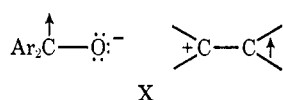


results above, be essentially nil. In fact, $k(\text{IIIc})/k(\text{III d}) = 1.10 \pm 0.01$, indicating a healthy preference for deuterium going next to oxygen, and ruling out the possibility that step 1 is an elementary reaction. The only obvious interpretation consistent with all the isotope effects is that the intermolecular competitions reflect some (irreversible) step k_1 and that the intramolecular competition reflects another step, k_2 . The results for the intramolecular competition are readily interpreted on the basis of the preferential collapse of X to IIc over II d, expected on the basis of hybridization arguments³ as long as L_1 and L_2 are chemically identical in X.

The substituent effects reported in Table I show that the rate of quenching diaryl ketone triplets by *cis*-2-butene increases markedly as electron attracting groups are introduced, even though the triplet energy decreases in this direction. Arnold⁴ has observed that the competition between energy transfer and oxetane formation with acetophenones and norbornene is extremely sensitive to ring substituent; the present results suggest that much of this sensitivity may reside in the oxetane-forming reaction.

If the substituent effects reflect the nature of intermediate X, they suggest that it involves significant electron transfer from olefin to ketone. However, Yang^{13,14} and Wagner¹⁵ have provided examples of ketone hydrogen-abstraction reactions in which substituent effects similar to these operate, and have concluded that the effects are due to interactions of π - π^* levels with the n - π^* level in the triplet; those triplets which are "purer n - π^* " react faster. While such an explanation would account for our observations, the available spectroscopic evidence (phosphorescence excitation spectra^{14,16} and phosphorescence lifetimes¹⁴) suggests only rather slight π - π^* contributions to these diaryl ketone triplets. We accordingly prefer to consider that our substituent effects support the intermediacy of an electron-transfer complex. Electron transfer has for some time been implicated in the



quenching of excited states by amines,¹⁷ and more recently by hydrocarbons as well.¹⁸

Further work on the development of model systems for isotope effects on electron-transfer reactions is planned, as well as other experiments to test the proposed intermediate.

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Acknowledgment. Support of this work by the donors of the Petroleum Research Fund (Grant No. 3031-A4), administered by the American Chemical Society, is gratefully acknowledged.

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Received October 24, 1969

Discovery of a σ Radical in X-Irradiated Malonic Acid

Sir:

We wish to report the discovery by esr of a new σ -radical species in the well-studied system of X-irradiated malonic acid.¹ The existence and structure of a relatively small number of carbon-based σ radicals such as CO_2^- ,² formyl,³ phenyl,⁴ and acetyl⁵ have generated considerable interest in recent years. However, only the former two have been studied as oriented molecules in a single crystal.^{2,3d} We have determined carbon-13 and proton hyperfine tensors as well as the g tensor for the oriented σ radical trapped in the malonic acid crystal, and we show that it can be characterized as a monosubstituted acetyl radical, $\text{RCH}_2\dot{\text{C}}=\text{O}$ ($\text{R} = -\text{COOH}$).

Freshly X-irradiated malonic acid has two distinct characteristics: (1) the radiation-induced pink coloration of the crystal disappears within hours; (2) the relaxation time T_{1e} increases dramatically in about the same period.⁶ These facts, together with the observation of a more intense pink color from perdeuterated malonic acid, stimulated us to search for unusual features in the spectrum of the deuterated crystal.

An esr spectrum of a malonic acid- d_4 crystal irradiated for 15 min is shown in Figure 1. The previously known $\text{R}\dot{\text{C}}\text{D}_2$ radical^{1b,d} gives rise to the five-line pattern marked A at the low-field side of the central spectrum and is the parent of a set of carbon-13 satellites marked B. The single line marked σ is from the new radical and is the parent of two sets of carbon-13 satellites, marked $\sigma(\text{I})$ and $\sigma(\text{II})$ in the figure. These four lines have the same g tensor and decay at the same rate as σ .

Diagonalized tensors are (500, 384, 373 MHz) for the $^{13}\text{C}(\text{I})$ hyperfine, (172, 133, 132 MHz) for the

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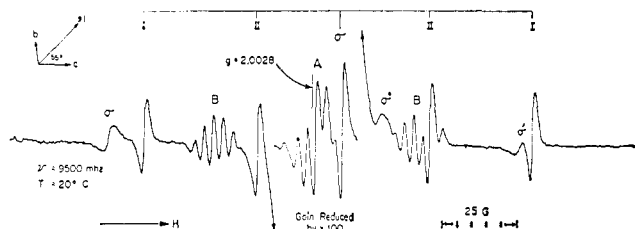
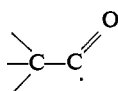


Figure 1. ESR spectrum of a malonic acid- d_4 crystal recorded 90 min after a 15-min exposure to X-rays. The magnetic field lies approximately in the C-C-C plane.

$^{13}\text{C}(\text{II})$ hyperfine, and (1.9964, 2.0019, 2.0040) for the g value. The similarity of the $^{13}\text{C}(\text{I})$ tensor to those of the radicals $\text{CO}_2^{\cdot-}$ and $\text{HC}=\text{O}^{\cdot}$ indicates that the bulk of the unpaired spin density is localized in a σ orbital on carbon. An angle of about 130° between the two bonds to this carbon can be deduced from the tensor.⁷ The low g value along one canonical axis corresponds well with the characteristic behavior of $-\text{C}=\text{O}$ σ radicals^{2,3,5c,d} suggesting some delocalization of the σ -unpaired electron onto the oxygen of a $\text{C}=\text{O}$ group.^{3a} The presence of the large second carbon-13 splitting eliminates $\cdot\text{COOH}$ as a possibility, and in fact leads to



as the most plausible framework.

