[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

One-Electron Oxidation of Copper Phthalocyanine

BY ALLEN E. CAHILL AND HENRY TAUBE

Oxidation of tetrasulfonated copper phthalocyanine in water by certain agents produced a fugitive red intermediate which has a lifetime of several seconds. One-electron oxidizing agents of sufficient potential produce the intermediate most efficiently. A similar stage is observed in the oxidation of the Co(II), Fe(III), Al(III) and Zn(II) complexes but not of the unmetallated sulfonated phthalocyanine. In 85% H_3PO_4, the half-life of the intermediate derived from tetrasulfonated copper phthalocyanine is *ca.* 15 min. at 25°. The spectrum of the red intermediate differs markedly from that of the parent copper complex. It has been shown that a net one-electron change produces the intermediate quantitatively. The red substance disproportionates, regenerating in part the original compound, or if excess oxidizing agent is present, undergoes net oxidation by a further one-electron change. The kinetics of disappearance of the red intermediate in phosphoric acid solvents has been studied, and interpreted recognizing the colloidal nature of the system.

The work of Dent, Linstead and Lowe has shown[1] that phthalocyanines can be oxidized quantitatively in acid by strong oxidizing agents such as ceric ion. The equation for the half-reaction describing the oxidation of the copper derivative, for example, may be represented as

$$(C_8H_4N_2)_4Cu + 8H_2O + 4H^+ = Cu^{++} + 4C_8H_5O_2N + 4NH_4^+ + 2e^-$$

Two equivalents of oxidizing agent are consumed for the net oxidation to phthalimide and other products, of each mole of phthalocyanine. In the present paper, experiments are reported which show that under some conditions a well defined one-electron oxidation of metal phthalocyanines takes place. The experiments were carried out with sulfonated phthalocyanines[2] since these are more readily dispersed in water and the other solvents used than are the unsulfonated complexes. The intermediate derived from the parent substance by one-electron oxidation is recognized by its magneta red color. The unoxidized sulfonated phthalocyanines are blue to green, the color depending on the solvent, and the final products on net two-electron oxidation at equivalent concentrations are essentially colorless.

The first part of the paper deals with quantitative experiments performed with tetrasulfonated copper phthalocyanine (TSCP) in phosphoric acid–water mixtures as solvents. In a later part of the paper, significant qualitative observations on TSCP and other phthalocyanines are presented.

Experimental

The potassium salt of tetrasulfonated copper phthalocyanine (TSCP) was used as supplied, without further purification.[3] The principal impurities are residues of inorganic salts introduced during preparation of the compound. The material was analyzed by three methods: oxidation by ceric ion in water, oxidation by ceric ion in 85% H_3PO_4 and determination of copper content. The values of the apparent molecular weight as determined by the three methods were 1204, 1203 and 1242. The theoretical molecular weight is 1049.7. Ions such as Cl^-, SO_4^-, and others which with reference to the method of preparation, could reasonably be expected as impurities, were tested for their effect on the observations, and proved to be without influence even at concentrations considerably higher than contamination levels. It was also shown that the observations are qualitatively the same when a sample of less completely sulfonated material is used in place of TSCP.

(1) Dent, Linstead and Lowe, *J. Chem. Soc.*, 1033 (1934).

(2) These were supplied through the courtesy of Dr. E. M. Bigelow, Jackson Laboratory, E. I. du Pont de Nemours and Co.

(3) The description accompanying the sample was: "potassium salt of essentially pure tetrasulfonated copper phthalocyanine; sample contains inorganic salts."

The system TSCP in phosphoric acid gives reproducible absorption data, obeys Beer's law, shows fairly reproducible rate behavior, and appears to be homogeneous on ordinary visual examination. It is quite certain, however, that it is a suspension of TSCP in the solvent, rather than a solution. A Tyndall effect can be observed, and, after long standing, solute collects in a flocculent form.

