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AN ESR STUDY OF SOME GROUP IVB FREE RADICAL ADDUCTS OF DIETHYLKETOMALONATE

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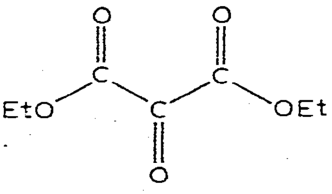
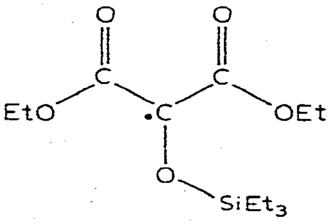
Summary

Diethylketomalonate (DEKM) reacts with triethylsilyl, tri-n-butylstannyl and tricyclohexylplumbyl radicals to give adduct radicals detectable by ESR. This is the first observation of the addition of a lead-centred radical to a carbonyl group. The hydrogen atom adduct of DEKM exhibits line broadening effects attributed to rotational isomerism of the hydroxyl group. The dynamics of this process have been determined.

The addition of group IVB metal-centered radicals to carbonyl compounds produces paramagnetic intermediates detectable by ESR and the reactions of organosilicon, organogermanium and organotin radicals with a variety of ketones and esters have been reported [1—3]. Diethylketomalonate (I) is a tricarbonyl compound with two ester-carbonyl groups and one keto-carbonyl group. We should expect adduct radicals formed by DEKM to be stabilised by the presence of the ester groups, and have accordingly investigated its reaction with triethylsilyl, tri-n-butylstannyl and tricyclohexylplumbyl radicals. We have also found that DEKM readily forms a hydrogen atom adduct and have studied the temperature dependence of its ESR spectrum.



(I)



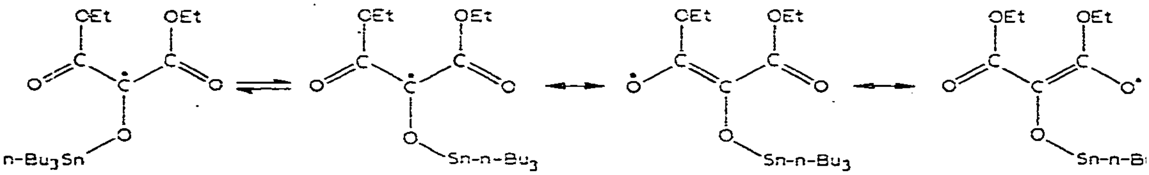
(II)

Results and discussion

Preliminary attempts were made to add triethylsilyl radicals to DEKM by photolysis of a mixture of triethylsilane, t-butyl peroxide and DEKM in the cavity of an ESR spectrometer. The ESR spectrum produced consisted of a doublet (3.7 G) of quintets (0.93 G) inconsistent with the expected structure (II). This spectrum has since been assigned as the hydrogen adduct $HO{-}\dot{C}(CO_2Et)_2$ (III), we return to the question of its method of formation later. By lowering the temperature to −70°C, we were able to minimize formation of III and obtained an ESR spectrum consisting of a 1.0 G quintet which we assign to the triethylsilyl adduct II with hyperfine structure from the four equivalent methylene protons of the ethoxy groups.

$$Et_3SiH \xrightarrow{t\text{-}BuO\cdot} Et_3Si\cdot \xrightarrow{O{=}C(CO_2CH_2CH_3)_2} \underset{\text{(II)}}{Et_3SiO\dot{C}(CO_2CH_2CH_3)_2} \qquad (1)$$

Tri-n-butylstannyl radicals also react with DEKM to give a radical with a quintet splitting of 0.95 G. Weaker lines flanking the main spectrum (Fig. 1) have been assigned to ^{117}Sn and ^{119}Sn satellites with a splitting of 4.05 G. We attribute this spectrum to the carbonyl group adduct IV. One can also write cyclic structures such as V for this species (a structure of this type has been proposed for the adduct formed by $\dot{S}nMe_3$ and benzil [3]), but the observed equivalence of the four methylene protons indicates a low barrier for rotational isomerism about the C—O bond (IVA ⇌ IVB) and suggests pentacoordination



