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THE ELECTRON SPIN RESONANCE SPECTRA AND STRUCTURES OF SOME ALUMINIUM DERIVATIVES OF 3,6-DI-t-BUTYL-1,2-BENZOQUINONE

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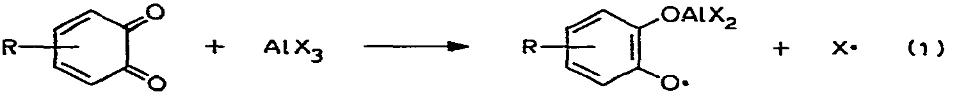
Summary

ESR spectra are reported for the aluminium derivatives of the semiquinones which are formed when the compounds Et_nAlCl_{3-n} (n = 0, 1, or 3) react with 3,6-di-t-butyl-1,2-benzoquinone. The conditions (solvent and other ligands about the metal) are identified under which three different types of spectra can be observed, which are assigned to monodentate non-fluxional, monodentate fluxional, and bidentate structures respectively.

Introduction

A number of studies have been reported of the interaction of aluminium compounds with orthoquinones. The overall reaction which occurs is illustrated in eq. 1, and the reactive radical X$^•$ which is liberated can induce the polymerization of vinylic monomers (1).



The aluminium derivatives of semiquinones which are formed are long-lived, and the electron spin resonance spectra have been reported for the products of the reaction of aluminium trihalides in tetrahydrofuran with 4,6-di-t-butyl-3-nitro-1,2-benzoquinone, 3,5-di-t-butyl-1,2-benzoquinone [2], 3,6-di-t-butyl-1,2-benzoquinone [3], 3,4,5,6-tetrachloro-1,2-benzoquinone (orthochloranil) [4], and 9,10-phenanthraquinone [5], and of triethylaluminium in toluene with 3,5-di-t-butyl-1,2-benzoquinone and 3,6-di-t-butyl-1,2-benzoquinone [6].

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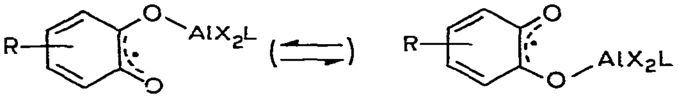
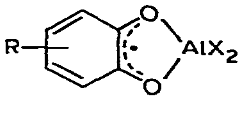
In principle, the quinone could act as a monodentate ligand to give a derivative which is static or fluxional on the ESR time scale as illustrated in I, or it could act as a bidentate ligand as in II. The existence of three-coordinate aluminium in an electron-donor solvent is unlikely, and under these conditions, if the quinone acts as a monodentate ligand, the fourth coordination site will presumably be occupied by a solvent molecule (L).



(I)



(II)

The ESR spectra of the products from all the above reactions showed hyperfine coupling to aluminium (^{27}Al, 100% abundance, $I = 5/2$), and with the symmetrically substituted (C_{2v}) quinones, coupling to the ring protons implied that the aluminium was symmetrically situated with respect to the two oxygen atoms. This does not distinguish between the fast-fluxional monodentate structure I or the bidentate structure II.

Our previous studies on the corresponding tin derivatives of semidiones have shown how their structure can vary with the nature of the ligands about the tin [7]. Thus, with biacetyl, the radicals $\cdot SnCl_3$ and $\cdot SnBuCl_2$ gave adducts which showed hyperfine coupling to chlorine and which were inferred to involve bidentate dione, whereas the radicals $\cdot SnBu_2Cl$ and $\cdot SnBu_3$ gave adducts with no coupling to the ligands, and which were believed to carry monodentate dione which was non-fluxional or fluxional, respectively.

The strong tendency of aluminium compounds to form complexes with electron donors suggests that the solvent, as well as the ligands, might play a part in determining the structures of the aluminium derivatives of the semiquinones. We report here a study by ESR spectroscopy of the structures of the semiquinone products which are formed when 3,6-di-t-butyl-1,2-benzoquinone or, more briefly, 3,4,5,6-tetrachloro-1,2-benzoquinone react with aluminium compounds, as the nature of the ligands (Et and Cl) about the aluminium and of the solvent, are varied. The results provide the first examples of non-fluxional monodentate aluminium complexes, and throw some light on the question of fluxional monodentate versus bidentate structures.

