

STABILITY OF PEROXY RADICALS IN THE PRESENCE OF TRANSITION METAL IONS.

AN ESR INVESTIGATION

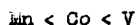
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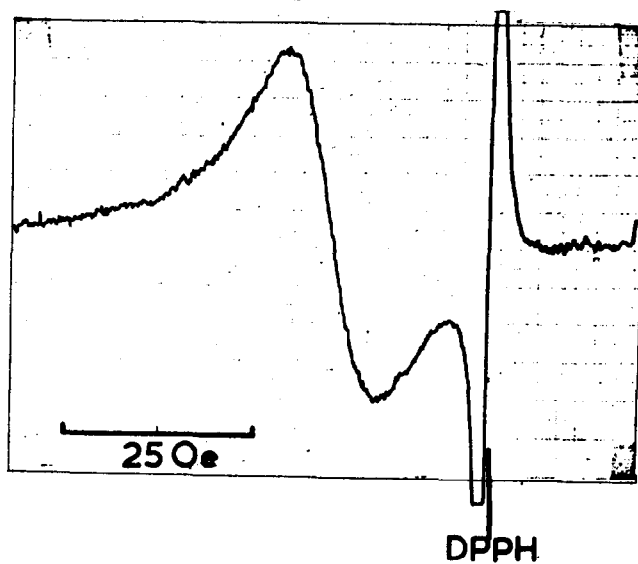
This preliminary communication describes the generation and stability of t-peroxy radicals in non-aqueous solvents. t-Butyl and cumene hydroperoxides have been taken as model compounds and ESR spectra were recorded with a Varian V4502 X-Band spectrometer. Peroxide decomposition catalysts in the form of their naphthenates, soaps, and acetylacetonates have so far been used.

Addition of a small excess of hydroperoxide to a benzene solution of the metal compound (Mn, Co or V) in situ in the ESR cavity, produces a single line ESR spectrum, width ≈ 10 G, g value 2.0154 ± 0.0004 . The spectrum due to the Mn^{2+} or VO^{++} moieties disappears. The above g value falls in the range quoted as being characteristic of peroxy radicals (1,2). The single line is also generated in other solvents such as cumene, nitrobenzene and nitropropane. The stability of the radical however is dependent on the identity of the metal present and qualitatively follows the order:-



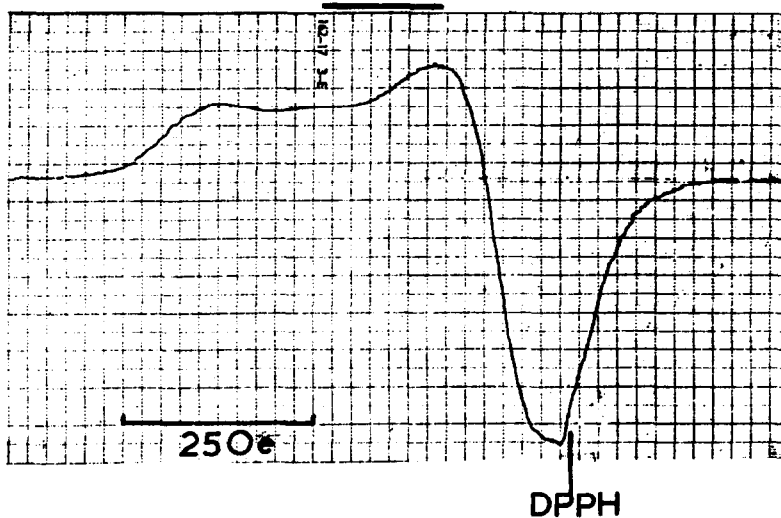
Quantitative data are not yet available but the decay rate in the presence of manganese is considerably greater than that in the presence of vanadium. Though somewhat reduced in intensity, the peroxy radical signal in the presence of vanadium was still present after 60 hrs at room temperature. The decay rate is increased at higher temperatures. With both manganese and cobalt there is a short induction period before the rapid build up of the single line. During this induction period the Mn^{2+} signal is absent. No induction period was observed with vanadium.

