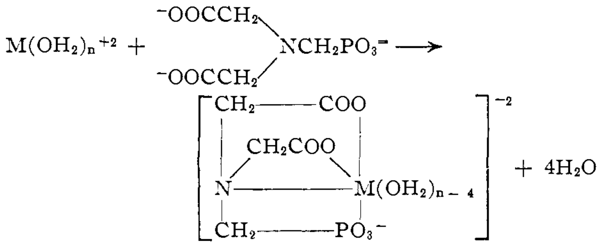

It can be seen that two metal ions Ca(II) and Mg(II) have stabilities which differ considerably from the normal values. The behavior of the calcium ion is similar to that noted with other aminopolycarboxylic acids capable of forming a number of chelate rings with the metal ion.[10] In such cases the stabilities of the calcium chelates are always much higher than the values predicted by any type of empirical correlation. A plausible explanation for this interesting behavior of the calcium ion has not yet been given.

A reasonable explanation can be offered for the lower-than-normal stability of the magnesium chelate. Since the magnesium ion may be considered as having a coördination number of 4 in its aqueous complexes, the chelate compound would be tetrahedral, with the metal ion ideally at the center of a regular tetrahedron, and with the four electron-donor groups at the corners. For all the other metal ions investigated the coördination compounds have more-or-less octahedral arrangements of donor groups, four positions being occupied by the ligand, and the remaining two *cis*-positions occupied by water molecules.[11] Inspection of formulas V and VI indicates that a ligand which could readily conform to formula VI, would not necessarily be able to provide the distribution of donor groups required by V. An examination of molecular models indicates that this difference in behavior is indeed the case, and that the strain resulting from the formation of the magnesium chelate would consequently involve an energy contribution in the direction of decreased stability.

**Acknowledgment.**—The authors are indebted to Mrs. Sonya Westerback of Clark University for the synthesis of aminomethylenephosphonic-N,N-diacetic acid.

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[10] A. E. Martell and M. Calvin, ref. 8, p. 193.

[11] The authors do not hereby specify a rigid structure for the coördination spheres consisting of ligand groups and solvated water. It is recognized that the tetrahedral and octahedral arrangements represent average or approximate positions as a consequence of the "essentially-ionic" nature of the metal-donor bonds. Such an interpretation is not inconsistent with the correlation of stability with ionization potential described above.

WORCESTER, MASS.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

# Mechanism of Racemization of Complex Ions. IV. Effect of Added Large Ions upon the Rates of Dissociation and Racemization of *Tris*-(1,10-phenanthroline)-iron(II) Ion[1,2]

BY ARNE JENSEN, FRED BASOLO AND H. M. NEUMANN

RECEIVED OCTOBER 25, 1957

The rates of dissociation and racemization of tris-(1,10-phenanthroline)-iron(II) have been measured at 25° in aqueous solutions containing various large anions and cations. Lauryl sulfate, *d,l*-10-camphor sulfonate, some alkaloid hydrochlorides and certain polyelectrolytes affect the rates. These effects are attributed to ionic association, and independent evidence for association has been obtained from studies of the ultraviolet spectra and by dialysis techniques. Structural features of the associations are discussed.

Several years ago Râу and Dutt[3] reported that the rates of racemization of aqueous solutions of *dextro*- and of *levo*-tris-(biguanidinium)-cobalt(III) chloride *dextro*-tartrate are slightly different. Davies and Dwyer[4] have observed that the presence of optically active ions have different effects on the rates of racemization of *dextro*- and *levo*-tris-(1,10-phenanthroline)-nickel(II) ions. They also found that the rate of racemization of this complex is likewise altered by the presence of large optically inactive ions.

This behavior of complex ions in the presence of large ions, polyelectrolytes and proteins may in some way be related to the biological activity of these metal complexes. For example it was found that although certain complex cations are stable and probably pass through the body unchanged, they also exhibit marked biological activity.[5] Certain metal complexes, when injected intraperitoneally into mice, cause paralysis and death by respiratory failure suggestive of curariform activity. There is reason to suspect that this activity results from their attachment to active sites in the biological system.

