Anal. Calcd. for $C_{15}H_{13}BrFNO_2$: C, 53.3; H, 3.85; N, 4.1. Found: C, 53.6; H, 3.7; N, 3.7.

1-Phenyl-1-chloro-2-bromo-2-fluoroethane (V, Hal = Br) was obtained from the above carbinol by reaction with thionyl chloride in 71% yield. The compound, b.p. 96–97° (3 mm.), could not be prepared analytically pure and retained a faint pink color even after repeated distillation.

Anal. Calcd. for C_8H_7BrClF: C, 40.4; H, 2.95. Found: C, 41.5; H, 3.15.

Dehalogenation of this chloride with zinc dust gave a 60% yield of β-fluorostyrene (VI).

Polymerization of β-Fluorostyrene.—To a solution of β-fluorostyrene (5 g.) in petroleum ether (25 ml.), cooled to 0°, was added dropwise a solution of $SnCl_4$ (2 ml.) in the same solvent (10 ml.). Each drop produced a strong exothermic reaction and formation of a precipitate. The mixture was left overnight, then the polymer was centrifuged and washed with petroleum ether. For purification it was dissolved in benzene and precipitated by addition of methanol. The white, granular material softened at 240–260°.

No polymerization occurred when β-fluorostyrene—in bulk or in benzene solution—was treated with benzoyl peroxide or *t*-butyl hydroperoxide. Likewise, β-fluorostyrene was not attacked by ethanolic potassium hydroxide at temperatures up to 60°.

***p*,β-Difluorostyrene.**—*p*,α-Difluoro-α-chloroacetophenone[21] was reduced by lithium aluminum hydride to 1-(*p*-fluorophenyl)-2-chloro-2-fluoroethanol, b.p. 68–70° (2 mm.), in 74% yield.

Anal. Calcd. for $C_8H_7ClF_2O$: C, 49.9; H, 3.6. Found: C, 50.2; H, 3.9.

This carbinol was converted by thionyl chloride in 70% yield into 1-(*p*-fluorophenyl)-1,2-dichloro-2-fluoroethane, b.p. 55–56° (2 mm.), $n^{20}D$ 1.5102.

Anal. Calcd. for $C_8H_6Cl_2F_2$: C, 45.5; H, 2.8. Found: C, 46.0; H, 3.2.

Dehalogenation with zinc dust gave a 55% yield of *p*,β-difluorostyrene, b.p. 33° (2 mm.), $n^{19}D$ 1.5040, $d^{19.5}$ 1.0345, *MR*D 40.06.

Anal. Calcd. for $C_8H_6F_2$: C, 68.6; H, 4.3. Found: C, 68.9; H, 4.3.

The polymer of *p*,β-difluorostyrene was prepared as described above.

Conversion of α,α-Dichloroacetophenone into β-Chlorostyrene.—Reduction of the above ketone with lithium aluminum hydride gave 85% of 1-phenyl-2,2-dichloroethanol, b.p. 170° (16 mm.) or 117° (4 mm.), m.p. 56°.[22] This carbinol was converted by thionyl chloride into 1-phenyl-1,2,2-trichloroethane, b.p. 130° (17 mm.).[23] Dehalogenation with zinc gave β-chlorostyrene in 60% yield, b.p. 89–92° (15 mm.), $n^{13}D$ 1.5781.

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[21] F. Bergmann, A. Kalmus and E. Breuer, This Journal, **79**, 4178 (1957).

[22] M. O. Forster and W. B. Saville, *J. Chem. Soc.*, **121**, 2595 (1922).

[23] H. Biltz, *Ann.*, **296**, 219 (1897).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY]

The Reaction of Olefins with Oxygen and Phosphorus[1]

BY CHEVES WALLING, FRANK R. STACEY, SAUNDERS E. JAMISON AND EARL S. HUYSER

RECEIVED MARCH 24, 1958

The reaction of white phosphorus and oxygen with olefins, first described by Willstätter, has been found to be a radical chain process, accelerated by azobisisobutyronitrile and inhibited by hydroquinone. The slower oxidation of benzene solutions of phosphorus alone shows similar properties. The initial products have an approximate composition olefin·P_2O_4 and are proposed as having a polymeric anhydride structure containing one P per unit as a phosphonic anhydride, and one P as a phosphite anhydride. When these initial products are benzene-soluble further oxidation occurs to olefin·P_2O_5.

