

RADICAL ANIONS OF UNSATURATED ESTERS. THE MALEIC-FUMARIC AND PHTHALIC SYSTEMS

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(Received in USA 7 June 1967)

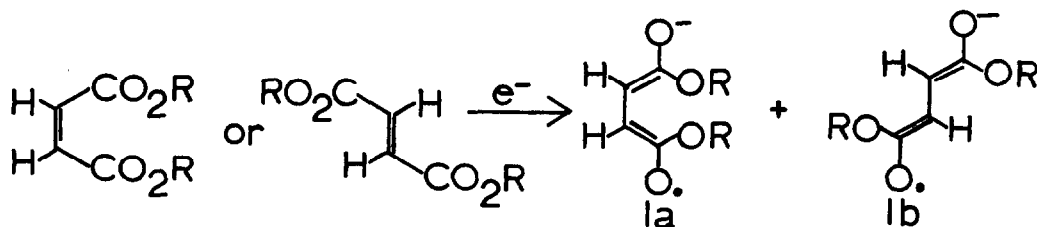
The great stabilizing effect of conjugated carbonyl groups upon radical anions is well known. We here report e.s.r. spectra of unsaturated esters, which illustrate the effects of cis-trans isomerism on e.s.r. spectra.

When diethylmaleate (ca. 3×10^{-3} M in DMSO which is 5×10^{-2} M in tetrabutylammonium perchlorate) is electrolytically reduced in the e.s.r. cavity (1) at room temperature, a spectrum showing three groups of lines appears (spectrum A). Inspection shows that spectrum A is composed of two separate species in approximately 2:1 ratio, each a wide-spaced triplet of quintets, with slightly different splitting constants and g-factors. The spectrum fades in 5-10 min., and is not particularly well resolved.

When the initial spectrum (A) containing three groups of lines fades, it is replaced by a second spectrum (B) containing two groups of lines. B is also caused by two separate species (2.4:1 ratio) with slightly different splitting constants and g-factors. Each has splittings by two non-equivalent protons and one pair of protons--an ethyl splitting has been lost. Spectrum B is much stabler toward further electrolysis and lasts for at least an hour. Spectrum B is also obtained when monoethylmaleate is reduced at high potentials (far exceeding that of solvent breakdown); no preliminary spectrum was observable from the half-acid. The e.s.r. spectra observed upon reduction of diethyl fumarate are the same as those from the maleate. Dimethyl maleate and fumarate behave as the ethyl esters, but there are two more protons in the initial spectrum (although we did not resolve well enough to report splittings for the minor component, it is clearly present), and one more in the second spectrum. Dimethyl and diethyl phthalate also give initial anion

spectra followed by dealkylated radicals, but here we could not resolve the small ortho ring splittings in the initial spectra. There were "accidental equivalences" in the small splittings of the dealkylated spectra, which appeared as four overlapping multiplets. There was no evidence in either of the phthalate esters for each spectrum containing two species as was observed in the maleate-fumarate cases. The splittings observed are summarized in Tables I and II.

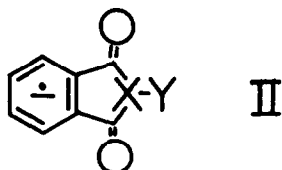
Maki (2) was the first to observe cis-trans isomerism by e.s.r.; finding two different sets of splittings upon reduction of terephthalaldehyde, but identical g-factors. Corvaja, Nordio, and Giacometti (3) recently reported different g-factors as well as splittings for a substituted phenylglyoxal anion. There are in principle six possible isomers in the maleate-fumarate "A" spectra ("double bond" cis or trans, and carbonyl oxygens cis-cis, cis-trans, or trans-trans to the vinyl hydrogens). We take the identical double spectra from maleates and fumarates but only single spectra from the phthalates as proof that it is double bond isomerism which causes the doubled spectra, and that the species causing "spectrum A" are Ia and Ib (with the stipulation that relative positions of O and OR are unknown) (4).



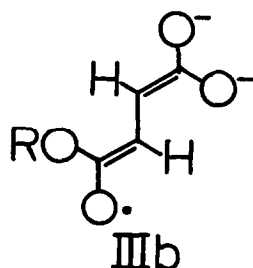
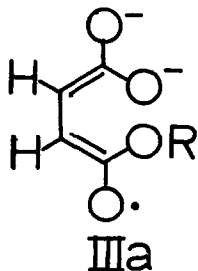
The spectra require that in the anion rotation about the central bond is rapid compared to minutes, but slow compared to ca. 10^{-6} sec.

