peaks identified as P − CO (*m/e* 375) and P − NO (*m/e* 373) were both observed, but the ion P − CO was present in much greater abundance (8:1) than the ion P − NO. Thus, the carbonyl group is much more readily lost from the parent ion than is the nitrosyl group, as is usually found in mixed carbonyl–nitrosyl complexes. The preferential loss of carbonyl groups is also a common feature in the chemical reactions of mixed carbonyl–nitrosyl complexes. The reactions described above are typical: when other ligands such as tertiary phosphines or arsines react with complexes containing both nitrosyl and carbonyl groups, carbon monoxide is almost always the ligand which is displaced. Exchange reactions between carbon monoxide have been studied and the rates of exchange are rather rapid. However, the exchange between nitric oxide and the nitrosyl group is very much slower, if it takes place at all.[15,16] These facts all point to the conclusion that the metal–nitrogen bond in nitrosyls is substantially stronger than the metal–carbon bond in metal carbonyls. Infrared studies also show that the metal–nitrogen force constants are greater than metal–carbon force constants in this class of compounds.[17]

The infrared spectra of these complexes were obtained, and the carbonyl and/or nitrosyl frequencies are listed in Table IV. The decrease in the stretching frequencies of the carbonyl and nitrosyl groups indicate that there is a substantial increase in the π bonding between the metal and the carbonyl or nitrosyl group on replacement of CO groups by the arsine ligand.

TABLE IV

INFRARED SPECTRAL DATA FOR DISUBSTITUTED DERIVATIVES OF $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$, AND $Ni(CO)_4$

Compd	Str freq, cm^{-1}	Ref
$Fe(NO)_2(das)$	1716 (NO), 1660 (NO)	*a*
$Fe(NO)_2[As(C_6H_5)_3]_2$	1732 (NO), 1690 (NO)	*b*
$Co(CO)(NO)(das)$	1940 (CO), 1710 (NO)	*a*
$Co(CO)(NO)[P(C_6H_5)_3]_2$	1957 (CO), 1717 (NO)	*c*
$Ni(CO)_2(das)$	1996 (CO), 1931 (CO)	*d*
$Ni(CO)_2$(*cis*-edas)	2000 (CO), 1935 (CO)	*a*

[a] This work. [b] D. W. McBride, S. L. Stafford, and F. G. A. Stone, *Inorg. Chem.*, **1**, 386 (1962). [c] W. D. Horrocks, and R. C. Taylor, *ibid.*, **2**, 723 (1963). [d] Reference 6.

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Racemization and Oxygen-18 Exchange Studies of Heterochelate Chromium(III) Complexes. II. The Cations Oxalatobis(2,2′-bipyridine)chromium(III), Oxalatobis(1,10-phenanthroline)chromium(III), and Oxalatobis(ethylenediamine)chromium(III)

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The kinetics of racemization and oxygen-18 exchange for $Cr(ox)bipy_2^+$, $Cr(ox)(phen)_2^+$, and $Cr(ox)(en)_2^+$ (where ox = oxalate ion, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline) have been studied in acid solution. Racemization of $Cr(ox)(bipy)_2^+$ is markedly acid dependent whereas $Cr(ox)(phen)_2^+$ shows little acid dependence. Both complexes show distinct racemization rate dependences on addition of various anions or cations. An intramolecular racemization mechanism accounts for the overall behavior. The $Cr(ox)(en)_2^+$ complex is hydrolyzed readily in acid media and this contributes largely to loss of optical activity. All three cationic complexes show acid-catalyzed exchange of all their oxalate oxygens with solvent water. The four oxalate oxygens are kinetically indistinguishable. The exchange reactions are uniformly first order in acid and in complex. Arrhenius parameters for oxygen exchange and for racemization have been measured. Two mechanisms for oxygen exchange are consistent with the data and involve either oxalate ring opening or rapid carbonyl–carboxyl oxygen interchange.

Introduction

In a previous paper[2] we described racemization and oxygen-18 exchange behavior for anionic chromium(III) complexes as part of a systematic study on metal–oxalate complexes. In this paper we give results of work with the cationic complexes $Cr(ox)(bipy)_2^+$ and $Cr(ox)(phen)_2^+$ (bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, ox = oxalate ion) together with a reinvestigation of $Cr(ox)(en)_2^+$ (en = ethylenediamine).