In 1681, Robert Boyle reported that the glow accompanying the oxidation of phosphorus in air was not observed with solutions of phosphorus in turpentine,[2] an observation which may be considered the first on the effect of olefins on the oxidation of phosphorus. The similar effect of ethylene on the slow combustion of solid white phosphorus was studied by Graham, in 1829,[3] and the subject continued to excite interest well into this century, providing one of the important bases for the theory of chain reactions developed by Semenoff.[4] In 1914, Willstätter and Sonnenfeld[5] published a short paper on the products obtained on exposure of benzene or cyclohexane solutions of phosphorus and olefins (chiefly cyclohexene) to oxygen, but the only subsequent work[6] we know of is the report by Montingnie[7] of the formation of an organophosphorus derivative from phosphorus and oxygen in the presence of an unsaturated steroid.

Willstätter[5] reported that phosphorus–cyclohexene mixtures in benzene rather rapidly took up oxygen on shaking to yield initially a product $C_6H_{10}P_2O_3$. Further oxygen absorption was "slower," giving finally a product $C_6H_{10}P_2O_4$. This "phosphorate" was a white or pale yellow, benzene-insoluble, hygroscopic solid which reacts vigorously with water, dissolving with evolution of heat. The only product identification involved treating the phosphorate with 40% HNO_3. Under these conditions the phosphorus was further oxidized and approximately half was liberated as phosphoric acid, precipitable by magnesium ion. The lead salt of an organophosphorus acid was precipitated from the filtrate with a lead analysis corresponding to $C_6H_9PO_3Pb$. These observations were rationalized by the formula scheme shown, although an intermediate β-hydroxyphosphonic acid was also postulated.

This and the following paper[8] describe some fur-

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[1] Work supported by the Chemical Corps, U. S. Army.

[2] R. Boyle, "New Experiments and Observations Made upon the Icy Noctiluca," London, 1681/2.

[3] T. Graham, *Quart. J. Science*, 83 (1829).

[4] For further bibliography and discussion see K. C. Bailey, "The Retardation of Chemical Reactions," Edward Arnold & Co., London, 1937, Chapters 3 and 6.

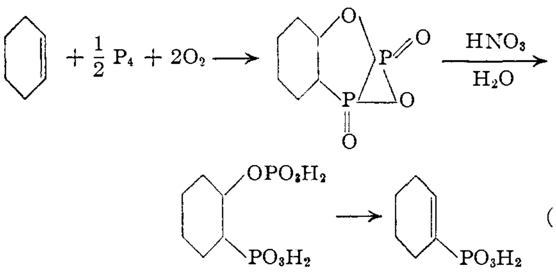
[5] R. Willstätter and E. Sonnenfeld, *Ber.*, **47**, 2801 (1914).

[6] Willstätter explains his rather incomplete results as follows: "Durch den Eintritt meines Mitarbeiters in den Militardienst bin ich gezwungen worden, die Arbeit abzubrechen, . . ." Apparently the investigation was never resumed.

[7] Montingnie, *Bull. soc. chim.*, **49**, 73 (1931).

[8] C. Walling, F. R. Stacey, S. E. Jamison and E. S. Huyser, This Journal, **80**, 4546 (1958).

ther observations on this neglected, but striking and facile reaction, which, while incomplete, we present in the hope of drawing it to the attention of other investigators.



(1)

Characteristics of the Cyclohexene–Phosphorus–Oxygen Reaction.—When a solution of white phosphorus in benzene containing ordinary cyclohexene is vigorously stirred in an atmosphere of oxygen at 40–50°, a rather rapid uptake of oxygen begins, often after a short induction period, and the creamy white solid "phosphorate" soon begins to precipitate. Most of our experiments were run using slightly over one mole of cyclohexene per two gram atoms of phosphorus, and typical oxygen uptake curves are shown in Fig. 1. Oxygen uptake stops at two atoms per gram atom of phosphorus, and the "phosphorate" with the approximate composition $C_6H_{10}P_2O_4$ is obtained in essentially quantitative yield. Although the oxidation is mildly exothermic, so that a stirred reaction mixture maintains itself a few degrees above the surrounding bath, the reaction is easily controllable and it is interesting that benzene solutions of phosphorus, which tend to fume (and may even ignite) in air, lose these properties when they contain a small amount of olefin. The only difficulties we have had with the reaction are when too vigorous stirring splashes solution onto the vessel walls. Under these circumstances the drops may dry and the residual phosphorus burn off. For preparative purposes we also find that the reaction can be run conveniently by simply drawing a slow stream of dry air through a phosphorus–olefin–benzene solution.