Two methods of dispersing TSCP in H_3PO_4 were used. In one method, the material was dissolved (or dispersed) in a minimum volume of water, and the solution was then diluted with 85% phosphoric acid; in the second method, phosphorus pentoxide was added to TSCP in water, adding enough to make the final solution 85% in phosphoric acid. The results obtained with both methods are essentially the same. The stock solutions prepared were *ca.* 10^{-3} *M* in TSCP and, for most of the experiments, were diluted further with solvent of desired composition. A stock solution of $Ce(SO_4)_2$ in 85% H_3PO_4 was also prepared.

Absorption Measurement on TSCP.—Figure 1 presents the results of measurements of the absorption coefficient of TSCP in water and in 85% H_3PO_4. This change in medium produces a visual color change from blue to bluish-green, and the change in spectrum is observed also to be quite marked. The change in color from blue to green is brought about also by adding concentrated sulfuric acid or perchloric acid to the solution in water. Data on the absorption coefficient of TSCP in phosphoric acid outside the range covered by Fig. 1, particularly on the long wave length side, proved to be irreproducible. However, there appeared to

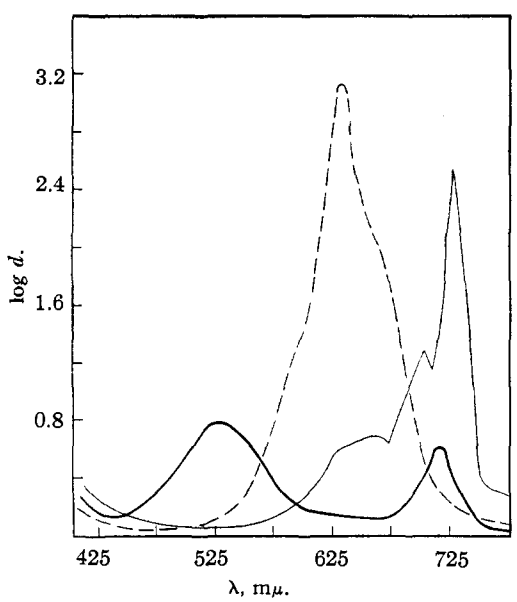

Fig. 1.—Optical density of TSCP and $TSCP^+$, concentration, 4.0×10^{-5} *M*, cell thickness, 1 cm.: — — — —, TSCP in water; ——, TSCP in 85% H_3PO_4; ——, $TSCP^+$ in 85% H_3PO_4, generated by adding 1 eq. Ce(IV) for each equiv. TSCP, and by adding 2 equiv. Ce(IV) for each equiv. TSCP.

be no correlation between variations in these measurements and any other observations made on the systems, and the effects were not further explored.

It is of interest to record that in general features the absorption curve for tetrasulfonated phthalocyanine in 85% H_3PO_4 resembles that of TSCP, with only a slight shift of the high peak. The maximum for the parent acid is at 710 mμ.

Table I presents results obtained in testing whether Beer's law is obeyed by TSCP in 85% H_3PO_4. The data show that there is no significant departure from the requirements of the relation over the eighty-fold range in concentration studied.

TABLE I

TEST OF BEER'S LAW FOR TSCP IN 85% H_3PO_4

λ = 625 mμ, temp. 25°

(TSCP), mole/l.	$\alpha^a \times 10^5$
4.2×10^{-5}	3.4
1.1×10^{-5}	3.4
5.3×10^{-6}	3.5
5.3×10^{-6}	3.7
4.2×10^{-6}	3.6
5.3×10^{-7}	3.3
Mean	3.5

[a] $\alpha = \frac{2.3}{lC} \log \frac{I_0}{I}$.

Stoichiometry of Production of the Red Oxidation Product.—The extinction coefficient in 85% H_3PO_4 of the red oxidation product generated from TSCP has been determined over a range of wave length. To make ready comparison with the spectrum of the parent substance possible, the results are also presented in Fig. 1. The measurements were made at 2°, since the half-life of the substance is considerably increased by decrease in temperature. The decomposition was followed as a function of time, and the absorption data have been corrected back to zero time. Two sets of measurements were made. In one experiment, only 1 mole of Ce(IV) was added for each mole of TSCP, in the second the ratio of oxidizing agent to TSCP was doubled. The spectra obtained for the red substance are identical for the two systems, and the curve in Fig. 1 combines the data of the two experiments. It should be pointed out that the initial reaction of TSCP and Ce(IV) is complete in a few minutes even at 2°. The half-life of the red form in the experiment with excess Ce(IV) was shorter than for the one with no excess Ce(IV), 65 min. as compared to 245 min., but was long enough to make it possible to obtain data of reasonable precision.

