ses 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.

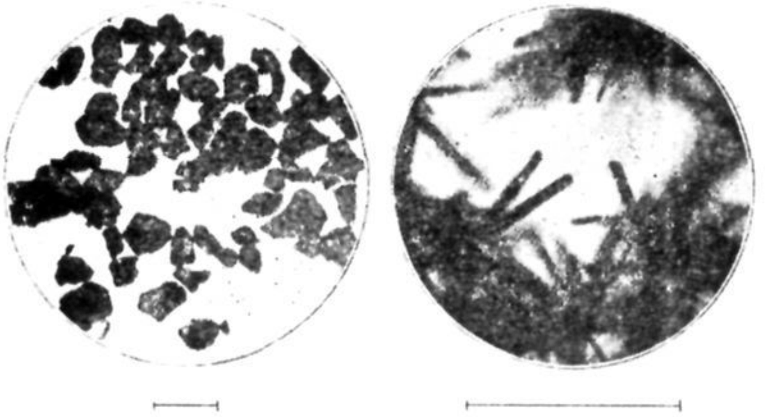
A positive assignment of the other two crystal forms could not be made. It appears probable that the tetragonal crystals were form IV and the hexagonal crystals were either II or III. Extended heating of samples of crystal-growth material with patterns approximating those of form II resulted in the formation 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.

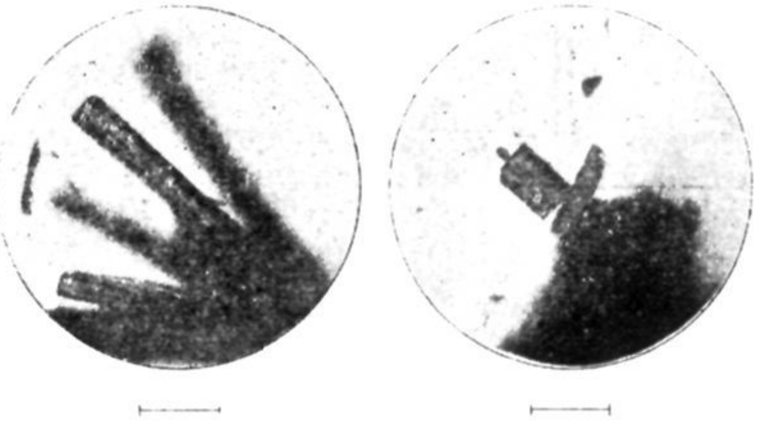
Summary

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.



50 microns
Amorphous

50 microns
Tetragonal



50 microns
Hexagonal

50 microns
Triclinic

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

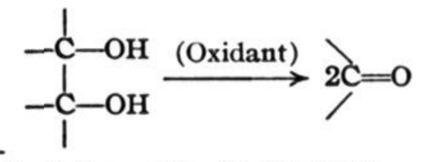
SCHENECTADY, N. Y. RECEIVED MAY 21, 1947

[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).

and he noted that both this oxidant and periodate ion could act as coördination centers. Price[6] suggested that a cyclic periodate–glycol ester might be an intermediate in the periodate oxidation. Heidt, Gladding and Purves[5] discussed and enlarged editorially on Criegee's original ideas concerning the mechanism of the reaction. Generally, it can be said that these investigators agree that an intermediate which might be considered a coördination compound of the oxidant with the reductant is involved in the reaction.

