801. *The Radiolysis of Tri-n-alkyl Phosphates.*

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Electron irradiation of trialkyl phosphates leads to the corresponding dialkyl hydrogen phosphate as a major product, the absolute yield decreasing in the series trimethyl to tripentyl ester. Yields of the respective mono-alkyl dihydrogen phosphates are less by ten-fold and formation of phosphoric acid is negligible. Hydrocarbon products include alkenes and alkanes, but the yields do not account quantitatively for the loss of organic fragments in acid formation. Yields of hydrogen generally increase with molecular weight of the ester. These results are interpreted in terms of reactions involving the parent molecule-ion. There is mass-spectral evidence that organic phosphate ions can undergo simple rearrangement accompanied by fragmentation of the alkyl chain; in the liquid state the latter reaction leading to formation of acid phosphate is assumed to compete with other ionic processes leading to hydrogen production.

The chemical effects of ionizing radiation on many classes of organic compounds have been explored in recent years [1] but no information was available at the outset of this investigation relating to the alkyl esters of phosphoric or other inorganic oxy-acids. In the crystalline state, the sulphate anion has considerable chemical stability to electron bombardment as shown [2] by the absence of formation either of oxygen or of sulphide, sulphite, and thiosulphate anions on prolonged irradiation of cæsium sulphate. Also, in studies on the radiation of aqueous solutions, appreciable concentrations of sulphate and phosphate anions have often been used without apparently contributing to the induced reactions.[3] Thus, the inert nature of these anions to direct irradiation seems established. It is therefore of interest to study esters of inorganic oxy-acids to determine whether the radiation-induced changes are confined to the organic groups. A preliminary note concerning the radiolysis of tributyl phosphate has been published; [4] this paper describes a more detailed study on the homologous series of tri-n-alkyl phosphates extending from trimethyl to tripentyl esters. Since tributyl phosphate is utilized in the processing of nuclear fuels by solvent extraction, the radiation decomposition incurred by this solvent has also been widely studied in multicomponent systems which approximate to those obtained under technical conditions.[5-7] Concerning the radiolysis of pure tributyl phosphate, the formation of monobutyl and dibutyl acid phosphates reported earlier [4] has been confirmed by other workers,[6-8] and Burr [8] has suggested a tentative free-radical mechanism for the decomposition. However, some recent information [9,10] on the mass-spectral pattern of

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[1] Collinson and Swallow, *Chem. Rev.*, 1956, **56**, 471.
[2] Williams, unpublished work; cf. Hennig, Lees, and Matheson, *J. Chem. Phys.*, 1953, **21**, 664.
[3] Johnson, Scholes, and Weiss, *J.*, 1953, 3091.
[4] Williams, Wilkinson, and Rigg, *Nature*, 1957, **179**, 540.
[5] Williams and Wilkinson, A.E.R.E. Report C/R 2179, 1957.
[6] Burger and McClanahan, *Ind. Eng. Chem.*, 1958, **50**, 153.
[7] Wagner, Kinderman, and Towle, *Ind. Eng. Chem.*, 1959, **51**, 45.
[8] Burr, *Radiation Res.*, 1958, **8**, 214.
[9] McLafferty, *Analyt. Chem.*, 1956, **28**, 306.
[10] Quayle, "Advances in Mass Spectrometry," Pergamon Press, London, 1959, p. 365.

organic phosphates indicates a correlation with the radiolysis results which suggests that the liquid-phase decomposition may also involve the fragmentation and rearrangement of the primary ion before neutralization; this interpretation is discussed below.

EXPERIMENTAL

Materials.—Trimethyl, triethyl, and tributyl phosphate, supplied by L. Light and Co. Ltd., were purified by several distillations at low pressure over anhydrous sodium carbonate, a Widmer column being used. Tripropyl and tripentyl phosphate were prepared by the action of the corresponding alcohol on phosphorus oxychloride;[11] increased yields were obtained if the reaction was carried out in the presence of a solution of pyridine in benzene to remove the hydrogen chloride as formed. The products were then fractionated and the trialkyl ester distilled as before. The purified samples had the following b. p.s: $(MeO)_3PO$, 73°/10 mm.; $(EtO)_3PO$, 90°/10 mm.; $(PrO)_3PO$, 121°/10 mm.; $(BuO)_3PO$, 148°/10 mm.; $(C_5H_{11}O)_3PO$, 162°/5 mm.

Dialkyl hydrogen phosphates were prepared by hydrolysis of the corresponding trialkyl phosphates with concentrated sodium hydroxide solution; under these conditions only a very small amount of the monoalkyl ester was formed and the dialkyl ester could be isolated as the sodium salt. A mixture of monoalkyl and dialkyl acid phosphates was obtained by hydrolysis with sulphuric acid of the appropriate trialkyl ester. These acidic esters were used for the preparation of derivatives and the standardisation of analytical procedures as described below.