An experiment was also performed in which one-half mole of ceric ion was added for each mole of TSCP. The optical density of this solution was then measured (zero time measurement obtained as before by extrapolation) using light of wave length 530 mμ. At this wave length the red substance absorbs much more strongly than does the parent substance. The optical density was observed to be that expected for the conversion of one half of the TSCP to the red form. This result, taken together with the demonstration that ceric ion in excess of the 1:1 ratio does not affect the optical density of the oxidation product proves that the red substance is derived from the parent substance by a net one-electron oxidation. This conclusion is supported also by the additional observations on stoichiometry reported in the following paragraph.

When a solution in which TSCP has been transformed to the red form $TSCP^-$, and containing no excess ceric ion, is allowed to stand, the bluish-green parent substance is regenerated by the disproportionation reaction

$$2TSCP^+ = TSCP + \text{stable products}$$

The optical density of the final green solution at each wave length of the range covered in Fig. 1 is one-half that of the original green solution—correction having been applied for the change in volume caused by addition of the ceric reagent. The stable products, which are presumably Cu^{++}, NH_4^+ and phthalimide, contribute nothing to the absorption in comparison either to $TSCP^+$ or TSCP. It was shown furthermore that the stoichiometry expressed by the preceding equation is maintained, not only for the over-all reaction, but also at all intermediate stages of the disproportionation reaction.

When two or more moles of Ce(IV) is added for each mole of TSCP, the parent substance is not regenerated, and the net change describing disappearance of $TSCP^+$ becomes

$$TSCP^+ + Ce(IV) = Ce(III) + \text{stable products}$$

Kinetics of the Disproportionation and Oxidation of the Red Intermediate.—The rate of disappearance of $TSCP^+$ has been studied as a function of its concentration, the concentration of ceric ion, of solvent composition and of temperature.[4] The reaction was followed spectrophotometrically, using the wave length 530 mμ. In most of the experiments, the course of the reaction was followed over at least 4 half-lives of the red form. The applicability of rate law I and of rate law II to the data obtained in each experiment was tested in the appropriate manner.

Rate law I has the form

$$t = \frac{2.303}{k_1} [-\log(d - D)] + C_1$$

d is the optical density at time t, D is the final optical density, C_1 is an integration constant and k_1 is defined by $-d(TSCP^+)/dt = k_1(TSCP^+)$. If the data conform to the first order rate law, k_1 is obtained from the slope of the straight line obtained in a plot of t *vs.* $\log(d - D)$. Rate law II is based on the assumption of a second order dependence of the rate of decomposition of $TSCP^+$ on its concentration, and for the disproportionation reaction was tested in the form

$$t = \frac{(\alpha_R - \alpha_G/2)}{k_2(d - D)} + C_2 \qquad \text{II}$$

k_2 is defined by $-d(TSCP^+)/dt = k_2(TSCP^+)^2$. α_R and α_G are the extinction coefficients of $TSCP^+$ and TSCP, respectively, C_2 is a constant of integration. When this equation applies to the data of an experiment, t plotted against $1/(d - D)$ yields a straight line, from the slope of which k_2 can be determined. The equation can apply also when net oxidation rather than disproportionation of $TSCP^+$ takes place if α_G is replaced by 0. In general, the data of each experiment define k_1 or k_2, whichever applies, within a few per cent. The agreement between duplicate experiments however is no better than 10%. The imprecision is due in part to variation in temperature, and in part to variation in composition of the solution. The solvent is viscous, and volumes are not easily reproduced precisely.

