titanium which is removed less efficiently. The procedure is rapid and may be easily adapted to large scale procedures. It is especially valuable for removing last traces of impurities to give a highly purified product.

G. E. Boyd, E. R. Russel, J. Schubert and A. W. Adamson[3] have found that if a solution containing zirconium in low concentrations, in the order of 10^{-10} M, is passed through an ion exchange column the zirconium is removed from the solution and held very strongly by the resin, presumably by true surface adsorption. In the experiments in which zirconium is present in moderate concentrations (0.1 M) as in the above experiments, the zirconium seems to be adsorbed only to a very slight extent. This behavior could be explained by making the following assumptions: (1) The zirconium is present entirely as the colloidal form and has no ionic charge. Therefore it can be removed from solution only by true adsorption on the resin. (2) The surface adsorption capacity of the resin is very small. In the experiment described above, it was shown that the break-through capacity was approximately 0.00084 mole per 100 cc. of resin. This may be compared with the ion exchange capacity which is given as approximately 0.020 mole per 100 cc. of resin.

When the element is removed by ion exchange, the procedure is reversible in the manner shown below for sodium and hydrogen.

$$\mathrm{NaR} + \mathrm{H}^+ \rightleftarrows \mathrm{Na}^+ + \mathrm{HR}$$

where R represents the resin. Thus as an acid solution is poured down a column of sodium resin, the sodium ion goes into the solution and the hydrogen ion is removed. Since the procedure is reversible, as more hydrogen ion is poured through the column the sodium ion moves slowly down the column.

On the other hand, if the element is present as a colloid, insoluble in the solvent used, it will be removed by surface adsorption. This process will be irreversible unless a solvent is used in which the colloid forms a true solution. Thus zirconium nitrate, when dissolved in water, forms a colloidal solution of the hydrous oxide in dilute nitric acid. This hydrous oxide is adsorbed irreversibly on the ion exchange resin and is readily removed only by some solution, such as oxalic acid, which complexes and thus dissolves the zirconium.

The adsorption process is independent of the exchange process. Colloidal zirconium when present in very low concentrations is entirely adsorbed on the resin even if a high concentration of ions is present. Conversely, a small amount of cations may be completely removed by the resin even in the presence of high concentrations of colloidal zirconium.

Summary

1. A method has been developed for purification of zirconium by ion exchange columns.
2. In this procedure the zirconium is present in the colloidal form and is not adsorbed by the resin while the impurities which are present as positive ions are removed by ion exchange.
3. This method is rapid and easily adaptable to large scale procedures.
4. Results of several experiments are given to show the efficiency of purification of zirconium from iron, titanium, beryllium and lanthanum.
5. A procedure is described for obtaining a purified solution of zirconium salt from a typical ore.

AMES, IOWA

RECEIVED JULY 14, 1947

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(3) Unpublished reports on Manhattan Project.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION, CHEMICAL ENGINEERING DEPARTMENT, TENNESSEE VALLEY AUTHORITY]

Polymorphism of Red Phosphorus

BY W. L. ROTH,[1] T. W. DEWITT[2] AND ANTHONY J. SMITH

Elemental phosphorus exists in several allotropic modifications, classified loosely as white, red and black. The properties of red phosphorus are intermediate between those of the white and black forms. White phosphorus has a low melting point, is volatile, and is soluble in organic solvents. The structure of the solid has not been determined, but it probably is derived from the packing of tetrahedral P_4 molecules. Crystalline black phosphorus has a high melting point, is insoluble in organic solvents, and markedly resembles graphite in texture. The structure is built up from indented sheet-like layers in which each phosphorus atom is covalently bonded to its three nearest neighbors.[3]

Gingrich and co-workers[3,4] have calculated the radial distribution curve of "amorphous" red phosphorus. Each atom has three nearest neighbors at a distance of 2.29 Å. and somewhat over six neighbors at 3.48 Å. Because of the similarity of this distribution to that of crystalline black phosphorus, it has been suggested that red phosphorus is microcrystalline with an atomic arrangement similar to that of black phosphorus. An ex-

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[3] R. Hultgren, N. S. Gingrich and B. E. Warren, *J. Chem. Phys.*, 3, 351–355 (1935).