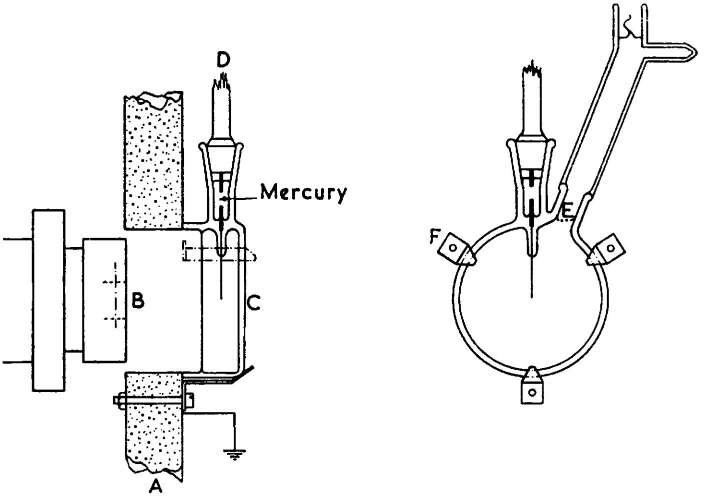

FIG. 1. *Irradiation cell and mounting.*

A, Graphite screen. B, van de Graaff beam. C, Cell. D, Current lead. E, Liquid level. F, Clamps.

Irradiation Procedure.—All irradiations were carried out with a horizontal beam of 1·25 Mv electrons emanating from a Van de Graaff accelerator. Two types of cell were generally used. In order to follow the kinetics of gas evolution during irradiation it was convenient to use a cell incorporating a bellows manometer which had been previously developed in this laboratory.[12] A simpler type of cell (Fig. 1) was used for runs involving the analyses of gaseous contents and liquid phase after the completion of the irradiation dose. The liquid was usually introduced directly into the cell and thoroughly de-gassed by vacuum pumping until the pressure in the associated gas space was about 10^{-4} mm., as measured with the liquid frozen at $-196°$; the cell was then sealed from the vacuum line and mounted for irradiation as shown in Fig. 1. All cells were made from " Pyrex " glass with windows of 0·5 mm. uniform thickness through which the electron beam penetrated into the liquid; the cell thickness was generally 8 mm. or more and therefore greater than the total range (*ca.* 4 mm.) of the electrons in these liquids.

Cell Dosimetry.—The incident energy of the electrons was given directly by readings on the generating voltmeter of the Van de Graaff machine. These values were proved to be reliable

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[11] Kosolapoff, " Organo-phosphorus Compounds," J. Wiley Co., New York, 1950, p. 226.
[12] Amphlett and Williams, *J. Sci. Instr.*, 1956, **33**, 64.

by two methods. First, by calorimetric measurement of total beam energy, and secondly, by recording the magnet current settings required to deflect the electrons of any given voltage from their original vertical path in the accelerator to a horizontal beam and comparing the data against a calibration of corresponding values obtained with photoelectrons of known energy.

Measurement of total charge input was given by a current integrator which recorded 12 counts/min. for any pre-set current in the range 0·01—10 μA. Total energy input was calculated as the product of electron energy and charge input, after corrections had been applied for the back-scattering effect and the energy loss sustained by the beam in passing through the machine and cell windows.[13] For the cells used in this investigation the total window thickness was 122 mg./cm.^{2} and the net energy loss for an incident beam of 1·25 Mv electrons amounts to 0·24 Mv. These data being used, an absolute calibration [14] of the ferrous sulphate actinometer in cells of identical construction gave a *G* value (100 ev yield) for oxidation of ferrous ion of 15·8, in excellent agreement with other absolute determinations of this quantity.[15, 16] Further confirmation of the accuracy of this dosimetry at higher dose rates was provided by measurements of the yield of hydrogen gas from benzene,[17] which agreed with accepted values.

Gas Analysis.—After irradiation, the cell was sealed to a conventional vacuum line, and the gaseous contents were separated into fractions by low-temperature distillation. The volumes of the two fractions volatile at −196° and −100°, respectively, were determined in each case by collection in a calibrated Toepler pump.[17] Gases volatile above −100° were similarly collected and then examined by infrared analysis; these fractions isolated from the irradiation of tripropyl and tributyl phosphate showed absorption bands at 6 μ, 10·3 μ, and 11·0 μ characteristic of olefin unsaturation. Detailed analyses of the −196° and −100° fractions were carried out by the microtechnique due to Blacet and Leighton [18] and independently by mass spectrometry. Oxygen or oxides of carbon were absent from these gas mixtures.