(IVA) (IVB)

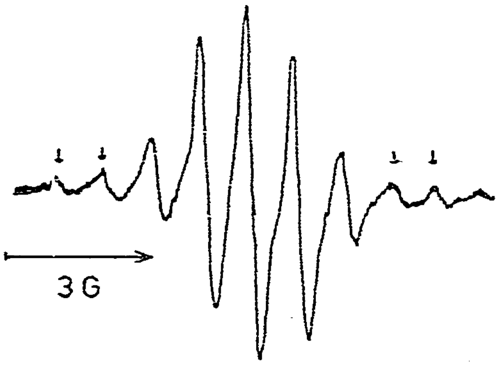
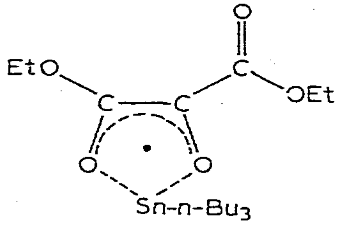
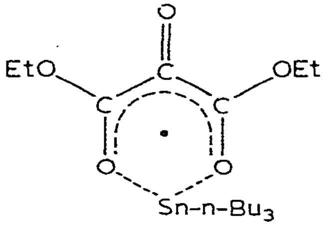


Fig. 1. ESR spectrum of the radical formed from DEKM and tri-n-butylstannyl radicals at 0°C. The arrows indicate satellite peaks due to ^{117}Sn and ^{119}Sn.

with the second carbonyl group is not a major factor. Equivalence of the two ethyl methylene groups could in principle also be achieved by forming a six-membered ring VI but we feel this is unlikely for two reasons. Firstly, Schroeder et al. [3] observed only a five-membered ring in the reaction of trimethylstannyl radicals with 1,3-diphenylpropanetrione, and secondly the similarity of splittings observed in the silyl adduct II and the tin adduct IV suggests a similar structure for both radicals.



(V)



(VI)

We have previously suggested [2] that the reaction of tin-centred radicals with α-diketones gives rise to radical anions which exist as contact ion pairs with a trialkylstannyl cation. On balance we now prefer to write these adducts as covalent structures such as IV but would stress that the Sn—O bond has substantial ionic character.

Adducts of lead-centred radicals to carbonyl compounds have not previously been reported but we find tricyclohexylplumbyl radicals react with DEKM and again a 0.95 G quintet is observed. In this case each line in the ESR spectrum (Fig. 2) is further split into a 0.21 G quartet. The only obvious origin for this additional splitting is from the three protons in the 1-positions of the cyclohexyl groups. We should also expect to observe a satellite splitting from ^{207}Pb ($I = 1/2$, 21% natural abundance) but poor signal to noise has so far precluded its detection. Splittings from this isotope have, however, been observed in a number of other adducts [4]. The structure of the Pb adduct is presumably similar to that of the Sn species since identical proton splittings were observed in each case.

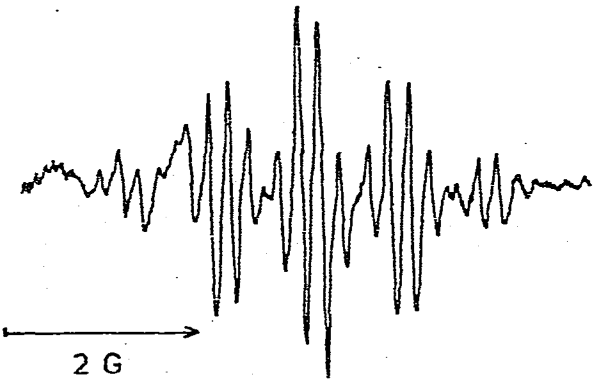


Fig. 2. ESR spectrum from DEKM and tricyclohexylplumbyl radicals at 20°C.