Some preliminary findings on oxygen-18 exchange have been published.[3] Werner[4] first reported that $Cr(ox)(en)_2^+$ racemized in aqueous solution and Bushra and Johnson[5] subsequently ascribed the rotation loss to

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[1] (a) Australian National University. (b) University of Queensland.

[2] J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, **9**, 1243 (1970).

[3] (a) J. A. Broomhead, N. Kane-Maguire, I. Lauder, and P. Nimmo, *Chem. Commun.*, 747 (1968); (b) J. A. Broomhead, I. Lauder, and P. Nimmo, *ibid.*, 652 (1969).

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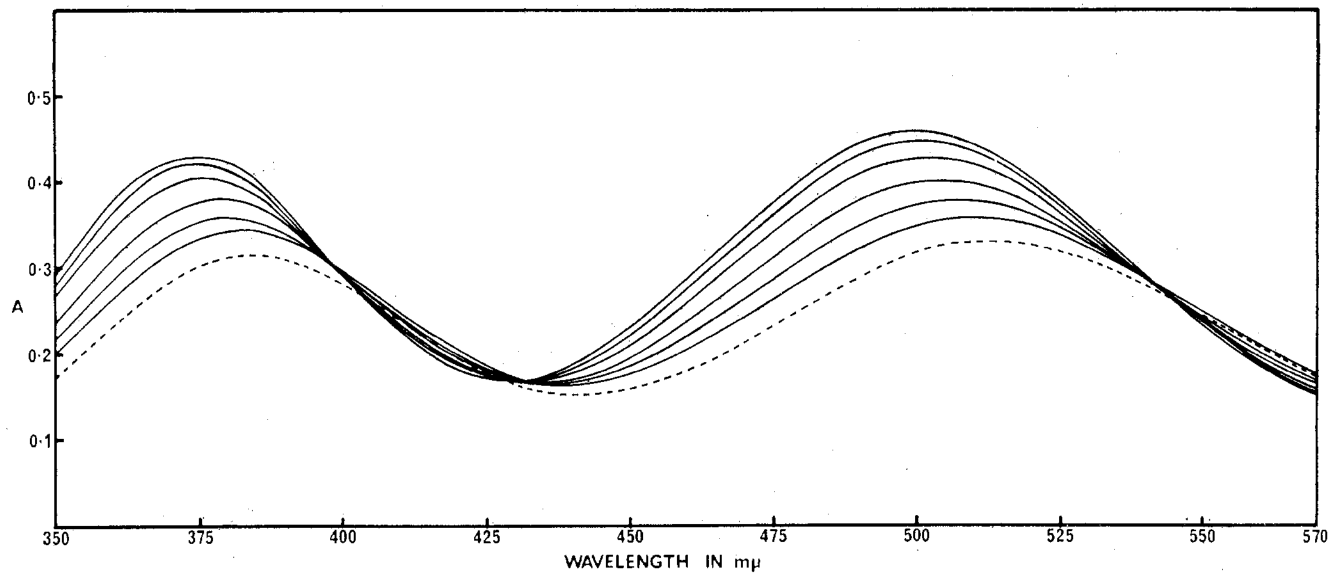

Figure 1.—Absorption spectral time scans for Cr(ox)(en)$_2^+$ in 1 *M* perchloric acid at 50°. Upper curve at zero time followed by scans at 5.5, 14, 27.5, 41, 55, and 72 min (lower curve), respectively.

decomposition. No kinetic studies have been made previously with Cr(ox)(en)$_2^+$ which was of interest for comparison with its aromatic amine counterparts.

Experimental Section

Materials.—Cr(ox)(bipy)$_2^+$, Cr(ox)(phen)$_2^+$, and Cr(ox)(en)$_2^+$ were prepared and resolved by literature methods.[4-6] Oxygen-18-enriched (by 1.55%) water was obtained from Yedda Research and Development Co., Rehovoth, Israel. Other reagents used were as described previously.[2]

Methods.—Racemization rates were determined using a Perkin-Elmer 141 automatic polarimeter and sodium or mercury lamp light sources. Initial rotations of about 1° in a 10-cm tube could be measured within ±0.002°. Rate constants calculated from the slopes of the log (degrees rotation) *vs.* time plots have a reproducibility of ±1% and an accuracy of ±2%. Reactions were studied for times corresponding to at least 90% racemization. Precautions were taken to protect Cr(ox)(en)$_2^+$ from the light.