The purpose of this investigation was to make a quantitative kinetic study on the effect of large ions, polyelectrolytes and proteins on the rates of dissociation and racemization of tris-(1,10-phenanthroline)-iron(II) ion. Data are presented to show that the effects are due to inter-ion-associations. Associated species are present even in dilute aqueous solution and even between ions of like charges.

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(1) Previous paper in this series. J. E. Dickens, F. Basolo and H. M. Neumann, THIS JOURNAL, **79**, 1286 (1957).

(2) This investigation was supported by a Grant-in-Aid from the National Institute for Health, Grant No. RG-4335 (C).

(3) P. Râу and N. K. Dutt. *J. Indian Chem. Soc.*, **20**, 81 (1943).

(4) N. R. Davies and F. P. Dwyer. *Trans. Faraday Soc.*, **50**, 24 (1954).

(5) For a brief summary and references see F. P. Dwyer, E. C. Gyarfas, R. D. Wright and A. Shulman, *Nature*, **179**, 425 (1957).

Table I

| Compd. having little or no effect[a] | Compd. having a large effect |
|---|---|
| Triethanolamine hydrochloride (1.0 *M*) | Brucine hydrochloride |
| *n*-Octadecyl-trimethylammonium chloride (0.10 *M*) | Quinine hydrochloride |
| *t*-Dodecylbenzylbenzyldimethylammonium chloride (0.14 *M*) | Strychnine hydrochloride |
| *t*-Octylphenoxyethoxyethylbenzyldimethylammonium chloride (0.40 *M*) | Sodium lauryl sulfate |
| Poly-[ethyl-(2-methyl-5-vinylpyridinium) bromide](2.0%) | *d,l*-10-camphor sulfonate |
| Naphthalene-β-sulfonic acid (0.15 *M*) | Sodium polystyrene sulfonate |
| Polyvinylpyrrolidone ("0.45 *M*") | Polymethacrylic acid |
| Serum albumin (*p*H 2.5-3.0) (1.0%) | Serum albumin (*p*H 9) |

[a] The concentrations given in parentheses are the maximum concentration used.

## Experimental

**Compounds.**—Solutions of the complex ion Fe(phen)$_3^{2+}$ used for dissociation studies were prepared *in situ* by the addition of three equivalents of 1,10-phenanthroline to one of ferrous sulfate. The optically active salt, *l*-[Fe(phen)$_3$](ClO$_4$)$_2$, was prepared and resolved through the antimonyl tartrate by the method of Dwyer and Gyarfas.[6] The polyelectrolytes used were kindly supplied by the Monsanto Chemical Company, the quaternary ammonium salts by the Rohm and Haas Company and the sulfonates and sulfates by the Procter and Gamble Company. The authors wish to thank these companies for giving them free samples of these materials.

**Rates of Dissociation.**—The rates of dissociation of Fe(phen)$_3^{2+}$ in aqueous solutions containing large ions were determined spectrophotometrically at 25 ± 0.05° by the method previously described.[7] The initial concentration of Fe(phen)$_3^{2+}$ was $2.7 \times 10^{-5}$ *M* and measurements of optical density at a wave length of 510 mμ were made at suitable time intervals. Unless otherwise stated, all reaction mixtures were 0.02 *N* HCl in order to assure essentially complete dissociation of the complex ion. The rate constants, $k_{\text{diss}} \pm 1\%$, were obtained from a plot of the log of the optical density *vs.* time.

