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Electron Spin Resonance Studies of Photo-irradiated Aroylphosphonates

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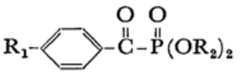
In a preceding paper,[1] we have shown that *para*-substituted benzoylphosphonates have a moderately strong n–π^* transition of the carbonyl group, involving a transition with the phosphorus d-orbitals in the 320—390 mμ, and that the n–π^* absorption maxima of these compounds are considerably affected by the powerful electron inductive abilities of *para*-substituents, such as the methoxy and chloro functions. The present investigation was undertaken to see if the ESR spectra of irradiated aroylphosphonates exhibit the effects of *para*-substituents on the aromatic ring in the magnetic parameters.

Another point of interest was the fact that there have been very few ESR studies of the organic phosphorus compounds[2] compared to those of the inorganic phosphorus compounds; especially little has yet been done with the ESR study of the UV-irradiated organophosphorus compounds.[3] In this paper, we wish to report the results obtained by the ESR measurements of UV-irradiated *para*-substituted aroylphosphonates Ia-d, which have never before been investigated by means of the ESR technique.



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Ia, $R_1=H$; $R_2=C_2H_5$
b, $R_1=Cl$; $R_2=C_2H_5$
c, $R_1=t\text{-Bu}$; $R_2=C_2H_5$
d, $R_1=CH_3O$; $R_2=C_2H_5$

On UV-irradiation at 77°K through the filter cutting off below 3200 Å, each of the aroylphosphonates employed in this work showed unsymmetrical ESR signals. These ESR spectra have a large anisotropic doublet with a 53—128 gauss separation which is thought to be due to the interaction between an unpaired electron and the phosphorus nucleus, and a g value almost close to the free spin value. All of these spectra were quite stable at 77°K; upon a subsequent elevation of the temperature the hyperfine structure did not show any significant change except for a great decrease in the intensity during the ESR measurements. However, these signals completely vanished at 156°K. The observed g and A values in Compounds Ia—d are summarized in the Table 1.

TABLE 1. ESR RESULTS FOR THE PHOSPHORUS-CONTAINING RADICALS
(The A values are in gauss.)

Compound	$\bar{g}$	$A_{\perp}$	$A_{\parallel}$
Ia	2.004	127.8	5.33
b	2.005	143.4	36.9
c	2.005	125.7	52.3
d	2.005	124.6	58.6

As is obvious from the table, the *para*-substituents on the aromatic ring participate considerably in both the isotropic and anisotropic splittings of these radicals. Although such substituent effects have been extensively studied in mono- or disubstituted benzene radical anions by Bowers *et al.*,[4] it is of particular interest that similar effects have been found in the ESR spectra of irradiated aroylphosphonates.

These observations suggest that the extent of the anisotropic hyperfine interaction of substituted aroylphosphonates vary over a considerable range, depending upon the electron-withdrawing or electron-donating properties of the substituent groups on the aromatic ring. Thus, when calculating the orbital spin densities on the phosphorus atom of the observed radicals from the isotropic and anisotropic parts of the hyperfine coupling tensors, we have obtained the values of 0.30, 0.22, 0.29, and 0.32 for Ia, Ib, Ic, and Id respectively.

These results support the idea that the powerful electron-inductive abilities of the methoxy and chloro functions on the aromatic ring undoubtedly cause a change in the spin density on the phosphorus atom. Therefore, it seems interesting to compare these results with other spectroscopic data, such as the results of infrared, UV, or dipole moment measurements. Although it is recognized that ESR study, which involves excited states,

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[1] K. Terauchi and H. Sakurai, This Bulletin, **42**, 821 (1969).

[2] F. Ramirez and S. Dershovity, *J. Am. Chem. Soc.*, **78**, 5614 (1956); E. Müller, H. Eggensperger and K. Scheffer, *Ann.*, **658**, 103 (1962); *Z. Naturforsch.*, **16b**, 764 (1961); E. A. C. Luchen, *J. Chem. Soc.*, **1963** 5123; M. W. Hanna, *J. Chem. Phys.*, **37**, 685 (1962).

[3] F. J. Adrian, E. L. Cochran and V. A. Bowers, *Advan. Chem. Ser.*, **36**, 50 (1962); U. Schmidt, K. Kabitzke, K. Markau and A. Müller, *Chem. Ber.*, **99**, 1497 (1966); K. Terauchi and H. Sakurai, This Bulletin, **41**, 1736 (1968).

[4] *Cf.* E. T. Kaiser and L. Kevan, "Radical Ions," Interscience Publishers, New York (1968), p. 211.

cannot normally be related to infrared or dipole moment data, which involve ground states only, the above findings are consistent with the view which has been suggested; in the dipole moment data, the values reported as 2.64D for Ib and 3.20D for Id,[5] it has been postulated that the powerful electron-inductive abilities of the methoxy and chloro functions induce a change in the electron density on the carbonyl carbon atom, and that the more the electron density on the carbonyl carbon increases, the more the lifetime of the conformation in which the carbonyl and phosphoryl groups are opposite increases. The UV and infrared data also provide evidence for the electron density on the C–P bond depending considerably upon the properties of those functions on the aromatic ring.[1] Therefore, it can be concluded that the findings of the ESR measurements are in comparatively good agreement with the other spectroscopic data.

On the other hand, these phosphorus hyperfine splittings prompt a question as to the preferred structure of the observed radicals. Since the n–π^* absorption maxima of benzoylphosphonates Ia–d show an average bathochromic shift of 50 mμ in comparison with those of the corresponding benzaldehydes, the π orbital on the carbonyl carbon atom might overlap with a vacant d orbital on phosphorus. Therefore, it may be reasonable to assume that the radicals which are produced photochemically from Compounds Ia—d contain such an extended conjugation that the electronic n–π^* excitation produces an unpaired electron, one which is probably partially delocalized over the P–O group, perhaps through the vacant d orbitals on phosphorus.

In connection with these observations, we will later report in detail on the results of our photochemical study of these compounds.

Experimental

The aroylphosphonates were synthesized by the reaction of triethylphosphite with acid chloride.[6] Repeated distillation under reduced pressure was used to purify all the compounds needed. The tests for purity were the same as those employed in a previous work.[1] A DMF solution of aroylphosphonate was pipetted into a Pyrex ESR tube; then the tube was degassed by conventional vacuum techniques before being sealed and irradiated at 77°K through a Toshiba UV-35 filter for 2 hr with a Toshiba 400-watt high-pressure mercury arc (Model HLS-4002A type). The ESR spectra were measured with a TDS Electronics Co. X-band ESR spectrometer (Model T-1000AX type), using a field modulation of 100 kc/sec and conventional elevating-temperature instruments.

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5) L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Cambridge, Mass. (1948).

6) K. D. Berlin and H. A. Taylor, *J. Am. Chem. Soc.*, **86**, 3862 (1964).