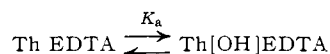
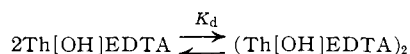


zirconium ion, it is surprising that the Zr(IV)-HEDTA chelate undergoes less hydrolysis and polymerization than its Th(IV) analog. This behavior is not completely without precedent, however. Whereas Bogucki and Martell²³ have calculated values of $pK_a = 7.04$ and $\log K_d = 4.3$ for the reactions



and



similar values obtained by Intorre and Martell¹⁶ for the hydrolysis and dimerization reactions of Zr(IV)-EDTA were $pK_a = 6.2$ and $\log K_d = 3.5$, respectively. Although the tendency toward hydrolysis of the Zr(IV)

(23) R. F. Bogucki and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 4170 (1958).

chelate is greater than that of the Th(IV) compound, the latter chelate dimerizes to a greater extent. The observed behavior in the cases of both Zr(IV)-EDTA and Zr(IV)-HEDTA chelates may be due to steric effects (associated with the smaller size of the Zr(IV) ion) which make it more difficult for additional donor atoms to approach the central metal ion.

The behavior of the Zr(IV)-EDTA-Tiron system is similar to that of Zr(IV)-EDTA in that both apparently form binuclear complexes. In the latter case hydroxide ions serve as bridging groups, while in the case of the mixed chelate bridges are presumably formed through the use of the phenolate groups of the Tiron molecules. Comparison with the data of Intorre and Martell¹⁶ on these systems shows that the less basic phenolic groups of Tiron interact with the Zr(IV) ion at a lower pH than do the more basic hydroxide ions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WIS.]

The Kinetics of the Oxidation of Bis-(2,3-dimercapto-1-propanolato)-iron(II) by Cystine in Alkaline Solutions¹

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RECEIVED JUNE 20, 1963

In alkaline solutions containing an excess of DMP (2,3-dimercapto-1-propanol) one mole of cystine (CSSC) is reduced by two moles of $\text{Fe(II)(DMP)}_2^{-2}$ to give two moles of cysteine and two moles of the intense red Fe(III) complex of DMP. The principal reaction path consists of two steps: the first is the reaction of CSSC with DMP to give the mixed disulfide CSDMP, and the second involves the displacement of DMP coordinated to an Fe(II) nucleus by CSDMP. The mixed complex is involved in the electron transfer. This second step shows both a first- and a second-order dependence on Fe(II). A slow, parallel reaction in which CSSC reacts directly to give Fe(III)³ is also present. As an aid in verifying the mechanism and the values of the rate constants, the reactions were simulated with an analog computer.

Thiols are usually quantitatively oxidized to the disulfide by iron(III). This is the case for mercaptoacetate,³ which in coordinating metal ions serves as an oxygen-sulfur donor, but with cysteinate, which is a sulfur-nitrogen donor, the oxidized form cystine has been found to react with the iron(II) complex to form a low, but detectable, concentration of the iron(III) cysteinate.⁴ This reaction has been used to evaluate the potential of the cysteine-cystine couple.⁴

Finally, with the sulfur-sulfur donor, 2,3-dimercapto-1-propanol, the iron(III) mercaptide in alkaline solutions is found to be highly stable with regard to the oxidation of mercaptide to disulfide and reduction of iron(III) to iron(II).⁵

The kinetics of the iron(III) oxidations of mercaptoacetate and cysteinate have been studied and it was found in these reactions that the electron transfer proceeds via a bimolecular reaction between two iron(III) complexes.⁶⁻⁸ The activated complex apparently consists of a binuclear species in which two electrons are transferred from coordinated mercaptide groups to the two iron(III) nuclei. Similar reactions of this type involving a two-electron oxidation of coordinated ligands with the concomitant reduction of two metal ions have been reported.⁹⁻¹⁴ The iron(II)-DMP sys-

tem offers an opportunity of studying the reverse reaction where an oxidized form of a ligand may be reduced in a two-electron step by metal ions which undergo a one-electron oxidation. In the present work this process was studied by adding cystine to ammoniacal solutions of Fe(II) containing an excess of DMP and following the formation of the intense red Fe(III)-DMP complex spectrophotometrically at a wave length of 507 m μ . Under these conditions Fe(II) is bound as the light red Fe(DMP)_2^{-2} ¹⁵ and Fe(III) forms the intensely colored species Fe(DMP)(OH) and $\text{Fe(DMP)(OH)(NH}_3\text{)}$.⁵

Experimental

The techniques used in conducting the kinetic studies under air-free conditions were similar to those previously described.^{5,8,15} In a typical experiment an ammonia buffer was placed in a reaction flask, the flask was capped, and the contents de-aerated. Aliquots of air-free partially neutralized DMP and ferrous ammonium sulfate solutions were added. The concentrations were adjusted so the final solution had a volume of 100 ml. and was 0.10 M in NH_4Cl .