Oxygen-18 exchange experiments followed methods previously described and involved precipitation of the complexes from acid solutions as their triiodide salts. For Cr(ox)(en)$_2^+$ there was no contamination due to the precipitation of hydrolysis products. Thermal decomposition and isolation of the CO_2 liberated followed the methods previously given,[2] except that an extra trap (acetone–Dry Ice) was needed in the vacuum line to condense iodine liberated early in the combustion. The complexes were also dissolved in unbuffered oxygen-18-enriched water at 33° and samples isolated after 25 hr. The values of the 46/44 ratios for the carbon dioxide obtained on thermal decomposition of each complex were all 430×10^{-5}. These are to be compared with the value of 421×10^{-5} which is found for normal carbon dioxide and the value of 2760×10^{-5} calculated on the basis of complete oxygen exchange under the same conditions.

Absorption Spectral Studies.—Since acid solutions were necessary to effect oxygen-18 exchange, the spectra of the cations Cr(ox)(bipy)$_2^+$ and Cr(ox)(phen)$_2^+$ in 1 *M* hydrochloric acid at 25° were recorded on a Cary 14 spectrophotometer. The spectra were scanned repeatedly over a time interval of 37 hr and were found to be unchanged. However evidence for aquation at higher acidities was found for 8 *M* nitric acid solutions. The spectra of Cr(ox)(phen)$_2^+$ after 13 hr and Cr(ox)(bipy)$_2^+$ after 7 hr at 25° in 8 *M* HNO_3 agreed with published spectra of Cr(H_2O)$_2$(phen)$_2^{3+}$ and Cr(H_2O)$_2$(bipy)$_2^{3+}$, respectively.[7,8]

The ethylenediamine complex Cr(ox)(en)$_2^+$ shows significant acid hydrolysis even in 1 *M* acid in contrast to the aromatic base analogs. Spectral changes take place in either nitric, hydrochloric, or perchloric acid media with displacement of the parent absorption peaks to longer wavelengths. A typical reaction spectrum is shown in Figure 1 for 1 *M* perchloric acid solutions at 50°. In the initial stages of reaction three isosbestics are evident at 400, 432, and 540 mμ. After approximately 1 hr these begin to shift ultimately producing three new isosbestics at 428 and 578 mμ (not shown). It appears likely that the ethylenediamine ligands are involved in these changes. This conclusion is based on the close similarity of the spectrum of hydrolyzed Cr(ox)(en)$_2^+$ with that reported by Veigel[9] for hydrolyzed α-Cr(ox)(trien)$^+$ together with the failure of the similar Cr(ox)(bipy)$_2^+$ and Cr(ox)(phen)$_2^+$ to undergo an analogous reaction. Veigel found evidence for a single hydrolysis product Cr(ox)(H_2O)trienH^{2+} (where trienH = triethylenetetramine with one end uncoordinated but protonated). A comparison of the spectra of the complexes and of their hydrolysis products is made in Table I. The ethylenediamine complex was obtained by ion-exchange chromatography of the cooled reaction mixture from the hydrolysis of [Cr(ox)(en)$_2$]Br (0.04 g) at 70° for 28 min in perchloric acid (20 ml, 2.5×10^{-2} *M*). At this stage the reaction spectrum indicated completion of the initial hydrolysis and participation of the subsequent stage. Two bands were eluted from the column (Bio-Rad Ag 50W-X4) using 1 *M* perchloric acid. The first fraction when mixed with Cr(ox)(en)$_2^+$ gave the same three initial isosbestic points as were generated in the hydrolysis reaction, thus suggesting that the first fraction corresponded to the primary hydrolysis product Cr(ox)H_2O(en)enH^{2+} (enH = half-bonded ethylenediamine with the uncoordinated nitrogen protonated).

TABLE I
ABSORPTION MAXIMA (λ_{max}, mμ) AND EXTINCTION COEFFICIENTS (*E*, M^{-1} cm^{-1}) FOR Cr(ox)(en)$_2^+$ AND α-Cr(ox)trien$^+$ AND THEIR ACID HYDROLYSIS PRODUCTS

Complex	λ_{max}	*E*	λ_{max}	*E*
Cr(ox)(en)$_2^+$	371	87	493	91
α-Cr(ox)trien^{+} [a]	370	104	495	147
Cr(ox)H_2O(en)enH^{2+}	391	65	521	64
Cr(ox)H_2OtrienH^{2+} [a]	392	63	520	63

[a] Reference 9.

