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Mechanism of Racemization of Complex Ions. V. The Dissociation and Racemization of Tris-(2,2'-bipyridine)-iron(II) and Tris-(1,10-phenanthroline)-iron(II) Ions in Water–Methanol and Methanol Solutions[1,2]

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The rates of racemization of tris-(2,2'-bipyridine)-iron(II) and of tris-(1,10-phenanthroline)-iron(II) increase continuously with increasing methanol content of water–methanol mixtures, while the rates of dissociation display a maximum. The differences in the two rates suggest that in alcohol rich solvents racemization takes place essentially by an intramolecular process. There is a specific anion catalysis on the rates of dissociation. The observed results are discussed in terms of ion-pair formation and solvation of the complexes.

Detailed kinetic studies have been carried out on the rates of dissociation and racemization of the complexes of nickel(II) and iron(II) with 2,2'-bipyridine and 1,10-phenanthroline, respectively, e.g., $M(bipy)_3^{2+}$ and $M(phen)_3^{2+}$. In aqueous solution nickel(II) complexes were found to racemize by a dissociation mechanism[4] whereas the iron(II) complexes racemize largely by an intramolecular process and only in part by dissociation.[5]

Davies and Dwyer[6] have investigated the racemization of these complexes in several non-aqueous solvents and in water–organic solvent mixtures. Recently Wilkins and Williams[7] studied the exchange of 1,10-phenanthroline in the system Ni-$(phen)_3^{2+}$-*phen in various solvents. They observed that the dissociative path for racemization also persists in these solvents.

Except for a few preliminary observations[6] on the rates of racemization, the iron(II) complexes had not previously been studied in non-aqueous

(1) Previous paper in this series, A. Jensen, F. Basolo and H. M. Neumann, THIS JOURNAL, 80, 2354 (1958); presented in part at the Chicago Meeting of the American Chemical Society, September, 1958.

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

(3) Taken from a dissertation submitted by L. Seiden in partial fulfillment of the requirements for the Ph.D. at Northwestern University, Evanston, Illinois, 1957.

(4) F. Basolo, J. C. Hayes and H. M. Neumann, THIS JOURNAL, 75, 5102 (1953).

(5) F. Basolo, J. C. Hayes and H. M. Neumann, ibid., 76, 3807 (1954).

(6) N. R. Davies and F. P. Dwyer, Trans. Faraday Soc., 50, 1325 (1954).

(7) R. G. Wilkins and M. J. G. Williams, J. Chem. Soc., 1763 (1957).

solvents. The purpose of this paper is to report the results of kinetic studies on the rates of dissociation and racemization of $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ in water–methanol and methanol solutions.

Experimental

Materials.—The compounds used in this study were $[Fe(bipy)_3]Cl_2$, $[Fe(phen)_3]Cl_2$, $d-[Fe(bipy)_3](ClO_4)_2\cdot 2H_2O$ and $d-[Fe(phen)_3](ClO_4)_2\cdot 3H_2O$. The racemic chlorides were prepared by the method of Blau.[8] The complexes were resolved through the antimonyl tartrates and isolated as the perchlorates, as described by Dwyer and Gyarfas.[9]

The water–methanol solvent mixtures were prepared for each run as needed by direct weighing, using distilled water and anhydrous methyl alcohol, reagent grade absolute, further dehydrated by refluxing with magnesium turnings for several hours and then distilled from the residue of magnesium methoxide and magnesium hydroxide.[10]

Most of the determinations were done in solutions of hydrochloric acid, prepared by appropriate dilution from either an aqueous or an anhydrous methanolic HCl solution. The concentrations of both solutions were determined by titration with standard NaOH. Although the aqueous stock solution retained its standardization almost indefinitely, it was found that the HCl concentration ($4\ M$) in the methanol solution decreased appreciably after several days' storage at room temperature. This apparently was due to the reaction $CH_3OH + HCl \rightarrow CH_3Cl + H_2O$. This reaction was retarded by storage of the alcohol solution in a cold room at 5°. In this manner, it was possible to keep such solutions for periods of approximately one month without any appreciable change in titer.

(8) F. Blau, Ber., 21, 1077 (1888); Monatsh. Chem., 19, 647 (1898).

