

Electron Spin Resonance Studies of Stable Radicals Generated by Oxidation of *s*-Butyl-lithium with Transition-metal Ions

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Summary Stable radicals are generated by oxidation of *s*-butyl-lithium with transition-metal ions; the e.s.r. spectra of these radicals are discussed.

THE oxidation of intermediate anions to radicals has been postulated in many oxidation reactions catalysed by metal ions.¹ Using a flow system, the e.s.r. spectrum has been obtained for the radical $\cdot\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$, a rearranged oxidation product of the anion of 1-methoxycyclopropanol.²

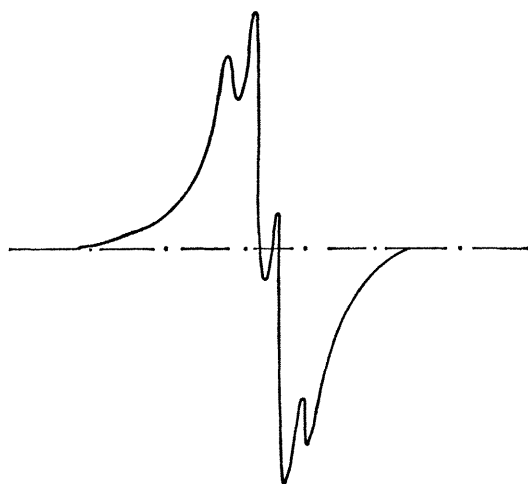


FIGURE. E.s.r. signal of $\text{Bu}^{\text{s}}\text{Li}$ -DIPS.

This hemiacetal is quantitatively oxidized by Ce^{4+} , Cu^{2+} , and Fe^{3+} , ions; the process is catalytic as the oxygen

present restores the original valence of the reduced ions. We now show that *s*-butyl-lithium can be oxidized by Cu^{2+} , Fe^{3+} , and La^{3+} ions to quite stable radicals easily detectable by e.s.r. These radicals are probably coordinated with the transition-metal ion.

2,4-Di-isopropyl salicylates (DIPS) or acetylacetonates of Fe^{3+} , Cu^{2+} , and La^{3+} are dissolved in benzene, and the resulting solutions mixed with *s*-butyl-lithium in *n*-pentane (1M-solution, Metallges. AG, Langelsheim, Germany). The solutions obtained in this way are homogeneous. Rigorous drying of all chemicals and glassware is necessary to prevent decomposition of the *s*-butyl-lithium. The e.s.r. spectrometer is assembled from a Varian microwave bridge and a Newport 7 in. magnet (field homogeneity 0.1 G); the electronic part is home-built. The apparatus works at a frequency of ca. 9.5 GHz (3 cm). In the cavity the sample-tube is placed in a quartz Dewar tube in which the temperature can be varied by means of a nitrogen flow.

The e.s.r. signals of mixtures of *s*-butyl-lithium and the complexes of the transition metal used are stable over a period of weeks at room temperature. On increasing the temperature to ca. 70 °C, the spectral lines become sharper. The *g*-values and hyperfine structure splitting constants are listed in the Table; a typical spectrum is given in the Figure. From the intensity of the absorption, which can be compared with that of a known sample of diphenylpicrylhydrazyl (DPPH), it is estimated that the quantity of radicals generated is of the same order of magnitude as the number of transition-metal ions present.

The *g*-values of the spectra observed, added to the non-existence of a clear interaction with the nuclei of ^{63}Cu , ^{65}Cu , and ^{139}La ($I = \frac{3}{2}$, $\frac{3}{2}$, and $\frac{7}{2}$, respectively), seem to indicate that the unpaired electron is concentrated in a molecular

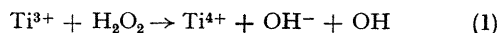
orbital on carbon atoms only. However, alkyl radicals are generally unstable, unless there is some delocalization in an extended π -system. It must be assumed, therefore, that the observed radicals are complexed to the transition-metal ion.

Oxidation with Cu^{2+} yields a hyperfine structure in which the unpaired electron is in interaction with two equivalent protons, while the hyperfine structure obtained by oxidation with Fe^{3+} and La^{3+} shows the unpaired electron to interact with three protons; in the case of iron, these latter protons

TABLE

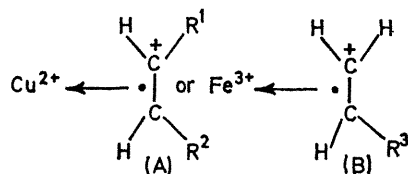
Transition metal ion	Complex	Complex (mol l ⁻¹)	Bu ^s Li (mol l ⁻¹)	<i>g</i> -Value	Hyperfine structure
Cu^{2+}	DIPS	0.005	0.1	2.0034 ± 0.0002	2 equiv. H, $a = 2.8$ G
La^{3+}	DIPS	0.0012	0.012	2.0034 ± 0.0002	2 equiv. H, $a = 2.4$ G 1 H, $a = 4.8$ G
Fe^{3+}	DIPS	0.004	0.06	2.0034 ± 0.0002	3 equiv. H, $a = 4.8$ G
Fe^{3+}	Acac	0.004	0.06	2.0034 ± 0.0002	3 equiv. H, $a = 4.0$ G

A similar complex formation is observed in the reaction of Ti^{3+} with H_2O_2 (reaction 1),³ and in the reaction of TiCl_3



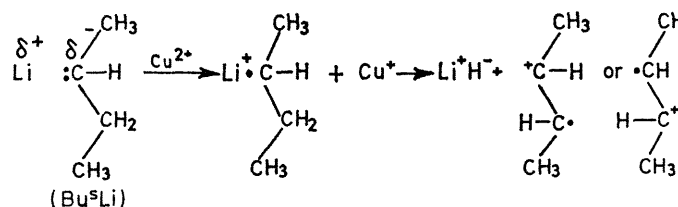
and H_2O_2 in MeOH which produces $\cdot\text{CH}_2\text{OH}$, the radicals probably being co-ordinated to the Ti^{4+} ion. Furthermore, a greatly increased stability of peroxy-radicals in the presence of transition-metal ions has been reported.⁴

The values of the hyperfine splitting constants of the protons suggest that the unpaired electron is situated in a



π -orbital. On this basis, the structure of the radicals may be as shown in (A) and (B). The Scheme shows how such structures can be formed.

are equivalent, whereas in the case of lanthanum they are not. This leads to the supposition that the elimination of LiH is governed by the transition metal or, if not, that only



SCHEME

one of the two types of radicals can be co-ordinated and stabilized, the other type getting lost in one of many possible ways. Nevertheless, the stability of the radicals is caused by the transition-metal ions, without a detectable influence of the metal on the e.s.r. spectrum.

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