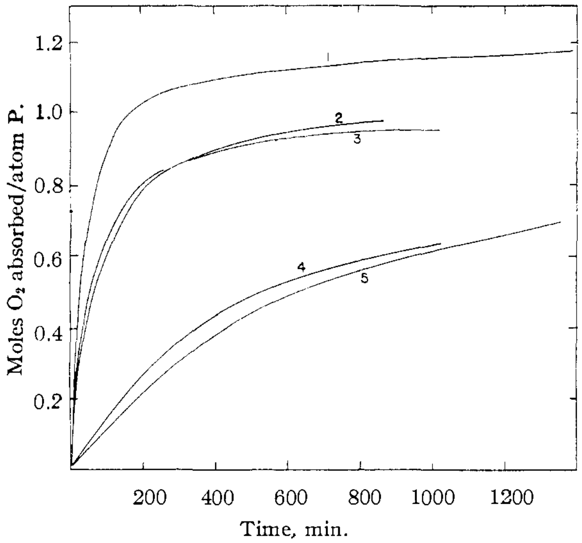


Fig. 1.—Reaction of phosphorus and olefins with oxygen: 1, 1-dodecene; 2, cyclohexene; 3, styrene; 4, *cis*-dichloroethylene; 5, phosphorus alone.

Although our results to this point parallel Willstätter's observations, we have been unable to confirm his conclusion of a stepwise oxidation. Our oxygen uptake curves show no sharp break at the point corresponding to a P:O ratio of 2:3 (Fig.1). Analysis of aliquots of reaction mixture for unreacted phosphorus by bromine titration after removal of olefin shows that an atom of phosphorus is consumed per molecule of O_2 absorbed from the beginning of the reaction, Fig. 2. Further, systems which have absorbed 1.5 moles of O_2 per mole of cyclohexene still contain approximately 0.5 mole of olefin.

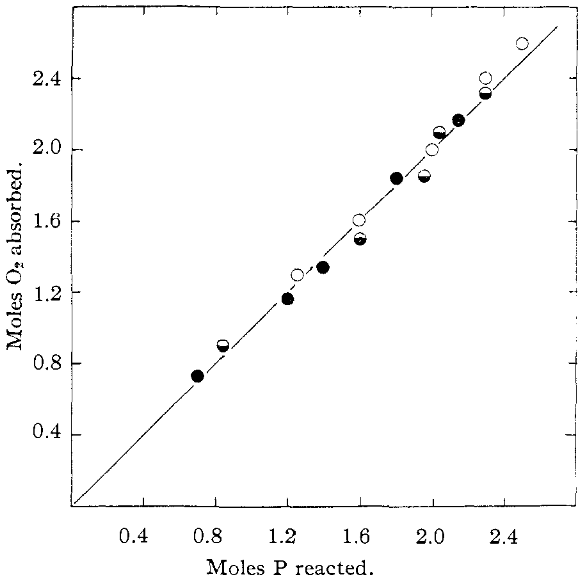


Fig. 2.—Comparison of oxygen and phosphorus consumption in reaction with cyclohexene. Different symbols indicate different reactions.

Several observations convince us that the oxidation is a radical chain process, probably involving very long chains. While old, peroxide-containing samples of cyclohexene begin to absorb oxygen at once, freshly distilled, peroxide-free samples show significant induction periods which in turn disappear upon the addition of azobisisobutyronitrile as a radical source, Fig. 3. If we assume that all chains at 80–100 min. are still being initiated by the azonitrile and that the temperature has risen to 50°, the kinetic chain length can be calculated as at least 7000. This need for some sort of initiator is shown even more strikingly with some of the other olefins discussed below. Hydroquinone is also an efficient inhibitor for the oxidation as shown by the second curve of Fig. 3.