**Rates of Racemization.**—The rates of racemization of *l*-[Fe(phen)$_3$](ClO$_4$)$_2$ in aqueous solutions containing large ions were determined at 25 ± 0.1° by the method previously described.[7] Solutions of approximately $1 \times 10^{-4}$ *M* complex were prepared by its dissolution in the appropriate solution at 0°. This cold solution was then immediately poured into a 1-dm., water-jacketed, polarimeter tube which was maintained at 25 ± 0.1° with circulating water. As soon as this temperature was reached measurements were taken by means of a Bellingham and Stanley polarimeter with a photomultiplier attachment. The optical rotation at zero time was approximately 0.3° at 589 mμ. The rate constants, $k_{\text{rac}} \pm 10\%$, were obtained from the slope $m$ of the first-order plot of log $\alpha$ *vs.* $t$ (min.), $k_{\text{rac}} = 2.303m$.[8]

**Analysis of Data.**—In cases where the rates varied with the concentration of added large ion attempts were made to analyze the data quantitatively in terms of the rate constants and equilibrium constants of the associated species. In the simplest systems where association does not go beyond the addition of one ion to the complex the relationship

$$k = k_1 + \frac{k_0 - k}{K_1[\mathrm{X}]}$$

is satisfied, where $k$ is the observed rate constant, $k_0$ is the rate constant for the free complex, $k_1$ is the rate constant for the associated ion, $K_1$ is the equilibrium constant for the association, and [X] is the concentration of added ion. The constants for such a system can be obtained from a plot of $k$ *vs.* $(k_0 - k)/[\mathrm{X}]$.

For systems where association is more extensive a trial and error fitting was used. For these systems $k_i$ is the rate constant and $K_i$ the equilibrium constant for the aggregate containing $i$ large ions.

**Spectra of Complexes.**—The absorption spectrum of Fe(phen)$_3^{2+}$, over the range 220–600 mμ, in water solution was compared with that in solutions containing either 0.10 *M* *d,l*-10-camphor sulfonate or 0.001 *M* lauryl sulfate ions. These spectra were recorded using a Beckman DK spectrophotometer and 1 cm. fused silica cells. Some difficulty was experienced with solutions containing *d,l*-10-camphor sulfonate ions which absorb in the ultraviolet region. In this case the result reported represents the average of several determinations.

**Dialysis.**—Dialysis measurements were made essentially by a method described earlier.[9]

Cellophane bags were prepared from commercial sausage casing sold under the trade name Nojax by the Visking Corporation, Chicago, Illinois. These bags were filled with 10 cc. of polyelectrolyte solution of approximately 0.005–0.50% concentration. The filled bags were then suspended in 10 cc. of $2.73 \times 10^{-5}$ *M* [Fe(phen)$_3$]SO$_4$ solution such that the liquid level inside and outside the bag are equal. In order to minimize the Donnan effect, all solutions used were 0.1 or 0.2 *M* in NaCl. The large test-tube containing the outside solution and the suspended bag and its contents was placed in a thermostat at 25 ± 0.05°. This was mechanically shaken for a period of approximately 12 hr. to ensure equilibration.

Measurements were also made on control tubes, in one case with the complex alone and no polyelectrolyte in the bag so that a correction could be made for the complex bound to the bag. In the other case the complex was omitted so that colored impurities in the bag and the polyelectrolyte might be determined. In all cases the optical density of the outside solution was determined at the absorption maximum of the complex ion, 510 mμ.

From the corrected optical density of the outside solution it was possible to calculate the concentration of unbound Fe(phen)$_3^{2+}$. This permits an estimate of the complex bound to the polyelectrolyte, [CX] as well as the unbound polyelectrolyte, [X]. The binding constant is then determined from the expression $K = [\mathrm{CX}]/[\mathrm{C}][\mathrm{X}]$ with a precision of ±5%.

## Results and Discussion

It was reported earlier[1] that ions such as chloride, nitrate and bisulfate were capable of decreasing the rate of dissociation of Fe(phen)$_3^{2+}$. This effect, although measurable, was relatively small; one molar solutions of these ions causing decreases of the order of 10%. The rate has now been measured in solutions containing a wide variety of large ions. In Table I the compounds are divided into two classes; those having little or no effect, and those having a large effect. A compound is placed in the latter group if it caused a change of greater than 10% in any of the experiments involving it. Since it is possible that some of the compounds in the first group might show effects this large if used at higher concentrations, the maximum concentration employed with each is included in the table.