[4] N. S. Gingrich and C. D. Thomas, *J. Chem. Phys.*, 6, 659–665 (1938).

cellent review of the literature on phosphorus is presented in a recent book by Yost and Russell.[5]

The physical properties of red phosphorus have not been susceptible of exact definition. The material has been variously described as red, metallic, scarlet and violet phosphorus; its structure has been considered to be amorphous, microcrystalline, cubic, hexagonal, monoclinic and triclinic.[6] Frost[7] has shown that red phosphorus crystallized from lead or bismuth has a different X-ray diffraction pattern from that crystallized from a melt of red phosphorus. The vapor pressure data in the literature are derived from measurements in which the reversibility of the vaporization reaction could not be demonstrated.[8] The vapor pressure, heat of sublimation, and density reportedly depend on the conditions under which the red phosphorus is prepared.

Since it appeared reasonable that red phosphorus might exist in polymorphic forms and that the inconsistencies in the literature might be ascribed to transitions between these forms, portions of red phosphorus that had been prepared in various ways were studied by thermal analysis and with X-rays and the microscope. The present paper describes the results of the study.

Experimental Methods

Red phosphorus, subsequently shown to be amorphous, was prepared (1) by heating distilled white phosphorus at 280° for six to eight hours in an inert atmosphere and freeing the product of residual white phosphorus by low-temperature distillation,[9] or (2) by heating a tungsten wire to about 900° in phosphorus vapor supplied from a reservoir of white phosphorus at a temperature near the boiling point and condensing the product on a surface at a temperature just above the dew-point of white phosphorus. Some work was done with commercial red phosphorus that had been washed with water and vacuum-dried.

Thermal Aging.—Pyrex or quartz tubes were filled with red phosphorus, degassed at 0.1 mm. pressure and 300°, sealed under vacuum and heated for fifteen minutes to eighty-seven days at controlled temperatures of 350 to 600°.

Crystal Growth from the Vapor.—Reaction tubes 15 to 45 cm. long were made from 8- to 11-mm. Pyrex tubing. About 4 g. of red phosphorus was placed in one end of each tube and degassed, and the tubes then were sealed off under vacuum. Bundles of the tubes were heated in a furnace in which the desired temperature gradient could be maintained. The charge usually was vaporized at 425 to 550° and condensed at the opposite end of the tube at 380 to 545°. After significant deposition had occurred, the tubes were opened under benzene to recover the product.

Crystallization from the Melt.—Quartz tubes 8 mm. in diameter were filled with amorphous red phosphorus, degassed and sealed under vacuum, heated above the melting point of the phosphorus, and cooled at a rate of about 1° per minute. The tubes were opened under benzene.

Seeding.—Distilled white phosphorus was seeded with crystalline red phosphorus that had been prepared by thermal aging or growth from the vapor, and the mixture was heated at 250 to 280° until a significant proportion of red phosphorus was formed. The product was recovered by distilling off the white phosphorus under vacuum.

Differential Thermal Analysis.—Thin-walled Pyrex bulbs, approximately 1.5 cm. in diameter and each having a re-entrant thermocouple well, were filled with a weighed quantity of red phosphorus, usually 1.5 g., and were degassed and sealed under vacuum. The weight of the glass was about 0.8 g. The reference bulb contained grain Alundum. Weights were so adjusted that the total heat capacities of the unknown and reference bulbs were the same.

The two bulbs were mounted directly on a differential Chromel-Alumel thermocouple, each bulb completely supported by a junction which fitted snugly in the thin-walled thermocouple well.

The furnace was so regulated that the temperature of the reference bulb increased linearly with time. Regulation was accomplished with a Tag photoelectric controller that maintained a constant difference in temperature between the two hot junctions of a differential thermocouple, one junction at the center of the furnace and the other adjacent to the heating element. A heating rate of 1.0° per minute generally was used.

The furnace was equipped with an explosion vent, because the bulbs frequently failed at the higher temperatures where the vapor pressure of red phosphorus may be 30 atmospheres or more. For subsequent examination, the bulbs were quenched by a blast of air introduced through the explosion vent.

X-Ray Analysis.—Powder photographs were made with the samples held in thin-walled glass capillary tubes. The camera radius was 70 mm. A copper target with a nickel filter was used. Intensities were estimated visually, and values of *d*, the interplanar distance, were calculated from the Bragg equation, using $\lambda_{K\alpha} = 1.541$ Å.

