The Radical Cation of Ethyl Dithioacetate

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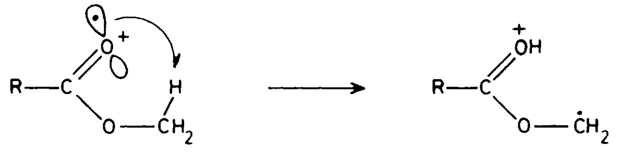
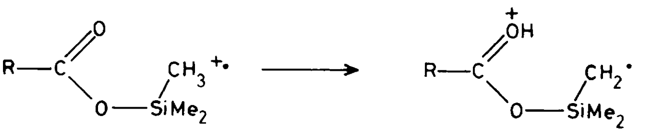
In contrast with ester cations (RCO_2R) which rearrange spontaneously at 77 K *via* intramolecular hydrogen atom transfer, stable π-radical cations of ethyl dithioacetate ($MeCSSEt^{+\bullet}$) have been observed by e.s.r. spectroscopy, following γ-irradiation of dilute frozen solutions in $CFCl_3$ at 77 K.

Radical cations of carboxylic esters have been the subject of debate and after some controversy, it is generally agreed that the e.s.r. spectra observed following γ- or X-irradiation of esters in freon solvents at 77 K are not due to the primary cations, but to radicals arising from intramolecular hydrogen atom transfer,[1—5] (*e.g.* Scheme 1) following ionisation of the in-plane oxygen lone-pair orbital. Exceptions to this are trimethylsilyl[6] and neopentyl[4] esters, in which the positive hole is largely confined to the Me_3Si– or $Me_3C{-}CH_2$– group, rather than to the RCO_2– moiety, and are stable at 77 K. On allowing the freon matrix to warm from 77 K, rearranged cations are observed, but these have been proposed[6] to arise from the proton transfer reaction (Scheme 2), which is apparently less facile than Scheme 1.

In view of these results, we were interested in studying the behaviour of a second-row analogue, *viz.* the dithioester, MeCSSEt; we are unaware of any previous report of an e.s.r. study of a thioester radical cation. Following γ-irradiation of the title compound as a dilute frozen solution in $CFCl_3$ at 77 K, e.s.r. spectra such as that shown in Figure 1 were recorded, from which the following data were extracted: $g_x = 2.055$, $g_y = 2.008$, $g_z = 2.000$; $A(2H) = 16$ G.† In contrast with the results for $RCO_2R^{+\bullet}$ cations, the spectrum is clearly not due to carbon centred radicals, given the extent of the g-anisotropy, and has an overall appearance similar to that reported previously for R–S$^\bullet$ radicals in the solid state[7,8] with a low field $g_\parallel$ (g_x) feature which is well separated from g_y and g_z; R–S$^\bullet$ radicals could be accounted for by fragmentation of the parent cation (Scheme 3). However, the value of g_x (2.055) is much less than that reported for R–S$^\bullet$ radicals (2.1—2.3, depending strongly on their environment) and the triplet splitting [A(H) = 16 G] would appear very low for $MeCH_2{-}S^\bullet$ radicals on the basis of both a recent correlation of π-bond energies with β-proton couplings[9] and a liquid phase study of $R_2C(Mu){-}S^\bullet$ radicals[10] by the μSR technique, in which muon couplings of 40—50 G were measured. We therefore consider that the spectrum is due to intact $MeCSSEt^{+\bullet}$ cations.



Scheme 1



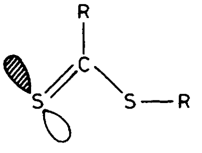
Scheme 2

$$MeCSSEt^{+\bullet} \longrightarrow Et{-}S^{\bullet} + Me{-}C{\equiv}S^{+}$$

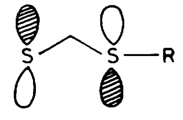
Scheme 3

CNDO/2 calculations[11] predict that the HOMO in MeCSSMe is the in-plane orbital (**1**) comprising mainly of the sulphur $3p_y$ orbital. However, the cation which is formed cannot be that with an in-plane SOMO of the type (**1**), since a negligible coupling to the two $MeCH_2$– protons would be expected, in contrast with that observed (16 G). We therefore assign the cation as being the π-form in which the unpaired electron is 'allylically' delocalised, and occupies the non-bonding π_2 orbital (**2**).

According to photoelectron results,[12] the HOMO in RCO_2R esters is the in-plane (n_o) orbital, and the chemistry of $RCO_2R^{+\bullet}$ cations, both in freon matrices[1—5] and in the gas-phase,[13] is compatible with ionisation of this orbital to form an oxygen centred radical which rapidly abstracts a hydrogen atom in an intramolecular step (Scheme 1) (In some higher esters, fragmentation of the rearranged species occurs[2,4]). The reaction of Scheme 1 is expected to be exothermic on the basis of typical O–H bond energies (110 kcal/mol)[14] compared with C–H bond energies (*ca.* 98 kcal/mol).[14] In the case of the dithioester, a radical transfer step of this kind would be endothermic (and have a higher activation energy) given typical S–H bond energies (*ca.* 82 kcal/mol);[14] we note that addition of muonium atoms to thiocarbonyl compounds occurs preferentially at carbon with the formation of



(1)



(2)

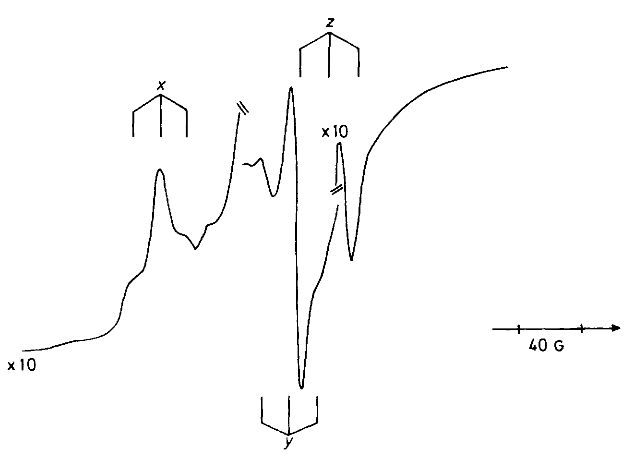


Figure 1. X-Band e.s.r. spectrum recorded following γ-irradiation of MeCSSEt as a dilute solution in $CFCl_3$ at 77 K, and assigned to the parent π-radical cations.

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† 1 G = 10^{-4} T.

$R_2C(Mu){-}S^{\bullet}$ radicals rather than at sulphur to form $R_2\dot{C}{-}SMu$ radicals[10] in contrast with carbonyl derivatives which form $R_2\dot{C}{-}OMu$ radicals.[15]

It seems possible, then, that ionisation might take place from the lone-pair orbital (**1**) as expected from the CNDO/2 order of orbitals, but the intramolecular H-atom transfer step is sufficiently slow compared with the oxygen case (Scheme 1) that relaxation of the cation can occur to form the delocalised (π_2) state.

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