Theory

Based upon the very logical hypothesis that coördination intermediates are necessary to the reaction, the kinetics equations for the general oxidation may easily be derived. Since coördination equilibria are generally known to be rapidly established, the slow reaction must be the disproportionation of the coördination compound involving the oxidant and the reductant

$$-d[A]/dt = k[AC]$$

where [A] is total oxidant (coördination number taken as two for simplicity), k the rate constant, t the time and [AC] the concentration of the coördination compound involving oxidant, A, and reductant, C. AC arises from the equilibrium reaction: $AB_2 + C \rightleftarrows AC + 2B$, where B is the base coördinated to A as the oxidant exists in solution. (B is taken as monodentate since it usually is water, hydroxyl or acetate or other univalent anion. C is necessarily bidentate since it is 1,2 oxygenated.) Further, $[AC] + [AB_2] = [A]$. Substituting $[A] - [AC]$ for $[AB_2]$ in the equilibrium expression $K = [AC][B^2]/[AB_2][C]$ and solving for [AC], we obtain $[AC] = K[C][A]/K[C] + [B]^2$, where it should be noted that [C] and [B] are the uncoördinated portions of C and B.

For the case of the oxidant having a coördination number greater than two, more than one coordination compound of the oxidant containing the reductant may be present. With a coördination number of six, for example, the complexes AB_6, AB_4C, AB_2C_2 and AC_3 might exist; each could be expressed in terms of total oxidant, [A] and the three equilibrium constants relating them. Generally, if there are a number of such complexes which might disproportionate, $-d[A]/dt = \sum_i k_iC_i$, where k_i is the rate constant for the disproportionation of the coördination compounds C_i.

The Trivalent Manganese–Oxalate Reaction

The trivalent manganese–oxalate reaction was chosen to test the theory for the following reasons: Oxalate has been shown to require a specific oxidant, being unattacked by such reagents as alkaline permanganate and nitric acid; the nature and properties of some of the coördination complexes of trivalent manganese and oxalate have been ascertained.[7] Experiments were designed to measure the rate of disappearance of trivalent manganese from solutions of known oxalic acid content maintained at known hydrogen ion concentrations and constant temperature and ionic strength. The oxalic acid and hydrogen ion concentrations were varied independently and the rates determined at two temperatures.

Experimental.—The best grade of C. P. reagents was used. The general procedure for the rate measurements was as follows: The amount of 1.0 M oxalic acid to make the desired final concentration, 5.0 ml. of 2.0 M nitric acid (or 3.0 ml. nitric acid and 2.0 ml. 2.0 M sodium nitrate) and 2.0 ml. of 0.08 M manganese nitrate were added to a 25-ml. volumetric flask bearing a 24-ml. calibration line in addition to the 25-ml. one. Water was added to the 24-ml. mark and the solution placed in the constant temperature bath (maintained to 0.1°) and allowed twenty minutes to come to temperature. Then 1.0 ml. of 0.04 M potassium permanganate was carefully layered over the other reactants and another ten minutes allowed for the contents of the flask to come to constant temperature. The flask was thoroughly shaken and the Sargent electric timer started. Four samples were removed at different times by means of a 5-ml. pipet, and each sample was quenched in a special quenching solution. The time reading was taken when the barrel of the pipet was about two-thirds empty as the liquid meniscus passed a special mark.

The quenching solution consisted of 10 ml. of a solution prepared from 100 g. of citric acid adjusted to a pH of 8.5 with ammonium hydroxide and diluted to 400 ml. The trivalent manganese citrate complex has a yellow color with maximum extinction at 430 mμ and a molar extinction of 310. The color is stable for a number of hours and obeys the Beer–Lambert law over the range used. The concentration of trivalent manganese was determined by measuring the extinction of the citrate complex after dilution to 25 ml. with water. A Cenco–Sheard Spectrophotometer was used for all extinction measurements.

Because light and oxygen have been reported to effect the reaction,[8] the experiments were run in artificial light, and amber glass vessels were used interchangeably with colorless ones without altering the results; running the reaction in a nitrogen atmosphere produced results identical within experimental error with those run in the presence of air.

Results and Discussion

A plot of log Mn^{3+} *vs.* t resulted in a series of straight lines whose slope, k', was reproducible to within 5%. In every determination, the starting trivalent manganese concentration was no greater than one-tenth that of the oxalate or hydrogen ion, allowing the assumption that both of these quantities remained constant during an experiment. Data obtained are listed in Table I, the trivalent manganese varying from approximately

TABLE I

PSEUDO CONSTANTS (1/SEC.)