Characterisation and Analysis of Liquid-phase Products.—The development of irradiation-induced acidity was general in the phosphate esters examined. The estimation of acidity was carried out by electrometric titration against a standard solution of 0·0994N-sodium hydroxide, a direct-reading Pye pH meter being used. The volume of ester per run was generally about 10 ml. and this was diluted (with water) to a total volume of 50 ml. before titration; for the higher members of the series, the esters were immiscible with water and these were dissolved in 50% ethyl alcohol–water. Some typical titration curves for trimethyl phosphate are shown in Fig. 2; the rate of change of pH per constant increment of added alkali is plotted in Fig. 3 as a function of the total alkali added and shows two distinct peaks which correspond to two end-points for the titration. A similar qualitative behaviour was observed for the other irradiated esters. The titre to the first end-point in Fig. 3 is considerably greater than the subsequent difference between the two end-points; this observation suggests that the acidic behaviour is not due to the presence of a single dibasic acid but that two acids are formed.

In order to characterize the acids formed from tributyl phosphate, they were extracted with sodium hydroxide solution which was then washed with carbon tetrachloride to remove any trace of tributyl phosphate; the aqueous solution was acidified whereupon oily drops formed which could be readily extracted with carbon tetrachloride. The infrared spectrum of the dried extract ($CaSO_4$) was identical with that of dibutyl hydrogen phosphate. Isolation of the sodium salts of the acids as described above from each irradiated ester enabled the corresponding *S*-benzylisothiouronium derivatives to be prepared. After several recrystallisations from dilute alcohol the m. p. of the isolated derivative accorded with that obtained

TABLE 1.

Dialkyl hydrogen phosphate	Dimethyl	Diethyl	Dipropyl	Dibutyl	Dipentyl
M. p. (authentic derivative)	189°	186°	188°	138°	148°
M. p. (isolated derivative)	188	187	188	139	148

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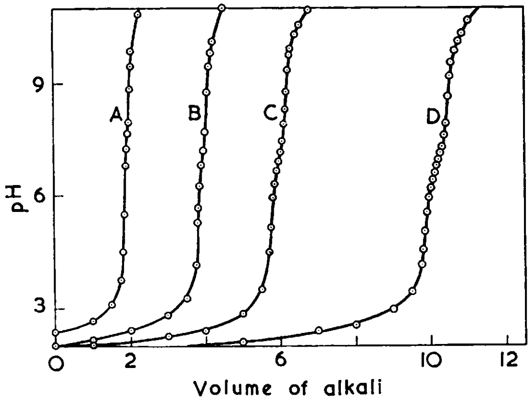
[13] Wilkinson and Williams, *J. Chim. phys.*, 1955, **52**, 600.
[14] Wild and Williams, unpublished work.
[15] Donaldson and Miller, *J. Chim. phys.*, 1955, **52**, 578.
[16] Schuler and Allen, *J. Chem. Phys.*, 1956, **24**, 56.
[17] Bates, Burns, Morris, Wilkinson, and Williams, A.E.R.E. Report C/R 2121, 1957.
[18] Blacet and Leighton, *Ind. Eng. Chem. Anal.*, 1931, **3**, 266.

by a similar preparation from the corresponding dialkyl hydrogen phosphate, as shown in Table 1.

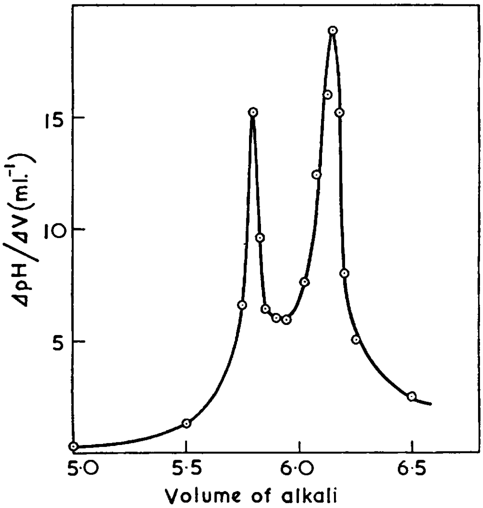
As the dialkyl hydrogen phosphate was easily identifiable among the irradiation products, it seemed reasonable to suppose that it was the acid present in highest yield. The acid phosphate products were further characterised by paper chromatography, pyridine–butanol–water being used as solvent.[19] After being dried, the paper was sprayed with ferric chloride solution in butanol, followed by a solution of sulphosalicylic acid. Two spots were observed having the same R_F values as known samples of the corresponding monoalkyl and dialkyl phosphate. From the relative magnitude of the spots it was evident that the latter was formed in much higher yield by radiolysis.

