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The ESR Spectra of Alkyl Radicals Formed in UV-irradiated Trialkyl Phosphate Glasses

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We have recently reported the results of ESR studies of the intermediate radicals formed in UV-irradiated glasses of alkylalcohols,[1] alkanethiols,[2] and alkyl dithiophosphates.[3] As part of our continuing study of the photochemical production of intermediate radicals, we have now made a similar investigation into a series of tri-*n*-alkyl phosphates. As a result, we have found that alkyl radicals are formed rather selectively during the UV-irradiation of trialkyl phosphates at 77 K. In the present note we wish to communicate briefly the results of this investigation, since the photo-production of alkyl radicals from trialkyl phosphates has not yet been reported.

Experimental

The trialkyl phosphates employed in this work were $(CH_3O)_3PO$, $(C_2H_5O)_3PO$, $(n\text{-}C_3H_7O)_3PO$, and $(n\text{-}C_4H_9O)_3PO$. They were all commercial reagents supplied by the Tokyo Kasei Kogyo Co., and all were used without further purification. Each of the trialkyl phosphates showed a weak absorption spectrum in the region of 220—280 nm,[4] with a steep absorption edge below 220 nm. Thus, the UV light of the 253.7 nm wavelength from a low-pressure mercury lamp (Ushio Electric Co., Ltd., UL-200W) housed with a Vycor glass filter was thought to be effective. The UV-irradiation and ESR measurements were carried out at 77 K. Each sample gave a cracked-free glass upon cooling, and a few minutes' irradiation gave rise to an intense signal with a good S/N ratio. The other experimental details were similar to those of the previous report.[3]

Results and Discussion

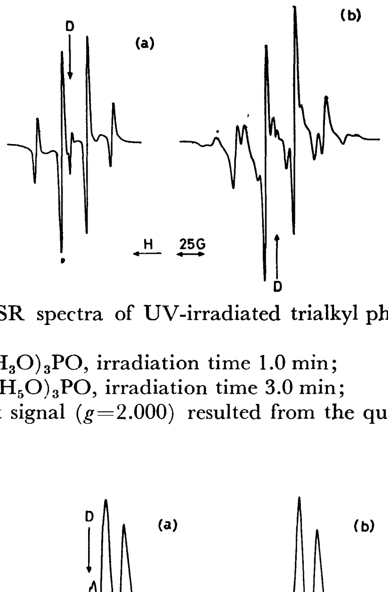

Fig. 1. ESR spectra of UV-irradiated trialkyl phosphates at 77 K.
(a) $(CH_3O)_3PO$, irradiation time 1.0 min;
(b) $(C_2H_5O)_3PO$, irradiation time 3.0 min;
D, defect signal (g=2.000) resulted from the quartz Dewar vessel.

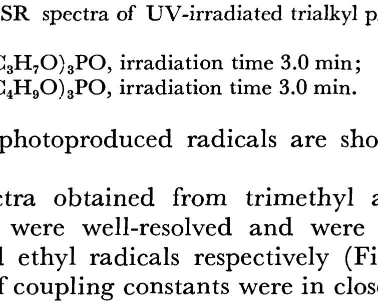

Fig. 2. ESR spectra of UV-irradiated trialkyl phosphates at 77 K.
(a) $(n\text{-}C_3H_7O)_3PO$, irradiation time 3.0 min;
(b) $(n\text{-}C_4H_9O)_3PO$, irradiation time 3.0 min.

ESR Spectra of Intermediate Radicals. Typical ESR spectra of photoproduced radicals are shown in Figs. 1 and 2.

The spectra obtained from trimethyl and triethyl phosphates were well-resolved and were assigned to methyl and ethyl radicals respectively (Fig. 1). The following hf coupling constants were in close agreement with those previously reported:[5]

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[1] K. Hatano, M. Yanagita, Y. Fujita, and T. Kwan, *Kogyo Kagaku Zasshi*, **72**, 123 (1969).

[2] M. Yanagita, Y. Fujita, and T. Kwan, *Nippon Kagaku Zasshi*, **91**, 898 (1970).

[3] M. Sato, M. Yanagita, Y. Fujita, and T. Kwan, This Bulletin, **44**, 1423 (1971).

[4] This band can tentatively be assigned to a (n-π^*) transition after M. Halman and I. Platzner (*J. Chem. Soc.*, **1965**, 1440).

[5] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

$\dot{C}H_3$ $A^H = 23.0$ Gauss

$CH_3\dot{C}H_2$ $A_\alpha^H = 21.9$ Gauss, $A_\beta^H = 27.0$ Gauss

It follows from Fig. 1, however, that ethyl radicals give hf lines with an unequal linewidth; moreover, the intensity distribution differs from the theoretical one, while the quartet hf lines of methyl radicals are equal in linewidth and their relative intensities are very close to the theoretical ratio of 1: 3: 3: 1. Such an unequal linewidth as observed in the spectrum of the ethyl radical has already been interpreted by Cochran *et al.*[6] as arising from the effect of the anisotropic hf interaction with the α-protons. It seems, therefore, probable that the motional character of the ethyl radical differs from that of the methyl radical; such a supposition is in accordance with the decay behavior of these radicals, as will be described below.