Results and Discussion

Differential Thermal Analysis.—Exploratory thermal analyses were made of various samples of red phosphorus, including commercial samples, laboratory samples made by the conversion of liquid white phosphorus at 280°, and samples deposited from the vapor with the aid of a heated tungsten filament. All samples behaved similarly. The first curve in Fig. 1 illustrates a typical analysis.

Three reproducible peaks appeared in the heating curve between room temperature and 550°, the first breaking at about 460°, the second at about 520°, and the third at about 540° as an additional hump on the second peak. (The breaking temperature is temperature at which the rate of change of temperature of the sample bulb begins to differ from that of the reference bulb.) All the peaks were caused by the red phosphorus increasing in temperature relative to the Alundum; that is, the effects were exothermic. An endothermic peak noted with some samples at about 80° probably was due to impurities such as phosphorus oxides and acid, because the magnitude of the peak was reduced by carefully washing and drying the samples.

To simplify the subsequent discussion, the notation shown on the first curve in Fig. 1 has been adopted. The region preceding the first peak is termed I, the regions between the three peaks are II and III, respectively, and the region immediately beyond the third peak is IV. It will be shown that these regions probably correspond to

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(5) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, pp. 158-168.

(6) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green and Co., New York, N. Y., 1931.

(7) A. V. Frost, *J. Russ. Phys. Chem. Soc.*, **62**, 2235-2241 (1930).

(8) A. Smits and S. C. Bokhurst, *Z. physik. Chem.*, **91**, 249-312 (1916).

(9) S. Skolnik, G. Tarbutton and W. E. Bergman, This Journal, **68**, 2310-2314 (1946).

different polymorphs of red phosphorus. The concept that the three peaks are due to the transitions of forms I→II, II→III, and III→IV, respectively, is introduced conveniently at this point.

The transitions could not be reversed on cooling, nor could they be obtained a second time by reheating the same sample. Thus the reverse transitions either proceed at extremely slow rates or do not occur at all in the experimental temperature range. Consequently, the temperatures at which the peaks appear do not have any thermodynamic significance but merely show the temperature at which the transition becomes rapid with respect to the method of experimental measurement.

An estimate of the heat liberated in transition I→II has been made by evaluating a cooling constant from the latter part of the curve, assuming all the red phosphorus was at essentially the same temperature, and performing a graphical integration. An order-of-magnitude value of 200 cal./gram-atom was obtained. The other transitions involve smaller energy changes, roughly proportional to the areas under the peaks.

A series of thermal analyses was made on samples of red phosphorus that had been heated for various periods of time at different temperatures. To facilitate comparison, a single reproducible source of red phosphorus (liquid-phase preparation) was used. A typical sampling of the data (Fig. 1) shows that the peaks could be progressively eliminated by heating at temperatures below the normal breaking temperatures.

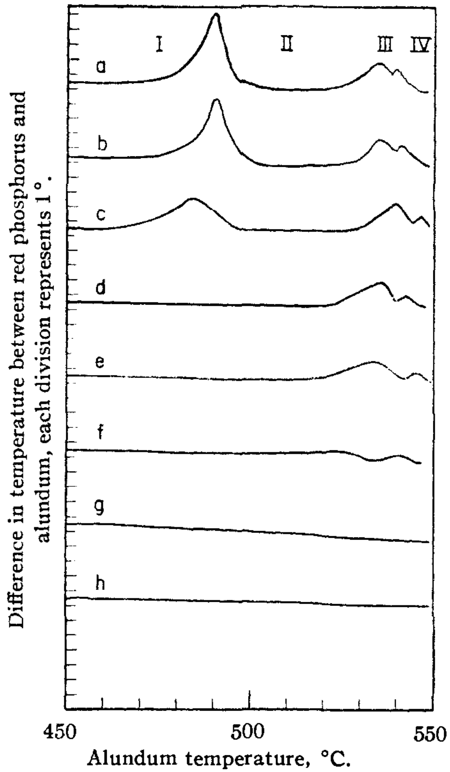


Fig. 1.—Thermal analysis of red phosphorus: 1.5 g. of red phosphorus; heating rate, 1° per min.; curves a and b, untreated; c, heated at 458° for 2 hours; d, 459° for 5 hours; e, 495° for 0.75 hour; f, 481° for 7 hours; g, 499° for 7 hours; h, 550° for 0.25 hour.