In 85% H_3PO_4, the disproportionation of $TSCP^+$ proceeds as a first order reaction. Data illustrating this behavior for a typical experiment are shown plotted in Fig. 2. Even when excess Ce(IV) is added initially, so that net oxidation of $TSCP^+$ rather than its disproportionation is being studied, the data of a given experiment conform to the first

TABLE II

KINETICS OF DISAPPEARANCE OF RED FORM IN 85% H_3PO_4 DISPROPORTIONATION AND OXIDATION

	(TSCP) × 10^5	Temp., °C.	No. of half-lives	$(Ce\ IV)_0/(TSCP)_0$	k_1
1	3.7	25 ± 0.2	5	1.0	0.051
2	2.5[a]	25 ± 0.2	4	1.0	.045
3	4.0	25 ± 0.2	4	1.0	.050
4	3.7[b]	25 ± 0.2	3	1.14	.039
5	2.7	25 ± 0.2	4	2.0	.054
6	2.7	25 ± 0.2	5	2.0	.050
7	2.0	25 ± 0.2	4	2.8	.11
8	1.25	25 ± 0.2	4	5.5	.22
9	4.0	2 ± 0.5	1	1.0	.0028
10	4.0	2 ± 0.5	2	2.0	.011

[a] 5×10^{-4} *M* $Fe_2(SO_4)_3$ added. This experiment proves that the rate of oxidation of $TSCP^+$ by Fe(III) is very slow. [b] The value of k_1 was obtained from the data after the reaction had proceeded far enough to consume Ce(IV) completely.

(4) A thermostated cell compartment of the type described by Bell and Stryker, *Science*, **105**, 415 (1947), was used.

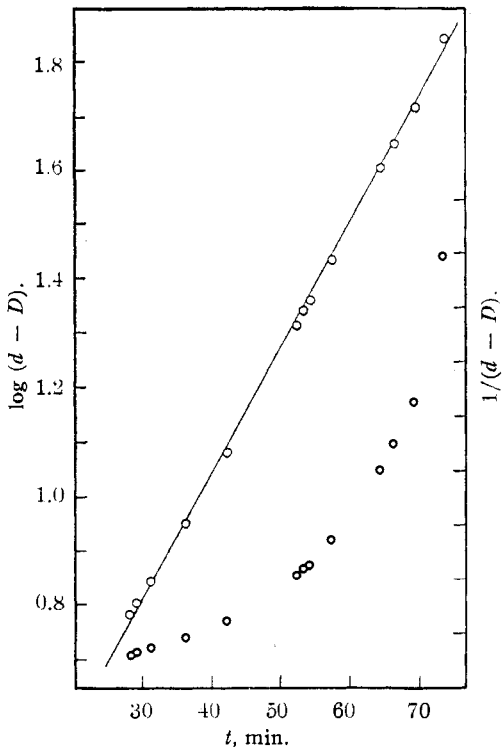

Fig. 2.—Kinetics of the disproportionation of $TSCP^+$ in 85% H_3PO_4; data of expt. 3, Table II: O, governed by ordinates on the left; O, governed by ordinates on the right.

order law. The specific rate from experiment to experiment increases, however, as initial Ce(IV) is increased. The results of the kinetic experiments in 85% H_3PO_4 as solvent are summarized in Table II.

In a solvent medium less rich in H_3PO_4, the disproportionation of $TSCP^+$ proceeds as a 2nd order reaction (*cf.* Fig. 3, which presents data for an experiment in 68% H_3PO_4). With excess Ce(IV), the disappearance of $TSCP^+$ again becomes first order in $TSCP^+$. If only a small excess of Ce(IV) is present initially, the reaction remains second order in $TSCP^+$, but proceeds at a much greater rate. The data pertaining to a solvent medium *ca.* 69% in H_3PO_4 are summarized in Table III.

