

E.S.R. Spectra of the Radicals $\text{Me}_2\dot{\text{C}}\text{CN}\cdot\text{AlMe}_3$ and $\text{Me}_2\dot{\text{C}}\text{CO}_2\text{Me}\cdot\text{AlMe}_3$ in Solution

Steven Brumby

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 0511

The radicals $\text{Me}_2\dot{\text{C}}\text{CN}\cdot\text{AlMe}_3$ (**3**) and $\text{Me}_2\dot{\text{C}}\text{CO}_2\text{Me}\cdot\text{AlMe}_3$ (**4**), generated in solution by the photolysis of azo compounds in the presence of trimethylaluminium, have been studied by e.s.r. spectroscopy.

Lewis acids have been shown to exercise intriguing effects on certain reactions in which free radicals are involved, such as homopolymerization,¹ copolymerization,² and the decomposition of the azo compound (**1**).³ Interest in these effects prompted the present investigation, in which free radicals formed during the photolysis of solutions of azo compounds [(**1**) and the dimethyl ester (**2**)] and trimethylaluminium in

toluene were studied by e.s.r. spectroscopy. It is hoped that a knowledge of the e.s.r. spectra of the complexed radicals generated under these conditions will be helpful to an understanding of the various kinetic effects observed when Lewis acids are present.

Sample solutions were prepared by combining the azo compound and trimethylaluminium, both with toluene as

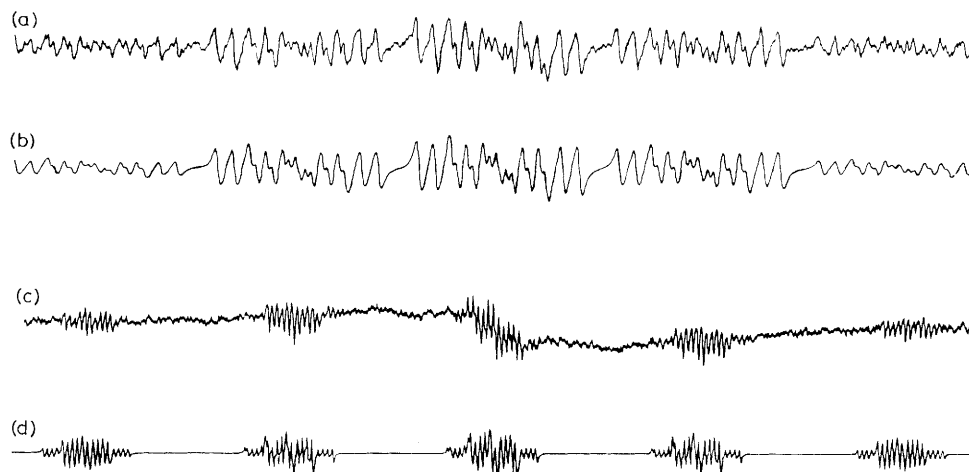
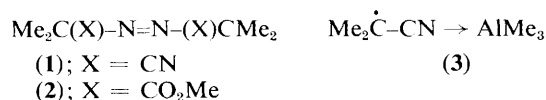


Figure 1. E.s.r. spectra recorded during *in situ* photolysis of a solution of (a) (1) and AlMe_3 (1 : 2) in toluene at -25°C and (c) (2) and AlMe_3 (1 : 1) in toluene at -50°C . (b) and (d) Second-order simulated spectra, using data in Table 1.

solvent, in an atmosphere of helium. E.s.r. spectra were recorded while irradiating the sample with light from a Hg-Xe lamp.

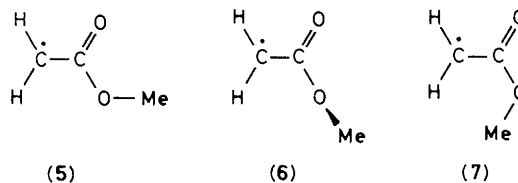
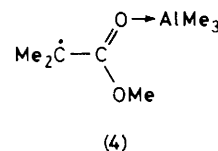
Using (1), closely similar spectra were obtained over the temperature range -25 to $+50^\circ\text{C}$, and with 1–2 mol



(calculated as AlMe_3) of trimethylaluminium per mol of (1). These spectra evidently belonged to a transient species, since their intensities decayed to zero within a few seconds when irradiation was interrupted. The complete spectra consisted of seven multiplets, but the outer multiplets were of low intensity. A spectrum comprising the central five multiplets, recorded at -25°C , is shown in Figure 1a. The spectrum exhibits splitting by a ^{27}Al ($I = 5/2$) nucleus, and is attributed to the co-ordinated species (3). Parameters used in the simulation (Figure 1b) are reported in Table 1, where they may be compared with previously reported⁴ data for the radical $\text{Me}_2\dot{\text{C}}\text{CN}$. It seems possible that unresolved splitting by the protons of the methyl groups attached to aluminium may contribute to the effective linewidth in the spectrum of (3).