(9) F. P. Dwyer and E. C. Gyarfas, J. Proc. Roy. Soc. N. S. Wales, 83, 263 (1950); 85, 135 (1951).

(10) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 360.

Essentially this same procedure was followed to prepare reaction mixtures containing HBr instead of HCl. All other chemicals used in this study were of reagent grade.

Rates of Dissociation.—Rates of dissociation of Fe(bipy)$_3^{2+}$ and Fe(phen)$_3^{2+}$ at the different experimental conditions were determined spectrophotometrically by the method previously described.[5] The changes in optical density with time were measured at 520 mμ for Fe(bipy)$_3^{2+}$ and 510 mμ for Fe(phen)$_3^{2+}$. The initial complex concentrations were approximately 5 × 10⁻⁵ M, as this concentration afforded the most convenient absorbancy readings.

In the majority of experiments an acid was added to combine with bipyridine as it dissociated; acid concentrations ranged from 0.01 M to as high as 5 M. Swiss workers[11] have described an alternative procedure in which another transition metal ion is used to react with the dissociated bipyridine. Following this method we have in some cases used excess Ni²⁺ salts instead of acid. Under these conditions the iron(II) complexes are essentially completely dissociated at equilibrium. Since the optical density of the nickel(II) complexes formed is much less than that of the iron(II) complexes at the chosen wave lengths, only minor corrections had to be made.

Excellent first-order behavior was obtained in all cases with the Fe(bipy)$_3^{2+}$ complex. However, at low H⁺ concentrations in methanol, the plots for Fe(phen)$_3^{2+}$ showed curvatures which indicated that the dissociation was not proceeding to completion. In such cases, the initial slope of the line was used to compute k_{diss}. It also was observed that although the acidified solutions of both complexes in water go to a colorless equilibrium mixture, those in alcohol-rich solvents retain a yellowish tinge. The absorption of these residual solutions at the wave lengths used, however, was negligible, so that only minor corrections were necessary. The color was perhaps due to the oxidation of Fe²⁺ and the formation of some chloro complex of iron(III). Tests with SCN⁻ gave the characteristic red color for iron(III).

Racemization.—The rate of change of optical activity of the complex at different experimental conditions was followed using a Bellingham and Stanley polarimeter with a photomultiplier attachment and a sodium vapor lamp light source. Polarimetric measurements with these compounds are hampered by one experimental difficulty. Even when present in relatively low concentrations, the complexes yield highly colored solutions. Thus in order that sufficient light be transmitted, the solutions must be dilute so that the angle of rotation observed is low and the precision of kinetic data is poor. This limitation has been mentioned previously, and examination of the data obtained using the normal visual method of measurements shows considerable scatter.[12] By using the photomultiplier attachment, it was possible to make measurements on more concentrated solutions at lower light intensities and obtain greater precision.

The procedure for making optical rotation measurements on these solutions was essentially that previously described.[13] However, several complicating factors necessitated some modifications. The usual technique requires that the rotation of the sample and the light intensity remain constant during the time of measurement. In the cases studied, however, the complex ion is racemizing at a rapid rate, and in some solutions it is also simultaneously dissociating, so that the light intensity is rapidly changing. In such cases an arbitrary intensity value was selected, and readings were taken at 30 sec. intervals on alternate sides of the minimum at this prechosen intensity value. After the data for a given kinetic run had been collected, a plot of the two sets of values (readings on either side of the minimum) vs. time was made. The correct minimum position, the angle of rotation, at any given time then was calculated by averaging the points on the two curves corresponding to that time. These values of α were then plotted in the usual fashion, log α vs. time, and rate constant for racemization, k_{rac}, determined from the slope of the straight line, k_{rac} = −slope × 2.303.

The majority of the racemization runs were carried out in a one decimeter jacketed polarimeter tube, through which

(11) P. Lauger, S. Fallab and H. Erlenmeyer, *Helv. Chim. Acta,* **37,** 1050 (1954); H. Brintzinger, S. Fallab and H. Erlenmeyer, *ibid.,* **38,** 557 (1955).

(12) J. C. Hayes, Thesis, Northwestern University, Evanston, Illinois, 1953.

