first double bond is the most exothermic of any yet recorded.[14]

Acknowledgment. The author is greatly indebted to R. Hoffmann for many stimulating discussions and to National Science Foundation and Public Health Service Research Grants GP-7479 and 10495-01 (National Cancer Institute) for financial support.

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On the Radiation-Induced Polymerization of Isobutylene under Anhydrous Conditions and the Effect of Solid Additives[1]

Sir:

There have been persistent claims from several laboratories that the rates of the radiation-induced ionic polymerization of isobutylene can be markedly increased in the presence of certain solid additives.[2] Most of the detailed quantitative work on this subject refers to the use of silica, alumina, and zinc oxide powders with high surface areas.[2] It has been argued that the mechanism of the reaction is essentially heterogeneous, and that the role of the solid is to provide electron traps[2a] or some other ill-defined means of positive-ion stabilization,[2b] thereby acting to extend the ionic chain. In addition, a recent correlation of this enhancement effect with the semiconductor properties of solids has been proposed.[2d]

Because it has been established[3] that low concentrations of water exert a strong retarding effect on the rates of many radiation-induced ionic polymerizations, our interest was inevitably drawn to the above subject[2] by the lingering suspicion[3a] that the reason for the observed effects could be trivial in origin, deriving only from the action of the solid as an efficient dehydrating agent for the liquid monomer. In an attempt to resolve this question unambiguously,[4] isobutylene samples of extreme dryness have been prepared in the present study without bringing the monomer into contact with a dispersed solid adsorbent at any stage, either before or during irradiation. This avoids the possibility of any adventitious carryover of finely divided solid into the irradiation cell.

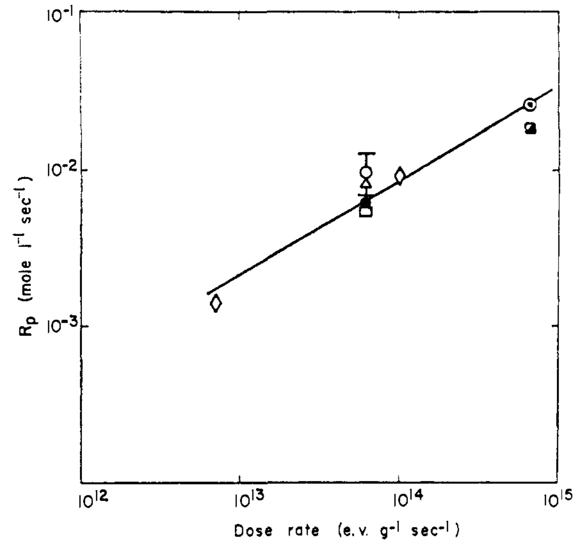

Figure 1. Dose rate dependence of rate of polymerization of isobutylene: O, mean of nine separate runs at 0° (the horizontal bars represent the average deviation from the mean); ●, mean of two runs at 0° from batch 9; ⊙, mean of two runs at 0° from batch 9; ◪, mean of four runs at −78°; □, mean of four runs at −78°; △, mean of three runs at 27°; ◇, taken from ref 2b at −78 and 0° (see text). The straight line is drawn between the data points marked by ● and ⊙.

Full details of experimental technique will be described elsewhere.[5]

Isobutylene (Phillips Research Grade, 99.59 mole %) was distilled *in vacuo* over refluxing sodium–potassium alloy[6] at 300° in a greaseless apparatus constructed of Pyrex glass and metal valves. The dry monomer was then distilled from a reservoir held at −78° through a breakseal into an all-glass manifold with attached sample tubes which had been previously baked out for up to 150 hr at 500° and 10^{-7} torr by means of an ultrahigh-vacuum pumping installation.