At this point we are unable to propose any detailed formulation of the chain involved. However, some observations on the hydrolysis of the phosphorate from isobutylene described in the following paper suggest that it involves attack of a radical with the partial structure P–O· upon the olefin, followed by attack of a hydrocarbon radical on a phosphorus atom.

Other Olefins.—We find that the reaction of phosphorus with olefins and oxygen is quite general, in most cases yielding the same sort of phosphorate as is obtained with cyclohexene. Our results are summarized in Table I and typical O_2 absorption curves appear in Fig. 1. Liquid olefins were allowed to react under the same conditions as cyclohexene. Ethylene was allowed to react by circulating a mixture of olefin and oxygen through a benzene solution of phosphorus. For obvious reasons the oxygen concentration in the gas mixture was kept below the explosive limit, the oxygen being replenished as it was consumed. Isobutylene reacted in the same manner as ethylene, but no analytical data were obtained on the product. Dichloroethylene and the gaseous olefins showed no reaction in the absence of azobisisobutyronitrile, and all of the experiments listed in Table I were carried out in its presence.

TABLE I

REACTION OF OLEFINS WITH PHOSPHORUS AND OXYGEN

Benzene solution, 40°, in presence of initiator

Olefin	O:P ratio[a]	Yield, %[b]		Analyses, %[c] C	H	P	O
Ethylene	..	..	Found	15.7	2.7	40.1	41.5
			Calcd.	15.6	2.6	40.2	41.4
Cyclohexene	1.96	99	Found	30.6	4.55	29.4	35.4
			Calcd.	34.6	4.84	29.8	30.8
1-Octene	2.55	103	Found	35.1	6.80	25.5	32.6
			Calcd.[d]	37.8	6.35	24.4	31.4
Styrene	2.04	109	Found	41.8	3.50	29.9	24.8
			Calcd.	42.0	3.80	26.8	27.4
1-Dodecene	2.25	99	Found	44.4	7.56	21.1	26.9
			Calcd.[d]	46.4	7.79	20.0	25.8
1-Hexadecene	2.35	93	Found	52.3	8.90	16.8	22.0
			Calcd.[d]	52.4	8.80	16.9	21.9
cis-Dichloroethylene	1.51	71	Found	16.2	1.23	37.5	4.33[f]
			Calcd.[e]	15.8	1.33	40.8	0[f]
3-Hexyne	2.05	..	Found	29.0	4.44	31.3	35.3
			Calcd.	34.6	4.84	29.8	30.8

[a] Ratio of gram atoms O absorbed to gram atoms P initially present (olefin present in slight excess). [b] On basis of calculated formula and phosphorus used. [c] Calculated values for olefin·P_2O_4 unless otherwise noted; found O by difference. [d] For olefin·P_2O_5. [e] For $C_2H_2P_2O_4$. [f] % Cl.

In the case of 1-octene and olefins of higher molecular weight there was a rapid uptake of two atoms of oxygen, followed by additional absorption, Fig. 1, and the products approximate the composition $C_nH_{2n}P_2O_5$. With dodecene and hexadecene the reaction products remain in solution, and it seems probable that oxidation stops at the olefin·P_2O_4 stage with lower olefins because of the extreme insolubility of the product. Similarly, in an experiment with isoprene, only two atoms of oxygen were taken up (corresponding to the reaction of only one double bond) before reaction ceased, and only two atoms were absorbed by 3-hexyne. In the case of dichloroethylene the product (which was not investigated further) contains little chlorine, and the reaction appears to take a more complicated course.