(13) C. Djerassi, E. W. Foltz and A. E. Lippman, THIS JOURNAL, **77,** 4354 (1955).

water at the appropriate temperature, ±0.1°, was circulated. This technique was not suitable for maintaining low temperatures during warm weather. For the low temperature experiments, a special apparatus was constructed. This consisted of a polarimeter tube sealed into an insulated vessel which contained a mixture of crushed ice and water. Attached to the polarimeter tube was a sintered glass funnel. The solvent was placed in this funnel and after it had come to temperature the solid complex was added and the solution filtered into the polarimeter tube. Measurements of optical rotation were taken as soon as the tube was full of solution.

Results and Discussion

The greater part of this investigation deals with Fe(bipy)$_3^{2+}$, but sufficient data were collected also on Fe(phen)$_3^{2+}$ to show its behavior under similar experimental conditions.

Dissociation.—Previous work[5,14] has shown that in aqueous solution the rate of dissociation of Fe(bipy)$_3^{2+}$ increases with H⁺ concentration, reaching a limiting value at 1 M acid, while the rate of dissociation of Fe(phen)$_3^{2+}$ decreases slightly with increasing acidity and ion concentration.[15]

The rate constants for the dissociation were measured in various methanol-water mixtures and at various HCl concentrations. It can be observed from Table I that for any given solvent composition the rate of dissociation of Fe(bipy)$_3^{2+}$ increases with increasing H⁺ concentration. Data in Table II permit a comparison of the rates of dissociation

TABLE I

DISSOCIATION OF Fe(bipy)$_3^{2+}$ IN WATER, WATER-METHANOL MIXTURES AND METHANOL AT 25.5°

Mole % CH₃OH	[HCl]	k_{diss} × 10² (min.⁻¹)	Mole % CH₃OH	[HCl]	k_{diss} × 10² (min.⁻¹)
0	1.2M	5.13	60	0.6	4.56
20	0.2	1.86		0.8	5.02
	.4	2.35		1.2	5.53
	.6	2.82	84	0.6	8.65
	.8	3.18		0.8	9.35
	1.2	3.50		1.2	10.6
40	0.2	1.99	100	0.8	13.9
	.4	2.67		1.2	15.4
	.6	3.11		1.6	16.4
	.8	3.48		2.0	16.9
	1.2	3.90		2.5	17.8
				3.0	17.7

of Fe(bipy)$_3^{2+}$ with Fe(phen)$_3^{2+}$ in 1.0 M HCl as a function of water–methanol solvent composition. The two complexes show a similar behavior in that their rates of dissociation rapidly increase in the region of high methanol content. One noticeable difference, however, is that for Fe(phen)$_3^{2+}$ there is a continual increase in rate of dissociation with increase in mole per cent. alcohol, whereas the rate of Fe(bipy)$_3^{2+}$ first decreases and then rapidly increases.

The effect of electrolytes other than HCl is shown in Table III. These data indicate that the effect is primarily a specific anion effect and that the effectiveness in accelerating the rate is approximately

Cl⁻ >> Br⁻ ~ CH₃C₆H₄SO₃⁻ > HSO₄⁻ ~ NO₃⁻ > ClO₄⁻

(14) J. H. Baxendale and P. George, *Trans. Faraday Soc.,* **46,** 736 (1950).

(15) J. E. Dickens, F. Basolo and H. M. Neumann, THIS JOURNAL, **79,** 1286 (1957).

TABLE II

DISSOCIATION OF $Fe(bipy)_3^{2+}$ AND $Fe(phen)_3^{2+}$ IN 1.0 M HCl WATER-METHANOL SOLUTIONS

Mole % CH₃OH	$Fe(bipy)_3^{2+}$, $k \times 10^2$ (min.$^{-1}$) 25.5°	30.4°	$Fe(phen)_3^{2+}$, $k \times 10^2$ (min.$^{-1}$) 25.5°
0	5.05	11.1	0.442
10	3.63	8.35	...
20(19)^a	3.46	7.60	0.603
30	..	7.83	...
40(37)	3.88	8.55	1.24
49	..	9.64	...
52(54)	..	9.90	2.42
60	5.32	11.6	...
70(68)	..	14.5	5.41
80	..	19.2	...
84(87)	10.2	...	12.6
90	..	24.8	...
100	14.7	31.5	...