The spectra obtained from UV-irradiated tri-*n*-propyl phosphate and tri-*n*-butyl phosphate are shown in Fig. 2. The two spectra are very similar in appearance and both consist of six broad hf lines resolved only poorly, with a splitting of 22—23 Gauss. By analogy with the spectra of radicals with the general formula of $RCH_2\dot{C}H_2$, as interpreted by Ayscough and Thomson,[7] the two spectra can be assigned to $CH_3CH_2\dot{C}H_2$ and $CH_3CH_2CH_2\dot{C}H_2$ respectively. The six hf lines may be explained on the assumption that the hf coupling constant for one of the β-protons is almost twice as great as that of the other β-proton and that of the α-protons ($A_\alpha^H=22$ Gauss, $A_\beta^{H_1}=22$ Gauss, $A_\beta^{H_2}=44$ Gauss). The unequivalence of the β-protons in contrast to the ethyl radical indicates that these radicals are rather strongly constrained in the matrices, without any averaging movements of the CH_2 group. Such an interpretation is consistent with that reported by Shimada *et al.*,[8] who studied the ESR of radicals of the $CH_3\dot{C}HCH_2$-ᴧᴧ- trapped in γ-irradiated polyethylene.

In general, the signal intensities of alkyl radicals were found to increase almost linearly with an increase in the irradiation time. No signal other than alkyl radicals was detected within 15 min irradiation of triethyl phosphate, tri-*n*-propyl phosphate and tri-*n*-butyl phosphate or within 2 min irradiation of trimethyl phosphate.[9] It appears from these results that alkyl radicals are formed primarily.

Since the trialkyl phosphates employed in the present work showed UV-absorption bands in the region of 220—280 nm assignable to a (*n*-π*) transition, it is tempting to suppose that the electronic excitation of trialkyl phosphate molecules is associated with the rupture of the C–O bond rather than that of the C–H or P–O bond. It should be noted here that such an effect of UV-irradiation has a close resemblance, as far as the ESR information is concerned, to that of the γ-irradiation recently reported by several workers.[10,11]

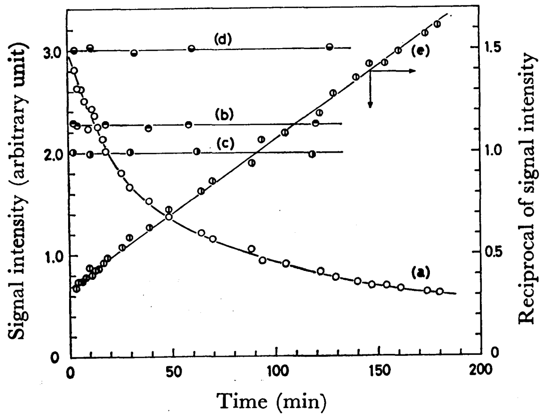
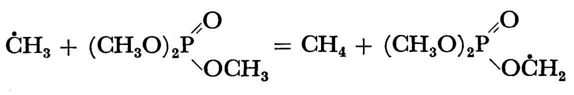


Fig. 3. Decay curves of alkyl radicals UV-produced and trapped in trialkyl phosphates at 77 K.
Signal intensity *vs.* time after UV-irradiation, (a) $\dot{C}H_3$, (b) $CH_3\dot{C}H_2$, (c) $CH_3CH_2\dot{C}H_2$, (d) $CH_3CH_2CH_2\dot{C}H_2$; Reciprocal of signal intensity *vs.* time after UV-irradiation, (e) $\dot{C}H_3$.

Stability of Alkyl Radicals. The signal intensities of the alkyl radicals trapped in the matrices were examined as a function of the time after the termination of the UV-irradiation. The results are shown in Fig. 3. It was found that ethyl, *n*-propyl, and *n*-butyl radicals did not decay at all within the period of observation, indicating that these radicals are stable in the matrices.

On the other hand, methyl radicals were found to decay, as is shown in Fig. 3, according to this equation: $-d[\dot{C}H_3]/dt=k[\dot{C}H_3]^2$. The second-order kinetics may imply that the radical recombination (1) takes place rather than the hydrogen-atom abstraction in the matrix (2).

$$\dot{C}H_3 + \dot{C}H_3 = C_2H_6 \qquad (1)$$



$$\dot{C}H_3 + (CH_3O)_2P\begin{matrix}\nearrow O \\ \searrow OCH_3\end{matrix} = CH_4 + (CH_3O)_2P\begin{matrix}\nearrow O \\ \searrow O\dot{C}H_2\end{matrix} \qquad (2)$$

However, the minor decay process due to the hydrogen-atom abstraction was proved by the appearance of a three-line spectrum (average splitting, 20 Gauss) ascribable to $(CH_3O)_2PO(O\dot{C}H_2)$ only after a considerable decay of the methyl radicals.

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[6] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **34**, 1161 (1961).

[7] P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, **58**, 1477 (1962).

[8] S. Shimada, H. Kashiwabara, and J. Sohma, *J. Polym. Sci.*, *A-2*, **8**, 1291 (1970).

[9] In the case of trimethyl phosphate, anisotropic doublet hf lines due to the formyl radical (HCO, $A^H=135$ Gauss) were observed on further irradiation.

[10] A. Begum, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc.*, *A*, **1970**, 1334.

[11] C. M. L. Kerr, K. Webster, and F. Williams, *J. Phys. Chem.*, **76**, 2848 (1972).