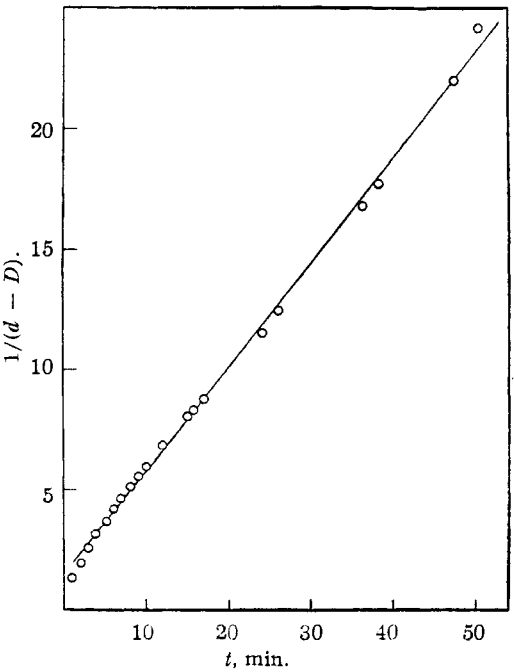

Fig. 3.—Kinetics of disproportionation of $TSCP^+$ in 68% H_3PO_4; data of expt. 1, Table III.

TABLE III

KINETICS OF DISAPPEARANCE OF THE RED INTERMEDIATE IN *ca.* 69% H_3PO_4

No.	$(TSCP)_0 \times 10^5$	% H_3PO_4 solvent	Temp., °C.	$(Ce^{+4})_0/(TSCP)_0$	No. of half-lives	$k_2 \times 10^4$	k_1
1	12.0	68	25	0.5	4	2.0	...
2	12.0[a]	68	25	0.5	4	2.0	...
3	3.7	71	25	1.0	4	1.7	
4	12.0	68	25	1.0	3	1.6	
5	12.0	68	25	1.15	3	10.0	
6	12.0	68	2	0.5	1	0.15	
7	23.0	69	25	2.0	8	...	0.22
8	12.0	68	25	2.0	5	...	.23
9	12.0	68	2	2.0	5		.017

[a] 6×10^{-4} *M* $Th(SO_4)_2$ present.

Figure 4 shows the variation of rate of disappearance of $TSCP^+$ in the presence of an equivalent amount of Ce(IV) as a function of solvent composition. A minimum rate is observed in *ca.* 85% H_3PO_4. A sharp increase in rate takes place in the phosphorus pentoxide richer systems beyond this minimum. If concd. sulfuric acid is added to 85% H_3PO_4, 1 part to 10, the rate of disappearance of $TSCP^+$ becomes too rapid to measure.

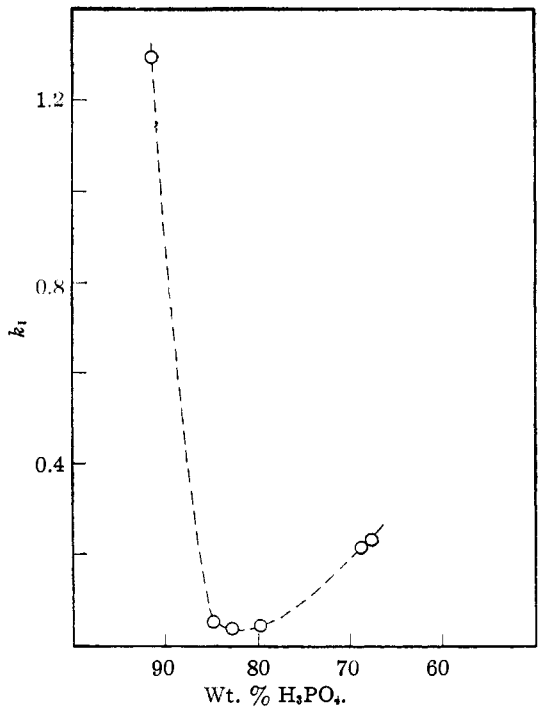

Fig. 4.—The rate of oxidation of $TSCP^+$ by Ce(IV) as function of solvent composition: temp., 25°, $(TSCP^+)_0$ = (excess Ce(IV))$_0$.

