The salient feature of Figure 1 is the reasonably close correspondence in the rates obtained by the two different techniques (with and without solid additive) in the vicinity of a dose rate of 10^{14} ev g^{-1} sec^{-1} where the results can be compared. It is also seen that the straight line offers a reasonable fit to the result[2b] obtained at the lowest dose rate. These findings immediately call into question the validity of the various explanations which have been proposed[2] for the *intrinsic* role of solid additives in radiation-induced ionic polymerization, and the general concept should be reconsidered in its entirety. The present work bears out the suggestion[3a] that the rates of radiation-induced ionic polymerization of isobutylene are frequently limited by the residual water content, in keeping with extensive studies on other monomers.[3b]

The highest $G(-m)$ values obtained in individual runs during the present work at the lower dose rate of 3500 rads/hr are 2.4×10^7 (0°) and 1.5×10^7 (−78°). These results correspond to the highest kinetic chain lengths recorded in studies of radiation-induced ionic polymerization at this dose rate under any conditions,[3b] and it is probable that these values are extremely close to the limiting yields which would apply in the case of negligible impurity termination. The comparative and theoretical aspects of this work will be taken up in a subsequent publication since this communication is mainly intended to convey the significant practical findings.

Acknowledgment. We wish to express our appreciation to Dr. D. J. Metz and Mr. C. L. Johnson for helpful discussions on the subject of experimental techniques.

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A Mechanism Involving Pseudo-Rotation for the Hydrolysis of Dimethylphosphoacetoin[1]

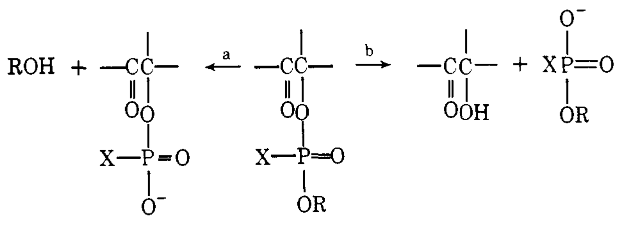
Sir:

It has been shown recently that the apparently anomalous hydrolytic behavior of some five-membered cyclic phosphonates and phosphinates can be adequately accounted for[2] if it is assumed that (1) the hydrolyses proceed *via* a pentacoordinate species which has the geometry of a trigonal bipyramid,[2,3] (2) positional exchange by means of a pseudo-rotation[4] can occur between the axial and the equatorial positions, (3) the occupying of an axial position by an alkyl group is energetically unfavorable,[2,5] and (4) groups enter at or leave from the axial positions only.[2]

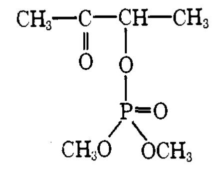
In the initial intermediate formed during hydrolysis of a cyclic ester such as methyl ethylene phosphate, one axial position is occupied by the incoming water molecule,[2] the other by one of the ring oxygens;[2,3,6] thus the phosphoryl oxygen is by default forced to take up an equatorial position. However, if a similar trigonal bipyramid is reached *starting from an acyclic compound*, there is not necessarily this restriction, and three extreme cases can be distinguished: (1) the phosphoryl oxygen can initially take up either an axial *or* an equatorial position, (2) it can take up an axial position only, (3) it can take up an equatorial position only. If one of these possibilities applies to the first formed intermediate, by the principle of microscopic reversibility it therefore may apply to the final intermediate from which one of the groups departs; the geometry of any other species formed by pseudo-rotation[4] of the first formed intermediate is not specified. Case 2 can already be excluded for acid-catalyzed hydrolysis.[2]

We report here our initial results on the application of these proposals to the mechanism of participation by a neighboring carbonyl group in the *base-catalyzed* hydrolysis of fully esterified phosphates and phosphonates.

