allowed to warm and distil slowly from one trap to another through the vacuum line. Approximately the first 1% and last 5% were set aside.

This procedure was repeated on the middle fraction several times until the product was found to be free from impurities on the basis of its infrared spectrum[5] and fractional codistillation[6] of a sample.

Irradiations were carried out in a 2-l. Pyrex glass flask equipped with a quartz finger containing a water-cooled Hanau 350-w mercury-arc lamp.

In a typical run 13.2 mmoles of oxalyl fluoride was condensed into the irradiation flask, 59.3 mmoles of oxygen was added, the flask was allowed to warm to room temperature, and irradiation was begun. After about 12 hr, irradiation was terminated. The products were bled through a trap held at $-183°$ and substances volatile at that temperature were pumped away. The remaining materials were separated by fractional codistillation and identified by infrared spectroscopy. The amounts were: 5.0 mmoles of COF_2 and SiF_4 (combined), 9.9 mmoles of CO_2, 0.4 mmole of $C_2O_4F_2$ impure with $C_2O_2F_2$, and 6.1 mmoles of pure $C_2O_4F_2$ (46% yield).

Bis(fluorocarbonyl) peroxide was identified by comparison of its infrared spectrum[7] with that of a sample prepared using Schumacher's synthesis, by its vapor density molecular weight (theoretical 126, found 129), and by liberation of iodine from aqueous potassium iodide.

It is probable that higher yields of the peroxide could be obtained by irradiating for shorter times and recycling the unreacted oxalyl fluoride after separation from $C_2O_4F_2$. Quantitative conversion is unlikely, however, since both oxalyl fluoride and bis(fluorocarbonyl) proxide decompose irreversibly under prolonged ultraviolet irradiation.

$$(FCO)_2 \xrightarrow{h\nu} COF_2 + CO$$

$$(FCO_2)_2 \xrightarrow{h\nu} COF_2 + CO_2 + {}^1/_2O_2$$

Bis(fluorocarbonyl) peroxide has been reported to decompose, and even explode at elevated temperatures.[1] Though no difficulties were encountered during this work, the compound was treated as if hazardous, and care was taken to maintain sample temperatures below 30°, with adequate shielding during manipulations.

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Rate-pH Profile for the Dissociation of Iron(II)- and Cobalt(II)-2,2′,2′′-Terpyridine Complexes

BY R. FARINA, R. HOGG, AND R. G. WILKINS[1]

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The dependence on pH of the rates of acid dissociation (hydrolysis) of metal complexes with a variety of bidentate ligands has been well studied.[2,3] It is believed that the proton acts as a scavenger for one released end of the bidentate ligand, giving a moderate accelerating effect on the rate with decreasing pH. Eventually a limiting rate is reached in sufficiently high acid concentration and the first-order rate constant in these conditions is equated to that of the metal–ligand bond rupture. The mechanism for acid dissociation of bidentate ligands capable of protonation should be equally adaptable to multidentate ligands also.[2] We report here on the effect of acid concentration on the dissociation of metal complexes containing the terdentate ligand 2,2′,2′′-terpyridine, using mainly $M(terpy)_2^{2+}$ ions and M = Fe and Co

$$M(terpy)_2^{2+} \rightleftharpoons M(terpy)(H_2O)_3^{2+} + terpy \qquad (1)$$

Experimental Section

Kinetics.—The rate of dissociation of $Fe(terpy)_2^{2+}$ in $[H^+] < 0.2\ M$ and of $Co(terpy)_2^{2+}$ in neutral (pH ~6) solutions was measured by ^3H–terpy exchange experiments.[4] The dissociation of $Co(terpy)_2^{2+}$ in dilute acid was effected by addition of ferrous ions.[5] Complete dissociation of $Fe(terpy)_2^{2+}$, $Co(terpy)_2^{2+}$, $Co(bipy)_3^{2+}$, and $Co(terpy)^{2+}$ in suitable concentration occurs at $[H^+] > 0.1\ M$ and was easily followed with a Cary 14 or a glass Lucite stopped-flow apparatus spectrally at 550, 520, 425, and 420 mμ, respectively. Dissociation of $Fe(terpy)_2^{2+}$ in high base concentration was also followed at 550 mμ in the presence of EDTA ($\sim 10^{-4}\ M$) to maintain a homogeneous solution,[6] although apparently this is not essential.[7] Complexes used in this study were prepared as described previously.[4] Excellent first-order kinetic plots were obtained in all cases. In all runs $[H^+]$ remained constant.