Results and discussion

The ESR spectra of the semiquinone derivatives which are formed when aluminium compounds, Et_nAlCl_{3-n} (n = 0, 1, or 3) react with 3,6-di-t-butyl-1,2-benzoquinone, in various solvents, are listed in Table 1. The analyses of the spectra were refined by computer simulation, and some examples of the observed and simulated spectra are given in the figures. The reactions involving ethylaluminium dichloride or aluminium trichloride always gave identical spectra which we assign to the $AlCl_2$ derivative of the semiquinone.

We consider first the spectra of the products from triethylaluminium. With toluene as solvent, the two protons of the aromatic ring showed equal coupling constants (Fig. 1). When ether was added, this spectrum could still be observed,

TABLE 1

ESR SPECTRA OF THE SEMIDIONE RADICALS FORMED FROM THE REACTION OF ALUMINIUM COMPOUNDS WITH 3,6-DI-t-BUTYL-1,2-BENZOQUINONE AT —40°C

AlX_3	Solvent	$a(^{27}Al)$ (G)	a(nH) (G)	g	Γ (G) [a]
Et_3Al	PhMe	2.14	3.80 (2 H)	2.0040	0.17
	Et_2O	2.15 2.40	3.78 (2 H) 3.32 (1 H) 4.48 (1 H)		0.3
$EtAlCl_2$	PhMe	2.11	4.50 (2 H)	2.0038	0.5
or	Et_2O	2.32	3.27 (1 H) 4.60 (1 H)	2.0039	0.3
$AlCl_3$	Bu_2O	2.30	3.23 (1 H) 4.65 (1 H)		0.3
	$CH_2{=}CMeCO_2Me$	2.30	3.35 (1 H) 4.50 (1 H)	2.0041	0.2
	THF	2.38	3.90 (2 H)	2.0041	0.3
	Me_2CO	2.42	3.85 (2 H)		0.4
	$CH_2{=}CHC{\equiv}N$	2.52	3.88 (2 H)		0.3

[a] Peak-to-peak line width in the first-derivative spectrum.

together with a second spectrum showing a higher hyperfine coupling to aluminium, and now inequivalent hydrogen atoms in the aromatic ring, the relative intensities of these two spectra depending on the ratio of the reagents, the concentrations, and the temperature.

If tetrahydrofuran is used as the solvent, a rapid reaction occurs to give, in a few seconds, a colourless solution which does not show an ESR signal. The possible significance of this is referred to below.

The inequivalence of the two hydrogen atoms when ether is the solvent indicates the monodentate structure III. If we discount the possibility of 3-coordi-

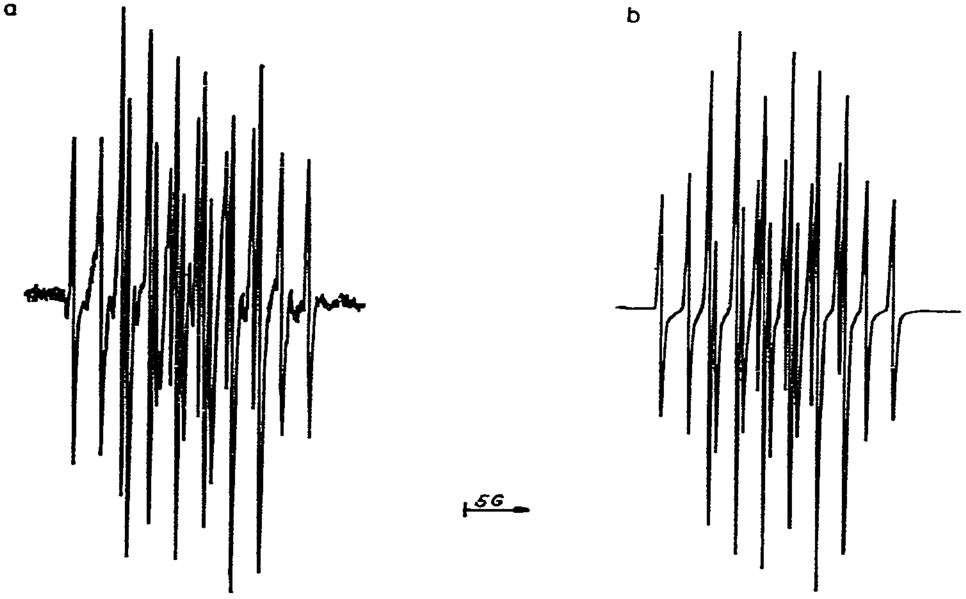
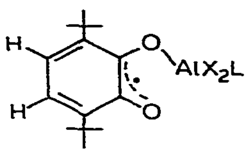
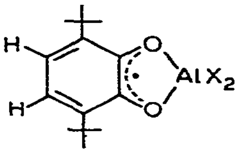