A light red color was noted immediately on mixing, but it was found necessary to equilibrate the solutions for 12 hr. at 25.0° in order for the initial values of absorbance to become constant. The color changes apparently result from the fact that the iron(II)-DMP system is relatively slow to equilibrate: dark red polynuclear species¹⁵ appear to be formed rapidly on mixing. Traces of disulfides which are present initially also contribute to the absorbance. A typical initial absorbance at 507 m μ is of the order of 0.1-0.2 unit.

(1) This work was supported by a grant from the National Science Foundation.

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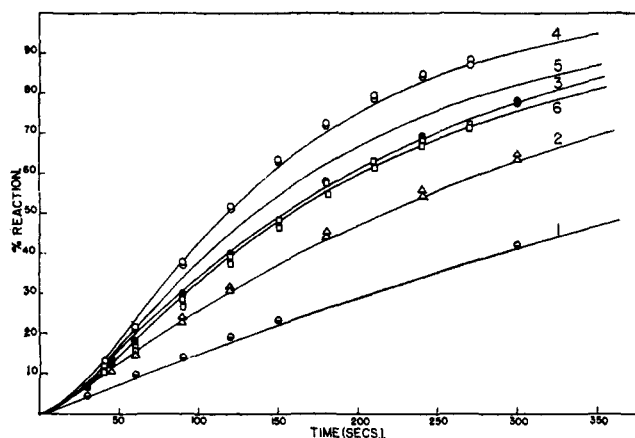


Fig. 1.—The reduction of cystine by $\text{Fe(II)(DMP)}_2^{-2}$, pH 10.38, $1.20 \times 10^{-3} M$ Fe(II): \ominus , $\text{DMP}_\Sigma 0.10 \times 10^{-3} M$; \triangle , $\text{DMP}_\Sigma 0.50 \times 10^{-3} M$; \bullet , $\text{DMP}_\Sigma 1.00 \times 10^{-3} M$; \circ , $\text{DMP}_\Sigma 3.00 \times 10^{-3} M$; \square , $\text{DMP}_\Sigma 6.05 \times 10^{-3} M$. The solid lines are the rates simulated with the analog computer.

After 12 hr., a measured volume of an air-free neutralized cystine solution at 25.0° was injected into the Fe(II)–DMP solution. The flask which was equipped with an optical side arm was then quickly placed in the cell compartment of a Cary 14 spectrophotometer. To give a time axis the recorder of the spectrophotometer was started simultaneously with the injection of the cystine. The absorbance at $507 m\mu$ was recorded as a function of time. Since the changes in the absorbance were fairly rapid, measurements in most experiments were continuously made until about 50% reaction, after which time the flask was returned to the water bath. The flask was removed from the bath at intervals thereafter for further absorbance determinations.

The percentage reaction at time t was calculated using the relationship $\% \text{ reaction} = (A_t - A_i)/(A_\infty - A_i) \times 100$ where A_t is the absorbance at time t , A_i is the initial absorbance, and A_∞ is the equilibrium absorbance measured after 24 hr.

Using the extinction coefficient⁵ of Fe(III) appropriate to the ammonia level of the buffer used in each run it was verified that the A_∞ values correspond quantitatively to the formation of 2.0 moles of Fe(III) per mole of cystine initially introduced. This indicates that the over-all stoichiometry is $2\text{Fe(II) (complex)} + \text{CSSC} \rightarrow 2\text{Fe(III) (complex)} + 2\text{CS}^-$.

At the pH levels of the present experiments only a very slight excess of DMP is necessary to suppress the formation of the polynuclear Fe(II) complexes to negligible levels relative to the concentration of $\text{Fe(II)(DMP)}_2^{-2}$.¹⁵ Therefore, the initial concentration of uncomplexed DMP was calculated using the simple relationship, $(\text{DMP})_\Sigma = (\text{DMP})_{\text{total}} - 2(\text{Fe(II)})$. The subscript Σ indicates that this term represents the concentration sum over all the various protonated species of DMP.