Results and Discussion

We can be certain that we are measuring reaction 1 in the acid dissociation experiments since the mono species both is less absorbing and dissociates at a slower rate than the bis. In the isotopic exchange experiments, also, only the equilibrium in (1) contributes to ligand interchange.[8] The first-order dissociation rate constants (k_{obsd}) for a number of complexes and conditions are shown in Table I. The variation of k_{obsd} with pH for the $Fe(terpy)_2^{2+}$ and $Co(terpy)_2^{2+}$ ions can be accommodated by the mechanism[9] shown in Scheme I. Stationary-state conditions are assumed, with B, C, D, and E in very small concentration.[10]

In the low $[H^+]$ region where dissociation follows the route $A \rightarrow B \rightarrow C \rightarrow$ products, the value of k_{obsd} is pH independent, and it is easily shown that

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[9] k_3, k_4, and k_5, as well as k_8, k_9, and k_{10}, may be composite first-order rate constants involving both terminal and middle nitrogen–metal bond rupture and formation. It is understood that another terpyridine molecule is coordinated to M throughout the reaction.

[10] As judged from pH measurements, there is no rapid production of protonated species when $Fe(terpy)_2^{2+}$ (0.01 M) is acidified (pH 2).

$$k_{\text{obsd}} = \frac{k_1k_3k_5}{k_2k_4 + k_2k_5 + k_3k_5} = k_a \tag{2}$$

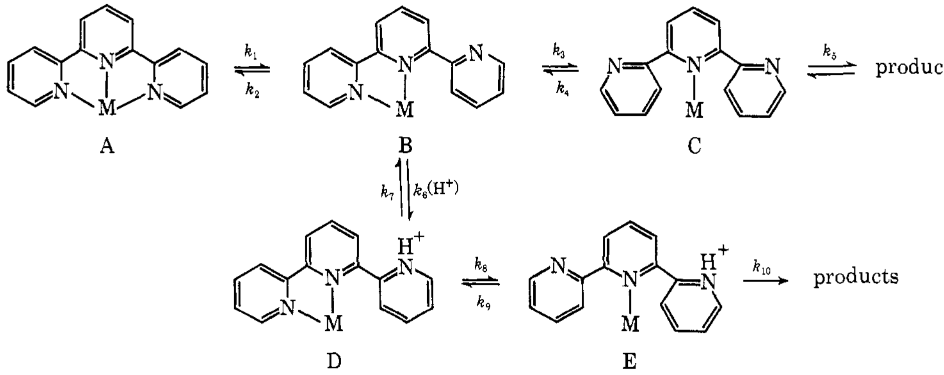
TABLE I

DISSOCIATION RATE CONSTANT FOR TERPYRIDINE AND BIPYRIDINE COMPLEXES

Complex ion	Temp, °C	$[H^+]$, M	k_{obsd}, sec^{-1}	k_{calcd},[e] sec^{-1}
$Co(terpy)_2^{2+}$	18.0	10^{-6}	8.0×10^{-4} [a]	1.0×10^{-3}
	18.0	3×10^{-5}	2.0×10^{-3} [b]	1.8×10^{-3}
	18.0	0.001	5.7×10^{-3} [b]	2.5×10^{-2}
	18.0	0.10	7.6×10^{-1} [b]	2.5
	18.0	0.5	12[b]	11
	18.0	1.0	22[b]	21
	0.2	1.0	2.9[b]	
	18.0	2.0	39[b]	43
	18.0	3.0	48[b]	47
$Co(bipy)_3^{2+}$	18.0	10^{-5}	0.7[c]	
	18.0	1.0	23	
	18.0	2.0	32	
$Co(terpy)^{2+}$	26.0	10^{-6}	10^{-4} [a]	
	26.0	0.5	0.3	