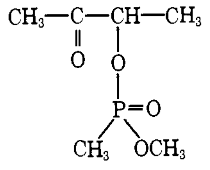
The presence of an α-carbonyl group has been shown by several workers to greatly enhance the base-catalyzed rate of hydrolysis of a variety of phosphate[7] and phosphonate[8] esters, and several mechanisms[7-9] have been advanced to account both for this acceleration and for the observed products. When the ester involved is that of a good leaving group (*e.g.*, I, R = *p*-nitrophenyl) the reaction typically[7a,b,8] goes by path a, but with a simple alkyl ester (*e.g.*, I, R = methyl) decomposition may occur *via* path b, a reaction first described[7c] in the case of dimethylphosphoacetoin (II).



I



II



III

At pH 8.6 and 25° about 3% of the reaction of II goes by path a, as shown by the production of methanol (2–3% estimated by vpc) and by quantitative paper chromatography[10] (3–4% of monomethylphosphoacetoin). The ratio of rates (b:a) for the two pathways

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[1] This research was partially supported by the National Institutes of Health under Grant GM 13335.

[2] E. A. Dennis and F. H. Westheimer, *J. Am. Chem. Soc.*, **88**, 3431, 3432 (1966); R. Kluger, F. Kerst, D. G. Lee, E. A. Dennis, and F. H. Westheimer, *ibid.*, **89**, 3918 (1967); G. Aksnes and K. Bergesen, *Acta Chem. Scand.*, **20**, 2508 (1966); see also D. G. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 2762 (1967).

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[4] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

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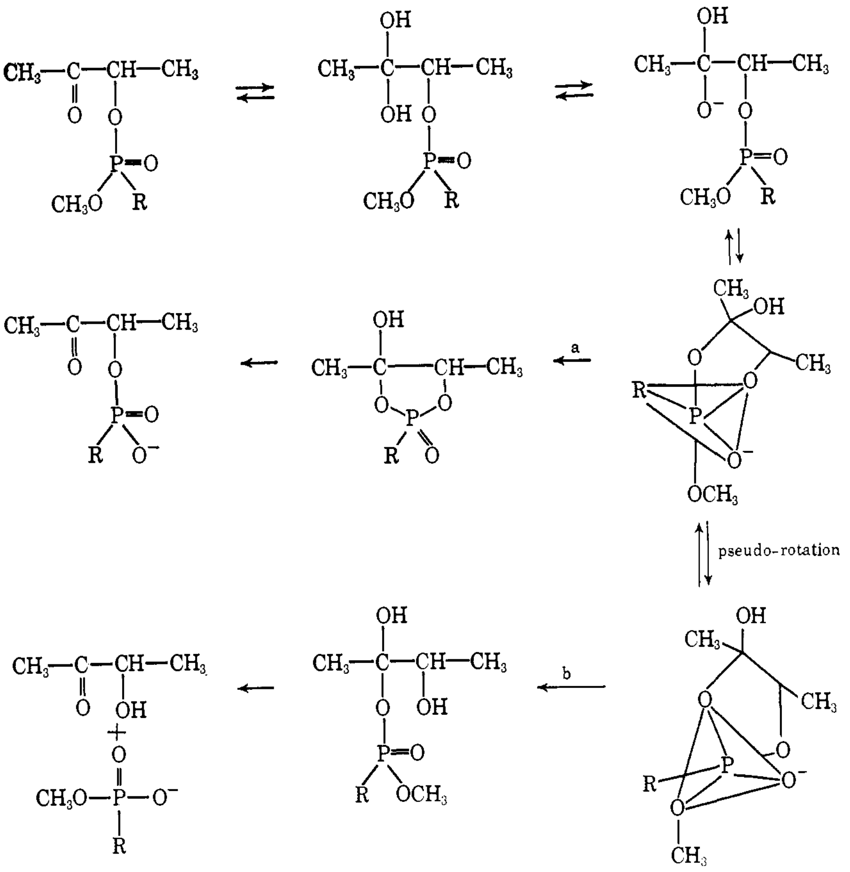
[7] (a) A. A. P. G. Archer and J. Harley-Mason, *Proc. Chem. Soc.*, 285 (1958); (b) D. Cohen, Ph.D. Thesis, Cambridge University, 1959; (c) F. Ramirez, B. Hansen, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 4588 (1962).