Most experiments were conducted in a pH 10.38 ammonia buffer, but runs at lower values of pH were also made in this same buffering system. To test for autocatalysis, experiments were run with either $2.5 \times 10^{-4} M$ Fe(III) or $8.4 \times 10^{-4} M$ cysteine added. The resulting curves coincided closely with those obtained under the same conditions in the absence of these additions, demonstrating that catalysis or inhibition by the reaction products is a negligible factor.

Results

The points for the experimentally observed values of $\% \text{ reaction vs. time}$ are shown in Fig. 1 for some of the experiments conducted at pH 10.38. In the series illustrated, the DMP level was varied while the initial concentrations of Fe(II) and cystine were maintained constant at 1.20×10^{-3} and $1.00 \times 10^{-4} M$, respectively. It is seen in Fig. 1 that as the DMP level is increased from the minimum to the maximum value investigated, the over-all rate of formation of Fe(III) first increases until a maximum rate is reached at about $3.0 M$ DMP, then decreases. Also, the curves, especially where the rate is a maximum, are seen to exhibit a slight induction period. This indicates the formation of a reactive intermediate. For two-step reactions, curve-matching methods have been used to obtain the rate constants¹⁶

(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, Chapter 8.

and this technique was used to obtain preliminary values for the production of Fe(III). Appropriate to the present system, for the reactions $A \xrightarrow{k'} B \xrightarrow{k''} 2C$ it is easy to show that the per cent of C as a function of time is given by the equation

$$\% C = 100 \left[1 + \frac{\kappa e^{-\tau} - e^{-\kappa}}{1 - \kappa} \right] \quad (1)$$

where τ is the dimensionless product $k't$ and κ is the ratio k''/k' . Equation 1 was used to construct a family of curves of $\% C$ vs. $\log \tau$ for various values of κ . When the observed rate curves were plotted as $\% \text{ Fe(III) vs. } \log t$ on separate graphs using the same scale, it was found possible to obtain close, but not exact, superimpositions between individual, theoretical, and observed curves.¹⁷ It was not possible to superimpose curves exactly because the observed curves were found to have somewhat higher values of per cent product over the first 15% reaction than those calculated.

Because of the nature of eq. 1, unique values of k' and k'' are not obtained for each observed rate curve. The theoretical family has the property that it is possible to fit an observed curve to a calculated curve having either a particular value of κ or its reciprocal. In either case the same two values are obtained for rate constants, but it is not possible to tell which corresponds to the first or second step. The tentative assignment of the values k' and k'' given in Table I was made on the basis of the following observations:

For experiments in which the DMP_Σ level was less than $3 \times 10^{-3} M$ the slower rate was found, within the experimental error, to increase linearly with increasing DMP_Σ . Also, this step very likely shows no dependence on the Fe(II) level.¹⁸ In this same DMP_Σ range the faster rate was found to vary inversely with DMP_Σ and, to a first approximation, directly with the square of the Fe(II) concentration.

Since Fe(III) is predominantly a reaction product of the second step,¹⁷ it is reasonable to assign the Fe(II)-dependent rate constants to k'' . Consistent with this, in a reaction involving cystine it is likely that a step which shows a direct dependence on DMP_Σ arises from thiol-disulfide exchange and signifies the first step of the reaction.

In the region $\text{DMP}_\Sigma \approx 3.6 \times 10^{-3} M$ the rates for the two steps "cross-over" and at higher DMP_Σ levels k' represents the faster step and k'' represents the slower. Because of the impossibility of exactly matching curves, the values of the faster step, that is the one which is less "rate-determining," is known with less precision. The discussion of the faster rates, therefore, has been limited to those values for which κ lies in the range 5 to $1/5$.

A plot of k' vs. DMP_Σ defines a straight line with a slope $3.81 \text{ mole}^{-1} \text{ sec.}^{-1}$. The intercept at zero DMP_Σ is equal to $1.7 \times 10^{-3} \text{ sec.}^{-1}$. This positive intercept indicates that a parallel DMP-independent reaction of cystine with Fe(II) also exists. This parallel reaction accounts for the high initial values observed in the rate curves.

Simulation of the Reaction with an Analog Computer.—Pseudo-first-order conditions were not maintained throughout the experimental ranges covered in Table I. The departure is particularly serious regard-

(17) In ref. 16 the equations for theoretical rate curves are given for reactions such as the hydrolysis of organic dihalides or diesters. In these reactions one halide ion or alcohol molecule is produced in each step of reaction. The curves derived for this type of mechanism are quite different from those based on eq. 1 and it was found impossible to fit more than but a few of the present results to the curves for this latter mechanism.