Similar experiments were performed by Hirano *et al.*,^{3b} who recorded the e.s.r. spectrum of a solution of (1) and triethylaluminium in benzene at 54°C . Surprisingly, their spectrum differs from the spectrum shown in Figure 1a. In an attempt to reproduce the results of Hirano *et al.*, experiments were conducted under various conditions, sometimes using benzene as solvent, but using only trimethylaluminium (not triethylaluminium). The spectra recorded were similar to the spectrum shown in Figure 1a.

Using (2), spectra were recorded over the temperature range -50 to $+50^\circ\text{C}$, with an azo compound to AlMe_3 ratio of 1 : 1. Two distinct species contributed to the spectra, one of the component spectra having broad lines and the other narrow lines. The contribution of the broad line spectrum increased with temperature. Whereas the narrow-line spectrum belonged to a transient species, the broad-line spectrum belonged to a persistent species, the concentration of which diminished slowly during several hours in darkness. The spectrum shown in Figure 1c was recorded at -50°C , when the contribution of the broad-line spectrum was minimal. The narrow-line



component spectrum shows splitting by a ^{27}Al nucleus, and is attributed to species (4). Parameters used in the simulation (Figure 1d) are reported in Table 1, where they may be compared with previously reported⁵ data for the radical $\text{Me}_2\dot{\text{C}}\text{CO}_2\text{Me}$. The species responsible for the broad-line spectrum could not be identified.

Previous studies of the e.s.r. spectra of aluminium-containing radicals and radical ions include species with ^{27}Al in α ,^{6,7} β ,⁸ and γ ⁷ positions. In (3) and (4), the ^{27}Al atoms are in δ positions with respect to the free-radical centre, and the aluminium hyperfine splitting constants are accordingly smaller. Using the calculated ^{27}Al splitting for a singly occupied 3s orbital,⁹ the observed splittings correspond to spin densities in the aluminium 3s orbitals of 0.17 and 0.05 % for (3) and (4), respectively. These spin densities may arise by spin delocalization or by spin polarization, or by a combination of both mechanisms. From the fact that the values of $a_{\text{H}(\beta)}$ are not greatly influenced by complexation (Table 1) it seems that spin delocalization is not important, and that the co-ordinate bonds do not have appreciable $p_{\pi}-d_{\pi}$ character. Begum *et al.*⁸ arrived at a similar conclusion regarding the C-X bond in radicals of type $\text{R}_2\dot{\text{C}}-\text{X}$ (X = alkyl substituted Al). In contrast with the β proton hyperfine splittings, the substituent splittings are markedly influenced by co-ordination to trimethylaluminium. With the nitrile radicals, this is not surprising, since co-ordination is expected to influence both the π orbital spin density near nitrogen and the exchange coup-

Table 1. E.s.r. spectral data.

Radical	Temperature/ $^{\circ}$ C	Hyperfine coupling constants/G				Linewidth/G
		$a_{H(\beta)}$	a_N	$a_{H(\delta)}$	a_{Al}	
$Me_2\dot{C}CN^a$	20	20.4	3.3	—	—	0.15
$Me_2\dot{C}CN\cdot AlMe_3$	-25	20.75	4.04	—	1.70	0.60
$Me_2\dot{C}CO_2Me^b$	20	21.3	—	1.25	—	0.15
$Me_2\dot{C}CO_2Me\cdot AlMe_3$	-50	21.08	—	2.12	0.49	0.25

^a Data from ref. 4. ^b Data from ref. 5.

ling between the π and the sp orbitals of nitrogen. As regards the ester radicals, the situation is complicated by the fact that a number of different conformations are possible, and INDO calculations¹⁰ were carried out for the radical $\cdot CH_2CO_2Me$. As expected¹¹ the most stable conformations were found to be those in which the $-CO_2-$ group is coplanar with the $\cdot CH_2-$ group. We considered three such conformations, (5), (6), and (7). Of these conformations, (5) was predicted to be the most stable, and (7) the least stable. The predicted methyl proton splitting constants were consistently too small, but it is significant that they varied widely between the different conformations. It seems possible that the formation of a co-ordinate bond between the carbonyl oxygen and trimethylaluminium might alter the relative stabilities of the different conformations, for steric reasons, and this might explain, at least in part, the observed effect on $a_{H(\delta)}$.

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