X-Ray Analysis.—The X-ray (copper, wave length 1.541 Å.) powder photographs of ordinary "amorphous" red phosphorus show a broad diffuse ring at $\sin \theta = 0.134$, corresponding to an interplanar spacing of 5.75 Å. Essentially identical patterns were obtained from all commercial samples and all laboratory samples prepared at low temperatures. Thus, red phosphorus made by thermal conversion of the liquid at 280° and red phosphorus deposited by means of a hot tungsten filament on a wall at 260° are the same and show little evidence of high-order structural regularity. This material corresponds to region I observed in the thermal analysis.

That heating induced structural changes in red phosphorus I, as indicated by thermal analysis, was confirmed by the X-ray patterns. Powder photographs of samples heated at different temperatures for various periods of time showed that the pattern development paralleled the extent of thermal treatment. The patterns at first consisted of a few very diffuse lines. As the heat-treatment continued, the lines sharpened and new lines appeared. Prolonged heating at low temperature developed the same pattern as brief heating at a higher temperature.

To some extent it was possible to correlate the peaks in the thermal analysis with the X-ray patterns. This was done by quenching samples at various points in the thermal analysis and examining the product with X-rays. In this manner, patterns were assigned to I, II, III and IV. The assignment of III is the least certain; because of the short temperature range of stability, it was difficult to quench a sample with assurance that it was in region III of the thermal analysis.

Numerous samples were aged thermally and their patterns compared. As long as the temperature was below 540°, all the patterns could be assigned to one of the four groups. These characteristic patterns are given in Table I.

Since the patterns of I, II and III were quite diffuse, some of the differences in the patterns may be due to lack of resolution. It is also possible, particularly with II and III, that mixtures of the forms may have been present. Although the patterns are similar, there appear to be significant differences that confirm the results of the thermal analyses and indicate the existence of four different polymorphs of red phosphorus. Of the four patterns, that of form IV agrees best with the one reported by Frost[7] for material obtained by cooling red phosphorus through the melting point.

Inspection of the photographs showed further that there was a fifth pattern, obtained from material heated to 550° and above, that was con-

Table I

X-Ray Powder Patterns of Red Phosphorus I, II, III and IV

Form I d, Å.	Form I Intensity[a]	Form II d, Å.	Form II Intensity[a]	Form III d, Å.	Form III Intensity[a]	Form IV d, Å.	Form IV Intensity[a]
						5.84	M
5.7	S	5.66	S	5.71	MS		
						5.58	M
		5.39	MW				
						5.21	M
				4.48	MW		
						3.43	VW
		3.30	VW	3.27	VW		
		3.08	VW	3.11	VW	3.15	W
				2.90	W	2.92	MW
		2.82	MW	2.81	W	2.79	W
						2.70	W
		2.62	MW	2.63	MS	2.65	MS
		2.45	VW				
						1.77	M
						1.73	W
						1.69	VW
						1.63	W

[a] S, strong; MS, medium strong; M, medium; MW, medium weak; W, weak; VW, very weak.

siderably different from those of forms I, II, III and IV. This form of red phosphorus, not detected by thermal analysis, will be called form V. The pattern, which is given in Table II, corresponds to those Frost[7] obtained with red phosphorus crystallized from lead at 525 to 590° and from bismuth at 570 to 580°.

The X-ray patterns of forms IV and V were sharp, and the particle size of many of the preparations was so large that the diffraction arcs varied markedly in intensity from point to point.

Crystal Growth from Phosphorus Vapor.—It was shown microscopically that heat-treatment changed the semi-transparent particles of amorphous red phosphorus to opaque particles, which, when viewed between crossed nicols, were observed to comprise countless submicroscopic to microscopic crystals. These anisotropic crystals appeared in random orientation in the particles and never exceeded 3 microns in size when the heat-treatment was conducted at temperatures below 550°.

The desirability of obtaining the various forms as well-defined crystals of a size suitable for single-crystal analysis was apparent. Attempts were made to grow crystals of red phosphorus from liquid white phosphorus by seeding with crystals of the red variety and effecting the normal thermal conversion at 250 to 280°. Only amorphous products (form I) were obtained. A few attempts to crystallize red phosphorus from the melt resulted in the formation of mixtures of the various forms, possibly because of temperature gradients within the sample at the time of crystallization.