From the distribution of compounds between the two groups it is obvious that no single factor is going to explain all the observed effects. Both groups of compounds contain large cations, large anions, polymeric substances and molecules with polar groups. The evidence to be presented is all

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(6) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 263 (1950).

(7) F. Basolo, J. C. Hayes and H. M. Neumann, This Journal, **76**, 3807 (1954).

(8) F. Basolo, J. C. Hayes and H. M. Neumann, *ibid.*, **75**, 5102 (1953).

(9) I. M. Klotz, F. M. Walker and R. B. Pivan, *ibid.*, **68**, 1486 (1946).

consistent with the view that association between a large ion and the complex is the cause of the kinetic effects. This association can be attributed in general to van der Waals forces, but in any specific case there may be other factors involved.

Before presenting the data for ions that affect the rates the following considerations seem helpful. The rigid, planar structure of phenanthroline lends certain geometrical characteristics to the complex. The complex is not spherical in shape, but rather the three perpendicular phenanthroline planes jut out from the center of the complex, leaving three major pockets between them. Models show that two water molecules fit rather compactly into each pocket, the whole aggregate now becoming generally spherical. This is in accord with the observation that many of the phenanthroline complexes appear as hexahydrates.

For these reasons we shall assume as a basis for further explanation that the normal form of the complex in aqueous solution is this hexahydrated ion. Because of the proximity of the water molecules, and because they are properly oriented for coördination, it seems likely that water molecules will immediately occupy any coördination positions made vacant by dissociation of phenanthroline molecules. In a general way, any new aggregate that loosens up the compact hexahydrated arrangement, hence giving greater freedom of motion to the phenanthrolines, should tend to increase the rate of dissociation. However, if the new aggregate results in removal of the water molecules from their close proximity the rate of dissociation should decrease.

Let us first consider the effect of cations (Table II). These are bound purely by van der Waals forces, and would be expected to occupy positions near the phenanthrolines, but without greatly affecting the hydrate structure. The electrostatic effect of the ion would then be to decrease the electron density on the coördinated nitrogen, similar to the effect caused by chloro-substitution on the phenanthroline. The increase in dissociation rate observed with cations is thus consistent with the increase observed for tris-(5-chloro-1,10-phenanthroline)-iron(II).[10]

TABLE II

RATES IN PRESENCE OF LARGE CATIONS AND 0.02 *M* HCl AT 25°

| Solution | $k_{diss} \times 10^3$, min.$^{-1}$ | $k_{rac} \times 10^2$, min.$^{-1}$ |
|---|---|---|
| ... | 4.55 | 4.0 |
| 0.013 *M* brucine hydrochloride | 4.82 | 4.4 |
| .025 *M* brucine hydrochloride | 5.02 | 4.7 |
| .050 *M* brucine hydrochloride | 5.32 | 5.1 |
| .100 *M* brucine hydrochloride | 5.73 | 7.6 |
| .025 *M* quinine hydrochloride | 4.68 | 4.8 |
| .050 *M* quinine hydrochloride | 5.03 | 6.0 |
| 0.100 *M* quinine hydrochloride | 5.65 | 10 |
| .200 *M* quinine hydrochloride | 6.24 | 12 |
| .300 *M* quinine hydrochloride | 7.02 | 14 |
| .025 *M* strychnine hydrochloride | 4.75 | .. |
| .050 *M* strychnine hydrochloride | 4.94 | .. |

The brucine hydrochloride data fit very well the assumption that only one brucine ion is attached to the complex. Graphical analysis of these data gives 6.8 × $10^{-3}$ min.$^{-1}$ and 6.8 × $10^{-2}$ min.$^{-1}$ for the rates of dissociation and racemization at 25°, respectively, for the ion-pair. The values obtained for $K_1$ were: 11 from the dissociation data and 13 from the racemization data. This is satisfactory agreement. Using these values of the respective constants, the calculated rate constants at the various concentrations are in good accord with the experimentally observed rate constants.