Fig. 1. (a) ESR spectrum obtained from triethylaluminium and 3,6-di-t-butyl-1,2-benzoquinone in toluene at —40°C. (b) Simulation.

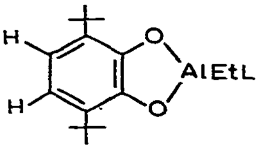
nate aluminium in an ethereal solvent, and of the coexistance of fluxional and non-fluxional III, the simpler spectrum with equivalent hydrogens must presumably be assigned to the chelated structure IV, as has been suggested previously [6]. It appears that, with a non-coordinating solvent, the aluminium is rendered 4-coordinate by intramolecular association by the quinone, but a coordinating solvent can compete with this association and break the chelation, converting IV into III.



(III)



(IV)



(V)

The spectra of the products from aluminium trichloride or ethylaluminium dichloride can be rationalised on an extension of this model. With toluene as solvent, intramolecular association by the quinone gives the structure IV (X = Cl), showing an equivalent pair of hydrogen atoms (see Table 1). A weakly coordinating solvent such as diethyl ether, dibutyl ether, or methyl methacrylate (L) can break this chelation, and give the monodentate derivative III (X = Cl) which is not fluxional on the ESR time scale (Fig. 2).

If the reaction is carried out in a more powerfully coordinating solvent like tetrahydrofuran, acetone, or acrylonitrile, or if, for example, tetrahydrofuran is added to the product in ether, a third type of spectrum now intervenes (Fig. 3): the hyperfine coupling to aluminium remains high, but the two hydrogen atoms now appear equivalent, with a hyperfine coupling lower than that which is observed in toluene solvent, but close to the average of the two values which are observed in a weakly coordinating solvent. The only reasonable interpretation of this new type of spectrum appears to be that strongly coordinating ligands L increase the mobility of the aluminium moiety between the two oxygen atoms, so that the two hydrogens appear equivalent by time-averaging. Unfortunately our attempts to observe both types of spectra for the solutions in diethyl ether, dibutyl ether, or tetrahydrofuran, by varying the temperature, have been unsuccessful.

Below about —40°C, general broadening of all the lines in the spectrum occurred, whereas above about 35°C, further chemical reaction took place to give other radicals which complicated the spectrum.

The implication is that the degenerate homolytic substitution shown in eq. 2 proceeds more readily when the ligand L is strongly bonding, at least when the entering and leaving groups and the metal centre have the geometry which is imposed on them by the orthoquinone.

$$RO^{\bullet} + AlX_2L{-}OR \rightarrow RO{-}AlX_2L + {\cdot}OR \qquad (2)$$

Studies have been carried out on the mechanism of bimolecular homolytic substitution at 3-coordinate boron and this is known to occur less readily when the metal is rendered 4-coordinate, but very little has been reported on homolytic reactions at aluminium, and there appears to be no relevant work