$Ni(terpy)_2^{2+}$	1.0	10^{-6}	7×10^{-8} [a]	
	1.0	2.0	5.8×10^{-3}	
$Fe(terpy)_2^{2+}$	35.0	10^{-6}	1.0×10^{-6} [d]	1.0×10^{-6}
	35.0	10^{-5}	1.0×10^{-6} [d]	1.1×10^{-6}
	35.0	0.0001	1.2×10^{-6} [d]	1.8×10^{-6}
	35.0	0.0004	4.0×10^{-6} [d]	4.2×10^{-6}
	35.0	0.0018	1.4×10^{-5} [d]	1.5×10^{-5}
	35.0	0.006	2.7×10^{-5} [d]	4.8×10^{-5}
	35.0	0.18	1.3×10^{-3} [d]	1.2×10^{-3}
	35.0	0.20	2.0×10^{-3} [b]	1.4×10^{-3}
	35.0	0.50	2.5×10^{-3} [b]	2.7×10^{-3}
	35.0	1.0	3.9×10^{-3} [b]	4.2×10^{-3}
	35.0	2.0	6.0×10^{-3} [b]	5.7×10^{-3}
	35.0	3.0	7.3×10^{-3} [b]	6.5×10^{-3}
	Temp, °C	p*H*	k_{obsd}, sec^{-1}	
	70.7	8.8	4.7×10^{-4}	
	70.7	10.7	1.3×10^{-3}	
	45.0	13.0	7.0×10^{-3}	

[a] Extrapolation of exchange data.[4] [b] $I = 3.0\ M$ using HNO_3–$NaNO_3$. [c] By adding terpyridine. [d] $I = 0.01\ M$ using HCl–NaCl. [e] On the basis of eq 4, see text.

SCHEME I



As the concentration of H^+ increases and when $[H^+] \sim K_D$ (the acid dissociation constant of D),[11] the route A → B → D → E → products becomes increasingly important. After it takes over (and then we justifiably assume that the A → B → C → E → products route is unimportant), relation 3 is obtained.

$$k_{\text{obsd}} = \frac{k_1k_6k_8k_{10}[H^+]}{k_2(k_7k_9 + k_7k_{10} + k_8k_{10}) + k_6k_8k_{10}[H^+]} = \frac{k_1k_b[H^+]}{1 + k_b[H^+]} \tag{3}$$

When $k_b[H^+] \ll 1$, $k_{\text{obsd}} = k_1k[H^+]$, and a first-order dependence on $[H^+]$ is predicted and observed. At sufficiently high $[H^+]$, $k_b[H^+] \gg 1$ and $k_{\text{obsd}} = k_1$. This limiting value is almost reached around $[H^+] \sim 3.0\ M$ with the $Fe(terpy)_2^{2+}$ system but the limiting trend is barely noticeable with $Co(terpy)_2^{2+}$. In the region where the limiting trend is commencing, *i.e.*, fairly high acidity, $k_b[H^+] \approx 1$ and therefore $(k_{\text{obsd}})^{-1} = (k_1)^{-1} + (k_1k_b[H^+])^{-1}$ so that the linear plot of $(k_{\text{obsd}})^{-1}$ against $[H^+]^{-1}$ gives an intercept of $(k_1)^{-1}$ and this is how this value was obtained.