[8] C. N. Lieske, E. G. Miller, Jr., J. J. Zeger, and G. M. Steinberg, *ibid.*, **88**, 188 (1966).

[9] D. A. Usher, Ph.D. Thesis, Cambridge University, 1963, pp 13–18; J. R. Cox, Jr., and O. B. Ramsay, *Chem. Rev.*, **64**, 348 (1964); M. J. Frearson, Ph.D. Thesis, Cambridge University, 1966; H. Witzel, A. Botta, and K. Dimroth, *Chem. Ber.*, **98**, 1465 (1965).

[10] D. A. Usher, *J. Chromatog.*, **12**, 262 (1963).



is therefore about 30. We now report that substitution of a methyl group for a methoxyl in II (to give the phosphonate III) causes a remarkable change in the product distribution. The reaction is still first order in hydroxide ion and in ester in the pH range 8.5–9.4 (0.07 *M* potassium perchlorate; 25°), but analysis of the products[10,11] shows that reaction by path a now accounts for about 95% of the total. This is not caused by a large increase in the rate of path a[12] but by a greater than 200-fold *decrease* in that of path b. The ratio of the relative rates (b:a) for the phosphate to that for the phosphonate is about 600. We suggest here a possible mechanism[14] for this reaction which does not appear to be inconsistent with any experimental facts at present available and which, if correct, would imply that for these compounds case 3 (see above) is more nearly correct than case 1 or 2.

If case 1 applied, then pseudo-rotation of the first formed intermediate about R as a pivot[2] would allow rapid reaction by path b even when $R = CH_3$. Case 2 can also be excluded since it would predict no reaction by path a for either compound.[15] Thus, if this mechanism is correct,[14] case 3 appears to apply, and path b is suppressed for the phosphonate since a pseudo-rotation about any pivot other than the methyl group would place the latter in an axial position.[2,5] An interesting prediction from this mechanism is that base-catalyzed migration of an intact dialkylphosphoryl group to a neighboring hydroxyl may occur; this has been excluded only for a monoalkylphosphoryl group[16] or the unsubstituted phosphoryl group[17] itself. We are currently extending this work to include some phosphinate esters and other neighboring groups.

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(11) The acetoin methylphosphonate was identified by nmr and infrared spectroscopy and by elemental analysis of the barium salt. *Anal.* Calcd for $C_5H_{10}Ba_{0.5}O_4P$: C, 25.69; H, 4.31; P, 13.25. Found: C, 25.46; H, 4.31; P, 13.20. The phosphonate III was identified by nmr and infrared spectroscopy. *Anal.* Calcd for $C_6H_{13}O_4P$: C, 40.00; H, 7.27; P, 17.19. Found: C, 40.13; H, 7.40; P, 16.98.

(12) The rate of reaction by path a for the phosphonate (27 activity^{-1} sec^{-1}) is about three times that for the phosphate. Similar small rate increases can be found[13] in other phosphonate–phosphate comparisons. However, phosphonate III and phosphate II^{7c} hydrolyze many orders of magnitude faster than dimethyl methylphosphonate and trimethyl phosphate, respectively.

(13) J. R. Cox, Jr., and O. B. Ramsay, *Chem. Rev.*, **64**, 317 (1964); R. F. Hudson and L. Keay, *J. Chem. Soc.*, 2463 (1956); but see A. Eberhard, Ph.D. Thesis, Harvard University, 1964, pp 6–8.

(14) For some of the other experimental facts that must be taken into account see ref 7–9. For simplicity, only one of the possible pseudo-rotations is shown here.

(15) It could be claimed that path a need not involve an intermediate and may instead take place by a direct displacement. However, the known[2] base-catalysed hydrolysis of phenyl ethylene phosphate to give ethylene phosphate also argues against case 2.

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A New Conformation for an Isolated Six-Membered Ring System[1]

Sir:

The reaction of monophenylphosphonitrilic fluoride trimer, $P_3N_3F_5(C_6H_5)$, with benzene in the presence of

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