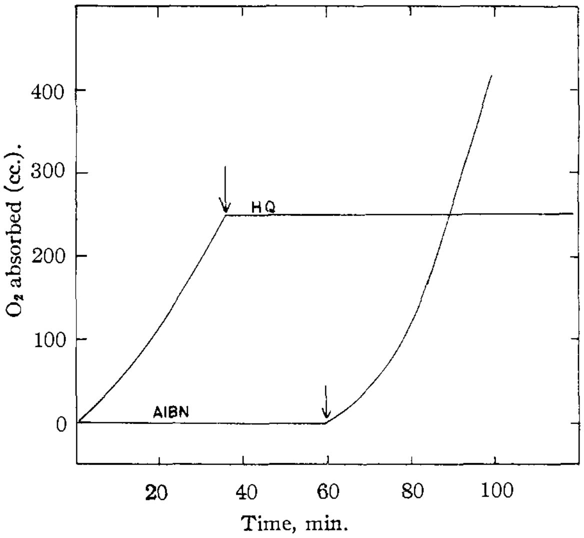
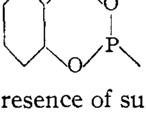


Fig. 3.—Hydroquinone inhibition and azobisisobutyronitrile initiation in reaction of cyclohexene with phosphorus and oxygen. Hydroquinone (HQ) and azobisisobutyronitrile (AIBN) added at times indicated by arrows.

For comparison with these olefin reactions we also have carried out some experiments on the autoxidation of benzene solutions of phosphorus alone. Oxygen uptake is again accelerated by azobisisobutyronitrile, consistent with the presumed radical chain nature of the gas-phase reaction,[4] but as is shown in Fig. 1, more slowly than in the presence of most olefins. Specifically, a solution containing 0.9 g. of phosphorus and 0.02 g. initiator absorbed oxygen initially at a rate of 0.68 cc./min. compared with 8.7 cc./min. in the presence of cyclohexene.

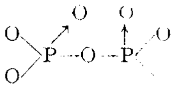
Properties of "Phosphorates."—The reaction products from olefins, phosphorus and oxygen which we have prepared are in general white to light yellow apparently crystalline solids, markedly hygroscopic but apparently indefinitely stable in dry air. They dissolve with reaction in water and alcohols and are soluble in dimethylformamide. While the stoichiometry of oxygen uptake is generally reproducible and consistent with an olefin·P_2O_4 or olefin·P_2O_5 product, analytical results (Table I) are generally somewhat low in carbon and high in oxygen and hydrogen, and a number of analyses on the cyclohexene product showed considerable scatter. A similar difficulty was noted by Willstätter,[5] and is probably due in large part to the extremely hygroscopic nature of the products.

Largely on the basis of hydrolysis studies described in the following paper we believe that our products are primarily polymeric anhydrides rather than having the structure advanced by Willstätter, and have one phosphorus atom bound to carbon as a phosphonic anhydride, with the other linked to carbon through oxygen and (for RP_2O_4 phosphorates) at the phosphite level of oxidation. As evidence for this polymeric structure, a sample of 1-hexadecene product (RP_2O_5) gave an apparent molecular weight by the Rast method corresponding to about 5 units. A possible structure incorporating these features for the cyclohexene product appears below with the nature of the end-groups



undecided. The presence of such end groups could also account for some of the discrepancies in analytical results mentioned above.

The nuclear magnetic resonance spectrum of P^{31} observed in a dimethylformamide solution of the cyclohexene product[9] partially substantiates this formulation. At 17 megacycles/sec. using H_3PO_4 as standard a strong signal was obtained at +26.3 ± 0.3 p.p.m., attributed to a



structure. A second signal at +12.75 ± 0.25 p.p.m. of approximately 1/3–1/5 the intensity of the first was attributed to terminal phosphorus atoms in the chain. The failure of any trivalent phosphorus to show up in the spectrum may be due to further atmospheric oxidation of the solution as observed with the benzene-soluble products noted above.

Experimental

Cyclohexene. Typical Preparation Using Oxygen.—White phosphorus (10.0 g., 0.32 g. atom) was dissolved in 500 ml. of dry, thiophene-free benzene under nitrogen in a flask equipped with a magnetic stirrer and placed in a thermostated water-bath at 40°. Cyclohexene (14.5 g., 0.18 mole) was added, the system swept out with a liter of oxygen and connected to a large oxygen-filled gas buret. Stirring was commenced, and the oxygen pressure maintained at approximately 810 mm. Oxygen absorption and product precipitation began immediately. After 10 hours, 6.4 liters (0.285 mole at S.T.P.) of oxygen had been taken up and the reaction mixture was filtered on a sintered glass filter, washed with 500 ml. of petroleum ether, and dried under vacuum on the filter. The yield was 30 g., 100% of theory based on oxygen consumed.