If the scheme is considered *in toto*

$$k_{\text{obsd}} = \frac{\dfrac{k_1k_3k_5}{k_2(k_4 + k_5)} + k_1k_b[H^+]}{1 + \dfrac{k_3k_5}{k_2(k_4 + k_5)} + k_b[H^+]} \sim \frac{k_a + k_1k_b[H^+]}{1 + k_b[H^+]} \tag{4}$$

The approximation in (4) can be made if the reasonable assumptions $k_2 \gg k_3$ and $k_4 > k_5$ are made. Our results over a 10^6-fold range of $[H^+]$ agree well with the approximate form of (4) if, for iron, $k_a = 1.0 \times 10^{-6}\ \text{sec}^{-1}$, $k_1 = 9.0 \times 10^{-3}\ \text{sec}^{-1}$, and $k_b = 0.9\ M^{-1}$ at 35° and, for cobalt, $k_a = 1.0 \times 10^{-3}\ \text{sec}^{-1}$, $k_1 = 125\ \text{sec}^{-1}$, and $k_b = 0.2\ M^{-1}$ at 18°. The agreement between k_{obsd} and k_{calcd} is shown in Table I and is seen to be very good except for the dissociation of $Co(terpy)_2^{2+}$ in the pH 1.0–3.0 region. This was affected by the addition of Fe(II) ion; the reaction did not go to completion and the rate was slightly dependent on $[Fe^{2+}]$, so that only an order for the dissociation rate was probably measured. From fragmentary data for $Ni(terpy)_2^{2+}$, $k_a = 7 \times 10^{-8}\ \text{sec}^{-1}$ and $k_1 \approx 5.8 \times 10^{-3}\ \text{sec}^{-1}$ at 0°.

In the neutral region, since $k_2 \gg k_3$ and $k_4 > k_5$, then (2) reduces to $k_{\text{obsd}} = k_1k_3k_5/k_2k_4$. We have previously used this value for k_{obsd} in conjunction with k_f (the reverse of k_5) to estimate K_2, the formation constant for the bis(terpyridine) complexes.[5] There is at least a 10^4-fold increase in the rate constant from neutral (k_a) to strongly acid solution ($\sim k_1$) and this simply reflects the high ratio for k_2k_4/k_3k_5 (formation rate constants/dissociation rate constants). The striking dependence of rate on pH is also shown (from a few experiments) by $Ni(terpy)_2^{2+}$ and even a mono species, $Co(terpy)^{2+}$.

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[11] From the results, this places $pK_D \sim 4$, which is understandably close to that of pK_2 for terpyridine (3.3 at 25°: P. O'D. Offenhartz, P. George, and G. P. Haight, Jr., *J. Phys. Chem.*, **67**, 116 (1963)).

The behavior contrasts strongly with that of the bipyridine complexes, $M(bipy)_3^{2+}$. The corresponding ratios are 6.0^{12} (M = Fe), 40 (M = Co), and 4.0^{12} (M = Ni). However the limiting values which we equate to k_1 are quite similar for the highest bipyridine and terpyridine complex of a particular metal, *e.g.*, $Fe(bipy)_3^{2+}$ dissociates[12a] in 1.5 *M* HCl with a first-order rate constant 3.5×10^{-3} sec^{-1} at 35°, remarkably close to that for $Fe(terpy)_2^{2+}$, 9.0×10^{-3} sec^{-1}. For $Co(bipy)_3^{2+}$, $k_1 =$ 32 sec^{-1} and, for $Co(terpy)_2^{2+}$, $k_1 \sim 125$ sec^{-1}, both at 18°. Finally for $Ni(bipy)_3^{2+}$, $k_1 = 3.8 \times 10^{-4}$ sec^{-1} [12b] and, for $Ni(terpy)_2^{2+}$, $k_1 \sim 5.8 \times 10^{-3}$ sec^{-1} at 1.0°. It thus appears that the rate constant for rupture of a pyridine nitrogen–metal bond is only slightly smaller when it is part of a single ring (bipyridine) than when it forms part of a double ring (terpyridine) system. Both are, of course, much smaller than in the metal–pyridine complex itself. The order of kinetic stability of the metal–nitrogen bond measured by k_1 is Fe > Ni > Co.