Concentrations in moles per liter.

	$k' \times 10^5$			
	$[H]^+ = 0.24$		$[H]^+ = 0.40$	
$[H_2C_2O_4]$	20°	14.8°	20°	14.8°
0.08	183	100	336	202
.16	131	68	211	121
.24	112	57	170	97
.40	100	51	138	75
.60	89	46	122	63

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(6) Price and Kroll, THIS JOURNAL, **60**, 2726 (1938).

(7) Cartledge and Ericks, THIS JOURNAL, **58**, 2061, 2065 (1936).

(8) Kolthoff, *Z. anal. Chem.*, **64**, 185 (1924).

0.008 to 0.003 M during an average run. The time of a run varied roughly from about a hundred and fifty to four hundred seconds.

The pseudo-constants are seen to decrease as the oxalate concentration increases, and to be hydrogen-ion dependent. (This is somewhat at variance with the interpretation of Launer,[4] who concluded that the rate was a straight inverse function of oxalate concentration, and was hydrogen-ion independent.) In light of the above theory, it must be assumed that two or more coördination compounds are disproportionating and that the more rapidly reacting one has the lower oxalate content. Cartledge and Ericks[7] have shown that $[Mn(C_2O_4)_3]^{-3}$ and $[Mn(C_2O_4)_2(H_2O)_2]^-$ may be isolated as potassium salts and that $[Mn(C_2O_4)_3]^{-3}$ exists only at relatively high pH values. The equilibrium appears to be

$$\underset{C_1}{[Mn(C_2O_4)_2(H_2O)_2]^-} + 2H_2O + 2H^+ \rightleftarrows \underset{C_2}{[Mn(C_2O_4)(H_2O)_4]^+} + H_2C_2O_4$$

The existence of non-oxalated trivalent manganese must be ruled out since the hydrated or hydroxylated complex is known not to exist. Therefore, $-d[Mn^{3+}]/dt = k_1C_1 + k_2C_2$. Utilizing the equations: $K = C_1[H^+]^2/C_2[H_2C_2O_4]$ and $[Mn^{3+}] = C_1 + C_2$, one can show that

$$\frac{-d[Mn^{3+}]}{dt} = \left[\frac{k_1K[H_2C_2O_4] + k_2[H^+]^2}{K[H_2C_2O_4] + [H^+]^2}\right][Mn^{3+}]$$

The portion in brackets may be identified with the pseudo-constant k'.

Launer[4] showed the necessity for having an oxalate to manganese ratio of at least two in order to stabilize trivalent manganese, and Cartledge and Ericks[7] did not find evidence for C_2 in their spectrophotometric investigations of the complexes. It may, therefore, be assumed that K is very large; in this case, the psuedo-constant reduces to: $k' = k_1 + (k_2[H^+]^2/K[H_2C_2O_4])$. A plot of k' *vs.* $1/[H_2C_2O_4]$ should result in a straight line whose slope is $k_2[H^+]^2/K$ and whose intercept is k_1. Such plots are shown in Fig. 1. The effect of $[H^+]$ is slight on k_1, but k_2/K varies approximately as the square of $[H^+]$. The complete kinetics expression is therefore

$$\frac{-d[Mn^{3+}]}{dt} = \left[k_1 + \frac{k_2[H^+]^2}{K[H_2C_2O_4]}\right][Mn^{3+}]$$

Approximate calculation of the energy of activation for the process involving the dioxalato complex may be made from the values of k_1, since the latter can be separated from the equilibrium constant. Substituting the values for k_1 obtained at the higher acidity into the Arrhenius expression

$$2.3 \log\left(\frac{k_a}{k_b}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_b} - \frac{1}{T_a}\right)$$

and solving for ΔH, one obtains 25 kcal. The nature of the reaction indicates that the high energy step is the breaking of the carbon-to-carbon bond in oxalate, a process which one would expect to take between 50 and 70 kcal. per mole. It would appear that coördination has lowered the activation energy for the process by some 25 to 40 kcal., and that without coördination, the activation energy would be far too high for the reaction to proceed. It is proposed that the following steps are involved in the reaction