FIG. 1

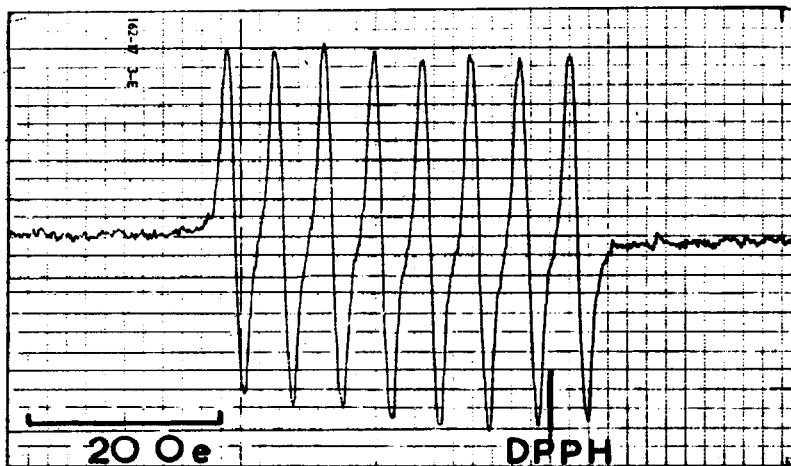


Co NAPHTHENATE + $\text{PhC}(\text{CH}_3)_2\text{OOH}$
IN BENZENE SOLUTION

FIG. 2



Mn NAPHTHENATE + $\text{C}(\text{CH}_3)_3\text{OOH}$
IN BENZENE AT -170°C .

FIG. 3

$\text{VO}(\text{Acac})_2 + \text{C}(\text{CH}_3)_3\text{OOH}$ IN ETHANOL
AT ROOM T.^o

Addition of small amounts of hydroperoxide causes a very rapid drop in the VO^{++} signal intensity. On standing the signal is autocatalytically regenerated, though not reaching its original intensity. The peroxy radical has not been detected in the presence of Mn^{2+} or VO^{++} ions. The ESR spectra from these paramagnetic ions could, however, have masked the signal from the radical. Addition of 4-methyl-2:6-di-tert-butyl phenol immediately removes the peroxy radical. A typical peroxy radical single line spectrum is shown in Fig. 1.

The stability of the radical suggests that it is associated with the metal ion, as was observed by Fischer (3) in the system $H_2O_2/Ti^{3+}/Ti^{4+}$ where the H_2O_2 radical is stabilised by the Ti nucleus. Manganese and vanadium have nuclear spins of $5/2$ and $7/2$ respectively and attempts have been made to observe the hyperfine interaction with the metal nucleus by cooling the benzene solutions to $-170^\circ C$. No hyperfine splitting was observed.

In the rigid benzene lattice at low temperatures the ESR line becomes asymmetric showing g value anisotropy (Fig. 2). Thus, with manganese naphthenate in benzene solution, for $tBuOO$.

$$g_{\parallel} = 2.0260 \text{ and } g_{\perp} = 2.0104$$

giving $(g)_{\text{isotropic}} = 2.0156$

When the sample is slowly warmed from $-170^\circ C$ the ESR spectrum becomes isotropic.

When $tBuOOH$ is added to solutions of vanadium naphthenate or acetylacetonate in ethanol an 8 line spectrum (Fig.3) is observed. These spectra are not inconsistent with interaction of the free electron on the peroxy radical with the vanadium nuclear spin. The hyperfine coupling of 50e and $g = 2.0116$ are to be compared with the normal values of ca. 100e and $g = 1.98$ for the VO^{++} species.

References

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- (3) H. Fischer "Applications of ESR in the Study of Reactive Intermediates in Chemical Reactions". Discussion Meeting at the Royal Society, London on 4th May, 1967.