The quinine hydrochloride data lead to no simple analysis. It appears that there is wide variety in the extent of association, with little change in rates for the various forms.

Although ion-pair formation of metal complexes in solution can often be detected by shifts of the ultraviolet absorption spectrum of the complex,[11] this method could not be used for these large cations because of their strong absorption in the ultraviolet region.

With anions the effects are more complicated. The data, shown in Table III for *d,l*-10-camphor sulfonate ion are particularly interesting; the rate of dissociation first rising slightly and then decreasing, while the rate of racemization increases. Evidence of ion-pair formation was observed in the spectrum of $Fe(phen)_3^{2+}$ in 0.1 *M* *d,l*-10-camphor sulfonate. The maximum of the principal absorption peak is shifted from 266 to 268 mμ. It is of interest that the absorption maximum of 1,10-phenanthroline (*p*H 9) itself shifts from 265 to 267 mμ in the presence of 0.1 *M* *d,l*-10-camphor sulfonate. Since the spectral shifts observed are much the same for neutral phen as for $Fe(phen)_3^{2+}$ it would seem that the interaction binding the sulfonate anion to the complex cation is not simply the electrostatic attraction between an anion and cation.

TABLE III

DISSOCIATION AND RACEMIZATION OF $Fe(phen)_3^{2+}$ IN PRESENCE OF CAMPHOR SULFONATE AND 0.02 *M* HCl AT 25°

| Camphor sulfonate, *M* | $k_{diss} \times 10^3$, min.$^{-1}$ |  |  | $k_{rac} \times 10^2$, min.$^{-1}$ |  |  |
|---|---|---|---|---|---|---|
|  | Na salt | Acid | Calcd. | Na salt | Acid | Calcd. |
| 0.0000 | 4.55 | 4.55 | 4.55 | 4.0 | 4.0 | 4.0 |
| .0005 | .. | 4.65 | 4.67 |  |  |  |
| .001 | .. | 4.63 | 4.65 |  |  |  |
|  |  | 4.67 |  |  |  |  |
| .002 | .. | 4.56 | 4.64 |  |  |  |
|  |  | 4.60 |  |  |  |  |
|  |  | 4.62 |  |  |  |  |
| .005 | 4.58 | .. | 4.57 |  |  |  |
| .01 | .. | 4.51 | 4.51 |  |  |  |
| .05 | 4.00 | .. | 4.03 | 4.6 | 4.5 | 4.5 |
| .10 | 3.65 | 3.68 | 3.66 | 5.2 | 4.8 | 5.0 |
| .20 | 3.28 | 3.30 | 3.19 | 6.0 | 5.8 | 6.1 |
| .30 | 2.84 | 2.96 | 2.88 | 6.3 | 6.2 | 7.0 |
| .40 | 2.54 | 2.68 | 2.62 | 7.8 | 8.1 | 7.8 |
| .50 | 2.33 | .. | 2.42 | 7.7 | 8.6 | 8.6 |
| .60 | 2.21 | .. | 2.24 | 9.2 | 9.4 | 9.2 |

Attempts to analyze the dissociation and racemization data lead to the conclusion that aggregates

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[10] W. W. Brandt and D. K. Gullstrom, THIS JOURNAL, **74**, 3532 (1952).

[11] M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

containing one, two and three sulfonates are present in the solutions used. The data can be fit reasonably well by the constants:

Equilibrium constants: $K_1$, very large
$K_2$, 14
$K_3$, 1
Dissociation rate constants: $k_1$, $4.68 \times 10^{-3}$ min.$^{-1}$
$k_2$, $3.30 \times 10^{-3}$ min.$^{-1}$
$k_3$, $0.00 \times 10^{-3}$ min.$^{-1}$
Racemization rate constants: $k_1$, $4.0 \times 10^{-2}$ min.$^{-1}$
$k_2$, $4.5 \times 10^{-2}$ min.$^{-1}$
$k_3$, $18.0 \times 10^{-2}$ min.$^{-1}$

