Tetrahedron Letters No.58, pp. 5073-5076, 1969. Pergamon Press. Printed in Great Britain.

RADIOLYSIS OF PHOSPHOROUS ACID ESTERS

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(Received in Japan 30 October 1969; received in UK for publication 18 November 1969)

Although the γ-ray induced oxidation of aqueous phosphorous acid had been investigated by the several groups of workers,[1] the radiation chemistry of organic phosphorous acid esters has not been studied so extensively and only a few papers dealing with the γ-ray catalysis of the oxidation of triisopropyl phosphite in the presence of air[2] and the synthetic application of phosphoryl compounds, e.g., under the influence of ionizing radiation, the addition reaction of dialkyl phosphite to the double bond of chlorofluoroolefins leading to the corresponding dialkyl chlorofluoroethylphosphonates[3] have been reported. However, in all reported cases, radiation induced rearrangement of trialkyl phosphite system has never been observed. In the present paper, we wish to report the preliminary results of the γ-ray radiolysis of pure liquid trialkyl phosphites, affording alcohol, trialkyl phosphate and rearranged products.

The degassed sample of neat triethyl phosphite was irradiated by γ-ray from Co^{60} source to a total dosage of 2.10×10^{21} $ev\cdot g^{-1}$ for a period of 72.3 hours at ambient room temperature.* GLC analysis of the reaction mixture showed the presence of unreacted Ib, ethanol IIb (14.1%), diethyl phosphite IIIb (22.4%), triethyl phosphate IVb (5.9%) and diethyl ethylphosphonate Vb (1.4%). In addition to these products, the mass spectrum of the reaction mixture showed the peaks with M/e values characteristic of IIb, IIIb , IVb and higher molecular weight products.

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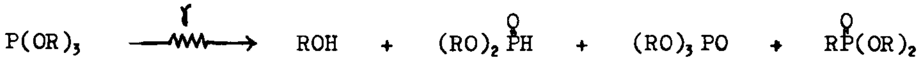
* Unless otherwise noted, all of the samples were degassed and the radiolysis was carried out at a dose rate of 4.844×10^{17} $ev\cdot g^{-1}\cdot min^{-1}$.



$$P(OR)_3 \xrightarrow{\gamma} ROH + (RO)_2\overset{O}{P}H + (RO)_3PO + R\overset{O}{P}(OR)_2$$

I II III IV V

a, $R{=}CH_3$; b, $R{=}C_2H_5$; c, $R{=}iso\text{-}C_3H_7$; d, $R{=}n\text{-}C_3H_7$

The radiolysis of trimethyl (Ia), triisopropyl (Ic) and tri-n-propyl (Id) phosphites under the identical conditions led to similar products. The observed results are summarized in the Table.

Table. Radiolysis of Trialkyl Phosphite

G Values of Reaction Mixture Composition

(at dose rate: 4.844×10^{17} $ev \cdot g^{-1} \cdot min^{-1}$)

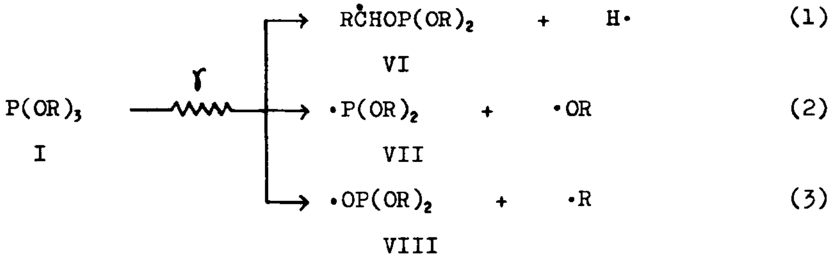
R	CH_3 (a)	C_2H_5 (b)	$i\text{-}C_3H_7$ (c)	$n\text{-}C_3H_7$ (d)
ROH (II)	14.71	24.93	10.80	8.05
$HP(O)(OR)_2$ (III)	11.83	39.57	27.06	47.94
$RP(O)(OR)_2$ (IV)	10.59	2.43	1.23	1.45
$OP(OR)_3$ (V)	9.73	15.72	1.37	1.52

As is shown in the Table, it is of particular interest that the formation of radiolytic products has the remarkably high G values and suggesting that the γ-ray induced reaction of trialkyl phosphite is much more effective than the UV-induced Arbuzov rearrangement.[4,5] In this connection, on the basis of the photolysis products composition, the production of alcohol and trialkyl phosphate by irradiating of γ-ray is significant fact and another characteristic findings are the facts that the observed G values of formation of III are greater than those of formation of IV in each of all cases. The mass spectra of reaction mixtures from the radiolysis of Ia, Ic and Id indicated the presence of a highly complex mixture of high molecular weight materials (for example, in the case of Ib, M/e values showed at 274, 290 and 302. These values correspond to the compounds of $(C_2H_5O)_2P(O){-}(O)P(OC_2H_5)_2$, $(C_2H_5O)_2(O)P{-}O{-}P(O)(OC_2H_5)_2$ and $(C_2H_5O)_2(O)PCH_2CH_2P(O)(OC_2H_5)_2$, respectively).

On the basis of this reaction mixture composition, it seems reasonable to assume at the present stage that the initial homolysis of three bonds of

C-H, C-O and P-O linkages in I occurs simultaneously by the γ-ray irradiation.

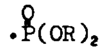
Consequently, this reaction may contain three modes of fragmentation as described below.



This interpretation can be also deduced to postulate from the results of the ESR study providing direct evidence to substantiate the existence of these intermediates (VI, VIII and VII). That is, the ESR spectra of γ-irradiated trialkyl phosphite I at 77° K have been observed the signals corresponding to all of the radical intermediates produced from the processes as mentioned above.[6]

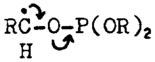
Among these processes, with respect to the nature of the fragmentation process (3), it had been postulated in previous papers of photo-induced reaction of I.[5,7] However, it might be preferable to assume that the excited molecule with excess vibrational energy of I exists as a precursor of these fragmentations from a consideration of the results obtained in a study of dose rate effects on this reaction.[8]

The formation of trialkyl phosphate IV can most probably be attributed to the attack of alkoxy radicals generated by the process (2) on I.[9] On the other hand, the large amount of dialkyl phosphite III formed in the reaction will be able to be reasonably explained using hydrogen-abstraction reaction of dialkyl phosphoryl radical (IX) from the phosphite molecule I or the excited one. The action of such an abstracting process in the reaction is thought to be consistent with the facts of the observed high G values, which suggesting a possibility of the radical chain mechanism as follows.



$$\text{VIII} \longrightarrow \underset{\text{IX}}{\cdot\overset{O}{\overset{\|}{P}}(OR)_2} \qquad (4)^{7}$$

$$\text{IX} + \text{I} \longrightarrow \text{III} + \text{VI} \qquad (5)^{5}$$



$$\underset{H}{R\dot{C}}\text{-O-P(OR)}_2 \;\; \text{VI} \longrightarrow R\ddot{C}H + \text{IX} \qquad (6)$$

It is well known that the phosphorus atom in trivalent phosphorus compound possesses high electron affinity because of the vacant d-orbitals, and have a strong tendency to form pentavalent derivative containing p -d bonding; especially the high bond energy, 151 kcal/mol,[10] of P=O linkage is considered to accelerate the reaction process (6). On the other hand, the termination reaction may be by the radical coupling of two species of IX or by the attack of the alkyl radical upon IX.

Further studies for an elucidation of the mechanism of this reaction and its synthetic application for the formation of the phosphoryl compounds are in progress.

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