

## Radical Cations of Diesters: Generation by Irradiation and Detection by Electron Spin Resonance

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Exposure of dilute solutions of a range of dimethyl diesters in trichlorofluoromethane to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K gave the corresponding radical cations. For the oxalate, malonate, and succinate esters the primary cations were detected. This is in contrast with results for various monoesters, which generally gave alkyl-radical-derived cations formed by hydrogen-atom migration to the carbonyl oxygen. The primary diester cations are characterised by fairly large positive  $g$ -shifts, small proton hyperfine splittings and, in some cases, intense violet colours. Rearranged products were detected from the malonate and succinate esters on annealing above 77 K.

The extra stability of the parent cations is attributed to delocalisation between the two carbonyl groups, which confers extra stability on the primary cations and inhibits hydrogen-atom transfer. For the malonate and succinate cations, weak bonding between two adjacent carbonyl oxygen atoms is proposed.

Dimethyl maleate and fumarate cations have also been studied. The former was also violet and had a triplet spectrum similar to that for the succinate. However, the latter, which cannot readily form an oxygen-oxygen bond, was colourless, the e.s.r. spectrum comprising an anisotropic triplet characteristic of an  $\text{H}_2\dot{\text{C}}\text{O}-\text{R}$  radical formed by hydrogen-atom transfer. Thus, in this case, it seems that the primary cation has a localised SOMO, facilitating rearrangement.

During the past few years there have been many successful studies of organic radical cations using matrix isolation techniques coupled with electron spin resonance spectroscopy.<sup>1</sup> However, there have been a number of surprising results, which include the formation of solvent complexes, such as (1) from methyl formate cations,<sup>2,3</sup> the rearrangement of nitroalkane cations,<sup>4</sup> and intra-cation hydrogen transfer.<sup>5-7</sup>

One of the most difficult areas has been that of ester radical cations, which have been widely studied.<sup>2,3,5-9</sup> For various apparently compelling reasons which have been discussed elsewhere,<sup>6,7</sup> it was originally thought that when the methyl formate cation adduct shown in (1) was lost on annealing above 77 K, a  $\pi$ -cation (2) was formed, and that for many other ester cations, the  $\pi$ -structure was formed directly at 77 K. Furthermore, Iwasaki *et al.*<sup>5</sup> suggested that the  $\pi$ -cation of methyl formate was directly formed on exposure at 4 K.

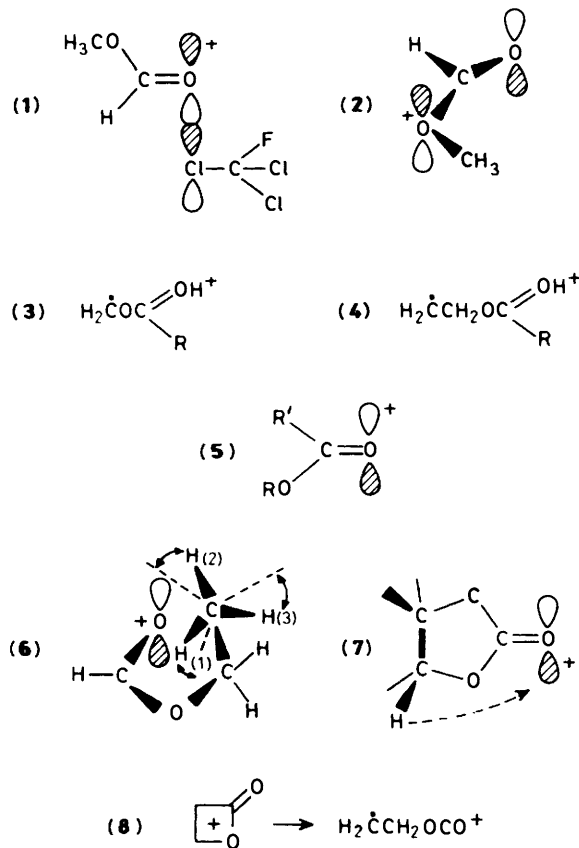
In fact, it now seems that these species are not  $\pi$ -cations, but are rearranged cations almost certainly having structures such as (3) or (4) for methyl and ethyl ester cations.<sup>6,7</sup> Indeed, it is our view that the preferred SOMO for the parent cations is actually the non-bonding ( $\text{O}_{nb}$ ) in-plane orbital (5), as deduced from photoelectron spectroscopic studies,<sup>10</sup> similar to that for aldehyde and ketone radical cations,<sup>11</sup> and to that thought to be utilised in the methyl formate cation- $\text{CFCl}_3$  adduct.<sup>2,3,8</sup>