(18) Because of departure from pseudo-first-order conditions, it is not possible to attach significance to the low value of k' in Table I for $0.60 \times 10^{-3} M$ Fe(II).

TABLE I

THE RATE CONSTANTS FOR THE CYSTINE-Fe(II)(DMP)₂⁻² REACTION
 pH 10.38, initial cystine = 1.00 × 10⁻⁴ M, NH₃ buffer, 0.10 M NH₄Cl, 25°; values obtained graphically
 Variation of DMP₂, Fe(II) initial = 1.20 × 10⁻³ M

DMP _{total} , M × 10 ³	DMP ₂ free, M × 10 ³	k', sec. ⁻¹ × 10 ³	k'', sec. ⁻¹ × 10 ²	k'''[DMP]/ [Fe(II)] ² , l. mole ⁻¹ sec. ⁻¹
2.80	0.40	2.9
2.80	.40	2.0
2.80	.40	2.5
2.80	.40	3.2
2.80	.40	3.2
2.90	.50	3.5
2.90	.50	3.6
3.32	.92	6.0	3.0	2.0
3.40	1.00	5.4	4.0	2.8
3.40	1.00	5.6	3.8	2.6
4.00	1.60	8.1	2.4	2.7
4.00	1.60	7.3	2.4	2.8
4.40	2.00	11	3.0	4.2
4.40	2.00	8.5	2.6	3.6
5.00	2.60	13	1.4	2.5
5.00	2.60	8.9	1.8	3.3
5.40	3.00	13	1.6	3.4
5.40	3.00	12	1.8	3.8
6.00	3.60	10	1.0	2.5
6.00	3.60	12	1.1	2.8
6.40	4.00	16	1.0	2.8
6.40	4.00	14	1.1	3.1
7.00	4.60	22	0.74	2.4
7.00	4.60	19	.62	2.0
7.40	5.00	22	.71	2.5
8.40	6.08	28	.59	2.5
8.40	6.02	29	.56	2.3

Variation of Fe(II)

Fe(II) _{init.} , M × 10 ³	DMP ₂ , M × 10 ³	k', sec. ⁻¹ × 10 ³	k'', sec. ⁻¹ × 10 ²	k'''(DMP ₂)/ [Fe(II)] ² , l. mole ⁻¹ sec. ⁻¹
0.60	0.90	3.9	1.7	4.3
1.00	.90	5.0	2.6	2.3
1.20	.92	6.0	3.6	2.3
1.60	.92	6.0	6.0	2.2
2.00	.90	5.5	13.0	2.9

ing DMP₂. Also, the complicating factor of the parallel DMP-independent reaction made it highly desirable to verify the mechanism and the values of the rate constants using an independent method. This was accomplished by simulating the reaction with an analog computer.¹⁹ The differential equations which were solved are

$$-d(\text{CSSC})/dt = k_1(\text{CSSC}) + k_2(\text{CSSC})(\text{DMP}_2)$$

$$\frac{d(\text{CSDMP})}{dt} = k_2(\text{CSSC})(\text{DMP}_2) - \frac{k_3(\text{Fe(II)})^2(\text{CSDMP})}{(\text{DMP}_2)}$$

$$\frac{d(\text{Fe(III)})}{dt} = 2k_1(\text{CSSC}) + \frac{2k_3(\text{Fe(II)})^2(\text{CSDMP})}{(\text{DMP}_2)}$$

with the restrictions

$$[\text{DMP}_2] = [\text{DMP}_2]_{\text{init}} - [\text{CSDMP}] + [\text{Fe(III)}]$$

$$[\text{Fe(II)}] = [\text{Fe(II)}]_{\text{init}} - [\text{Fe(III)}]$$

Successive approximations were used to evaluate the rate constants k_1 , k_2 , and k_3 from the experimental points plotted in Fig. 1.²⁰ The analogs of these rate constants on the computer were the resistances of three

(19) The National Bureau of Standards analog computer facilities were used. We are indebted to Dr. H. L. Mason and his staff for their assistance and cooperation in this undertaking.

(20) The Fe(II) dependence of the minor step involving k_1 could not be ascertained from the results, so this step was arbitrarily assumed to be zero order in Fe(II).

potentiometers. First, the initial conditions corresponding to curve 1 were used and the potentiometer corresponding to k_1 was adjusted (the two other rate potentiometers set to zero) until the generated curve coincided as closely as possible with the experimental points. The initial conditions were then reset to correspond to those of curve 2 and potentiometer k_2 was adjusted. A small adjustment of k_1 was made to improve the fit. Likewise, the data of curve 4 were used to find k_3 . The process was repeated until no further improvement was possible (about three cycles were required).