^{a} The mole % CH₃OH in parentheses refers to the solvent used for $Fe(phen)_3^{2+}$.

TABLE III

EFFECT OF ADDED IONS ON THE DISSOCIATION OF $Fe(bipy)_3^{2+}$ AND $Fe(phen)_3^{2+}$ IN METHANOL SOLUTION AT 25.5°

Solution composition	$Fe(bipy)_3^{2+}$ $k \times 10^2$ (min.$^{-1}$)
0.0005 M NiCl₂	1.31
.001 M NiCl₂	1.70
.005 M NiCl₂	3.47
.01 M NiCl₂	4.49
.01 M NiCl₂ + 1.0 M LiCl	15.0
.01 M HCl + 0.5 M LiCl	12.7
.01 M HCl + 1.0 M LiCl	15.2
.01 M HCl + 1.5 M LiCl	18.1
.01 M HCl + 2.0 M LiCl	19.2
.01 M HCl + 2.5 M LiCl	20.1
.5 M HCl + 0.5 M LiCl	14.7
.5 M HCl + 1.0 M LiCl	17.1
.01 M HCl + 1.0 M LiBr	1.63
.01 M NiBr₂	0.73
.01 M NiBr₂ + 0.5 M LiBr	1.49
.01 M NiBr₂ + 1.0 M LiBr	1.60
.05 M HBr	1.16
.25 M HBr	1.51
.50 M HBr	1.71
1.0 M HBr	2.84
1.0 M HCl + 1.0 M HBr	7.70
1.0 M HCl + 0.5 M HBr	9.75
1.0 M HCl + 0.25 M HBr	11.5
0.5 M H₂SO₄	0.39
1.0 M H₂SO₄	0.79
1.0 M p-toluenesulfonic acid	2.13
1.5 M p-toluenesulfonic acid	2.24
0.01 M Ni(NO₃)₂	0.50
.01 M Ni(NO₃)₂ + 0.1 M LiNO₃	.66
.01 M Ni(NO₃)₂ + 1.0 M LiNO₃	.77
.005 M Ni(ClO₄)₂	.25
.05 M Ni(ClO₄)₂	.25
	$Fe(phen)_3^{2+}$
0.1 M HCl	4.33^a
.1 M HCl + 0.4 LiCl	6.43^a
.5 M HCl	6.55^a
.5 M HCl + 0.5 M LiCl	7.96^a

^{a} These last four values in the table are for $Fe(phen)_3^{2+}$ in 80 mole % CH₃OH.

This is markedly different from the small retardation effect of added ions in aqueous solution.[15] It is apparent that the increasing rate of dissociation of $Fe(bipy)_3^{2+}$ with increasing HCl concentration, unlike the behavior observed in the water system, is due primarily not to increasing H^+ concentration, but rather to the increasing Cl^- concentration. Because of this fact and also because both complexes show an anion catalysis in methanol, it is unlikely that the half-bonded mechanism[5,16] proposed for the acid-catalyzed reaction of $Fe(bipy)_3^{2+}$ in water is of much importance in methanol.

The kinetic effect of anions can be explained if ion-pairs are formed, and if the pairs then dissociate with rate constants larger than that of the "free" complex. Although ion-pair formation of this type is not favored in water,[15] it should be extensive in methanol because of the lower dielectric constant of the latter. Experimental evidence in favor of ion-pair formation is provided by the apparent inhibition of k_{diss} by HBr in the presence of 1 M HCl. Normally one would expect that the effects of Br^- and Cl^- acting together would be additive, and since Br^- acting alone increases k_{diss}, a corresponding increase should be observable in the mixtures. However, if one assumes ion-pair formation, with the chloride-complex pair having a higher dissociation rate than the bromide-complex pair, this effect is readily explainable. The formation of bromide ion-pairs necessarily decreases the population of chloride ion-pairs, thus lowering the effective rate constant.