In an attempt to suppress hydrogen-atom transfer, we studied the radical cations of a range of lactones. In these, the transition states such as (6) cannot be utilised, and hydrogen atoms must perforce migrate over considerable distances in order to give the corresponding rearranged cation (7). In the event, we were able to slow hydrogen-atom transfer in some cases, but still the primary cations were not detected.<sup>12</sup> Instead, ring opening occurred as, for example, for the  $\beta$ -propiolactone cation (8).

In the present study, we have turned our attention to various diesters, in the hope that delocalisation of the SOMO would help to stabilise the parent cations.

### Experimental

Dilute solutions of the various substrates (*ca.* 1 : 1 000 molar ratio) in  $\text{CCl}_3\text{F}$  were frozen into small polycrystalline beads at



77 K and were irradiated with doses of up to *ca.* 1 Mrad. The samples were monitored at 77 K with a Varian E109 or E3 spectrometer. These samples were pulse-annealed by decanting the coolant and re-freezing when spectral changes had occurred. A Varian variable-temperature apparatus was used when required.

$\text{CD}_3\text{O}_2\text{CCH}_2\text{-CH}_2\text{CO}_2\text{CD}_3$  was prepared by the reaction of  $\text{CD}_3\text{OD}$  with succinic acid, with acid catalysis. The purity of the product was checked by measuring its b.p. and by proton n.m.r. spectroscopy.

All other diesters were obtained commercially and used as supplied.

## Results and Discussion

We studied a range of dimethyl and diethyl esters. Only the former gave well defined results, so attention is focused thereon.

**Dimethyl Esters.**—*Dimethyl oxalate.* This gave an intense, narrow singlet, showing well defined  $g_x$ ,  $g_y$ , and  $g_z$  features (Figure 1). Features for solvent adducts or the rearranged species ( $\text{H}_2\text{CO-X}^+$ ) were not detected under any conditions and it seems that the parent cations are remarkably stable relative to those for methyl monoesters and also that for dimethyl carbonate.<sup>13</sup>

There are two reasonable structures for the dimethyl oxalate

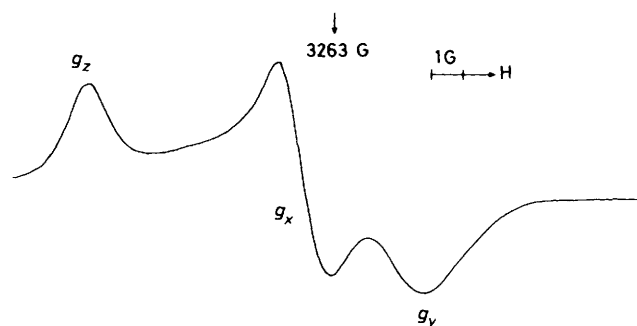


Figure 1. First-derivative X-band e.s.r. spectrum for dimethyl oxalate in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K, showing features assigned to the parent radical cations

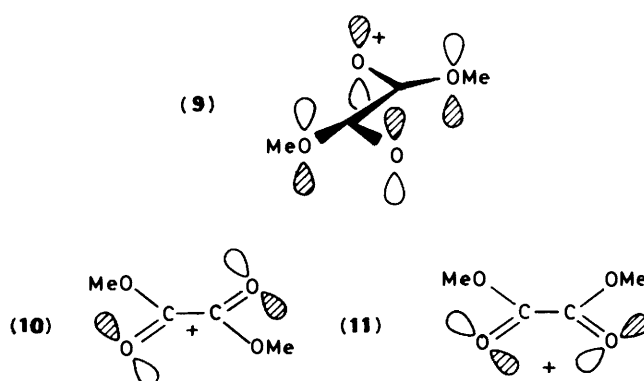


Table. E.s.r. parameters for some radical cations of diesters

Dimethyl ester cation	$^1\text{H}$ Hyperfine coupling (G) <sup>a</sup>	g Values		
		x	y	x
Oxalate		2.0090	2.0046	2.0023
Malonate <sup>b</sup>		2.0045	2.0026	2.0022
Succinate <sup>b</sup>	5.5 (2 H)	2.0043	2.0025	2.0022
Maleate	7.0 (2 H)	2.0060		2.0030
Fumarate <sup>c</sup>	ca. 19 (2 H)		ca. 2.0030	