Table II

X-Ray Powder Pattern of Red Phosphorus V

d, Å.	Intensity[a]	d, Å.	Intensity[a]
10.7	MW	2.15	VW
6.21	MS	2.11	VW
5.68	MS	2.06	VW
5.32	MS	2.01	VW
4.91	VW	1.84	MW
4.53	MW	1.83	MW
4.26	VW	1.79	MW
3.94	W	1.76	MW
3.59	W	1.73	VW
3.12	MW	1.68	W
3.03	MS	1.61	MS
2.89	MS	1.57	W
2.70	MS	1.45	VW
2.57	MS	1.42	VW
2.45	VW	1.40	VW
2.28	M	1.39	VW
2.17	VW	1.29	VW

[a] S, strong; MS, medium strong; M, medium; MW, medium weak; W, weak; VW, very weak.

Crystals of red phosphorus ranging up to 100 microns in length were grown by slow condensation from the vapor. At vaporization temperatures of 425° (approx. 1 atm. pressure) to 535° (approx. 20 atm.) and condensation temperatures of 380 to 510°, products containing two or more crystalline forms were obtained. The crystals were malformed, and their optical properties were obtained with difficulty. Microscopic examination led to the conclusion that the crystals belonged to the hexagonal and tetragonal classes. Photomicrographs of the crystals are shown in Fig. 2, and the optical properties are summarized in Table III.

Table III

Crystallographic and Optical Properties of Red Phosphorus

Form	Class	Principal refractive indexes (Li)	Optic sing	Angle 2V
Amorphous	....	2.7 to 3.0[a]	....	....
Tetragonal	Ditetragonal-dipyramidal (normal)	$n_\omega = 2.72$ $n_\epsilon = 3.15$	Uniaxial positive	....
Hexagonal	Trigonal	$n_\omega = 2.72$ $n_\epsilon = 3.15^a$ 3.20^b	Uniaxial positive	....
Triclinic	....	$n_\alpha = 3.11$ $n_\beta = 3.20$ $n_\gamma = 3.21$	Biaxial negative	24°26′

[a] Variable. [b] Close to 3.20.

At a vaporization temperature of 550° and a condensation temperature of 545°, there were developed well-formed crystals that were identified microscopically as belonging to the triclinic system. The products were free of other crystal forms. The crystals are shown in Fig. 2, and the optical data are summarized in Table III.

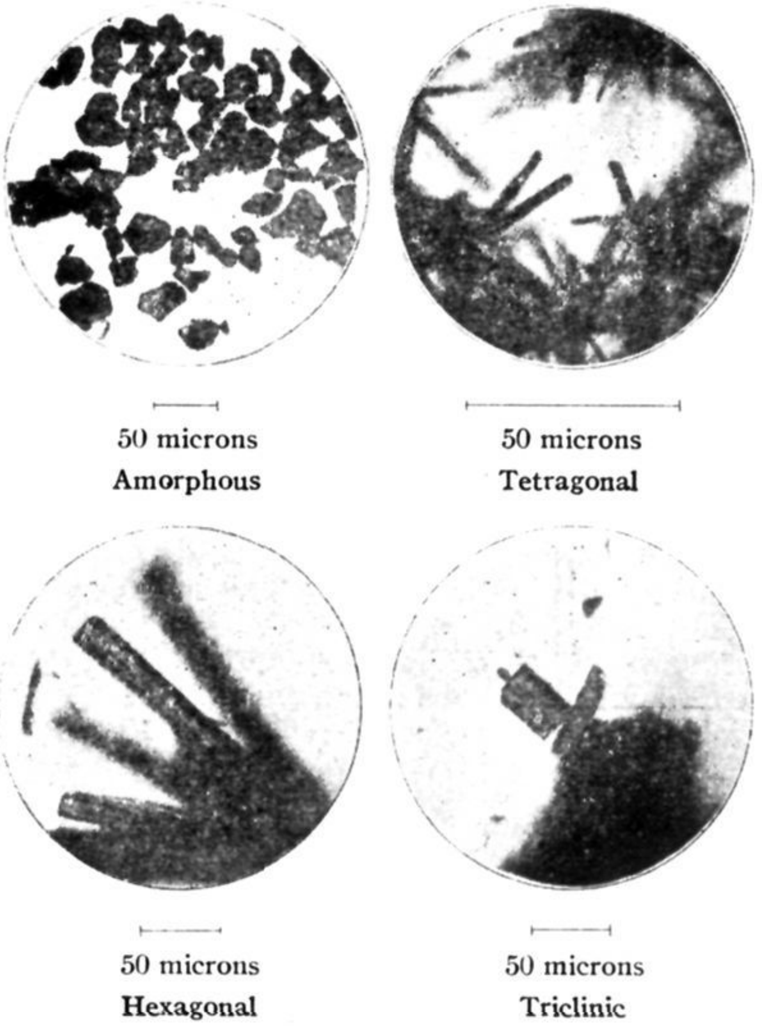
In an attempt to obtain pure samples of the various forms, the hexagonal and tetragonal crystals were separated mechanically. X-Ray powder photographs were taken, the various crystalline samples were heat-treated, and thermal analyses were made. The results can be summarized as follows:

