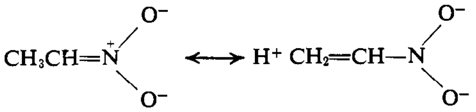

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lization by methyl groups, as in the final state. Superimposed on this will be the transition-state interaction of hydroxide ion with methyl groups which is destabilizing (inductive effect). As long as this destabilizing interaction (positive contribution to $\delta_R\Delta F^{\ddagger}$) exceeds the difference between the inductive and hyperconjugative interactions of the methyl and nitro groups in the transition state, $\delta_R\Delta F^{\ddagger}$ will be positive; since $\delta_R\Delta F^\circ$ is negative, α will be less than zero. Simple electrostatic calculations show that such a balance of effects is in fact reasonable for this system.

Deviant Brønsted relations such as these should be observed whenever the new transition-state interaction, which we shall call the intermolecular effect, exceeds the intramolecular effect of the substituent within the catalyst. This is especially likely to occur with nitroalkanes and other pseudoacids and -bases, which owe their acidity to the presence of groups capable of removing negative charge from the vicinity of the proton transfer site and usually also from the immediate neighborhood of substituents introduced for the purpose of varying acid strength. In more conventional catalysts, such as carboxylic acids, phenols, amine salts, etc., the charge either remains on the atom from which the proton is transferred or else moves nearer the substituent; in these cases, the intermolecular effect will be small compared to the intramolecular effect, and more normal Brønsted exponents will be observed. The intermolecular effect, however, will not be totally absent, and its presence will give α a value different from that of some other measure of the position of the transition state along the reaction coordinate, say x, the fraction of electronic charge transferred. Calculations, which will be reported in full later, show that an intermolecular effect only one-tenth of the intramolecular effect will, at $x = 0.5$, produce a 10% difference between α and x for proton transfer to a neutral or a negatively charged substrate, and the discrepancy will be greater for substrates of different charge types.

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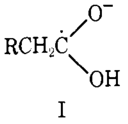
A New Type of Radical in Irradiated Single Crystals of Carboxylic Acids

Sir:

During the past decade extensive studies have been made of the electron spin resonance of irradiated single crystals of carboxylic acids. The radicals found so far may be classified into the following four categories. Irradiation at low temperature gives anion π radicals (I) produced by capture of an ejected electron[1] and neutral π radicals (II) produced by removal of the carboxylic group;[1a,2] while irradiation at room temperature, or elevation of the specimen temperature after irradiation at low temperature, gives a π radical (III) produced by rupture of the hydrogen atom attached to the α carbon of the carboxylic group, in the case of saturated compounds,[3] and π radicals (IV) produced by addition of H or R to the double bond, in the case of unsaturated compounds.[4]



I

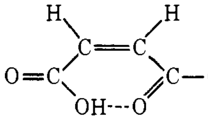
$RCH_2\cdot$ II

$R\dot{C}HCOOH$ III

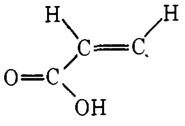
$R'CHX-\dot{C}R''COOH$ IV, X = H or R

Recently we have found a new type of radical which is believed to be a precursor of the radical of type II. The esr spectra of a single crystal of maleic acid irradiated at 77°K show that the anion π radical (C_π) of type I and the new type of radical (O_σ), having a large g anisotropy with a small hyperfine structure, are predominantly produced together with a minor product of the vinyl-type radical (V_σ) which corresponds to type II. O_σ is very unstable and disappears by subsequent exposure to a tungsten light or by warming slightly from 77°K. Instead, the signal due to V_σ was enhanced at the expense of the signal due to this unstable radical. Although both normal maleic acid and the deuterated one (DOOCCH=CHCOOD) were examined, the hyperfine and g tensors determined from the spectra of the latter are listed in Table I, since the hyperfine couplings due to the OH protons have not been analyzed yet.

It was found from comparison with the crystallographic data[5] that the direction of the maximum principal value (2.0261) of the g tensor of O_σ is approximately along the side C–O(H) bond and that of the minimum value (2.0035) is nearly perpendicular to the C–O(H) bond in the molecular plane. From this, together with the large g anisotropy, O_σ is assigned to the carboxyl radical produced by the removal of the OH proton which participates in intermolecular hydrogen bonding. The hyperfine coupling is due to a closer vinylene proton, since the direction of the maximum principal value is along the line connecting the side C–O(H) oxygen and the closer vinylene proton. The magnitude and the anisotropy of the hyperfine tensor are also consistent with this interpretation. Since the half-filled orbital lies in the molecular plane, this radical is a localized σ radical, in contrast to the π radical produced by the removal of the OH proton in



O_σ



V_σ

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Table I. The Principal Values and Their Directions of the Hyperfine and g Tensors in Irradiated Maleic Acid-d_2 (DOOCCHCHCOOD)