Qualitative Observations on $TSCP^+$ and Related Substances.—The red intermediate $TSCP^+$ is also formed efficiently in water solution by suitable oxidizing agents, but the lifetime in this medium is only of the order of a few seconds at room temperature. Among the oxidizing agents which react to form $TSCP^+$ efficiently are Ce(IV), MnO_4^- in acid, $Cr_2O_7^=$ in acid, HClO and Fe $(o\text{-phen})_3^{+++}$. With ClO_2, rapid but incomplete formation of the red intermediate takes place. When H_2O_2 is added to a strongly acid solution containing TSCP, the solution assumes a purplish color, and oxygen is slowly liberated. Bromine and thallic

ion oxidize TSCP slowly, without noticeable formation of the red substance; oxidation by ferric ion or an anode proceeds very slowly, again without noticeable production of the intermediate.

$TSCP^+$ is rapidly reduced by Fe^{++}, Sn^{++} or H_2O_2 and the resulting solution assumes the color of TSCP. From this solution or from that resulting on disproportionation of $TSCP^+$, a red intermediate of appreciable lifetime is regenerated when oxidizing agent is added.

Ceric ion generates a red intermediate also from the sulfonated phthalocyanines of Co(II), Al(III), Fe(III) and Zn(II). The lifetime of the intermediate resulting from the cobalt compound is longer than that of $TSCP^+$, but a higher concentration of Ce(IV) is required for complete, rapid reaction. The intermediate obtained from the aluminum derivative has a lifetime about as long as $TSCP^+$, that obtained from the ferric or zinc derivative is even more short-lived. The oxidation of unmetallated sulfonated phthalocyanine proceeds rapidly without noticeable formation of a red intermediate.

Only for the copper derivative is the lifetime of the corresponding intermediate greatly enhanced by changing from water to 85% H_3PO_4 as reaction medium. The group of oxidizing agents effective in 85% H_3PO_4 is about the same as it is in water; to the list can be added NO_3^-, which reacts only after an induction period, and NO_2^-, which reacts very rapidly. No system was encountered which presents an intermediate of longer life than is observed for $TSCP^+$ in H_3PO_4. Oxidation by Ce(IV) of TSCP in concentrated sulfuric acid or perchloric acid proceeds very rapidly, but the red intermediate is not observed. In concentrated citric or tartaric acid, the red substance derived from TSCP persists somewhat longer than it does in water.

Discussion

The quantitative experiments on the oxidation of TSCP in 85% H_3PO_4 have proven that the red substance is derived from the parent material by net one-electron oxidation. The similarity of the observations made with TSCP in water, and the other metal phthalocyanines makes reasonable the assumption that the red forms obtained in these systems also represent the one-electron stage of oxidation of the corresponding phthalocyanines. The phenomenon is therefore one of fairly great generality. It is clear from the experiments with the zinc and aluminum derivatives that the one-electron oxidation of the phthalocyanines should not be considered as taking place on the metal atom, but that it is a function rather of the highly conjugated organic ring. The metal ions do however affect the properties of the resulting radical, changing the rate of production from the parent substance, and the rate of disproportionation or further oxidation.

The fact that the substance formed when $TSCP^+$ is reduced or when it disproportionates behaves like the parent substance rather than like the unmetallated phthalocyanine, proves that the metal ion is retained in the ring during the one-electron oxidation. On further oxidation, the ring breaks, and the metal ion is released. Ejection of the metal ion may be involved in the rate-determining step of the further oxidation. This would account for the relatively high lability of the phthalocyanine itself as compared to the metallated derivatives.

Since Fe^{++} reduces $TSCP^+$ efficiently, and $Fe(o\text{-phen})_3^{+++}$ produces it, $E°$ for the couple: $TSCP = TSCP^+ + e^-$ is bracketted by the values -0.77 and -1.14. The observations made with ClO_2 as oxidizing agent, which indicate a measurable equilibrium between the ClO_2^-–ClO_2 and TSCP–$TSCP^+$ couples suggest as $E°$ for the latter couple a value of -1.0 ± 0.1. It is interesting to note that powerful one-electron oxidizing agents readily generate $TSCP^+$ from TSCP, but that two-electron oxidizing agents of equal strength —Tl^{+++} and Br_2 can be considered—do not bring about rapidly either the one-electron or two-electron oxidation. This is consistent with the view that the principal change in generating the red substance is removal of one electron. The two-electron oxidation requires in addition the rupture of a number of bonds.