The rates calculated from these constants are included in Tables III and IV. Because the number of constants is large it is possible that some other set might fit the data as well; the values stated give the best fit out of 40 sets tried. At the very least the different sets of values that were tried establish the magnitude of the equilibrium constants; show that for dissociation $k_1$ is $4.68 \times 10^{-3}$, $k_2$ is in the range $3.0–3.5 \times 10^{-3}$ and $k_3$ is less than $1.0 \times 10^{-3}$; for racemization $k_1$ and $k_2$ must be about the same as $k$ for the unassociated complex, whereas $k_3$ is several times larger.

TABLE IV

RATES IN SOLUTIONS OF POLY-ANIONS AND LAURYL SULFATE AT 25°

| Solution | $k_{\text{diss}} \times 10^3$, min.$^{-1}$ | $k_{\text{rac}} \times 10^2$, min.$^{-1}$ |
|---|---|---|
| ... | 4.55 | 4.0 |
| 0.01% Na polystyrenesulfonate[a] | 1.05 (1.02)[b] | 1.6 (2.0)[b] |
| 0.10% Na polystyrenesulfonate | 0.84 (0.80) | 1.7 (2.0) |
| 1.00% Na polystyrenesulfonate | .80 (0.73) | 1.7 |
| 2.00% Na polystyrenesulfonate | .75 (0.70) | .. |
| 0.01% polymethacrylic acid[c] | 4.68 | .. |
| .10% polymethacrylic acid | 3.59 | .. |
| .20% polymethacrylic acid | 2.88 | .. |
| .40% polymethacrylic acid | 2.08 | .. |
| 1.00% polymethacrylic acid | 1.24 | .. |
| 2.00% polymethacrylic acid | 0.88 | .. |
| 0.000125 $M$ Na lauryl sulfate[d] | 4.85 | .. |
| .00025 $M$ Na lauryl sulfate | 6.07 | 5.0 |
| .00050 $M$ Na lauryl sulfate | 7.23 | .. |
| .00100 $M$ Na lauryl sulfate | 7.80 | .. |

[a] Mol. wt. 10,000; 0.2 $M$ HCl. [b] The rates given in parentheses are for this same poly-anion of mol. wt. 70,000. [c] Mol. wt. 560,000; 0.02 $M$ HCl. [d] 0.02 $M$ HCl.

The trends displayed by the kinetic constants are consistent with the model previously presented if the anion is capable of changing the hydrate structure. Use of molecular models suggests that a sulfonate ion can conveniently occupy a pocket between two phenanthrolines, displacing the two water molecules. The aggregation is not as compact as the hydrate structure and allows greater freedom of movement of the two phenanthrolines. For an aggregate containing one sulfonate a slightly greater rate of dissociation is then expected as compared to the hexahydrate. The same trend must continue for the aggregate containing two sulfonates, but an additional factor now enters; one of the three phenanthrolines has no water molecules in position to replace it. A value of $k_2$ that is about two-thirds that of $k_1$ is the result. When three sulfonates are present there are no water molecules conveniently available and $k_3$ is small.

Racemization occurs predominantly by an intramolecular process for this complex.[7] The values of the rate constants make it clear that all of the water molecules must be replaced before the rate of intramolecular racemization is greatly affected.

The results obtained with solutions containing poly-anions are shown in Table IV. The rates observed suggest association between the complex and the poly-anions. Further evidence in support of association in these solutions has been obtained by a dialysis technique which makes use of a membrane permeable to ordinary ions but not to poly-anions.[9] In this way the association between polystyrene sulfonate (mol. wt. 70,000) and $Fe(phen)_3^{2+}$ was found to have an association constant of $4 \times 10^4$ at 25°. Thus with such a large binding constant, the complex is essentially all bound in the reaction mixtures studied kinetically. This then accounts for the abrupt decrease in the rate of dissociation of $Fe(phen)_3^{2+}$ and then its almost lack of dependence on the concentration of polystyrenesulfonate ion. The small value for the dissociation rate suggests that most of the water molecules in the complex have been displaced by sulfonate groups of the poly-anion. The fact that the sulfonate groups are also linked together by the skeleton of the poly-anion must lead to the rigidity that results in a decrease in the rate of intramolecular racemization.