FIG. 2. *Titration curves for irradiated trimethyl phosphate.*



Alkali, 0·0994N-sodium hydroxide; 10-ml. samples. Irradiation doses: A, 3·8; B, 7·55; C, 11·4; D, 19·0 × 10^{20} ev/ml.

FIG. 3. *Differential titration curve for irradiated trimethyl phosphate.*



Alkali, 0·099N-sodium hydroxide; 10-ml. [samples; dose, 11·4 × 10^{20} ev/ml.

Since the esters are identified as a mixture of monalkyl and dialkyl phosphate, their behaviour on titration can now be evaluated. The first neutralization point, corresponding to the formation of the acid salt of the monoalkyl dihydrogen phosphate, is obscured in the mixture by the much greater concentration of dialkyl hydrogen phosphate; the first end-point therefore corresponds to the combined titre required to form the acid salt of the monoalkyl dihydrogen phosphate and to neutralize the dialkyl hydrogen phosphate. The difference between the two end-points represents the additional titre to complete the neutralization of the monoalkyl dihydrogen phosphate and thus provides a determination of the amount of the last present in the mixture: the amount of dialkyl hydrogen phosphate can then be obtained by

TABLE 2.

Acid phosphate	pK_{a1}	pK_{a2}	N_1	N_2	pH$_1$ (calc.)	pH$_2$ (calc.)	pH$_1$ (obs.)	pH$_2$ (obs.)
Dimethyl	1·29		0·01		6·6		6·0	
Diethyl	1·39		0·01		6·7		5·9	
Dipropyl	1·59		0·01		6·8		6·6	
Dibutyl	1·72		0·01		6·9		6·8	
Monomethyl		6·31		0·001		8·7		8·8
Monoethyl		6·62		0·001		8·8		9·4
Monopropyl		6·67		0·001		8·8		9·5
Monobutyl		6·84		0·001		8·9		10·0

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[19] Wade and Morgan, *Nature*, 1953, **171**, 529.

subtraction. It is of interest to compare the pH_1 and pH_2 values observed experimentally at the two end-points with the values which would be obtained if the titration of the two acids were carried out separately at similar concentrations; the latter are evaluated from the appropriate dissociation constants [20] by means of the following relation [21]

$$pH_1 = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_{a1} + \tfrac{1}{2}\log_{10} N_1, \qquad pH_2 = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_{a2} + \tfrac{1}{2}\log_{10} N_2,$$

where K_{a1} and K_{a2} refer to the dissociation constant of the dialkyl hydrogen phosphate and the second dissociation constant of the monoalkyl dihydrogen phosphate, respectively, K_w is the ionic product of water, and N_1 and N_2 are the normalities of the two acids present. The experimental and calculated values are recorded in Table 2. The results obtained for the irradiation of tripropyl and tributyl phosphate may be affected by the presence of ethyl alcohol in the titration vessel.

An alternative estimation of alkyl acid phosphates involved the preliminary isolation of the acids from the irradiated trialkyl phosphate, as indicated above for the case of tributyl phosphate. Thereafter the acid esters were quantitatively hydrolysed by refluxing them with hydriodic acid (*d* 1·94; 66% by weight; 30 ml.) for 30 min., and the resulting inorganic phosphate was estimated spectrophotometrically.[5] The latter method was calibrated with twice-recrystallized potassium dihydrogen phosphate and gave excellent results for determinations based on the conversion of known amounts of tributyl phosphate and dibutyl hydrogen phosphate by the above procedure.

No inorganic phosphate was detected among the radiolysis products of trialkyl phosphates, even after prolonged irradiation. It is estimated that the yield must be less than 1·0% of the total acid alkyl phosphates formed.

The organic phosphate fraction left after the extraction of the acids from a sample of irradiated tributyl phosphate was shaken with dilute sulphuric acid for several days but this treatment failed to yield any more acidic phosphate esters as would be the case if pyrophosphates had been formed by irradiation.

RESULTS AND DISCUSSION

The concentrations of dialkyl and monoalkyl phosphate produced from the corresponding trialkyl ester as a function of irradiation dose are shown in Figs. 4 and 5, respectively. A linear relationship is generally valid, although at low doses the yields of monoalkyl dihydrogen phosphate are more uncertain owing to the low concentration in the irradiated solvent. The absolute yields of these products, defined as a *G* value in units of molecules per 100 ev, are therefore constant over the dose range examined; the values are recorded in Table 3. The determination of total acid phosphate by hydrolysis is in good agreement with the titration results for irradiated tributyl phosphate. Absolute yields of gas are also listed and these were similarly calculated from linear plots of macroscopic yield against dose. Extraction by the technique described of the gas fraction corresponding to C_3 and C_4 products was probably incomplete and the yields of these components in Table 3 represent lower limits.