One would expect the major component to be the trans isomer (Ib) since it has less steric strain and greater distance between the partially negative-charged oxygens, but the ratio is under 3:1 in all cases ($\Delta F_{\text{isom}} < 0.7$ kcal/mole). The major component always had the smaller g-factor and larger splittings (a larger splitting implies less spin density at oxygen which gives a lower g-factor (5)).

A detailed discussion of the spin density distributions of these anions cannot be given here. We shall note only that the large (β) ring splittings of the phthalate anions (3.4 G, see Table 1) are significantly larger than those of the cyclic analogs II. For II, where X = O, NH, "N⁻", N-Alkyl, "CH⁻", or "C-Alkyl⁻", the corresponding splittings all fall in the range 2.40-2.65 G (6).



The dealkylated spectra (B) clearly show the same sort of isomerism as the A spectra; we presume the simplest explanation, hydrolysis (by adventitious water?). The carboxylate group could accommodate much of the charge and would make the two ends of the molecule strongly non-equivalent, as observed. We would not expect exchange to be slow enough to see a carboxyl proton splitting if the acid anion were formed, but electrolysis does generate strong base and so we write the carboxylate anion. This is emphasized in the resonance structures IIIa and IIIb written for the isomers causing spectrum B.

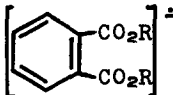


With three different types of oxygens for which one really does not know h and k parameters in structures like III, M.O. calculations are rather meaningless; we did find in calculations on the phthalate half-ester that the ring spin densities are quite sensitive to the unknown parameters. We do not feel the calculations either confirm or deny structure III for the second (B) spectra; more will have to be learned about treatment of heteroatoms before

meaningful calculations can be made. We are presently studying the variation of temperature and cation on these species to obtain activation parameters for the isomerizations. The facile hydrolysis during electrolysis was not expected, and the path this reaction takes is being studied.

Table I

Splitting Constants (in gauss) of Ester Anions

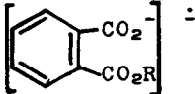
$[\text{RO}_2\text{C}-\text{CH}=\text{CHCO}_2\text{R}]^-$	Major	Minor	ΔH of centers
R = Methyl	6.6 (2H)	a	a
	ca. 1.17 (6H)	a	
R = Ethyl	16.65 (2H)	6.53 (2H)	0.2
	1.10 (4H)	1.06 (4H)	
			
R = Methyl ^b	3.40 (2H), 0.83 (6H)		
R = Ethyl ^b	3.4 (2H), 0.74 (4H)		

a. Not well enough resolved to measure.

b. The small ortho ring splittings were not resolved.

Table II

Splitting Constants (in gauss) of Half-ester Anion Radicals

$[\text{RO}_2\text{C}-\text{CH}=\text{CHCO}_2]^-$	Major	Minor	ΔH
R = Methyl	10.11 (1H)	10.03 (1H)	0.15
	2.81 (1H)	2.75 (1H)	
	1.02 (3H)	0.77 (3H)	
R = Ethyl	10.24 (1H)	10.13 (1H)	0.16
	2.78 (1H)	2.69 (1H)	
	0.91 (2H)	0.69 (2H)	
			
R = Methyl	ca. 7.35 (1H)		
	ca. 3.68 (1H)		
	ca. 0.88 (5H)		
R = Ethyl	7.33 (1H)		
	3.70 (1H)		
	0.98 (1H)		
	0.72 (3H)		

Acknowledgment is made to the Wisconsin Alumni Research Fund for support of this research.

References

1. A Varian V-4502 instrument with 9" magnet was employed, and electrolyses were conducted in a Varian flat quartz electrolytic cell. Fielddial calibration was used to measure the splittings.
2. A. H. Maki, J. Chem. Phys., 35, 761 (1962); E. W. Stone and A. H. Maki, ibid., 38, 1999 (1963).
3. C. Corvaja, P. L. Nordio, and G. Giacometti, J. Am. Chem. Soc., 89, 1751 (1967).
4. It is possible that this latter sort of isomerism has been observed in the phthalate system. The second spectrum from diethyl phthalate (which saturates remarkably easily) shows an unusual linewidth effect in that the outer two of the four equivalent patterns appear definitely sharper than the inner ones. Among the possibilities for such an effect is a rate of carbonyl rotation in the range 10^{-5} to 10^{-7} sec⁻¹.
5. A. J. Stone, Mol. Phys., 6, 509 (1962).
6. All in DMSO. To be published separately. R. E. Sioda and W. S. Koski, J. Am. Chem. Soc., 89, 475 (1967) have recently described the phthalic anhydride and phthalimide anion radical spectra in DMF.