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THE PHOTOLYSIS OF CARBETHOXYMETHYLTRIPHENYLPHOSPHONIUM SALTS[1]

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Recently we found that P-phenyl bond is broken first in the photolysis of ylids, I and II[2], and that bond fission in III depends on the wavelength of exciting light[3]. We have now examined the photolysis mechanism of phosphonium salt IV, a conjugated acid of I. Although the photolysis of a phosphonium salt V has been reported by Griffin et al[4], mechanistic investigations have not been made. We confirmed that the photolysis of IV occurs via the intramolecular charge transfer from an anion to a cation.

$Ph_3P{=}CHCO_2C_2H_5$ (I), $Ph_3P{=}CHCOCH_3$ (II), $Ph_3P{=}CPh_2$ (III)
$(Ph_3PCH_2CO_2C_2H_5)^+X^-$ (IV), $(Ph_3PCH_2Ph)^+Cl^-$ (V)

The solutions of IV (3.5 mmol) (X= Cl, Br and I) in 10 ml acetonitrile, degassed in quartz tubes, were irradiated with high pressure mercury lamp. Products identified and determined by glc were triphenylphosphine (TPP), carbethoxymethyldiphenylphosphine (DCP), a halobenzene (PhX), diethyl succinate, ethyl phenylacetate, diphenyl, benzene, ethyl acetate and a Brønsted acid (HX). All of them are the products expected from free radical reaction, and their formation is markedly quenched by the addition of iodine.

Quantum yields of the formation of the four primary products, TPP, ethyl acetate, benzene and DCP are shown in Table 1. Table 2 shows the relative reactivities of the salts[6].

Table 1 Quantum Yields of the Formation of the Products

Low pressure mercury lamp, Potassium ferrioxalate chemical actinometer.

X	TPP	DCP	CH_3CO_2Et	PhH
Cl	0.04	0.005	0.008	0.005
Br	0.04	0.001	0.03	0.001
BF_4	0.05	0.002	0.04	0.002
I[5]	0.0004	0	0.13	0.02

Table 2 The Relative Reactivities of the Salts

X	NO_3	Cl	Br	BF_4	I
conversion* (%)	12	18	24	33	45
relative reactivity	1	1.5	2	2.8	3.7

* calculated from recovered salts

It can be recognized from Table 1 and 2 that the photochemical reactivity of IV depends strongly on the anion species. The reactivity of IV increased with the change of anion in the order, ClO_4^-, $NO_3^- < Cl^- < Br^- < BF_4^- < I^-$[7]. An easily photo-oxidizable anion was shown to be effective except for BF_4^-[8].

Next, photolyses were carried out in various solvents, and the yields of TPP and DCP were determined (Table 3). Their yields increase as the solvents become less polar, while their ratio (TPP/DCP) decreases.

Table 3 Photolysis of IV (X=Br) in various solvents.

solvent	TPP*	DCP*	TPP/DCP	relative rate
MeOH	6	0	—	0.2
EtOH	98	6	16	1.2
i-PrOH	101	6	18	1.2
MeCN	79	6	14	1.0
DMF	165	15	11	2.1
PhH-EtOH	124	20	7	1.7

* $mmol \times 10^{-3}$

In order to clarify these results, the photolyses were carried out in benzene-ethanol mixed solvents in Pyrex tubes[9]. The yields of two phosphines increased linearly with the increase of the ratio of benzene to ethanol.

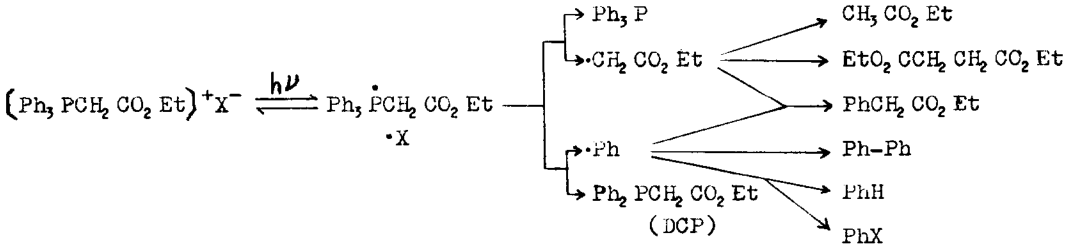
These results can be explained by considering that the degree of association will be larger in less polar solvents than in polar one[10] and, consequently, the charge transfer from an anion to a cation will occur more readily in less polar solvents. Actually IV was appreciably associated under the conditions employed[11].

All the evidences strongly support a direct charge transfer in associated ions.

Although alternative mechanism, a direct excitation of cation $Ph_3P^+CH_2CO_2Et$ or anion X^-, may be possible, such a possibility will be less important from our results.

In spite of the similarity in the first step of the photolysis mechanisms of phosphonium and anilinium salts[12], the modes of the bond fission are different between them, that is, $P\text{-}CH_2CO_2Et$ bond fission occurs in preference to P-phenyl bond fission in our photolysis, while N-phenyl bond breaks exclusively in the anilinium salt photolysis. In addition, the mode of bond fission of IV is also different from that of phosphine-ylid I previously reported by us, in which P-phenyl bond fission occurs mainly. The photolysis of sulfonium salt[13] has been reported to involve a charge transfer and a direct cation excitation yielding aryl radical and sulfinium cation radical.

Phosphoranyl radical formed by one electron transfer will decompose mainly to TPP and carbethoxymethyl radical and partly to DCP and phenyl radical. The reaction scheme will be as follows.



$$X\cdot \xrightarrow{\text{H donor}} X^- + H^+$$

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5) Because of their high reactivity to I_2 formed during the photolysis, the quantum yields of phosphines are exceedingly low. $Ph_3P + I_2 \longrightarrow Ph_3PI_2$.

6) In the following experiments, unless otherwise cited, degassed solutions of IV (1.6 mmol) in CH_3CN were irradiated with high pressure mercury lamp for 45 min.

7) Neither TPP nor DCP could be detected in the photolysis of ClO_4^- and NO_3^- salts.

8) In the photolysis of BF_4^- salt the probability of direct cation excitation yielding TPP cation radical may exist.

9) As the same results can be obtained both in Pyrex and quartz tubes, the possibility of benzene photosensitization can be ruled out.

10) The degree of association of $Ph_4P^+I^-$ has been reported to increase with the change of solvent in the order $H_2O < MeOH < CH_3CN$. A. Höniger and H. Schindlbauer, Ber. Bunsenges. Physik. Chem. **69**, 138 (1965).

11) The dissociation constant ($\alpha = \Lambda/\Lambda_0$) of IV (X=Br) in CH_3CN was 0.24.

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