The triclinic crystals corresponded to the red phosphorus V produced by heating the amorphous material to 550°. The X-ray patterns agreed, and further heat-treatment at 550° effected no change.

A positive assignment of the other two crystal forms could not be made. It appears probable that the tetragonal crystals were form IV and the hexagonal crystals were either II or III. Extended heating of samples of crystal-growth material with patterns approximating those of form II resulted in the formation of IV, as would be expected; with still further heating at higher temperatures, V was formed. The time required for development of these patterns was much greater, however, than that for the fine-grained material obtained in the heat-treatment of amorphous red phosphorus. Thermal analysis of crystal-growth products believed to be form II, for example, failed to show transitions below 550°.

Despite the similarity of some of the X-ray patterns, the occurrence of some significant differences in the patterns, the peaks in the thermal-analysis curves, and the result of the microscopic observations, all point to the existence of at least four, and probably five, different structures. The primary covalent bonding of phosphorus atoms probably is very similar in the different structures.

Acknowledgment.—The microscopic analyses of red phosphorus were made by W. A. Rice and J. R. Lehr. George Palmer of the University of Tennessee, Knoxville, made the X-ray diffraction photographs. The encouraging interest of J. W. H. Aldred and K. L. Elmore in the work also is acknowledged.



Amorphous Tetragonal

Hexagonal Triclinic

Fig. 2.—Photomicrographs of amorphous and crystalline red phosphorus.

Summary

Amorphous red phosphorus, when heated, undergoes irreversible exothermic transitions to crystalline modifications. The results of thermal analyses, X-ray diffraction studies, and microscopic observations indicate the existence of at least four, and probably five, polymorphic forms of red phosphorus. Triclinic, hexagonal and tetragonal crystals of red phosphorus have been grown from phosphorus vapor.

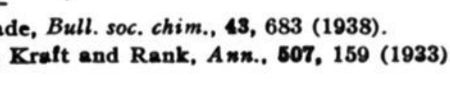
SCHENECTADY, N. Y. RECEIVED MAY 21, 1947

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

The Theory and Kinetics of Specific Oxidation. I. The Trivalent Manganese–Oxalate Reaction

BY FREDERICK R. DUKE

The work of Malaprade[1] with periodate and of Criegee[2] with periodate and lead tetracetate brought the phenomenon of specific oxidation into sharp focus. Either of these reagents was found to oxidize 1,2-glycols and related compounds according to the scheme



$$\begin{array}{l} -\overset{|}{C}-OH \\ -\underset{|}{C}-OH \end{array} \xrightarrow{\text{(Oxidant)}} 2\,{>}C{=}O$$

Ordinary alcohols and aldehydes are not attacked except exceedingly slowly. Other oxidizing agents which have been reported to act in a manner similar to periodate are tetravalent cerium,[3] tri- and tetravalent manganese,[4] bismuthate,[5] and trivalent silver.[5]

Criegee[2] proposed that a cyclic lead glycolate is an intermediate in the lead tetraacetate reaction,

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(1) Malaprade, *Bull. soc. chim.*, **43**, 683 (1938).

(2) Criegee, Kraft and Rank, *Ann.*, **507**, 159 (1933).

(3) Smith and Duke, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 120 (1943).

(4) Launer, THIS JOURNAL, **54**, 2597 (1932); Launer and Yost, *ibid.*, **56**, 2571 (1934).

(5) Heidt, Gladding and Purves, *Paper Trade J.*, **121**, No. 9, 35 (1945).