TABLE 3. *G-Values for radiolysis products.*

		Products						
Ester	Total acid phosphates	Dialkyl phosphate	Monoalkyl phosphate	H_2	CH_4	C_2H_6	C_2H_4	$C_3^* + C_4$
Trimethyl ...		2·83	0·20	0·47	0·85	0·11	0·12	—
Triethyl		2·01	0·14	0·77	0·12	0·37	0·33	—
Tripropyl ...		2·00	0·15	0·75	0·05	0·24	0·34	0·35
Tributyl	1·76 ± 0·08	1·52	0·12	1·11	0·05	0·12	0·12	0·45
Tripentyl ...		1·47						

* Mainly unsaturated.

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[20] Kumler and Eiler, *J. Amer. Chem. Soc.*, 1943, **65**, 2355.

[21] Kolthoff and Laitinen, "pH and Electro-titrations," J. Wiley Co., New York, 1944, p. 13.

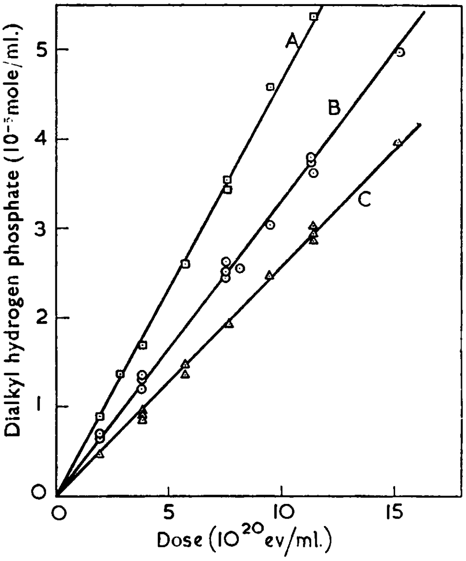
A comparison of our results obtained for tributyl phosphate with data obtained by other workers [6-8] is shown in Table 4.

TABLE 4. *G-Values for radiolysis of tributyl phosphate.*

	Radiation source	Dialkyl phosphate	Monoalkyl phosphate	H_2	CH_4	C_2	$C_3 + C_4$
This work	1·25 Mev electrons	1·52	0·12	1·11	0·05	0·24	0·45
Burger and McClanahan [6]	^{60}Co gamma	1·7—1·8	0·3				
Wagner, Kinderman, and Towle [7]	1 Mev electrons	2·25	0·39	1·59	0·07	0·13	0·75
		1·37	0·03				
Burr [8]	1·66 Mev electrons	2·44	0·14	1·73	0·07	0·18	0·65

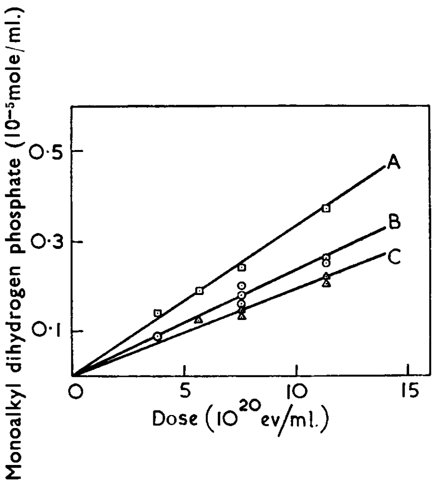
Since the ratios of our yields for dibutyl hydrogen phosphate and hydrogen to the corresponding values obtained by Burr [8] are 0·62 and 0·64, respectively, it seems likely that the discrepancy in absolute yield is due to the different dosimetric procedures employed. Burr [8] used the ceric sulphate dosimeter to establish that only 0·74 of the incident energy recorded by the charge input method was absorbed in the cell contents. On the other hand, we found that the Fricke (ferrous sulphate) dosimeter gave excellent agreement with the charge input method at low electron currents (about 0·01 μA) after suitable corrections were made for energy loss in the window materials and for back-scattering. Some of the *G*-values recorded by Wagner, Kinderman, and Towle,[7] which are again based on ceric dosimetry, are also higher than our data but their results show considerable variation depending upon the total dose received by the sample; we did not observe this type of behaviour. The results for dibutyl hydrogen phosphate obtained by Burger and McClanahan [6] are in closer agreement with our values. Since the measurement of energy absorption by means of the Fricke dosimeter in a gamma source, as used by these workers,[6] is generally much more reliable than the estimation of energy inputs from a fast electron beam, we conclude that their results have greater quantitative significance.