An important geometrical feature of these complexes, as pointed out in the previous article,[1] is the existence of three major pockets between the planar ligands. In water-methanol solution these pockets normally will be occupied by six solvent molecules. Two types of ion-pairs appear possible: an *internal ion-pair* in which the anion displaces one or more solvent molecules of the hexa-solvated species, and an *external ion-pair* in which association between anion and complex does not cause displacement of the solvent molecules. Ion-pair formation of complex ions in solution can sometimes be detected by changes in the ultraviolet spectrum.[17] The absorption spectra of $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ in methanol were examined from 220 to 800 mμ, both in the presence and absence of varying concentrations, up to 1 M, of LiCl, LiBr and LiI. However, in no case was any significant difference obtained. Therefore, if associated species are present, their spectra are essentially identical with the spectrum of the "free" hexa-solvated complex ion.

Since the perchlorate ion, of the ions tested, has the smallest effect on the rates of dissociation of these complexes, the rates were measured in methanol solutions containing a minimum concentration of Ni(ClO₄)₂. These data are given in Table IV.

Racemization.—Insofar as possible the racemization rate constants, k_{rac}, were measured under the same experimental conditions as k_{diss}, so that meaningful comparisons might be made. The racemization rate constants for $Fe(bipy)_3^{2+}$ and Fe-

(16) P. Krumholz, *J. Phys. Chem.*, **60**, 87 (1956).
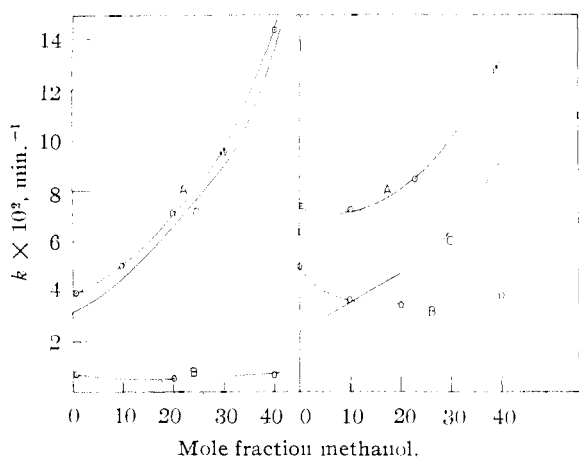
(17) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

Fig. 1.—Rates of negligible salt effects (left) end in 1 M HCl (right) for Fe(bipy)$_3{}^{2+}$ at 25°: A, k_{rac}; B, k_{diss}; C, $k_{rac} - k_{diss}$.

(phen)$_3{}^{2+}$ at various temperatures, acidities and solvent compositions are given in Table V. It is apparent from the data that the rate of racemization rapidly increases with an increase in methanol concentration of the solvent, in agreement with the earlier observations of Davies and Dwyer.[6]

TABLE IV

DISSOCIATION OF Fe(bipy)$_3{}^{2+}$ AND Fe(phen)$_3{}^{2+}$ IN 0.005 M Ni(ClO$_4$)$_2$ METHANOL SOLUTIONS AT 25.5°

Mole % CH₃OH	Fe(bipy)$_3{}^{2+}$ $k_{diss} \times 10^2$ (min.$^{-1}$)	Fe(phen)$_3{}^{2+}$ $k_{diss} \times 10^2$ (min.$^{-1}$)
0	0.70	0.44
20	.54	0.56
40	.75	..
60	1.08	1.19
80	1.20	1.23
100	0.25	0.25

TABLE V

RACEMIZATION OF Fe(bipy)$_3{}^{2+}$ AND Fe(phen)$_3{}^{2+}$ IN WATER, METHANOL AND WATER–METHANOL SOLUTIONS

Temp. (°C.)	Mole % CH₃OH	Fe(bipy)$_3{}^{2+}$ $k_{rac} \times 10^2$ (min.$^{-1}$)	Temp. (°C.)	Mole % CH₃OH	Fe(bipy)$_3{}^{2+}$ $k_{rac} \times 10^2$ (min.$^{-1}$)
3.8	0	0.087	25.5	20	7.14
	0	.076[a]		23	8.5[c]
	20	.115[a]		30	9.57
	40	.272		40	14.4[d]
	60	.73		39	12.8[a,d]
	79	1.26	30.4	0	9.68
	82	1.40		0	14.7[a,d]
	100	1.94[b]		10	11.9[d]
	100	1.85[a]		10	13.6[c,d]
	100	1.91		20	15.4[d]
7.4	100	3.15			Fe(phen)$_3{}^{2+}$
14.5	100	9.9	3.8	100	7.7
15.6	0	0.79	0.0	0	0.05
25.5	0	3.85		20	0.19
	0	7.4[c]		60	1.43
	10	5.03		80	3.19
	10	7.2[c]		100	4.33

[a] 1.0 M LiCl. [b] 2.0 M LiCl. [c] 1.0 M HCl. [d] Precision is low due to the rapidity of the reaction.