Burgess and Prince[7] have shown that the dissociation of $Fe(terpy)_2^{2+}$ is strongly base catalyzed and our own work is in agreement with this. There is no indication that a limiting rate is reached in strong base, but, for example, at 35° and in 0.12 *M* OH^-, the first-order rate constant[7] is 4.4×10^{-3} sec^{-1}, of the same order as the corresponding value in 0.1 *M* H^+. It appears that both OH^- and H^+ can prevent rejoining of severed M–N bonds in terpyridine complexes by attaching themselves to vacated positions of the metal ion or the basic nitrogen.[2]

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Further Evidence of Stereochemical Nonrigidity in Five- and Seven-Coordinate Structures

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We present evidence of stereochemical nonrigidity[1] in five- and seven-coordinate molecules.[2] The seven-coordinate species were derived from complexes of molybdenum and tungsten hexafluorides, and the five-coordinate molecule is $(C_6H_5)_2NPF_4$ kindly furnished us by Dr. R. Schmutzler.

The acceptor activity of metal hexafluorides has been established relative to fluoride ion[3] and organic donor molecules;[4] however, the structures of the resulting complexes have not been determined although in Na_2UF_8 preliminary analysis of X-ray data indicates the uranium atom is coordinated to eight fluorine atoms.[3b] We have reexamined the F^{19} spectra of tungsten and molybdenum hexafluoride complexes with organic bases and find a fairly rigorous demonstration of seven-coordination in $WF_6 \cdot P(CH_3)_3$.

The F^{19} spectrum (56.4 and 94 Mc) of $WF_6 \cdot P(CH_3)_3$ dissolved in acetonitrile or in sulfur dioxide consists of a major doublet due to PF coupling with W^{183}–F^{19} satellite doublets. The doublet resonance was unperturbed down to the lowest temperatures (∼−85°) possible with these solutions. These data are nearly conclusive[5] for a monomolecular complex with the phosphine and six fluorine atoms bound to the tungsten atom. Strict equivalence of fluorine atoms in $WF_6 \cdot P(CH_3)_3$ is not possible in any of the idealized seven-coordinate geometries.[2] Spectroscopic equivalence may be a reflection of a very small fluorine chemical shift or a rapid intramolecular rearrangement through which fluorine atom environments are averaged. We favor the latter alternative.[2,6] This observation of nmr spectroscopic equivalence of ligand atoms is characteristic of many seven-coordinate structures.[2,6]

Tungsten hexafluoride complexes with nitrogen bases were prepared, *e.g.*, $WF_6N(CH_3)_3$, and solution spectroscopic equivalence of fluorine atoms was observed; however, the possibility of equivalence having genesis in a fast base dissociation

$$WF_6N(CH_3)_3 \rightleftharpoons WF_6 + N(CH_3)_3$$

could not be eliminated because, unlike the nmr spectrum of the phosphine adduct, there was no observable spin–spin coupling between fluorine atoms and magnetic nuclei associated with the amine ligand. Interestingly the less sterically hindered amine, pyridine, yielded with WF_6 the complex $WF_6(NC_5H_5)_2$ in addition to a 1:1 adduct. The single-line F^{19} resonance of $WF_6NC_5H_5$ (−164 ppm) is shifted slightly to high field of WF_6 (−166 ppm) and the single line of $WF_6(NC_5H_5)_2$ appears at still higher field (−136 ppm, 25°). The chemical shift of the 1:2 adduct is temperature dependent (−122 ppm, −30°) and the change in chemical shift with temperature is consistent with the equilibrium

$$WF_6(NC_5H_5)_2 \overset{\Delta}{\rightleftharpoons} WF_6(NC_5H_5) + NC_5H_5$$

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[5] We found no other F^{19} resonance that could be attributed to a fluoride ion; and, in any case, a species such as $WF_5P(CH_3)_3{}^+F^-$ should exhibit fluorine atom nonequivalence for the octahedral cation. The P^{31} nmr spectrum would unequivocally establish the number of fluorine atoms bound to tungsten. However, we have not the spectrometer sensitivity to obtain the detailed fine structure with these dilute (with respect to number of phosphorus atoms) solutions.

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