The present work shows that the couple TSCP–$TSCP^+$ provides a path for the catalytic decomposition of hydrogen peroxide. Detailed kinetic experiments would, however, be required to determine whether the one-electron oxidation and reduction is the only path provided in the catalytic activity of phthalocyanines.[5] In view of the general similarity of the phthalocyanine and porphyrin rings, the observations made with the phthalocyanines raise the question of whether similar one-electron oxidation processes may not be important in the functioning of porphyrin complexes such as catalase.

The observations of the kinetics of disappearance of $TSCP^+$ in phosphoric acid solvents present some interesting and apparently anomalous features. These features can however be rationalized in a satisfactory manner if the point of view is accepted that $TSCP^+$ is present in the phosphoric rich media as a colloid rather than as a solute. This is a reasonable assumption in view of the known colloidal nature of TSCP in the same media. The disproportionation of $TSCP^+$ requires for its consummation a second molecule of $TSCP^+$. If the molecules are closely associated in a colloid, each molecule of $TSCP^+$ will always have other molecules as neighbors and a first order decomposition can be expected, no matter what the detailed mechanism of the reaction. To understand the results with ceric ion added, it need only be supposed that the red colloid once laid down does not readily adjust to changes in composition of the solution produced by continuing oxidation of $TSCP^+$. Its properties are therefore determined by the initial composition of the solutions, and any particular form will decompose at its characteristic first order rate. In this way, the observation that ceric ion increases the rate, but does not change the first order kinetics can be understood. Ceric ion may be incorporated into the colloid to an extent depending on its initial concentration, the ceric rich colloid having a more rapid specific rate of decomposition.

In the systems with 68% H_3PO_4, containing Ce(IV) equivalent to the $TSCP^+$ generated, the situation is presumably similar to that discussed for 85% H_3PO_4. A remarkable feature of the data obtained for 68% H_3PO_4 is that the reaction becomes second order in $TSCP^+$ when Ce(IV) is absent, or present in very slight excess. Even more remarkable is the fact that the rate of decomposition of $TSCP^+$ can be *decreased* by addition of Ce(IV). In experiment 4 of Table III,

(5) Cook, *J. Chem. Soc.*, 1761 (1938).

the initial rate by the second order path is 2.4×10^{-4} mole $l.^{-1}$ $min.^{-1}$. When a mole of Ce(IV) is added for each mole of $TSCP^+$ (expt. 7, Table III) the initial rate decreases to 2.5×10^{-5} mole $l.^{-1}$ $min.^{-1}$. It is evident that ceric ion wipes out the second order path completely, substituting for it the first order path, which, at certain concentration levels, is actually slower. A reasonable interpretation for the behavior is that Ce(IV) changes the state of $TSCP^+$ to a type of colloid in which the first order path can operate. This does not necessarily mean that $TSCP^+$ in 68% H_3PO_4 without excess Ce(IV) is homogeneously distributed. It may be present in a colloid structure highly diluted by the solvent, the separation of the molecules of $TSCP^+$ therefore depending on concentration.

The quantitative data discussed in the preceding paragraph show that the solvent exerts an important influence in determining the lifetime of the intermediate by affecting its physical state. The acidity of the medium is another important factor affecting the lifetime. The observations suggest that ring rupture in the phthalocyanine radical is an acid-catalyzed reaction. Another factor in determining lifetime apparently is the activity of water in the reaction medium. This influence is not unexpected since water is a reactant in the net two-electron oxidation. A consideration of these factors makes it seem likely that systems can be formed in which the phthalocyanine radicals have longer life than in those investigated. A promising possibility for further investigation would appear to be systems in which the phthalocyanines are adsorbed on surfaces.

Acknowledgment.—The work reported was begun as a result of a discussion with Dr. Thomas H. Davies. The authors wish to express their appreciation for his continued interest.

