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Preliminary communication

E.S.R. of some antimony and bismuth containing organometallic free radicals

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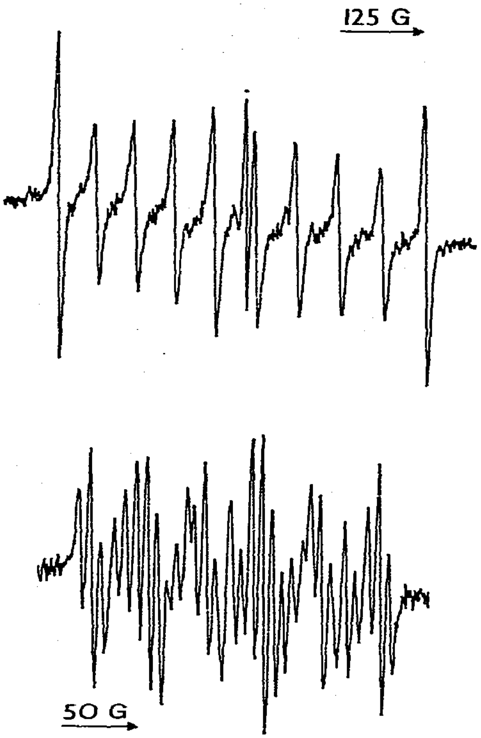
Organometallic radicals containing Sb and, for the first time, Bi have been characterised by e.s.r. The radicals are formed by the reaction at elevated temperatures of orthoquinones with metal (III) compounds.

Free radicals containing the Group VB elements P and, to a lesser extent, As have been extensively investigated by e.s.r. spectroscopy but little is known of organometallic free radicals containing the heavier Group VB elements Sb and Bi. We wish to report the preparation and e.s.r. spectra of a series of radicals exhibiting hyperfine interactions with the magnetic nuclei ^{121}Sb ($I = {}^5/_2$, 57%), ^{123}Sb ($I = {}^7/_2$, 43%) and ^{209}Bi ($I = {}^9/_2$, 100%). We are unaware of any previous reports of free radicals exhibiting ^{208}Bi hyperfine structure in solution. Unidentified radicals showing antimony hyperfine splittings have been noted in the reaction of $SbCl_3$ with quinonoid compounds[1].

The radicals have been prepared by the high temperature reactions of SbF_3, $SbCl_3$ and $BiPh_3$ with the orthoquinones 9,10-phenanthroquinone (PQ) and benzo[2-1, b ; 3-4, b'] dithiophen 4,5-dione (TQ). E.s.r. signals are readily observable on heating a solution of the Sb or Bi compound and PQ or TQ in diglyme to 160°C in the cavity of an e.s.r. spectrometer. In the case of SbF_3 and PQ more intense spectra were obtained in molten naphthalene at 200°C. Some spectra were also recorded in molten biphenyl but were generally less well resolved than those in diglyme.

In each case the dominant feature of the e.s.r. spectrum is hyperfine coupling to the metal nucleus (decets, octets and sextets for ^{209}Bi, ^{123}Sb and ^{121}Sb respectively). With SbF_3 coupling to two equivalent ^{19}F nuclei was also apparent and with PQ a further binomial quintet was resolvable. The radicals from $SbCl_3$ had broader lines than those from SbF_3 consistent with the presence of unresolved chlorine hyperfine structure. The hyperfine couplings (table) showed a slight variation with temperature and solvent. In the spectra of the bismuth containing species the hyperfine decet shows a pronounced variation in linewidth (figure) which we attribute to nuclear quadrupole relaxation. The line intensities are in good agreement with the linewidth ratios of 1.0 :



The e.s.r. spectra of Ic (top) and IIb (bottom) in diglyme at 160°C. The line marked + is due to an unidentified secondary radical.

Table

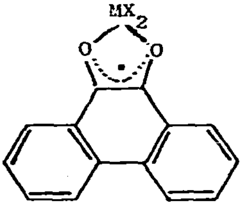
Hyperfine Coupling Constants (G) in diglyme at 160°C.

Radical	^{121}Sb	^{123}Sb	^{208}Bi	other h.f.c.c.
Ia	46.2	25.0	-	
Ib*	41.6	22.5	-	8.0(2F), 2.1(4H)
Ic	-	-	61.5	
IIa	46.9	25.3	-	
IIb	39.2	21.0	-	6.8(2F)
IIc	-	-	63.5	

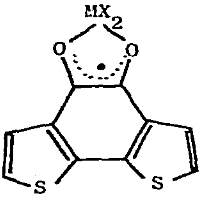
*in naphthalene at 200°C.

2.06 : 2.16 : 1.90 : 1.66 : 1.66 : 1.90 : 2.16 : 2.06 : 1.0 predicted for such a relaxation mechanism.

We assign the e.s.r. spectra to the radicals Ia - Ic and IIa - IIc formed by thermolysis of



I



II

a M = Sb, X = Cl
b M = Sb, X = F
c M = Bi, X = Ph

an intermediate five-coordinate donor-acceptor complex between the quinone and the Lewis acid

$$MX_3 + PQ \rightarrow MX_3(PQ) \xrightarrow{\Delta} [MX_2(PQ)]^{\cdot} + X^{\cdot}$$

The most compelling evidence for this assignment comes from the spectrum of Ib which shows, in addition to coupling to two fluorines and one antimony, coupling to four aromatic protons. The latter splitting is comparable in magnitude to the coupling observed in adducts of PQ with Group IVB organometallic radicals[2]. The magnitude of the metal hyperfine couplings corresponds to a small s-electron spin density at the metal nucleus, consistent with a structure in which the unpaired electron is mainly delocalised in the π-system of the quinone and the metal atom lies in the plane of the aromatic moiety

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References

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2. A. Alberti and A. Hudson, J.C.S. Perkin II, (1978) 1098.