Further, a pleasing internal consistency is achieved when the above tensors are compared with the malonic acid crystal structure.⁸ The major anisotropy axis of the $^{13}\text{C}(\text{I})$ tensor, the major axis of the $^{13}\text{C}(\text{II})$ tensor, and the g -minimum axis are parallel (respectively) to the C-O single bond, the C-C bond, and C=O double bond directions for one of the two carboxyl groups. The inescapable conclusion is that the trapped radical is $\text{RCH}_2\dot{\text{C}}=\text{O}$, and is produced by fission of the C-O single bond in that carboxyl group which is parallel to the C-C-C plane of malonic acid. The lines marked σ' in Figure 1 arise from the complementary σ radical whose carbon-13 and g tensors indicate⁹ that it is the species produced by C-O bond fission in the *other* carboxyl group (the one perpendicular to the C-C-C plane).⁸

The size of the $^{13}\text{C}(\text{II})$ splitting is at first very surprising, for it means that about 20% of the spin density is localized in the single bond between carbons. However, this is exactly analogous to the spin density distribution in the formyl radical ($\text{HC}=\text{O}$), whose extraordinarily large (380 MHz) proton splitting is explained by Adrian, *et al.*, on the basis of extensive mixing of a nonbonded structure into the radical ground state.^{3a} Application of the same model to $\text{RCH}_2\dot{\text{C}}=\text{O}$ predicts that the $^{13}\text{C}(\text{II})$ tensor should be about one-third the size of the $^{13}\text{C}(\text{I})$ tensor, as observed.

The most important unresolved question concerning acetyl radicals is the size of the hyperfine coupling to

(7) Using the s- and p-orbital parameters collected by J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

(8) J. A. Goedkoop and C. H. MacGillivray, *Acta Cryst.*, **10**, 125 (1957).

(9) The anisotropy of these tensors is reduced, apparently by a large amplitude motional averaging. ESR spectral changes observed upon cooling the crystal confirm the existence of a motional effect for the σ' radical and the absence of one for the σ radical.

the protons. Although Figure 1 shows no resolved deuteron splitting, the carbon-13 satellites from the σ radical in protonated crystals do reveal an excellent hyperfine pattern from two protons, as expected. The principal tensor elements for each proton (absolute signs assumed) are $(-)\text{12} \pm 1$, $(-)\text{16} \pm 1$, and $(+)\text{5} \pm 3$ MHz, with the axial direction in each case being roughly the line between the proton and C(I), the carboxyl carbon. This isotropic hyperfine coupling of $(-)\text{8} \pm 2$ MHz is smaller in absolute value than that obtained from randomly oriented acetyl radicals.¹⁰

The bright pink color which we associate with $\text{RCH}_2\dot{\text{C}}=\text{O}$ in these crystals compares nicely with the red coloration imparted to hydrocarbon glasses by acetyl radicals.^{5b} This absorption can be attributed to the $\sigma \rightarrow \pi^*$ electronic transition which is also responsible for the low g value when H is parallel to the C=O bond.^{3a} Both the color and $\text{RCH}_2\dot{\text{C}}=\text{O}$ ESR signal seem to decay at the same rate. The half-life of the latter (at 23°) is about 23 hr in malonic acid- d_4 but is only 1 hr in malonic acid- h_4 .

An additional striking isotope effect is apparent in the formation of the radicals themselves. In the limit of short X-irradiation at room temperature, fully 50% of the radicals trapped in malonic acid- d_4 are of the $\text{RCH}_2\dot{\text{C}}=\text{O}$ type whereas 10% is an upper limit in malonic acid- h_4 . It is thus possible that $\text{RCH}_2\dot{\text{C}}=\text{O}$ and RCHR (the latter is essentially absent in freshly irradiated malonic acid- d_4) are formed in a branching of paths from the same primary damage species, with the rate-determining step being C-O bond fission in the former case and H abstraction in the latter. Similarly the large isotope effect in the aging times hints that a H-abstraction process is rate determining for the decay as well. The observation that disappearance of the σ radical correlates with appearance of RCHR in the aging crystals lends support to this interpretation.

Acknowledgment. This work was supported by a grant from the National Science Foundation, GP 7428.

(10) The 14-MHz estimate of ref 5a may be passed over, for the g anisotropy, which was not considered, probably accounts for the structure in their spectrum. Tentative values of 14 and 22 MHz (ref 5c and 5d, respectively) for the isotropic component have recently been extracted from line shape studies of matrix-isolated acetyl radicals. Direct comparison of these various isotropic values is complicated by the possibility that part of the proton hyperfine may arise from hyperconjugation and thus depend upon the rotational position of the methyl group. As the C-H bond directions in $\text{RCH}_2\dot{\text{C}}=\text{O}$ are nearly orthogonal to the σ -orbital axis, we expect hyperconjugation to be at a minimum in this radical. To be compatible with the $(+)\text{14}$ -MHz matrix value,^{5c} an average hyperconjugative effect of $+22$ MHz is indicated for the rotating methyl group.

(11) National Science Foundation Predoctoral Fellow, 1964-1969.

(12) Alfred P. Sloan Fellow.

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The Low Barrier to Pyramidal Inversion in Phospholes. A Measure of Aromaticity¹

Sir:

The rate of pyramidal inversion at phosphorus in acyclic phosphines is remarkably insensitive to variations in structural parameters; expressed as ΔG_{130}^\ddagger , the

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.