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[CONTRIBUTION FROM THE DOW CHEMICAL COMPANY, MIDLAND, MICHIGAN]

The Dehalogenation Reaction. I. Dechlorination of Vinyl Chloride/Vinyl Acetate Copolymers[1]

BY TURNER ALFREY, JR., HOWARD C. HAAS[1] AND CHARLES W. LEWIS

The reaction of polyvinyl chloride and vinyl chloride/vinyl acetate copolymers with zinc, in dioxane, is accelerated by zinc chloride. Polyvinyl chloride dehalogenates to the extent of 86–87% in agreement with Marvel, *et al.*, and Flory. The dechlorination of the copolymers also proceeds to approximately 86%. This indicates that the reaction does not consist simply of the random removal of 1,3 pairs of chlorine atoms to form cyclopropane rings, with vinyl acetate acting as an inert spacer. Simultaneous removal of acetate and chloride, to form zinc chloride–acetate, would account for the high extent of dechlorination in the low-vinyl chloride copolymers; acetate ion is found in the reaction product.

Marvel, Sample and Roy[2] studied the dechlorination of polyvinyl chloride by zinc and observed that 84–86% of the chlorine was removed. The result was in good agreement with the theoretical value of 86.4% predicted by Flory[3] for a head-to-tail polymer and a random removal of pairs of adjacent chlorine atoms. Extension of Flory's theory to the case of vinyl chloride copolymers was made by Wall[4] and Merz, *et al.*[5] These latter treatments assumed that units of the co-monomer (*e.g.*, vinyl acetate) served as inert spacers between sequences of vinyl chloride units, and led to the prediction that the fraction of chlorine removed by zinc should decrease with decreasing mole fraction of vinyl chloride in the copolymer according to the expression

$$f = 1 - e^{-2P_{11}} \qquad (1)$$

(In the special case of vinyl chloride/vinyl acetate copolymers, P_{11} is very nearly equal to the *mole fraction* of vinyl chloride). Marvel and co-workers[6] carried out an experimental study of the dechlorination of vinyl chloride/vinyl acetate copolymers, and observed that the fraction of chlorine removed did decrease with decreasing vinyl chloride content, in approximate agreement with equation (1).

We have now studied this reaction in more detail, and have found that copolymers of different compositions differ in the *rate* of dechlorination, rather than in the final limiting extent of reaction. When sufficient time is allowed, copolymers ranging in composition from 40 to 100 mole per cent. vinyl chloride reach a limiting value for the removal of chlorine of about 87%. Furthermore, the dechlorination reaction has been found to be affected by zinc chloride. Traces of zinc chloride eliminate the induction period otherwise observed and markedly accelerate the dechlorination. By use of zinc chloride, copolymers of low vinyl chloride content, which underwent essentially no reaction with zinc alone within 400 hours, were dechlorinated to approximately the same extent as the other copolymers.

Experimental

Vinyl chloride (Monsanto) was purified as described previously.[7] Polyvinyl chloride was prepared by solution polymerization at 67° of the following mixture: C.P. methanol, 40 ml.; vinyl chloride, 15 g.; benzoyl peroxide, 50 mg. The polymer was purified by precipitation in hexane from a dioxane–methylethyl ketone mixture, filtered and dried in vacuum. *Anal.* Calcd. Cl, 56.7. Found: Cl, 56.6.

(1) Taken in part from the Ph.D. thesis submitted by Howard C. Haas, Polytechnic Institute of Brooklyn, November, 1948.

(2) C. S. Marvel, J. H. Sample and M. F. Roy, THIS JOURNAL, **61**, 3241 (1939).

(3) P. J. Flory, *ibid.*, **61**, 1518 (1939).

(4) F. T. Wall, *ibid.*, **62**, 803 (1940).

(5) E. Merz, T. Alfrey and G. Goldfinger, *J. Polymer Sci.*, **1**, 75 (1946).

(6) C. S. Marvel, G. D. Jones, T. W. Mastin and G. L. Schertz, THIS JOURNAL, **64**, 2356 (1942).

(7) P. Agron, T. Alfrey, Jr., J. Bohrer, H. C. Haas and H. Wechsler, *J. Polymer Sci.*, **3**, 156 (1948).