The solid lines in Fig. 1 are the final simulated results. Curves 1 through 5 were obtained using potentiometer settings corresponding to $k_1 = 0.0012 \text{ sec.}^{-1}$, $k_2 = 5.0 \text{ l. mole}^{-1} \text{ sec.}^{-1}$, and $k_3 = 33 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. Curve 6, which is in better agreement with the results at $6.0 \times 10^{-3} \text{ M DMP}$, was obtained by reducing k_3 to the value $26 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. The difference is greater than the experimental error and may result from changes in the ionic strength or from the formation of higher Fe(II) complexes.

In a separate experiment, not illustrated, the Fe(II) concentration was lowered to $0.60 \times 10^{-3} \text{ M}$ at DMP₂ equal to $0.90 \times 10^{-3} \text{ M}$ (see Table I). To reproduce the results it was found necessary to increase k_3 to $45 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. Thus, a model assuming only a second-order dependence on Fe(II) results in an "over-correction" when the iron concentration is reduced. An additional first-order path appears to be necessary. Assuming k_3 is a composite quantity according to the equation $k_3[\text{Fe(II)}]^{-2} = k_{1\text{CSDMP}}[\text{Fe(II)}] + k_{2\text{CSDMP}}[\text{Fe(II)}]^2$ and solving simultaneous equations using the k_3 values at 0.60×10^{-3} and $1.20 \times 10^{-3} \text{ M Fe(II)}$, $k_{1\text{CSDMP}}$ is found to be $14 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ and $k_{2\text{CSDMP}}$ is $21 \text{ l. mole}^{-1} \text{ sec.}^{-1}$.

The Reaction Rates of Possible Intermediates.—To study the reactions of the proposed intermediate CSDMP with Fe(DMP)₂⁻², unsuccessful attempts to prepare and isolate this compound were made. Since the evidence²¹ indicates that, except for cases where steric hindrance or strain exists, disulfide-mixed disulfide equilibrium constants are of the order expected for a statistical distribution of the species, attempts were made to prepare CSDMP-rich solutions by pre-equilibrating limited amounts of cystine with an excess of DMP. Solutions made up to be $2.00 \times 10^{-3} \text{ M}$ in CSSC and having a 5-fold excess of DMP were pre-equilibrated for a period of either 24 or 72 hr. This difference in the time was found to have no effect on the results. On injecting 3.00-ml. aliquots of these solutions into 100-ml. volumes of Fe(DMP)₂⁻² solutions having compositions similar to those described in Table I, a moderately fast generation of Fe(III) was observed. The kinetics were somewhat complicated and no attempt was made to resolve rate constants from the data.

When the cystine was pre-equilibrated with a 10-fold excess of DMP, however, the kinetics for the production of Fe(III) were somewhat simpler. The rate of formation of Fe(III) was found to be first order in disulfide computed as

$$[\text{disulfide}]_t = [\text{disulfide}]_{\text{init}} - 1/2[\text{Fe(III)}]_t$$

First-order plots for some of the experiments are shown in Fig. 2.

The pseudo-first-order rate constants, k'_{CSDMP} , obtained from the slopes in Fig. 2 and similar plots were found to adhere to the equation

$$k'_{\text{CSDMP}} = (k_{1\text{CSDMP}}[\text{Fe(II)}] + k_{2\text{CSDMP}}[\text{Fe(II)}]^2)/[\text{DMP}]$$

(21) See, for example, A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).

TABLE II
THE pH DEPENDENCE OF THE RATE CONSTANTS
NH₃ buffers, 0.10 M NH₄Cl, 25°, Fe(II)_{init} = 1.20 × 10⁻³ M, DMP_{init} = 1.60 × 10⁻³ M

pH	$k',^a$ sec. ⁻¹ , obsd.	k''	Fraction of					
			DMPH ₂	DMPH ⁻	DMP ⁻²	HCSSCH	HCSSC ⁻	-CSSC ⁻
10.38	0.0080 ^b	0.024	0.0048	0.565	0.430	0.00069	0.231	0.769
9.90	.0117	.018	.020	.781	.198	.0042	.472	.524
9.68	.0124	.068	.036	.836	.128	.0089	.594	.398
9.41	.0177	.071	.069	.861	.071	.020	.721	.259
9.19	.0237	.083	.111	.847	.042	.036	.792	.172
8.85	.0251	.099	.220	.762	.017	.084	.833	.083

^a Calculated on the basis that only the k_2 term is important (see text). ^b Calculated from the product, $k_2 \times (\text{DMP}_2)$ at pH 10.38.