Results

Methods of calculating rate constants for racemization and for ^{18}O exchange have been given previously.[2] The acid dependence of the racemization rate constants for Cr(ox)(bipy)$_2^+$, Cr(ox)(phen)$_2^+$, and Cr(ox)(en)$_2^+$

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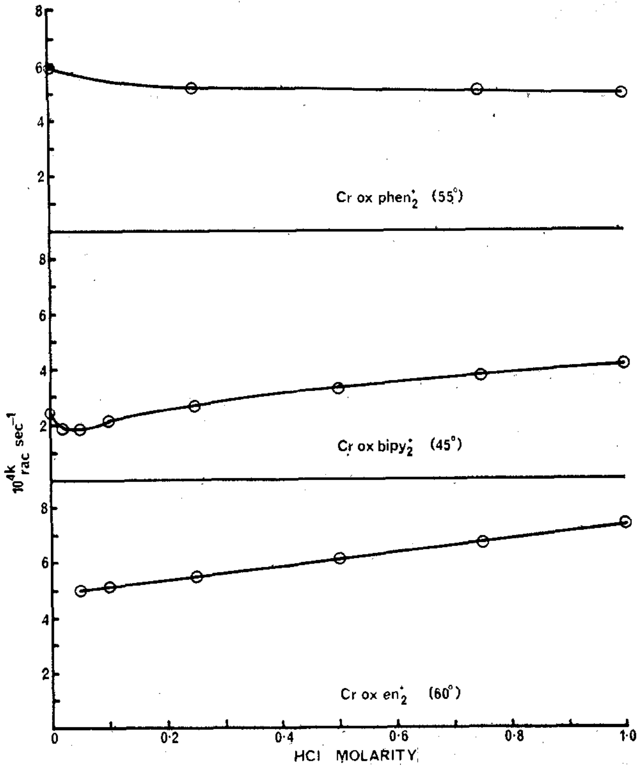

Figure 2.—Acid dependence of racemization rate constants for $Cr(ox)(phen)_2^+$, $Cr(ox)(bipy)_2^+$, and $Cr(ox)(en)_2^+$ at unit ionic strength in hydrochloric acid solutions.

is shown in Figure 2 for aqueous solutions and for solutions up to 1 *M* in hydrochloric acid.

Measurements of the temperature dependences of the rates lead to the Arrhenius parameters given in Table II. Good adherence to first-order kinetics was found for all three complexes in acid solutions. It is interesting that in the absence of acid the $Cr(ox)(en)_2^+$ complex behaves differently. Plots of log (rotation) *vs.* time are curved to smaller slopes initially and then become linear. The reaction is also accompanied by a color change from orange to red.

TABLE II

ARRHENIUS PARAMETERS FOR THE RACEMIZATION OF CHROMIUM(III) COMPLEXES IN 1 *M* HCl

Complex ion	10^4k,[a] sec^{-1}	E_a, kcal mol^{-1}	ΔS^*, eu
$Cr(ox)(bipy)_2^+$	10.6[b]	19.6 ± 0.2[d]	−14.5 ± 0.8[d]
$Cr(ox)(bipy)_2^+$	6.60[b,f]	20.6 ± 0.2	−12.6 ± 0.8
$Cr(ox)(phen)_2^+$	4.92[b]	20.4 ± 0.2	−13.6 ± 0.6
$Cr(ox)(en)_2^+$	7.35[c,e]	21.1 ± 0.2	−12.0 ± 0.6

[a] Reproducibility ±1%. [b] At 55°. [c] At 60°. [d] Errors are the standard deviations of the least-squares plots. [e] Includes hydrolysis reactions. [f] 1 *M* KCl, no acid.

Tables III and IV give the kinetic results on acid-catalyzed oxygen-18 exchange for each of the three complexes under investigation. From these data the Arrhenius parameters shown in Table V have been calculated. Exchange rate constants k_E have been calculated as described in part I with the exception that *n*, the number of kinetically indistinguishable oxygen atoms in the complex, has the value 4. Linear pseudo-first-order rate plots were obtained for each complex over at least 3 exchange half-lives thus demonstrating that all four oxalate oxygens were exchanging at the same rate. Typical rate plots for each complex are shown in Figure 3.