<sup>a</sup>  $1 \text{ G} \approx 10^{-4} \text{ T}$ . <sup>b</sup> Rearranged to give  $\text{H}_2\dot{\text{C}}\text{OR}$ -type radical at ca. 140 K. <sup>c</sup> Only the rearranged radical,  $\text{H}_2\dot{\text{C}}\text{OR}$ , detected at 77 K.

cation, that with a  $\pi$ -SOMO (9) and that with an in-plane non-bonding SOMO largely confined to the carbonyl oxygen atoms ( $\text{O}_{nb}$ ), (10) or (11). Since the spin density on the methoxy oxygen atoms is expected to be high for the  $\pi$ -cation (9), we would expect to detect considerable hyperfine coupling to the methyl protons. Since this was not observed, we favour one of the  $\text{O}_{nb}$  structures, (10) or (11). Since the parent ester normally exists in the *trans*-conformation (10), this seems to be the most probable structure for the cation. Also, the absence of visible absorption bands argues against structure (11) (see later).

*Dimethyl malonate.* Only a narrow singlet exhibiting even less  $g$ -anisotropy was obtained. This signal was accompanied by an intense purple colour, which we also assign to the parent cation. Once again, we rule out a localised or delocalised  $\pi$ -cation, since we would have expected considerable coupling to the methyl protons.

We therefore again propose a delocalised  $\text{O}_{nb}$  orbital but there are now several reasonable conformations. We consider only the two indicated in (12) and (13). Of these, we favour (13), primarily because we expect considerable  $\sigma$ -bonding interaction, because of favourable overlap between the two in-plane oxygen orbitals. This provides a ready explanation of the intense violet colour, since we expect an allowed transition,  $\sigma_1^2\sigma_2^1 \rightarrow \sigma_1^1\sigma_2^2$ , which could well fall in the visible region, if there is significant bonding. The small spread in  $g$ -values can also be understood in terms of such bonding.

Despite this postulated stabilisation *via*  $\sigma$ -bonding, this cation did appear to rearrange to give a carbon-centred radical ( $\text{H}_2\dot{\text{C}}\text{OX}^+$  type) in the 140 K region.

*Dimethyl succinate.* In this case we again observed a strong purple colouration, suggesting a structure similar to (13) but, in contrast with the malonate derivative, the e.s.r. spectra showed a weak interaction with two equivalent protons (Figure 2). These

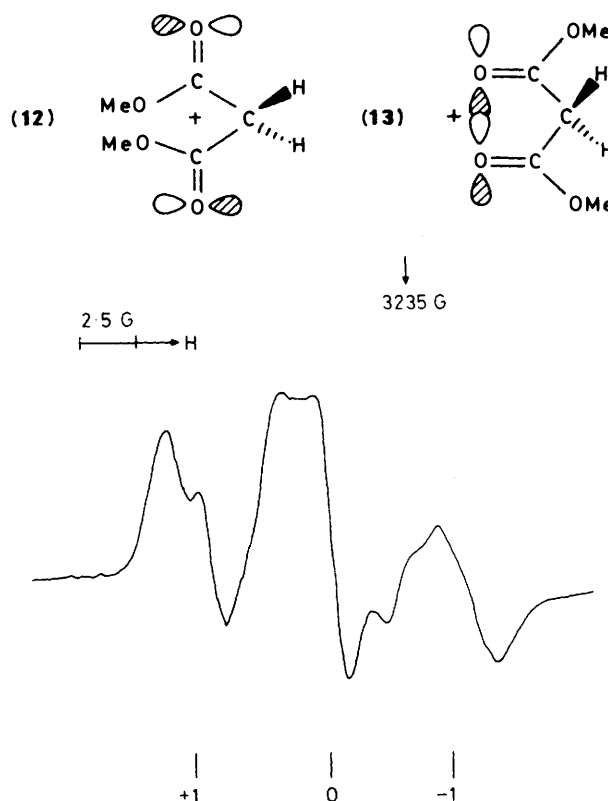


Figure 2. First-derivative X-band e.s.r. spectrum for  $[\text{}^2\text{H}_6]$ dimethyl succinate in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K, showing features assigned to the parent radical cations

components, with a splitting of 5.5 G, showed signs of extra splitting or anisotropy when the  $\text{CD}_3$  derivative was used but were otherwise unchanged. This shows that only slight broadening is caused by the six methyl protons, so again we strongly favour the oxygen-oxygen  $\sigma$ -bonded structure similar to that in (13) rather than a  $\pi$ -structure.