This is implied in Fig. 3 where a plot of $k'_{\text{CSDMP}}[\text{DMP}]/[\text{Fe(II)}]$ vs. $[\text{Fe(II)}]$ is seen to cause the points to fall along a straight line. The slope of the solid line drawn through the experimental points in Fig. 3 yields a value of $k_{2\text{CSDMP}}$ equal to 20–21 l. mole⁻¹ sec.⁻¹ while the intercept gives a value of $k_{1\text{CSDMP}}$ equal to 0.006 sec.⁻¹. The dashed line represents the trace using the rate constants obtained with the analog computer in the consecutive reaction studies. The two lines are seen to differ only by the somewhat uncertain value $k_{1\text{CSDMP}}$, giving strong support to the validity of the proposed mechanism.

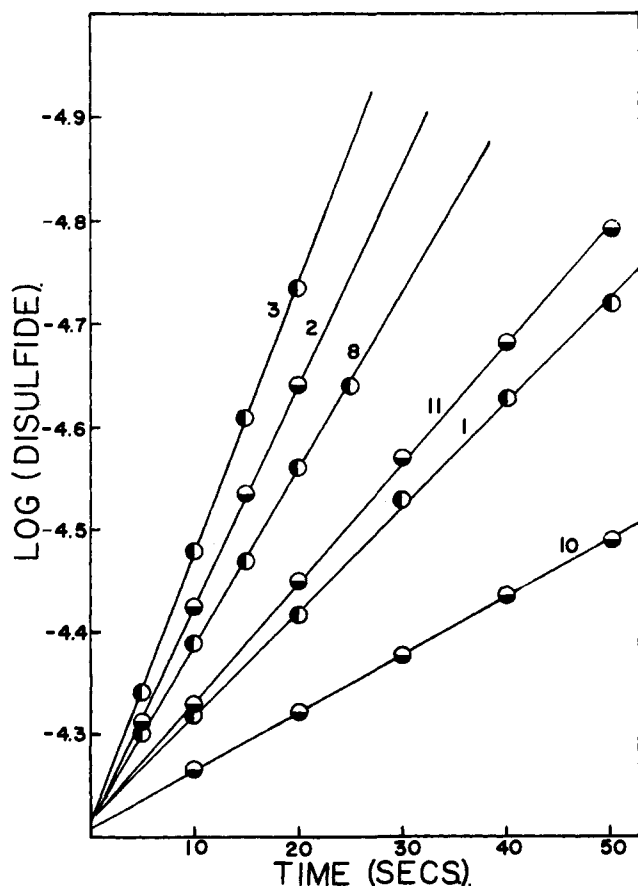


Fig. 2.—First-order plots for the reactions of pre-equilibrated solutions with Fe(DMP)₂⁻²; pre-equilibrated solutions: 2.90 × 10⁻³ M -CSSC⁻, 2.18 × 10⁻² M DMPH₂, 3.00 ml. injected into 100 ml. of the following at pH 10.4.

	Fe(II)	DMP ₂		Fe(II)	DMP ₂
1	0.00100	0.00106	8	0.00150	0.00106
2	.00200	.00206	10	.00100	.00206
3	.00300	.00306	11	.00150	.00206

In another set of experiments, solutions were prepared which contained an excess of cystine (5.00 × 10⁻³ M) over DMP (either 5.30 × 10⁻⁴ or 10.0 × 10⁻⁴ M). On injecting these mixtures (after 24 hr.)

into Fe(II)–DMP solutions almost instantaneous increases in the absorbances were noted. The rapid increases were followed by relatively slower rates of color development. The final equilibrium absorbances were the same regardless of the DMP level, but the initial rises corresponded to the production of about 1 mole of Fe(III) for each mole of DMP initially present.