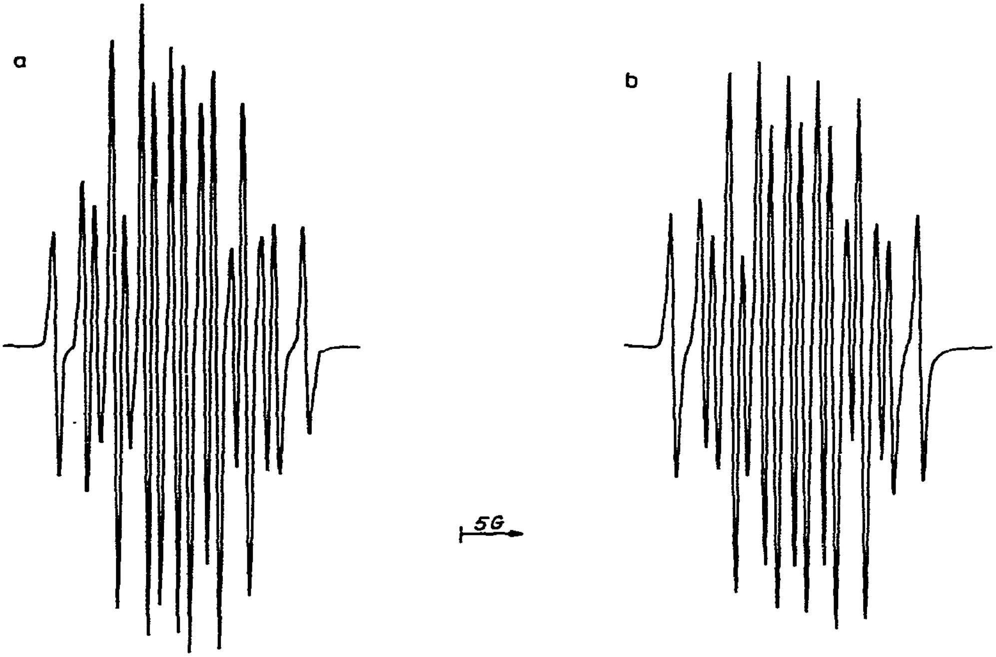


Fig. 2. (a) ESR spectrum obtained from aluminium trichloride and 3,6-di-t-butyl-1,2-benzoquinone in diethyl ether at —39°C. (b) Simulation.

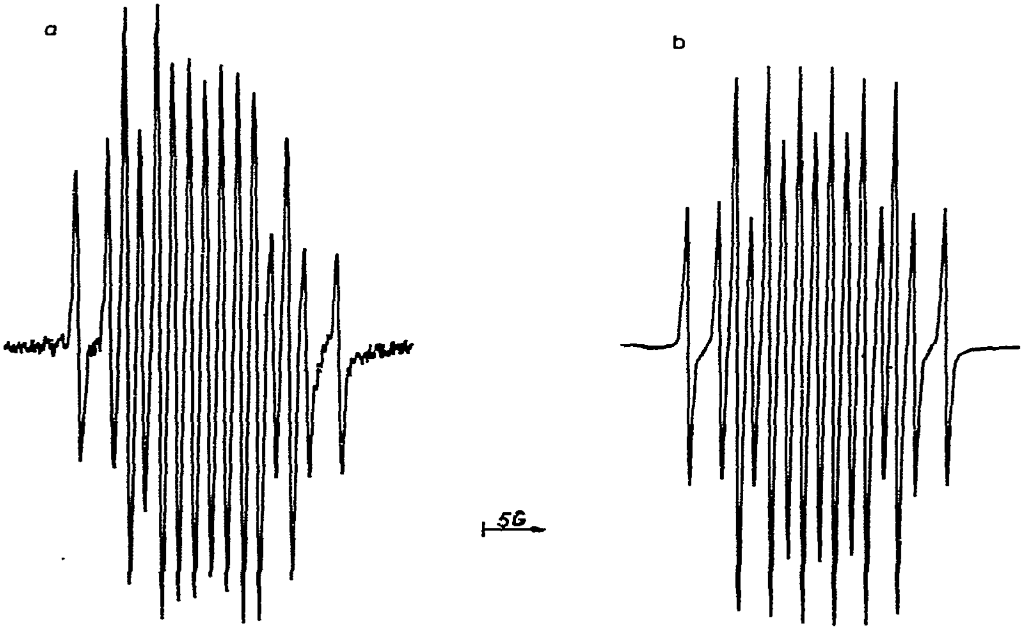


Fig. 3. (a) ESR spectrum obtained from ethylaluminium dichloride and 3,6-di-t-butyl-1,2-benzoquinone in acrylonitrile at —40°C. (b) Simulation.