Quantitative dialysis data at the same conditions of the rate experiments cannot be obtained with polymethacrylic acid which is only very slightly dissociated in 0.02 $N$ HCl. Since the iron(II) complex is completely decomposed in this acid solution during the time necessary for the dialysis experiment, the experiment was done with the analogous but stable ion, $Ru(phen)_3^{2+}$. An association constant of 60 was obtained. Thus the binding of the complex with polymethacrylic acid at the conditions of the rate experiment is considerably less than it is with polystyrenesulfonate ion. This is in accord with the rates of dissociation given in Table IV. This decreased binding is probably due in part to the fact that the polymethacrylic acid is only slightly ionized, so that the concentration of anionic sites is decreased. However, more recent experiments show that the smaller van der Waals interactions with the aliphatic polymer compared to the aromatic polystyrenesulfonate ion make even a greater contribution to the over-all binding of these metal complexes. Thus the dissociation data for the aliphatic polyelectrolyte system shows more similarity to the camphor sulfonate data than to the polystyrenesulfonate data. Unfortunately at the higher concentrations of complex required for the racemization studies the complex polymethacrylate separates from solution, so that it was not possible to study the effect on the racemization.

Dialysis experiments with polyvinylpyrrolidone and serum albumin are consistent with the kinetic data. The "cationic form" of serum albumin ($p$H 2.5–3.0) has no effect on the rate of dissociation, but in a borate buffer at $p$H 9 the rate is accelerated approximately 20%. Dialysis experiments show no association between the complex and the protein at $p$H 4, but some binding at $p$H 9. Both dialysis and rate experiments indicate no association with polyvinylpyrrolidone.

There is no ready explanation for the behavior with lauryl sulfate (Table IV). At concentrations of 0.0005 $M$ lauryl sulfate and greater the usual straight line first-order plot of the data is not obtained. Instead the line begins to decrease noticeably in slope beyond about the first 30% of the reaction. Therefore, the rate constants reported (Table IV) for the 0.00050 and 0.00100 $M$ lauryl sulfate reaction mixture were determined from the data collected during the initial 25% of the reaction. That association occurs is evident from the shift in the spectrum of the complex from 266 to 268 mμ found with solutions of 0.001 $M$ sodium lauryl sulfate. It may be significant that in this case the visible spectrum is also affected, being broadened and shifted 10 mμ toward longer wave lengths. The visible spectrum is generally unaffected by ionic association, and substitution in the phenanthroline rings themselves causes only small shifts.[10]

In all the previous discussion we have ignored the possibility of micelle formation by the large ions. The association between $Fe(phen)_3^{2+}$ and lauryl sulfate ions cannot be due to micelle formation because of the low concentrations used. However micelles are formed by 0.1 $M$ *d,l*-10-camphor sulfonate in 0.02 $M$ NaCl. Ultracentrifuge measurements[12] indicate an average molecular weight of a few thousand. The micelles would resemble the polyanions, and behave similarly with respect to their effect on the rate of dissociation. The less rigid structure of the micelle as compared to that of the polyelectrolyte would not be expected to cause a decrease in the rate of racemization as is caused by the polyelectrolyte.

**Acknowledgment.**—The authors wish to acknowledge that a few preliminary measurements on the effects of large ions were made by Dr. J. E. Dickens. They also thank Professor I. M. Klotz for many helpful suggestions, in particular with reference to the dialysis experiments.