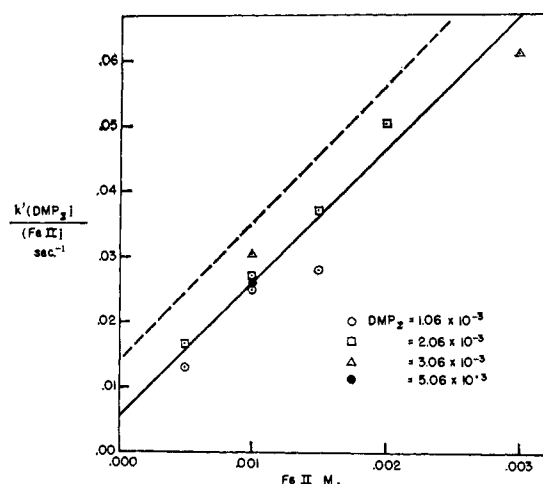


Fig. 3.—The dependence of the CSDMP rate constants on Fe(II) and DMP, pH 10.38: DMP₂: 1.06 × 10⁻³ M, ○; 2.06 × 10⁻³ M, □; 3.06 × 10⁻³ M, △; 5.06 × 10⁻³ M, ●.

The conditions in this last series favor the formation of higher disulfides of DMP. The results are best explained by a mechanism in which a polydisulfide such as CSDMPDMP₂ is rapidly attacked at the DMPDMP bond to give two Fe(III) ions and CSDMP.

The Effect of pH on the Rates.—The pH dependence of the rate constants was briefly investigated. The graphical method was used to obtain the constants since the results with the analog computer show that this procedure yields k' and k'' values which are sufficiently accurate for the present purposes.

The results are given in Table II for a series of solutions at constant initial concentrations of the reactants but buffered at different pH values.

It was found that as the pH decreases k' increases. At first k' decreases but then it too increases. A study of the DMP₂ variation at pH 9.90 showed that the increase in k' results from an increase in the k_2 term which is sufficiently large to compensate for a decrease in k_1 ; at pH 9.90 the k_1 term becomes negligible and is assumed to be negligible at lower values of pH.

At first glance the effect of pH on k_2 seems to be evidence against a mechanism involving thiol–disulfide exchange since these reactions usually show an inverse dependence on the hydrogen ion activity.²² This is because the thiol–disulfide exchange proceeds through an SN₂ mechanism involving the mercaptide ion. How-

(22) A. Fava, A. Illiceto, and E. Camera, *J. Am. Chem. Soc.*, **79**, 833 (1957).

ever, in the range pH 10.38–8.85 covered in the present experiments the predominant effect as far as the mercaptide group is concerned is the conversion of DMP^{-2} to DMPH^- . This can be seen in Table II where the fraction of each of the protonated forms of DMP and cystine is given.

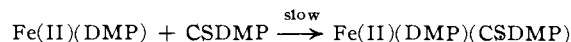
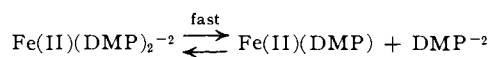
There are not sufficient data nor are the proton dissociation constants for cystine known with sufficient accuracy to warrant resolving the pH dependence of k' (i.e., k_2) into constants for all of the possible reactions between the various species. Since the values of k' increase as the pH decreases and since the concentrations of DMP^{-2} and CSCC^- profoundly decrease in this pH interval it seems unlikely that the path involving these species is important. Quite clearly the activated complexes are more or less protonated. Protonation would increase the reactivity both by decreasing the total negative charge of the activated complex and, through the inductive effect of the positive ammonium groups, increase the electrophilicity of cystine.

Some estimate of the maximum values of the individual rate constants can be obtained as follows. If at pH 8.85 the exchange proceeds only *via* reaction of the major species DMPH^- and HCSSC^- , the data would yield an absolute rate constant between these ions of about 0.04 l. mole⁻¹ sec.⁻¹. On the other hand, if DMP^{-2} and HCSSC^- were the only reactive species, the absolute value of the rate constant would be 17.6 l. mole⁻¹ sec.⁻¹. The former of these rate constants is somewhat smaller than those reported²² for thiol-disulfide exchange for unhindered, unstrained alkyl systems in methanol, while the latter is somewhat greater.

The second step of the consecutive $\text{CSCC-Fe}(\text{DMP})_2^{-2}$ reaction involves two parallel Fe(II) dependent paths both of which display an inverse dependence on DMP. This observation suggests that predissociation of coordinated DMP is involved. The over-all hydrogen ion dependence of k'' is also consistent with this provided DMP^{-2} is more basic than CSDMP^- . This seems to be likely since DMP^{-2} is

more basic than CSCC^- , and therefore CSDMP^- probably occupies an intermediate position.