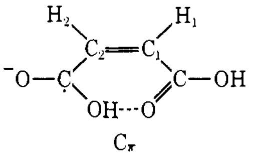
		Principal values, G[a]	Isotropic component	Direction cosines a	b	c'
O_σ		+6.4		+0.733	∓0.676	+0.078
	A_H	+3.6	+3.9	+0.639	±0.723	+0.264
		+1.7		−0.234	∓0.144	+0.962
		2.0261		+0.676	±0.737	−0.014
	g	2.0061	2.0119	−0.123	±0.131	+0.984
		2.0035		+0.727	∓0.663	+0.179
V_σ		+27.0		+0.573	±0.819	−0.025
	$A_{H\alpha}$	+9.6	+13.5	+0.814	∓0.565	+0.133
		+3.9		−0.095	±0.096	+0.991
	$A_{H\beta}$	58 ± 2 (nearly isotropic)				
		2.0032		−0.103	±0.120	+0.988
	g	2.0026	2.0025	+0.915	∓0.378	+0.141
		2.0018		+0.390	±0.918	−0.071
C_π		−13.0		+0.984	∓0.129	+0.128
	A_{H1}	−8.5	−8.2	−0.130	∓0.010	+0.992
		−3.2		+0.126	±0.992	+0.026
		−6.4		+0.807	±0.588	+0.047
	A_{H2}	−5.2	−4.5	−0.050	∓0.011	+0.999
		−1.9		−0.588	±0.809	−0.020
		2.0043		−0.475	±0.880	+0.002
	g	2.0040	2.0036	+0.877	±0.474	−0.085
		2.0024		+0.075	±0.039	+0.996

[a] The probable signs are determined from the hyperfine anisotropy.

potassium hydrogen maleate irradiated at room temperature.[6]

As for V_σ, it is evident that the anisotropic coupling having the isotropic component of 13.5 G and the nearly isotropic coupling of 58 G correspond to the α proton and the *trans* β proton, respectively, in the vinyl radical, as shown above. The g tensor also exhibits the characteristics of the σ radical of the vinyl type. From the principal directions of the hyperfine and g tensors, it was found that the radical carbon of V_σ is the one to which the $-C(=O)-O\cdot$ group of O_σ is attached. This strongly suggests that V_σ is produced by a loss of CO_2 from O_σ.

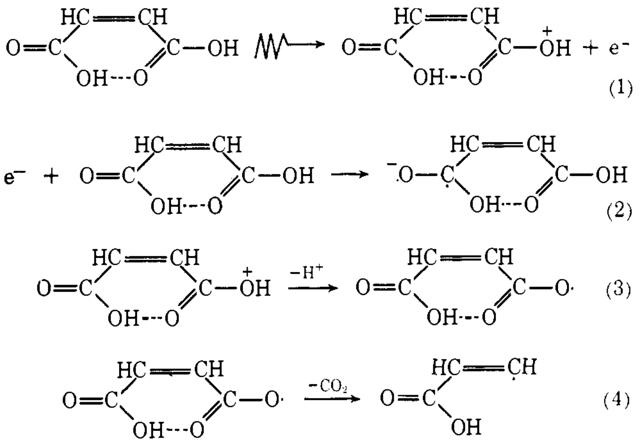
It is also concluded from the hyperfine and g tensors that the anion π radical (C_π) has the structure



C_π

where the unpaired electron is delocalized in the π system. From the hyperfine tensors characteristic of the α proton in π radicals, the spin densities on C_1 and C_2 are estimated to be 0.36 and 0.20, respectively.

From the formation of these radicals, the scheme shown in eq 1-4 may be proposed. In this scheme, O_σ is assumed to be produced from a cation by the ion-molecule reaction through the intermolecular hydrogen bond. Therefore, O_σ is considered to be a counterpart of the anion π radical formed by a capture of an ejected electron. The fact that O_σ is very unstable and converts into V_σ, accompanied by a loss of CO_2, suggests that the radical of type II found in saturated carboxylic acids might also have originated from the cation *via* O_σ-type radicals.



The existence of such an intermediate radical as O_σ has been also found in single crystals of potassium hydrogen maleate and fumarate irradiated at 77°K. Details will be given in subsequent papers.

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Structural Effects in Mass Spectrometry. Mechanistic Implications in the Dehydration of 26-Hydroxy-5α-furostan by Six- and Seven-Membered Cyclic Transition States

Sir:

It has been well established by deuterium-labeling studie sthat electron impact induced dehydration of acyclic alcohols ROH, where R = n-C_4H_9 or larger, proceeds preferentially ($\sim$90%) by 1,4-hydrogen abstraction *via* a six-membered cyclic transition state, with only approximately 5% each hydrogen abstraction by 1,3 and 1,5 processes.[1-4] The high degree of site specificity observed[1-4] for the hydrogen abstracted suggests that H-D scrambling in the alkyl chains[5] is not contributing significantly at least in 70-eV mass spectra.[1] Recently it has been shown[8,9] that loss of water can occur through much larger cyclic transitions states,[10]

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