FIG. 4. *Dialkyl hydrogen phosphate yield.*



A, trimethyl; B, triethyl; C, tributyl phosphate.

FIG. 5. *Monoalkyl dihydrogen phosphate yield.*



A, trimethyl; B, triethyl; C, tributyl phosphate.

In addition to the gaseous products and acid phosphates, material of higher molecular weight is also produced in the radiolysis.[8] This " polymeric " product was not investigated in our work, except insofar as it was shown not to contain pyrophosphates.

For chemical reactions initiated by ionizing radiation, it is logical to begin any discussion of mechanism by considering the fate of the parent ion. Much of the present literature arbitrarily assumes that the parent ion is neutralized in the liquid phase in a time (*ca.* 10^{-12} sec.) which does not allow that ion to react or re-arrange, leading to the formation of an excited molecule as a precursor of free radicals. However the radiation chemistry of liquid hydrocarbons has recently been discussed [22] in terms of ion-molecule and ion-dissociation processes; if these reactions are exothermic, they should precede neutralization, and it has been shown that this thermochemical criterion accounts qualitatively for many features regarding the variation of reactivity with molecular structure. For organic phosphates, similar thermochemical calculations cannot be carried out at present owing to lack of data but it is still possible to use mass-spectral information to determine the facility of fragmentation or rearrangement of the parent ion in the gas phase. An uncritical extrapolation of this evidence to the prediction of elementary processes in the radiation chemistry of liquids is generally unjustified because of the larger time interval (10^{-5} sec.) available in the highly attenuated gas phase for the unimolecular decomposition of the parent ion. Nevertheless useful correlations have been made.[23,24]

$(RO)_2P(OH){:}OH^{\cdot+}$ (I) $RO{\cdot}P(OH)_3^{\cdot+}$ (II) $P(OH)_4^{\cdot+}$ (III)

The mass spectra of triethyl [9] and tributyl phosphate [10] show certain general similarities which are taken to represent the general decomposition pattern for trialkyl phosphates; since these spectra were obtained independently, it is unlikely that the consistent rearrangement peaks which were observed arose from artefacts due to thermal or catalytic decomposition of the esters. The most important results can be summarized as follows: (*a*) the intensity of the parent ion is extremely low; (*b*) the largest peaks are due to the following rearranged ions (I), (II), and (III), where R represents the appropriate attached alkyl group; (*c*) where the alkyl groups are butyl, fragmentation by step-wise loss of carbon atoms is of minor importance compared with (*b*); (*d*) loss of a hydrogen atom, or of a hydrogen molecule, from the parent ion does not occur to any significant extent; and (*e*) the abundance of hydrocarbon ions is small. This information suggests that the ions referred to in (*b*) have considerable stability which could be due [25] to resonance of the positive charge between the attached hydroxyl groups; these ions are essentially oxonium ions as would be produced by proton addition to the singly-attached oxygen atom in the phosphate structure. Rearrangement ions involving the partial localisation of the positive charge on an oxygen atom are familiar in the mass spectra of aldehydes, ethers, carboxylic acids, and esters.[26] Also in thermal chemistry, the marked electronegativity of the oxygen atom in many compounds favours the attachment of a strong electrophilic species, such as a proton, to form oxonium ions.

The simplest interpretation of the mass spectral results quoted above is that the ion (I) is formed by an initial decomposition accompanied by re-arrangement, and that the other abundant ions (II) and (III) result from further step-wise fragmentation of ions (I) still possessing excess of energy; this process is aided by the increased resonance stability in the order (III) > (II) > (I). Thus for triethyl phosphate the abundances are found to be (I) > (III) > (II), whereas for tributyl phosphate the order is (III) > (II) > (I). By comparison with the gas phase, it is reasonable to infer that only

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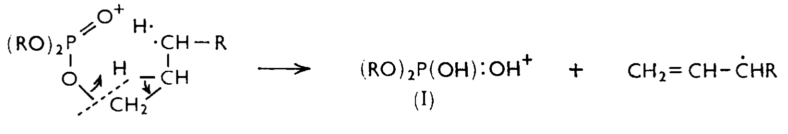
[22] Williams, *Trans. Faraday Soc.*, 1961, **57**, 755.
[23] McDonnell and Newton, *J. Amer. Chem. Soc.*, 1954, **76**, 4651.
[24] Burr, *J. Phys. Chem.*, 1957, **61**, 1483.
[25] McLafferty, " Advances in Mass Spectrometry," Pergamon Press, London, 1959, p. 383.
[26] McLafferty, *Analyt. Chem.*, 1959, **31**, 82.