The path first order in Fe(II) can be explained by reactions such as



The complex $\text{Fe(II)(DMP)(CSDMP)}$ may then react rapidly with $\text{Fe(II)(DMP)}_2^{-2}$ to give two Fe(III) in a two-electron transfer or may react in a one-electron transfer step to give a free radical.

The path second order in iron(II), which is the predominant path, shows the formation of a polynuclear activated complex. It is tempting to consider this activated complex to be analogous to the polynuclear intermediates formed in the oxidation of mercaptide by iron(III), with a two-electron transfer mediated by the complex.

The results can also be explained on the basis of the disulfide $(\text{DMP})_2$ being the reactive intermediate instead of CSDMP. This would be the case if CSDMP reacted rapidly with DMP to give $(\text{DMP})_2$. Although it does not seem likely that the second molecule of DMP would react faster than the first, this possibility cannot be ruled out. For CSDMP to be the intermediate the results of the pre-equilibration experiments require that $(\text{DMP})_2$ be appreciably less stable than CSCC^- . On the other hand, if $(\text{DMP})_2$ were the intermediate, a statistical distribution of species would be consistent with the observations.

The increase in the disulfide reactivities in the order $\text{CSCC}^- < \text{CSDMP}^-$ or $(\text{DMP})_2 < \text{CSDMPDMPCS}$ is another interesting observation of this work. The difference in reactivities may arise to some extent from the abilities of these ligands to coordinate to Fe(II). The order of reactivities, at least with CSCC^- and CSDMP^- or $(\text{DMP})_2$, is in the same order as their coordination tendency.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

The New Open-Chain Polyphosphines $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$ and $\text{CH}_3\text{P}\{\text{P}(\text{CF}_3)_2\}_2^1$

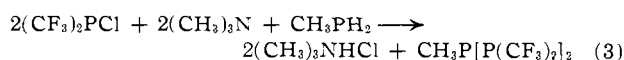
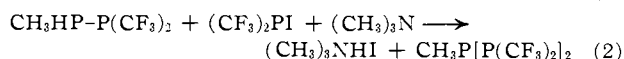
BY ANTON B. BURG AND K. K. JOSHI

RECEIVED JULY 31, 1963

The phosphine CH_3PH_2 reacts with $(\text{CF}_3)_2\text{PI}$ at -78° , quantitatively forming $\text{CH}_3\text{PH}_2\text{I}$ and the new diphosphine $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$ (b.p. est. 92°). This is decomposed by heat or light, quantitatively forming $(\text{CF}_3)_2\text{PH}$ and material having the composition of the $(\text{CH}_3\text{P})_n$ polymers. It is cleaved by HCl to make $\text{CH}_3\text{-PH}_2\text{Cl}$ and $(\text{CF}_3)_2\text{PCl}$; or by reaction with $(\text{CF}_3)_3\text{PI}$ and $(\text{CH}_3)_3\text{N}$ it is almost wholly converted to the somewhat stabler new triphosphine $\text{CH}_3\text{P}\{\text{P}(\text{CF}_3)_2\}_2$ (m.p. -66° , b.p. est. 151°). The same triphosphine is made almost quantitatively by the action of $(\text{CF}_3)_2\text{PCl}$ upon a mixture of CH_3PH_2 and $(\text{CH}_3)_3\text{N}$ at -40° . The ultraviolet absorption spectra of both new chain phosphines indicate delocalization of the lone-pair electrons, and their infrared spectra correspond to the expected structural components.

The P-P bond offers promise of many uniquely interesting compounds, each leading to a wide variety of new chemistry. The present work is concerned with two new types: the first of many possible trisubstituted diphosphines and the first fully substituted triphosphine. These were made by the virtually quantitative processes 1–3.

(1) This research was supported mostly by the United States Air Force through a subcontract under Contract AF 33(616)-6913 (terminated December 31, 1960), monitored by the Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Certain refinements were accomplished through support by Grant No. GP-199 from the National Science Foundation. We are also grateful to the National Science Foundation for providing our department with a Beckman IR7 infrared spectrophotometer through Grant No. G-14465 and for permission to obtain the related cesium iodide optics through Grant No. GP-199.



The new triphosphine is stable enough to encourage the search for many other P_3R_5 compounds, as well as a wide exploration of their chemical consequences. The formation of $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$ by reaction 1 may be closely analogous to an intermediate stage of the $\text{PH}_3-(\text{CF}_3)_2\text{PI}$ reaction to make $(\text{CF}_3)_2\text{PH}_2$,² for the decompo-

(2) G. S. Harris, *J. Chem. Soc.*, 512 (1958).