As with the malonate, there was some tendency to undergo hydrogen-atom transfer on annealing.

We conclude that for all three diesters the parent cation is stabilised by delocalisation and possibly weak in-plane bonding, and that hydrogen-atom transfer is greatly inhibited as a result.

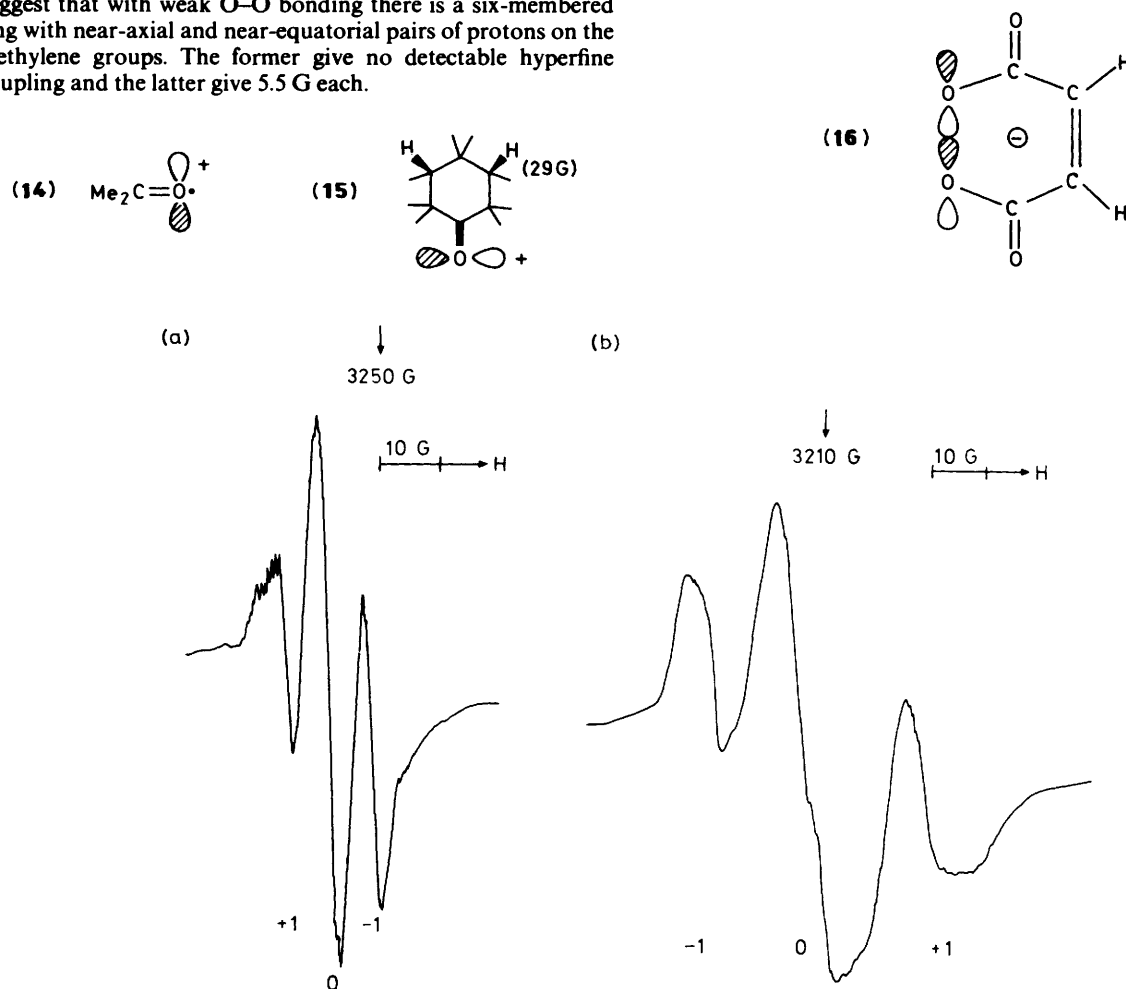
**Proton hyperfine coupling.** The absence of any coupling to the  $\text{CH}_2$  protons of the malonate cation is in good agreement with our results for aldehyde and ketone cations.<sup>11,14</sup> In particular, the methyl proton coupling for the cation (14) was found to be only *ca.* 1.5 G by ENDOR spectroscopy.<sup>15</sup> Thus, absence of any resolved coupling is in good accord with the proposed structure (13).