primary decomposition processes are important for the parent ion in the liquid, since neutralization occurs more rapidly, and also the increased collision rate favours both ion-molecule reactions and collisional deactivation of excited species. Hence we shall consider the formation of ion (I) to represent a primary rearrangement process also

$$[(RO)_2P(:O)\cdot O\cdot C_nH_{2n+1}]^+ \longrightarrow (I) + \cdot C_nH_{2n-1}\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

applicable to the liquid phase before neutralization. This re-arrangement of the parent ion occurs together with the loss of a hydrocarbon fragment as a radical, and it is consistent that hydrocarbon ions are not abundant in the mass spectrum; the process is represented in eqn. (1). Where *n* is 3 and 4, the corresponding radical species $C_3H_5\cdot$ and $C_4H_7\cdot$ can be stabilized by allylic resonance, *e.g.*, $C_3H_5\cdot$ could be $\cdot CH_2\text{-}CH{=}CH_2$, so that in these instances both products of reaction (1) display mesomerism; hence the endothermicity, if any, of the reaction will be reduced, thus assisting more rapid rearrangement. The actual mechanism of reaction (1) is likely to involve concerted movements of atoms and electrons helped by the formation of a cyclic transition state, as has been indicated for several other rearrangement reactions of positive ions in the gas phase.[26] In the representation given in eqn. (2), the odd electron is initially assumed to reside on the doubly bonded oxygen atom which thus carries a positive charge; the transfer of a hydrogen atom from the hydrocarbon chain to this oxygen atom leaves the free valency in the α-position with respect to the double bond formed concurrently by an olefin elimination.



········(2)

The formation of the ions (II) and (III) in the gas phase would follow by further olefin eliminations involving the remaining alkyl groups. The particular transition state illustrated in (2) cannot, of course, apply to trimethyl or triethyl phosphate but other cyclic transition states are probably valid for the same overall process (1) in these esters; the corresponding radicals CH and C_2H_3 would be expected to have greater reactivity than the allylic radicals.

According to Samuel and Magee's theory [27] for liquid water, the ejected electron in the ionization remains associated with the coulombic field of the cognate positive ion; this same model should have greater validity for an organic compound with a large number of vibrational degrees of freedom since this would result in a greater rate of energy loss for the electron. (We exclude consideration of effects due to electron capture by added solutes.) A thermalized electron represents a nucleophilic entity of high energy because of its highly concentrated negative charge; hence the interaction of the electron with the positive ion (I) could well involve the removal of a proton with the formation of a dialkyl hydrogen phosphate molecule and a hydrogen atom according to eqn. (3). Similar

$$(RO)_2P(OH)\overset{+}{:}OH + e^- \longrightarrow (RO)_2P(:O)\cdot OH + H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

reactions to eqn. (3) involving the elimination of a proton from carbonium ions have suggested by one of us [22] to account for the neutralization step in the radiolysis of branched alkanes. The processes of rearrangement (1) and neutralization (3) can be combined in the overall eqn. (4). Because of the short time (10^{-12} to 10^{-13} sec.) attending neutralization, the diffusion distance of the radical $\cdot C_nH_{2n-1}$ in the interval between rearrangement and neutralization would be insignificant so that both $\cdot C_nH_{2n-1}$ and H are formed in close proximity on this model, thus favouring combination. Hence the products of equation

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[27] Samuel and Magee, *J. Chem. Phys.*, 1953, **21**, 1080.

(4) may be amended to dialkyl hydrogen phosphate and C_nH_{2n}. A so-called " molecular " process for the formation of dialkyl hydrogen phosphate and olefin from tributyl phosphate was originally suggested [4] to account for our results.

$$(RO)_2P(:O)\cdot O\cdot C_nH_{2n+1} \rightsquigarrow (RO)_2P(:O)\cdot OH + \cdot C_nH_{2n-1} + H \quad . \quad . \quad . \quad . \quad . \quad (4)$$

An alternative mode of neutralization to that described above may apply in cases where the parent ion undergoes reaction or rearrangement to produce a more stable positive ion and an allylic radical; in this instance the electron could be captured by the radical to form an allylic carbanion. The resultant ion-pair could then have an appreciable lifetime before termination by proton transfer from the positive to the negative ion; such a scheme when applied to tripropyl and tributyl phosphate leads to the same products as the foregoing treatment. Intermediate ion-pair formation has also been advanced to account for the radiation-induced polymerization of β-pinene and α-methylstyrene.[28]

The observed small yield of monoalkyl dihydrogen phosphate must also devolve from a primary decomposition of the trialkyl phosphate and not from the secondary decomposition of the dialkyl hydrogen phosphate since the absolute yield of monoalkyl dihydrogen phosphate does not increase as the concentration of dialkyl hydrogen phosphate increases (Fig. 5). It is feasible, from the mass-spectral results, that a small fraction of rearranged ions (I) may retain sufficient energy in the liquid to undergo a further elimination of a C_nH_{2n} fragment with the formation of ion (II); its subsequent neutralization would be analogous to that for ion (I) in eqn. (3). The virtual absence of phosphoric acid in the radiolysis products is evidence that the additional rearrangement of ion (II) into (III) is not a significant process in the liquid. These results confirm our earlier proposition that only the elementary decomposition processes of ions are of major importance in condensed systems.