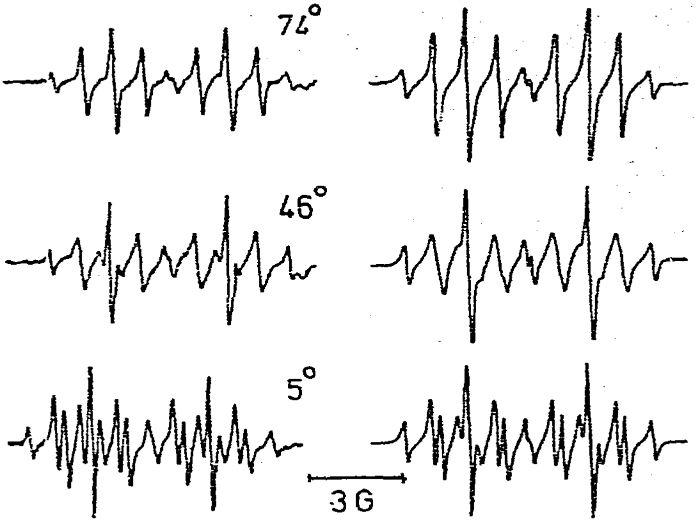


Fig. 3. ESR spectra of the hydroxy radical III at various temperatures together with computer simulations. The latter were calculated for exchange rates of 2.5, 0.25 and 0.01 MHz respectively (top to bottom).

As mentioned above, initial attempts to prepare the silyl adduct II produced instead a spectrum assigned to III. It was subsequently found that the same species could be prepared by photolysis of DEKM in diethyl ether, tetrahydrofuran, toluene, chloroform and carbon tetrachloride. We envisage that the keto-carbonyl group is excited, via a singlet, to a triplet state which abstracts a hydrogen atom from a solvent molecule. The observation that a spectrum is obtained in carbon tetrachloride demonstrates that abstraction from other molecules of I is also possible. It has been shown [5] that the triplet state of DEKM reacts as a diradical with tetramethylethylene to form an oxetane and presumably the same species is involved in the hydrogen abstraction reactions. The ESR spectrum of III is temperature dependent (Fig. 3). At +60°C it consists of a doublet of quintets but at +10°C it becomes a doublet of triplets of triplets. At intermediate temperatures linewidth alternation is apparent [6]. The hydroxyl proton splitting is temperature dependent and decreases from 3.51 G at −50°C to 3.27 G at +60°C. These observations are all consistent with a rotational isomerism of the hydroxyl group (IIIA $\rightleftharpoons$ IIIB) and we have performed a computer simulation of the spectra using the modified Bloch equations [6].

(IIIA) . (IIIB)

By matching computed spectra for known rates of exchange with the experimental traces (Fig. 3), we find an activation energy for the isomerisation, the mechanism of which probably involves the breaking of an intramolecular hydrogen bond, to be 49 kJ mol^{-1} with an Arrhenius factor of $10^{13.7}$. Our barrier is higher than values of 19 kJ mol^{-1} reported for the hydroxymethyl radical [7] and 9.6—11.7 kJ mol^{-1} for the biacetyl semidione [8] but this is not unexpected in view of the presence of the intramolecular hydrogen bond.

Experimental

All the experiments were performed by in-situ UV irradiation of solutions within the cavity of a Varian E3 spectrometer as previously described [2]. DEKM (Aldrich) and hexa-n-butyldistannane (BDH) were commercial samples. Triethylsilane and hexacyclohexyldiplumbane were prepared by standard procedures. DEKM is extremely hygroscopic and was kept in a vacuum desiccator when not in use.

Samples containing triethylsilane or hexa n-butyldistannane were a mixture of Group IVB compound and di-t-butylperoxide in the approximate ratio 1 : 2 (v/v) with 5—10 mg of carbonyl compound per ml. The reactions involving lead radicals were performed in benzene or toluene with 5 mg of DEKM per ml of solvent and a ratio of hexacyclohexyldiplumbane/DEKM of 3 : 1 (w/w).

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