in detail[3], in spite of the unique significance of these radicals in homolytic oxidation reactions.

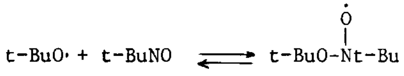
It is shown in this preliminary report that the 'spin trapping' of peroxy radicals using aliphatic and aromatic C-nitroso-compounds as scavengers gives rise to alkoxy rather than the expected alkylperoxy nitroxide adducts. In spite of this drawback the usefulness of the method is demonstrated by an investigation of the photo-oxidation of C-nitrosoalkanes and by the preparation of an alkoxy alkyl nitroxide labelled by ^{17}O specifically at the alkoxy oxygen atom.

When a dilute solution of 2-methyl-2-nitrosopropane (t-nitrosobutane) in benzene is irradiated in the absence of oxygen at a wavelength absorbed by the n^{-},π^{*}-band (500-800nm), the only paramagnetic species observable by e.s.r. is the well known di-t-butyl nitroxide (a_N=15.5G, g = 2.0063) formed as indicated by 1 via initial photo-dissociation of the weak C-N bond of the nitroso-compound.[4]

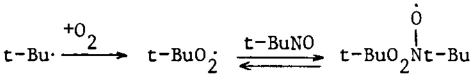
$$\text{t-BuNO} \xrightarrow{h\nu} \text{t-Bu}\cdot + \text{NO} \xrightarrow{\text{t-BuNO}} \text{t-Bu}_2\text{NO}\cdot \qquad (1)$$

In the presence of oxygen, however, this stable nitroxide is almost absent and the e.s.r. spectrum obtained during irradiation is dominated by another nitroxide triplet (a_N= 27.5G, g = 2.0058). The same unstable species is obtained in degassed solutions, when t-butoxy radicals are generated by photolysis of t-butyl hypochloride, di-t-butyl peroxide or t-butyl nitrite in the presence of a trace of t-nitrosobutane as scavenger. These precursors of t-butoxy radicals can be photolysed selectively in the ultraviolet at wavelengths where the scavenger does not absorb. These observations, in conjunction with previously measured e.s.r. parameters for this species[5], suggest that the unstable nitroxide observable when t-nitrosobutane is photolysed in the presence of oxygen is t-butoxy t-butyl nitroxide I.

This result is surprising as one would expect that the interception of t-butyl radicals by oxygen in reaction 1 should lead to the trapping of peroxy radicals with formation of a peroxy-alkyl nitroxide II rather than the scavenging of an alkoxy radical.

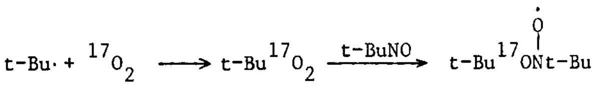


$$t\text{-BuO}\cdot + t\text{-BuNO} \rightleftharpoons \underset{\text{I}}{t\text{-BuO-}\overset{\dot{O}}{\overset{|}{N}}t\text{-Bu}} \qquad (2)$$



$$t\text{-Bu}\cdot \xrightarrow{+O_2} t\text{-BuO}_2\cdot \overset{t\text{-BuNO}}{\rightleftharpoons} \underset{\text{II}}{t\text{-BuO}_2\overset{\dot{O}}{\overset{|}{N}}t\text{-Bu}} \qquad (3)$$

The involvement of gaseous oxygen in this reaction can be demonstrated in two ways: first, by generating the t-butyl radicals from an independent source in the presence of oxygen, and second by a labelling experiment. Thus the 365nm photolysis of azo-isobutane in benzene with t-nitroso butane as scavenger gives a labile species identical in every respect with I if oxygen is present, but produces only the persistent di-t-butyl nitroxide if oxygen is absent. Moreover, when the photo-oxidation ($\lambda > 540$nm) of t-nitrosobutane is carried out using ^{17}O enriched oxygen, the e.s.r. spectrum observed exhibits additional clear hyperfine splitting (h.f.s.) due to a single nucleus with a spin of 5/2 splitting each nitroxide triplet branch into a sextet ($a_O = 1.53G$)[6]. The magnitude of this ^{17}O coupling[7] together with the nitrogen h.f.s. ($a_N = 27.4G$) indicates unequivocally that the label has been incorporated specifically as shown in (4).

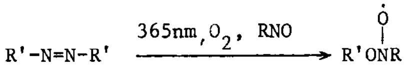


$$t\text{-Bu}\cdot + {}^{17}O_2 \longrightarrow t\text{-Bu}{}^{17}O_2 \xrightarrow{t\text{-BuNO}} t\text{-Bu}{}^{17}O\overset{\dot{O}}{\overset{|}{N}}t\text{-Bu} \qquad (4)$$

That t-butoxy t-butyl nitroxide rather than the t-butyl peroxy analogue is obtained is evident not only from the a_N- value, but also from the absence of further h.f.s. or broadening due to ^{17}O-^{17}O interaction. Both experiments with labelled and unlabelled oxygen were repeated in several inert solvents at different scavenger concentrations and at temperatures down to -80°C, however there was no evidence of II, and I was the only adduct observable apart from di-t-butyl nitroxide.