A comparison of our results with those of Dalton[2b] appears in Figure 1. It should be noted that each of the two data points taken from the latter work represents the maximum in the R_p–zinc oxide composition curve at the corresponding dose rate. Moreover, these particular rates are considerably higher than any of the other results, at similar dose rates, in the literature.[2] On the other hand, the points shown from the present work without additive refer to the mean of several runs, and the straight line denotes the dependence of the mean R_p on dose rate I for a set of samples prepared from the same batch of monomer and irradiated at 0°, for which the exponent $\Delta \log R_p/\Delta \log I$ is 0.6. An exponent close to 0.5 is expected[7] under conditions of negligible impurity termination. As observed for the reaction in the presence of zinc oxide,[2b] this study also suggests that the variation of R_p with temperature at constant dose rate is relatively minor between 27 and −78°.

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(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2968. This is AEC Document No. ORO-2968-26.

(2) (a) A review of the extensive earlier work in this field is given by S. H. Pinner, "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., Pergamon Press Ltd., Oxford, 1963, p 611; (b) F. L. Dalton, *Polymer*, **6**, 1 (1965); J. A. Bartlett and F. L. Dalton, *ibid.*, 7, 107 (1966); (c) C. David, F. Provoost, and G. Verduyn, *J. Polymer Sci.*, **C1**, 1135 (1963); (d) L. P. Mezhirova, A. D. Abkin, A. I. Popova, L. P. Tolstoukhova, and A. P. Sheinker, Abstract of Paper B21 presented at XXth International Congress of Pure and Applied Chemistry, Moscow, 1965, reproduced in AEC Document No. TID-22360; (e) for the alleged effect of additives on the polymerization rate of other monomers, see, *e.g.*, A. Charlesby and J. Morris, *Proc. Roy. Soc.* (London), **A281**, 392 (1964).

(3) (a) T. H. Bates, J. V. F. Best, and F. Williams, *Nature*, **188**, 469 (1960); *Trans. Faraday Soc.*, **58**, 192 (1962); (b) for a review of more recent work with detailed references, see F. Williams in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., John Wiley and Sons, Inc., New York, N. Y., in press.

(4) *Cf.* E. V. Kristal'nyi and S. S. Medvedev, *Vysokomol. Soedin.*, **7**, 1373, 1377 (1965). These authors concur with the suggestion[3a] that the solid additives serve to remove traces of water. They present evidence showing that after pretreatment with zinc oxide, isobutylene undergoes radiation-induced polymerization at −78° at the same rate as in the presence of zinc oxide. The highest polymerization rates and $G(-m)$ values obtained by these authors are about a factor of 10 lower than the results obtained in the present work under the same conditions of temperature (−78°) and dose rate (*ca.* 3.6 × 10^4 rads/hr).

(5) R. B. Taylor, M.S. Thesis, University of Tennessee.

(6) We use 78% potassium alloy corresponding to the eutectic composition. This pure liquid alloy is supplied by the MSA Research Corp., Callery, Pa. 16024.

(7) F. Williams, Ka. Hayashi, K. Ueno, Ko. Hayashi, and S. Okamura, *Trans. Faraday Soc.*, **63**, 1501 (1967).

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.

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

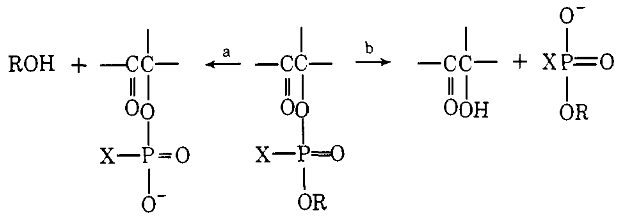
Sir:

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]

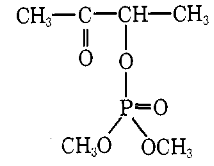
In the initial intermediate formed during hydrolysis of a cyclic ester such as methyl ethylene phosphate, one axial position is occupied by the incoming water molecule,[2] the other by one of the ring oxygens;[2,3,6] thus the phosphoryl oxygen is by default forced to take up an equatorial position. However, 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.

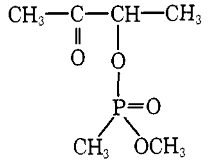
The presence of an α-carbonyl group has been shown by several workers to greatly enhance the base-catalyzed rate of hydrolysis of a variety of phosphate[7] and phosphonate[8] esters, and several mechanisms[7-9] have been advanced to account both for this acceleration and for the observed products. When 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.

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