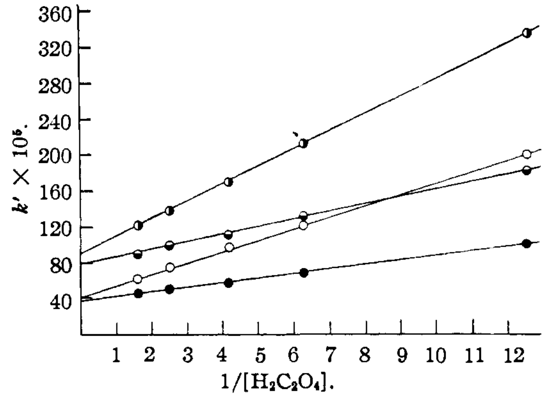
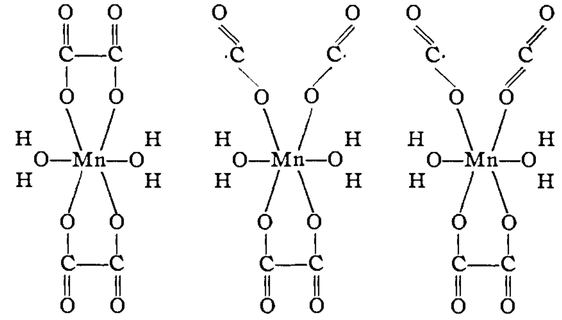


Fig. 1.—Plot of $k' \times 10^5$ *vs.* $1/[H_2C_2O_4]$: ◑, $H = 0.40$; $T = 20°$; ◒, $H = 0.24$; $T = 20°$; ○, $H = 0.40$; $T = 14.8°$; ●, $H = 0.24$; $T = 14.8°$.



Reactant (Mn^3) Activated complex (Mn^3) Product (Mn^2)

The activated intermediate may be considered to have a ruptured carbon–carbon bond, the odd electrons remaining paired to allow resonance with separation of charge as well as the formal bond type. (It is interesting to note in passing that this reaction may be one in which resonance plays an enhanced role in the activated complex.) The product, an unstable free radical ion, would be rapidly attacked by trivalent manganese to yield two molecules of carbon dioxide.

Summary

The kinetics of specific oxidation of glycols and related compounds is developed, based on the assumption that the slow reaction is the disproportionation of one or more intermediate coördination complexes. Substantiation is provided by an experimental study of the trivalent manganese–oxalate reaction which indicates that $[Mn(C_2O_4)_2(H_2O)_2]^-$ and $[Mn(C_2O_4)(H_2O)_4]^+$ are the two disproportionating complexes providing the reaction path.

The activation energy of the reaction is approximately 25 kcal., some 25 to 40 kcal. less than the energy required to break the carbon-to-carbon bond in oxalic acid; apparently coördination lowers the activation energy by this amount. Thus, the necessity of the intermediate to the specificity is explained.

EAST LANSING, MICHIGAN RECEIVED MARCH 28, 1947

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Reactions of Isopropyl Alcohol in the Presence of Catalysts Containing Magnesium Oxide[1]

BY LEON L. GERSHBEIN, HERMAN PINES AND V. N. IPATIEFF

The effect of metal oxide catalysts, having either dehydration or dehydrogenation properties, upon isopropyl alcohol has been the subject of extensive study by various investigators. Alumina or thoria, which are dehydration catalysts, converted isopropyl alcohol to propene, whereas copper or copper–zinc catalysts caused the dehydrogenation of this alcohol to acetone. The effect of the action of a catalyst composed of a mixture of oxides having dehydrating and dehydrogenating properties has been reported by Krause and Slobodin.[2] These authors did not reveal the composition of their catalysts; they reported, however, that under certain conditions isopropyl alcohol yielded a conjugated methylpentadiene.