Preparation using Air.—Cyclohexene (50 g., 0.61 mole) was added to 30 g. (0.97 mole) of phosphorus dissolved in dry benzene in a stirred flask and a slow stream of dry air drawn through the mixture for 48 hours. At the end of this time no phosphorus was present, as shown by the absence of white fumes on allowing a few drops of solution to evaporate on a watchglass. On isolation as previously described the phosphorate was obtained in 86% yield based on phosphorus.

Phosphorates of Other Olefins.—Products from other liquid olefins were prepared essentially as described above except that 0.1–0.5% azobisisobutyronitrile was added as initiator. Typical times required for absorption of the calculated amount of oxygen are indicated in Fig. 1. The soluble reaction products were isolated by evaporating off the benzene *in vacuo*, washing the residue with petroleum ether, and drying *in vacuo*. A Rast molecular weight determination on the 1-hexadecene phosphorate gave a value of 1521.

Gaseous olefins (ethylene and isobutylene) required a somewhat different apparatus. Thus in the preparation of ethylene phosphorate a solution of 10.4 g. of phosphorus (0.325 gram atom) in 600 ml. of benzene containing 0.2 g. of azobisisobutyronitrile was prepared and maintained at 40°. A 4:1 mixture of ethylene and oxygen contained in a reservoir system consisting of a gas buret and a 5-liter flask was circulated through the solution by means of a small diaphragm pump. As oxygen and ethylene were consumed they were replenished, maintaining the mixture below the explosive limit. After four days, the product was separated, washed with petroleum ether and dried. The yield was 22 g., 95% based upon phosphorus.

Determination of Oxygen–Phosphorus Ratio during Reaction.—The relative rates of consumption of oxygen and phosphorus in their reaction with cyclohexene were followed by periodically removing aliquots from a typical run, filtering off the product, evaporating benzene and cyclohexene from the filtrate, and determining residual phosphorus by titration with acidified bromide–bromate, a technique which gave good results in blank experiments with known amounts of phosphorus. Results have been plotted in Fig. 2 and indicate that the precipitate has the composition RP_2O_4 from the beginning of the reaction. Additional evidence was obtained by interrupting two experiments before oxygen absorption was complete, separating the residual olefin and benzene from product and phosphorus by filtration and vacuum distillation, and determining the unreacted cyclohexene by catalytic hydrogenation. Results are summarized in Table II, and while not entirely quantitative, indicate considerable unreacted cyclohexene with no evidence for any intermediate compound RP_2O_3.

TABLE II

PARTIAL OXIDATION EXPERIMENTS

Run[a]	1	2
C_6H_{10} taken	0.0177	0.0165
P_4 taken	.0342	.0320
O_2 absorbed	.0492	.050
RP_2O_4 formed	.0110	.0114
C_6H_{10} remaining	.008	.009

[a] All quantities in gram atoms.

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[9] The n.m.r. measurements and their analysis were obtained through the coöperation of the Chemical Warfare Laboratories, Army Chemical Center, Md.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY]

Chemical Properties of the Reaction Product of Cyclohexene with Phosphorus and Oxygen[1]

BY CHEVES WALLING, FRANK R. STACEY, SAUNDERS E. JAMISON AND EARL S. HUYSER

RECEIVED MARCH 24, 1958

Reactions of the product $C_6H_{10}P_2O_4$, obtained from cyclohexene, white phosphorus and oxygen, are described consistent with a polymeric anhydride structure. In water the product apparently is hydrolyzed immediately to β-phosphitocyclohexanephosphonic acid, which in turn undergoes rapid β-elimination of phosphorous acid and polymerization. In alcohols it is converted to a complex mixture of phosphorus esters, the structures of which have been only partially established.

Our preceding paper[2] described the reaction of a series of olefins with oxygen and white phosphorus in benzene solution to give white solid products of the approximate composition RP_2O_4 (or RP_2O_5) which reacted vigorously with water and alcohols and were suggested as having a polymeric anhydride structure, *e. g.*, for that from cyclohexene

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[1] Work supported by the Chemical Corps, U. S. Army.

[2] C. Walling, F. R. Stacey, S. E. Jamison and E. S. Huyser, THIS JOURNAL, **80**, 4543 (1958).