TABLE 2

ESR SPECTRA OF THE SEMIDIONE RADICALS FORMED FROM THE REACTION OF ALUMINIUM COMPOUNDS WITH 3,4,5,6-TETRACHLORO-1,2-BENZOQUINONE AT —40°C

	Solvent	$a(^{27}Al)$ (G)	g	Γ (G) [a]
Et_3Al	PhMe	2.5		1.8
	Et_2O	2.5	2.0056	1.8
Et_2AlCl	Et_2O	2.5		1.8
$EtAlCl_2$ or $AlCl_3$	PhMe	2.5		1.8
	Et_2O [b]	2.25 [c]	2.0052	0.6

[a] Peak-to-peak line width in the first-derivative spectrum. [b] Similar spectra were obtained with tetrahydrofuran or methyl methacrylate as solvent. [c] a (2 Cl) 0.78 G.

in the literature on reactions at 4-coordinate aluminium [8].

It is interesting to speculate that the lability of the radical III, when X = Et and L = tetrahydrofuran, may result from a rapid intramolecular S_H2 reaction by the free oxygen centre, at the solvated metal, to give an ethyl radical and the diamagnetic aluminium chatecholate V.

3,4,5,6-Tetrachloro-1,2-benzoquinone is also used in conjunction with organoaluminium compounds for initiating vinylic polymerization, and we have therefore investigated briefly the ESR spectra of the semiquinone derivatives which are formed. The relevant data are listed in Table 2.

These spectra are less informative than those obtained when the aromatic ring carries hydrogen, because hyperfine coupling to chlorine in the ring, which

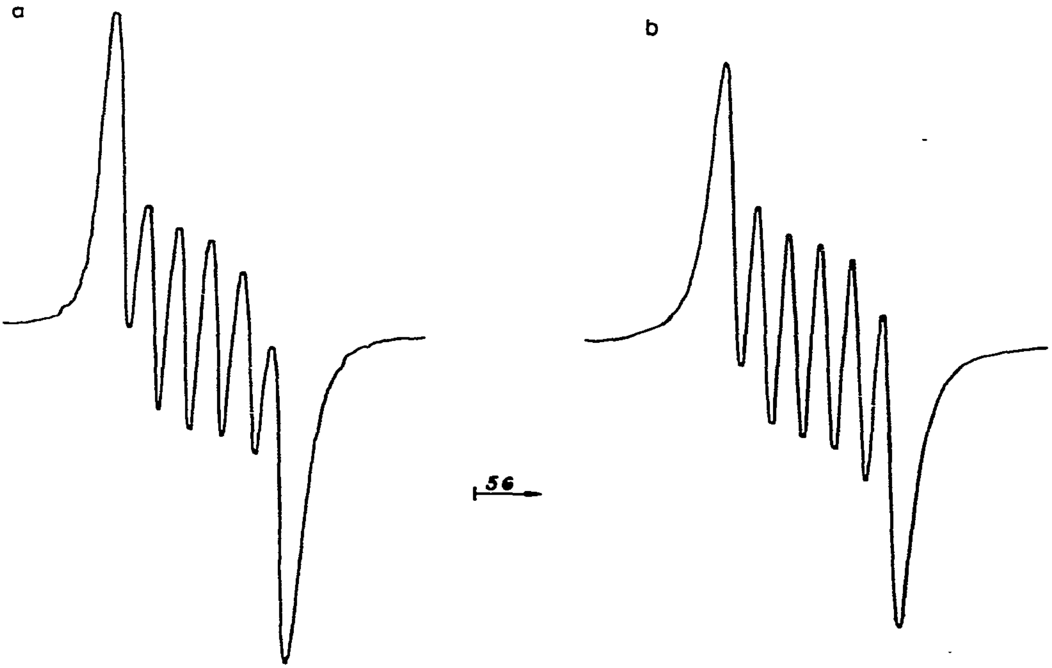


Fig. 4. (a) ESR spectrum obtained from triethylaluminium and 3,4,5,6-tetrachloro-1,2-benzoquinone in toluene at —35°C. (b) Simulation.