This mechanism accounts satisfactorily for the formation of the acid alkyl phosphates, but it is clear from Table 3 that the yields of gaseous carbon products account for much less than the corresponding loss of alkyl groups. For tributyl and tripropyl phosphate the measured yields of C_4 and C_3 olefin, respectively, may be low and could account for part of this inequality. Other reactions can be postulated to account for the non-olefinic hydrocarbons. Thus the high yield of methane from trimethyl phosphate could be due to two successive hydrogen abstractions instituted by a methylene radical, leaving behind two organic phosphate radicals which would then probably dimerize. The path of hydrogen formation remains to be clarified. Table 3 shows that the $G(H_2)$ yield tends to increase with the length of the alkyl chain. In unbranched alkanes dimerisation or cross-linking is important and is, of course, accompanied by hydrogen production. This process may be aided [22] by a primary ion-molecule reaction which involves hydrogen-atom or hydride-ion transfer from a neutral molecule to the parent ion, followed by the loss of a hydrogen molecule from the latter; subsequent combination of the ion and radical gives a dimeric ion (reactions 5—7). There is agreement [22,29,30] that olefin formation from linear alkanes is likely to involve the loss of molecular hydrogen directly from the parent ion. We surmise that hydrogen formation in the trialkyl phosphates most probably involves reactions analogous to those of hydrocarbons. If this is correct, then the rearrangement

$$RH^+ + RH \longrightarrow RH_2 + R^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$RH_2 \longrightarrow R\cdot + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$R^+ + R\cdot \longrightarrow R_2^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

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[28] Bates and Williams, *Nature*, 1960, **187**, 665; Bates, Best, and Williams, *ibid.*, 1960, **188**, 469.
[29] Dewhurst, *J. Phys. Chem.*, 1958, **62**, 15.
[30] Wagner, *J. Phys. Chem.*, 1960, **64**, 231.

(1) must also be competitive with the other reactions of parent ions resulting in hydrogen molecules. As a result, one would expect no correspondence between hydrogen and acid phosphate formation, and that the former should increase and the latter decrease as the alkyl groups increase in size. This conclusion is generally borne out by Table 3.

The results plotted in Fig. 6 show the variation of *G*-value for yield of acid phosphate with the electron fraction of tributyl phosphate in a kerosene–hydrocarbon diluent. It is evident that at low concentrations of tributyl phosphate, the yield of acid phosphate is enhanced above the value predictable on the basis of the fraction of energy absorbed in the phosphate ester. Similar non-linear relationships for hydrogen production in mixtures of olefins or aromatic compounds with cyclohexane have been recorded.[31] A possible explanation is that of positive-ion transfer from the hydrocarbon diluent to the tributyl phosphate, thus sensitizing the increased decomposition of the latter by the ion reactions discussed.

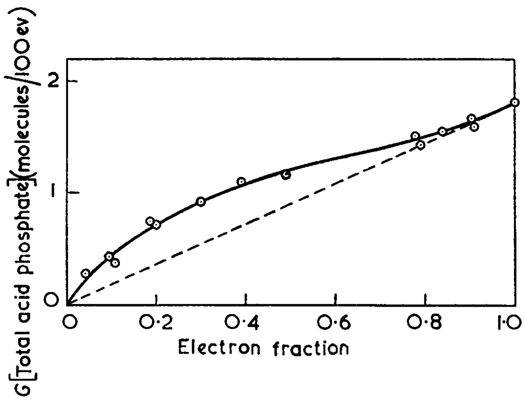

FIG. 6. *Absolute yield of acid phosphate as a function of fraction of tributyl phosphate in mixture.*

In conclusion, we comment on the possibility of a free-radical mechanism as indicated by Burr.[8] It is based on an analogy with the mass-spectral behaviour of butanol where the loss of a hydrogen atom from the parent ion is of primary significance; this does not, however, appear to be the case for the spectra of triethyl and tributyl phosphate. Further, the radical mechanism predicts a parallelism between the yields of hydrogen and dialkyl hydrogen phosphate, which is obviated by our results.

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[31] Manion and Burton, *J. Phys. Chem.*, 1952, **56**, 560.