For each solution the rate of racemization via a purely intramolecular mechanism can be obtained by subtracting the rate of dissociation from

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the observed rate of racemization (Fig. 1). For solutions both with and without HCl the rate of intramolecular racemization of Fe(bipy)$_3{}^{2+}$ increases with increasing methanol content of the solvent. For a given alcohol–water composition the intramolecular rate is more rapid in the absence of acid, as expected, since the ratio of dissociation events to intramolecular racemization for the half-bonded species increases with increasing acidity.[5,18]

Since the rate of racemization increases much more rapidly than does the rate of dissociation with methanol enrichment of the solvent, it is clear that the intramolecular racemization path makes an increasing contribution to the rate of loss of optical activity in such solvents.
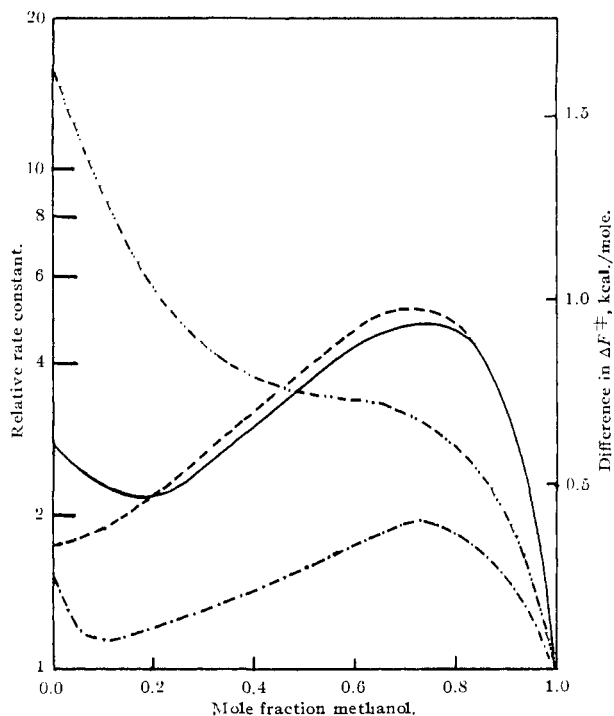

Fig. 2.—Dissociation rates for Fe(bipy)$_3{}^{2+}$ ————; Fe(phen)$_3{}^{2+}$, – – – –; Ni(bipy)$_3{}^{2+}$, —·—·—; Ni(phen)$_3{}^{2+}$ —··—··—; all in methanol–water mixture at 25°.

In aqueous 1 M HCl 32% of the racemization proceeds by intramolecular processes, but this rises to 70% in 40 mole % methanol. The corresponding values in the absence of HCl are 80 and 94%. Although the racemization rate in pure methanol at 25.5° is too rapid to be measured, a rate constant of 85 × 10^{-2} min.$^{-1}$ appears to be a reasonable estimate. Comparison with the dissociation rate of 0.25 min.$^{-1}$ (Table IV), demonstrates the great predominance of the intramolecular process in methanol.

In solutions of low methanol (Fig. 1) the rate of intramolecular racemization and the rate of dissociation differ significantly in their dependence on solvent composition. The increase in intramolecular rate with increasing methanol indicates that the replacement of water by methanol in the solvated ion increases the freedom of motion of the

(18) For a detailed mathematical treatment of the mechanism of racemization see reference 3.

ligands. Since it appears to be advantageous to consider the solvated species as the entity undergoing reaction, this effect will be referred to as an *ion-structure* effect.