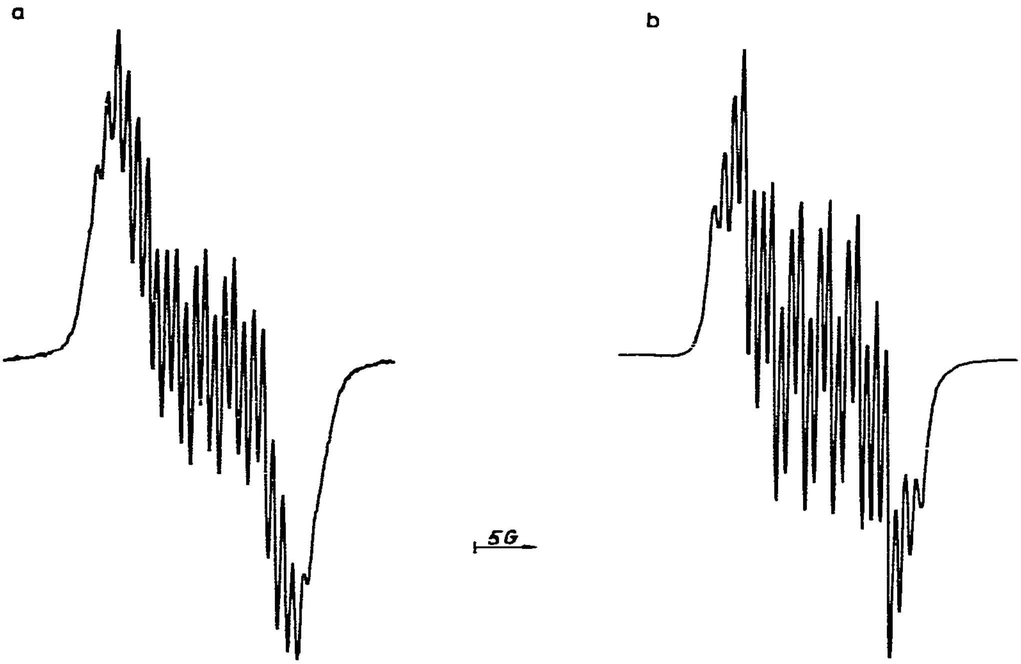


Fig. 5. (a) ESR spectrum obtained from ethylaluminium dichloride and 3,4,5,6-tetrachloro-1,2-benzoquinone in diethyl ether at —35°C. (b) Simulation.

would help to diagnose the structures, usually cannot be resolved. Thus, for example, triethylaluminium in toluene or ether gave a spectrum (Fig. 4) with a line width of 1.8 G which presumably conceals unresolved coupling to the chlorine atoms of the ring [4]. We were unable to resolve the spectra further by recording a higher derivative of the signals. The reaction of ethylaluminium dichloride or aluminium trichloride in ether at 0 to —40°C, however, gave a spectrum (Fig. 5) which could be analysed in terms of coupling to aluminium and to two equivalent chlorine atoms. Cooling the solution to —60°C led to general broadening of the lines of the spectrum, and, at 20°C, further reaction occurred to give other radicals which complicated the spectrum.

As other semidiones carrying the $AlCl_2$ groups show no evidence of hyperfine coupling to chlorine, and as the chloranil derivative carrying the $AlEt_2$ group apparently does show unresolved coupling to chlorine, it seems that this resolved coupling relates to two of the four chlorine atoms of the aromatic ring; the similar hyperfine coupling to two of the four chlorine atoms in the diphenylthallium derivative of the semiquinone of chloranil has been reported [9]. As these two chlorine atoms are magnetically equivalent, the static monodentate structure is excluded, but a decision cannot be made between the fast-fluxional structure I and the symmetrical bidentate structure II.

Experimental

All operations with organoaluminium compounds were carried out using dry, oxygen-free solvents under nitrogen. The quinones were recrystallised before use, and the aluminium chloride was purified by sublimation and the organoaluminium compounds by distillation under vacuum.

The aluminium chloride or organoaluminium compound in suspension or solution in the appropriate solvent was introduced at −80°C into a Suprasil silica tube containing an approximately equimolar amount of a solution of the quinone in toluene. The ESR spectra were recorded on a Varian E4 or E109 spectrometer.

Acknowledgement

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