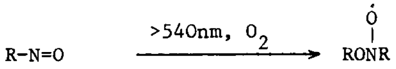
In a series of further experiments it was established, that this unexpected reaction is of general significance. Thus the 365nm photo-oxidation of azoalkanes in the presence of C-nitroso-compounds as scavengers gives rise to alkoxy alkyl or alkoxy aryl nitroxides III (equation 5, method A) whilst the photo-oxidation of C-nitrosoalkanes at 500-800nm generates alkoxy alkyl nitroxides of type IV (equation 6, method B).

Method A: R = alkyl or aryl, R' = alkyl



$$R'\text{-N=N-}R' \xrightarrow{365\text{nm}, O_2,\ \text{RNO}} \underset{\text{III}}{R'O\overset{\dot{O}}{\overset{|}{N}}R} \qquad (5)$$

Method B: R = alkyl but not aryl



$$R\text{-N=O} \xrightarrow{>540\text{nm},\ O_2} \underset{\text{IV}}{RO\overset{\dot{O}}{\overset{|}{N}}R} \qquad (6)$$

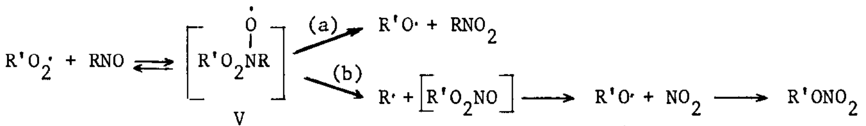
Table : e.s.r. parameters of alkoxy nitroxides III and IV

No.	Method	R'	R	$a_N(G)^{(a)}$	Solvent	Temperature(°C)
1	A	$(CH_3)_3C$	$(CH_3)_3C$	27.5	C_6H_6	18
2	B	-	$(CH_3)_3C$	27.5	C_6H_6	18
3	A	$(CH_3)_2CCN$	$(CH_3)_2CCN$	29.7	$C_6H_6/CFCl_3$	-30
4	B	-	$(CH_3)_2CCN$	29.7	$C_6H_6/CFCl_3$	-30
5	A	$(CH_3)_3C$	$(CH_3)_2CCl$	$23.6^{(b)}$	C_6H_6	18
6	B	-	$(CH_3)_2CCl$	$25.2^{(b)}$	$n\text{-}C_5H_{12}$	-86
7	A	$(CH_3)_2CCN$	$(CH_3)_2CCl$	$25.3^{(b)}$	C_6H_6	18
8	A	$(CH_3)_2CCN$	C_6H_5	$16.1^{(c)}$	C_6H_6	18

(a) nitrogen h.f.s. in Gauss (b) additional h.f.s. due to Cl present

(c) additional h.f.s. due to aromatic ring protons present.

It is clear from the known photochemistry of azo- and nitrosoalkanes and the close analogy in the two photo-oxidation reactions described here, that alkyl radicals are produced initially in both cases. Since oxygen scavenges alkyl radicals at a rate controlled by diffusion, peroxy alkyl radicals must invariably be produced in the subsequent step. It is necessary therefore to assume that peroxy radicals are converted to alkoxy radicals during the reaction. Kinetic considerations lead to the conclusion that the well known self-reaction of tertiary peroxy alkyl radicals via a labile tetroxide is of minor importance in this conversion, as compared to addition to the radical trap. For this reason it appears that the absence of an observable stationary state concentration of peroxy alkyl nitroxides indicates a rapid subsequent decay of this adduct rather than failure of the trap to scavenge. On this basis the following sequence is suggested implicating peroxy alkyl nitroxides and peroxy nitrites[8] as transient, but important intermediates in (5) and (6).



$$R'O_2\cdot + RNO \rightleftarrows \underset{\text{V}}{\left[R'O_2\overset{\overset{\cdot}{O}}{\underset{}{N}}R \right]} \begin{cases} \xrightarrow{(a)} R'O\cdot + RNO_2 \\ \xrightarrow{(b)} R\cdot + \left[R'O_2NO\right] \longrightarrow R'O\cdot + NO_2 \longrightarrow R'ONO_2 \end{cases}$$

The alkoxy radicals produced in this way by O-O and C-N fission[9] of the unstable adducts IV or V will give rise to the more persistent and therefore detectable alkoxy adducts as well as to the end products usually observed in the photo-oxidation of alkyl nitroso-compounds (nitroalkanes, alkyl nitrates etc.)[10,11]. In contrast it is to be expected that the removal of peroxy radicals by radical-radical reactions like RO_2 + NO prevails in the gas phase when $[RNO]$ is very small[12]. It should also be noted, that pathway (b) will be absent for R = C_6H_5 (No. 8 in table).

In conclusion, it is clear from these results, that the use of C-nitroso-compounds as spin-traps in homolytic oxidation reactions will not permit discrimination between peroxy and alkoxy radicals since both will give rise to alkoxy radical adducts.

Acknowledgement.

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