Effect of Solvent Composition on Rate of Dissociation.—The effect of solvent composition on the rate of dissociation presents a complicated situation. It is informative at this point to compare the dissociative behavior of the four complexes, $Fe(phen)_3^{2+}$, $Fe(bipy)_3^{2+}$, $Ni(phen)_3^{2+}$ and $Ni(bipy)_3^{2+}$, in methanol–water mixtures. This comparison is displayed graphically in Fig. 2. The relative rate constant is the ratio of the rate constant for a given complex in a given solvent mixture to the rate constant for the same complex in pure methanol. The logarithm of the relative rate constant has been plotted and, since the difference in the free energies of activation is proportional to this quantity, the ordinate has been marked in terms of both quantities. The rate constants for the iron(II) complexes are derived from the data of Table IV and hence are concerned with conditions where the salt effects have been kept as small as possible. The rate constants for the nickel(II) complexes are derived from the racemization data of Davies and Dwyer,[6] and it has been established[7] that the racemization rates are the same as the dissociation rates. These racemization measurements also were made under conditions where the salt effects were negligible.

At least three factors must be in operation here: one operating in the low methanol region tending to give decreasing rates, another in the intermediate region to give increasing rates, and the last to give decreases for high methanol content. An ion-structure effect, like that apparent from the racemization results, would be expected to favor increasing rates; this is probably the dominant factor in the intermediate region. The factor tending to give decreased rates in the low methanol region may be the disturbance of the solvent surrounding the ion caused by the necessary expansion of the dissociating species. Both the viscosity[6] and the volume shrinkage on mixing[19] suggest that the energy requirements of this *solvent-structure* effect would be greatest about mole fraction 0.3 methanol, if the solvent surrounding the ion had the same structure as the bulk solvent. Since the latter cannot be so, no exact correlation can be expected.

The remaining point to be explained is the decrease in rate in the high methanol content region. The simplest explanation is to correlate this with the deficiency of water in the solvated ion. If the dissociation mechanism includes participation by water, then the decrease is understandable. Some support for this view is to be found in the fact that the decrease in rate normally observed in high methanol content solutions is not evident when chloride is present (Table II). This could be accounted for by an internal ion-pair, in which the chloride ion is performing the function normally performed by a water molecule, *i.e.*, filling a vacated coördination site.

(19) C. Carr and J. A. Riddick, *Ind. Eng. Chem.*, **43**, 692 (1951).

Evanston, Illinois

The Reaction of Bis-(cyclopentadienyl)-titanium(IV) Bromide with Different Chlorides in Various Solvents*

By Arne Jensen and Fred Basolo

The rates of reaction of bis-(cyclopentadienyl)-titanium(IV) bromide with lithium chloride and with benzyldimethyloctadecylammonium chloride to give bis-(cyclopentadienyl)-titanium(IV) chloride were investigated. The rate of reaction with the quaternary ammonium chloride in tetrahydrofuran and in benzene shows a first-order dependence on the concentration of the chloride. This suggests that the reaction takes place by a displacement (SN2) process. Lithium chloride, under the same experimental conditions in tetrahydrofuran, reacts approximately one-twentieth as fast as does the quaternary ammonium chloride and the rate of reaction does not depend upon the concentration of lithium chloride. It is believed that in this case the rate-determining step involves a nucleophilic displacement by the solvent. The analogous bis-(cyclopentadienyl)-zirconium(IV) bromide was found to react much too fast to be studied by the spectrophotometric method used.

The mechanisms of substitution reactions of octahedral and of square metal complexes have been rather extensively investigated.[1] However, there is very little information on substitution reactions of tetrahedral metal complexes. These systems are not numerous and in general they react too rapidly to be amenable to kinetic studies by conventional techniques. Some progress has recently been made by the investigation of reactions of metal carbonyls and substituted metal carbonyls. Keeley and Johnson[2] found that the rates of carbon monoxide exchange with benzene solutions of $Ni(CO)_4$, $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$ decrease in that order. They suggest that the exchange takes place by a displacement (SN2) mechanism. Meriwether and Fiene[3] observe that the rate of reaction of $Ni(CO)_2(PR_3)_2$ with PR_3' to yield $Ni(CO)_2(PR_3)(PR_3')$ does not depend on

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958.

(2) D. F. Keeley and R. E. Johnson, Meeting of the American Chemical Society, Miami, Florida, April, 1957; D. F. Keeley, Doctorate Thesis, Florida State University, Tallahassee, Florida.

(3) L. S. Meriwether and M. L. Fiene, private communication.