(12) These measurements were made by Dr. L. Fuchs.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

# Complexes of Organic Phosphorus Compounds with Peroxymolybdic Acids[1]

BY ELLIS K. FIELDS

RECEIVED AUGUST 28, 1957

Organic compounds of phosphorus react with molybdenum trioxide and 90% hydrogen peroxide to form novel complexes that are derivatives of two peroxymolybdic acids, $H_2MoO_5$ and $H_2MoO_6$. Dialkyl and trialkyl phosphites, trialkyl phosphates, alkylphosphonic acids and triphenylphosphine have been converted in good yields. The complexes are shades of orange, from yellow to red. Heating to temperatures between 100 and 165° converts them to intense blue products that contain 1 or 2 oxygen atoms less. Orange and blue forms are soluble in most organic solvents; they are unaffected by light and air, but are decomposed by strong bases and acids.

Molybdenum compounds are of great industrial importance as catalysts in petroleum processes, as pigments and as enzymes. A series of molybdenum compounds that are relatively unknown are the molybdenum peracids. Peroxymolybdic acids $H_2MoO_5$, $H_2MoO_6$ and $H_2MoO_8$ have been mentioned, often without isolation of derivatives to prove the compositions.[2] Organic complexes of molybdenum with polybasic acids, polyhydric alcohols and phenols, β-diketones, aromatic amines, thiophenols and xanthates have been described.[3] However, no complexes of peroxymolybdic acids have appeared in the literature.

A variety of organic phosphorus compounds has been found to form complexes with molybdenum trioxide when reacting with hydrogen peroxide. These are the first complexes of organic phosphorus compounds with molybdenum to be reported. Twenty-four new complexes have been prepared in good yields from dialkyl and trialkyl phosphites, trialkyl phosphates, alkyl-phosphonic acids and triphenylphosphine. The properties of these complexes have been studied, and the probable structures have been deduced from elemental analyses, molecular weights, stoichiometry and infrared absorption data.

**Preparation of Complexes.**—The complexes formed upon adding 90% hydrogen peroxide to a stirred mixture of $MoO_3$ and the phosphorus compound. Less-concentrated peroxide also gave complexes, but 90% $H_2O_2$ was used to reduce hydrolysis effects. Such molybdenum compounds as $MoS_2$, $MoS_3$, $MoO_2$ and ammonium molybdate gave complexes, but $MoO_3$ gave the most consistent results; the other compounds functioned only insofar as they were first converted to $MoO_3$ by the hydrogen peroxide.

Phosphorus compounds were obtained commercially or synthesized. Six phosphate esters were obtained from Virginia-Carolina Chemical Corporation; tributyl phosphate and triphenylphosphine, from Eastman Kodak Co.; tri-2-ethylhexyl phosphate, from Carbide and Carbon Chemicals Company; and tri-butoxyethyl phosphate, from Ohio-Apex Company. The alkanephosphonic acids were prepared by peroxide-catalyzed addition of diethyl phosphite to 1-olefins to give alkanephosphonic esters in 74–80% yields[4] and hydrolysis of the resulting esters by stirring and refluxing with concentrated hydrochloric acid for 40 hours. 1-Olefins were obtained from Humphrey-Wilkinson Company. All esters were distilled *in vacuo*. The acids, ob-

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(1) Presented at the XVI International Congress of Pure and Applied Chemistry, Paris, France, July, 1957.

(2) E. Péchard, *Ann. chim. phys.*, [6] **28**, 537 (1893); G. Moeller, *Z. physik. Chem.*, **12**, 561 (1893); W. Muthmann and W. Nagel, *Ber.*, **31**, 1838 (1898); L. Pissarjewsky, *Z. anorg. Chem.*, **24**, 108 (1900); K. F. Jahr, *Chem. Zentr.*, **112**, **I**, 184 (1941); J. B. Martinez, *Anales fis. y. quim.* (*Madrid*), **40**, 348 (1944); *C. A.*, **44**, 968g (1950).

(3) A thorough bibliography is available in Bulletin Cbd-9, Climax Molybdenum Company, New York, New York, June, 1956.

(4) Dutch Patent 69,357, January 15, 1952, to N. V. de Bataafsche Petroleum Maatschappij.