In contrast, carbonyl cations having more remote protons often show well defined proton coupling, particularly to protons in a *W*-plan structure, as for the cation of cyclohexanone (15).<sup>14,16</sup> In this case the two strongly coupled protons (29 G) lie close to the radical plane. For the succinate cation the coupling is much smaller (5.5 G); delocalisation is probably reduced because of the O-O bonding. Also, the two coupled protons may not lie so close to the radical plane. Thus we suggest that with weak O-O bonding there is a six-membered ring with near-axial and near-equatorial pairs of protons on the methylene groups. The former give no detectable hyperfine coupling and the latter give 5.5 G each.

**Photolysis.** These violet radical cations are extremely sensitive to visible light. Photobleaching results in complete loss of the e.s.r. features assigned to the parent cations with concomitant growth of triplet features assigned to  $\text{H}_2\text{CO-R}$ -type radicals. We presume that the hydrogen-atom-transfer reactions so prevalent amongst the monoesters are greatly facilitated for the excited states of these cations.

**Dimethyl maleate.** The spectrum for the maleate radical cation is remarkably similar to that for the succinate, the hyperfine coupling to two equivalent protons being slightly increased to *ca.* 7 G [Figure 3 (a)]. The purple colouration again suggests a structure similar to (13), and coupling must be to the two olefinic protons. In this case, these must lie close to the radical plane, so the contrast with the carbonyl cations such as (15) probably reflects an enhanced localisation caused by bonding and probably by the electron-withdrawing effect of the OMe groups.

It is interesting to compare our results for dimethyl maleate cations with those for the isostructural unmethylated anions (16), studied some time ago by Iwasaki and his co-workers.<sup>17</sup> Using irradiated single crystals of potassium hydrogen maleate, these workers showed conclusively that the symmetrical  $\sigma$ -radical having a SOMO comprising the out-of-phase interaction of the two in-plane oxygen  $2p$  orbitals indicated in (16) was a primary product. Irradiation at room temperature is



**Figure 3.** First-derivative X-band e.s.r. spectra for (a) dimethyl maleate and (b) dimethyl fumarate in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K, showing features assigned (a) to the parent cation and (b) to the rearranged radical cation,  $\text{H}_2\text{COC}(\dot{\text{O}}\text{H})\text{CH}=\text{CHCO}_2\text{Me}$

thought to give the alternative  $\pi$ -radical, but this was not formed by an electron transition from the  $\sigma$ -radical.

Iwasaki *et al.* also suggested considerable O—O  $\sigma$ -bonding for this radical. They did not report on any visible absorption bands in the 500 nm region such as we observe, but they did find that the  $\sigma$ -radical was sensitive to visible light, which implies the presence of a transition in the visible region.

They obtained a fairly large  $g$ -shift,  $g_{\max}$  being 2.0079. This is slightly greater than our value for  $g_{\max}$  (2.007), but our errors are greater and, of course, the structures are different. Also, their proton coupling of  $5 \pm 1$  G (almost isotropic) is slightly smaller than ours ( $7 \pm 1$  G). Nevertheless, the agreement is good and we consider that the thorough results obtained by Iwasaki *et al.* strongly support our assignment.

*Dimethyl fumarate.* In marked contrast, these solutions remained colourless, and the e.s.r. spectrum was characteristic of a  $H_2\dot{C}OR$ -type radical [Figure 3(b)]. Evidently, delocalisation is inhibited for the primary cation, so that, as with the monoesters, hydrogen-atom migration from the methyl group takes place readily at 77 K.

*Diethyl Esters.*—All the corresponding diethyl esters have been studied. However, the spectra were complex, suggesting extensive proton hyperfine coupling and the presence of more than one type of radical. No compelling evidence for the presence of unrearranged primary cations was forthcoming. It will be necessary to study the mixed methyl ethyl esters and selected deuteriated esters before clear interpretations can be obtained. In the light of this uncertainty, we do not consider that these results should be included herein.

#### Acknowledgements

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