Because the study of the action of magnesium oxide upon secondary alcohols has not been reported in the literature, an investigation of the decomposition of isopropyl alcohol in the presence of magnesium oxide has been undertaken.

The magnesia catalysts were prepared from the magnesium nitrate by precipitation of the hydroxide with (a) ammonia at 85–95°, (b) ammonia at 25°, and (c) sodium hydroxide at 25°.

Although magnesia was considered as a dehydrogenation catalyst[3] on the basis of its action upon ethyl alcohol, it was found in this study that this catalyst at 490° caused both dehydration and dehydrogenation of isopropyl alcohol, the latter predominating. The reaction was very slow at a temperature of about 410°. The experiments were made at atmospheric pressure and the isopropyl alcohol was passed over the catalyst at an hourly liquid space velocity of 0.90.

The product obtained from this reaction consisted of a mixture of compounds that contained acetone, propene, liquid hydrocarbons, mesityl oxide, and some higher boiling oxygen-containing compounds. The extent of the formation of the various products obtained depended upon the type of magnesium oxide used; this is evident from the data summarized in Table I.

TABLE I

DECOMPOSITION OF ISOPROPYL ALCOHOL OVER MAGNESIA

Experiment no.[a]	1	2	3
Mode of preparation	NH_4OH @ 85–95°	NH_4OH @ 25°	NaOH @ 25°
Catalyst charged, g.	29.7	23.9	40.0
% of alcohol recovered	5.9	4.4	17.1
Alcohol passed, g.	347	306	357
Products obtained, mole %[b]			
Propene	11.4	12.3	12.8
Acetone	46.9	43.1	63.9
Liquid hydrocarbons	14.8	10.6	2.6
Mesityl oxide	7.7	8.2	5.0

[a] Duration of experiments was six hours, temperature 490°, liquid hourly space velocity 0.90. [b] Based on isopropyl alcohol reacted.

The compositions of the products given in this and other tables are reproducible within 0.5% in cases where the quantity of the product formed was greater than 5–8%. When the concentration of the various compounds analyzed was small, the error involved was larger.

The liquid hydrocarbons obtained contained 2-methylpentenes, 2-methyl-1,3-pentadiene, the latter amounting to 50–65% of the total liquid hydrocarbons, and a conjugated cyclohexadiene of the formula C_9H_{14}, probably 1,5,5-trimethyl-1,3-cyclohexadiene. The structure of the methylpentadiene was determined by means of its maleic anhydride adduct.[4] The proof of the structure of the C_9H_{14} hydrocarbon (b. p. at 130–135°) was based on the following facts: (a) on catalytic hydrogenation under pressure it absorbed two moles of hydrogen per mole of hydrocarbon to form a cyclic hydrocarbon of the formula C_9H_{18}. (b) It reacted with maleic anhydride, indicating the presence of a conjugated double bond. (c) The C_9H_{18} hydrocarbon did not undergo dehydrogenation at 240° in presence of platinized alumina. At 300°, however, the dehydrogenation proceeded with the formation of hydrogen, methane and *m*-xylene; the latter was identified through its nitro derivatives. The dehydrogenation results indicated the presence of a geminal carbon atom which contained two methyl groups.[5]

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(1) This investigation was supported in part by the Universal Oil Products Company.

(2) V. P. Krause and Ya. M. Slobodin, *J. Applied Chem.* (*U. S. S. R.*), **9**, 1278 (1936).

(3) Paul Sabatier, "Catalysis in Organic Chemistry," translated by E. Emmet Reid, D. Van Nostrand Company, New York, N. Y., 1923, p. 702.

(4) G. B. Bachman and C. G. Goebel, THIS JOURNAL, **64**, 787 (1942).

(5) V. N. Ipatieff, H. Pines and R. C. Olberg, *ibid.*, **68**, 1709 (1946).