TABLE III

KINETIC DATA FOR THE ACID-CATALYZED EXCHANGE OF OXYGEN BETWEEN WATER AND $Cr(ox)(bipy)_2^+$, $Cr(ox)(phen)_2^+$, AND $Cr(ox)(en)_2^+$ AT UNIT IONIC STRENGTH

[HCl], *M*	[Complex], *M*	Temp, °C	10^4k_E,[d,e] M^{-1} sec^{-1}
1.00	0.036[a]	25	2.75 ± 0.08
1.00	0.036[a]	33	5.86 ± 0.19
1.00	0.018[a]	33	6.13 ± 0.06
0.50	0.029[a]	33	3.20 ± 0.02
0.25	0.022[a]	33	1.67 ± 0.02
10^{-7}	0.036[a]	33	0.0
1.00	0.036[a]	40	12.0 ± 0.1
1.00	0.0024[b]	25	2.71 ± 0.01
1.00	0.0024[b]	33	5.76 ± 0.05
0.50	0.0024[b]	33	3.05 ± 0.03
10^{-7}	0.011[b]	33	0.0
1.00	0.0029[b]	40	11.3 ± 0.2
1.00	0.015[c]	25	2.76 ± 0.03
1.00	0.015[c]	33	5.64 ± 0.12
0.50	0.019[c]	33	2.69 ± 0.05
10^{-7}	0.015[c]	33	0.0
1.00	0.017[c]	40	11.0 ± 0.1

[a] $Cr(ox)(bipy)_2^+$. [b] $Cr(ox)(phen)_2^+$. [c] $Cr(ox)(en)_2^+$. [d] $k_E = k'[H^+]$; see ref 2. [e] Linear rate plots obtained by the method of least squares. The errors are the standard deviations of the slopes.

TABLE IV

COMPARISON OF CALCULATED AND OBSERVED 46/44 MASS RATIO VALUES ON THE ASSUMPTION OF COMPLETE OXYGEN EXCHANGE AT INFINITE TIME FOR 1 *M* HYDROCHLORIC ACID SOLUTIONS AT 33°

Complex	Reaction time, min	10^5R_∞ Obsd	10^5R_∞ Calcd
$Cr(ox)(phen)_2^+$	250[a]	2350	2600
$Cr(ox)(bipy)_2^+$	365[a]	1701	1825
$Cr(ox)(en)_2^+$	262[a]	2317	2600

[a] Approximately 3 half-lives based on k_E.

TABLE V

RATE CONSTANTS, ARRHENIUS PARAMETERS, AND ENTROPIES OF ACTIVATION FOR OXYGEN EXCHANGE BETWEEN WATER AND CHROMIUM(III) COMPLEXES IN 1 *M* HYDROCHLORIC ACID

Complex	10^4k_E,[a] sec^{-1}	E_a, kcal mol^{-1}	Log *A* (*A* in sec^{-1})	ΔS^*, eu
$Cr(ox)(bipy)_2^+$	2.75	18.0 ± 0.7[b]	9.6	−17 ± 2.3[b]
$Cr(ox)(phen)_2^+$	2.71	17.6 ± 0.4	9.3	−18 ± 1.4
$Cr(ox)(en)_2^+$	2.76	17.0 ± 0.6	8.9	−20 ± 2.0

[a] $k_E = k'[H^+]$; at 25°. [b] Errors are the standard deviations of the least-squares plots.

During these experiments the ionic strength was held constant by addition of potassium chloride. However no truly indifferent ionic medium could be found as is shown by the rate constant variations in the presence of various electrolytes (Table VI).

TABLE VI

EFFECTS OF VARIOUS IONS ON THE RACEMIZATION RATE CONSTANTS OF $Cr(ox)(bipy)_2^+$ AND $Cr(ox)(phen)_2^+$ AT 55°

	10^4k, sec^{-1}			10^4k, sec^{-1}	
Solution	$Cr(ox)(phen)_2^+$	$Cr(ox)(bipy)_2^+$	Solution	$Cr(ox)(phen)_2^+$	$Cr(ox)(bipy)_2^+$
H_2O	6.56	7.39	1 *M* KNO_3	4.88	5.30
1 *M* LiCl	7.86	8.80	0.23 *M* KNO_3	6.14	6.50
1 *M* NaCl	5.35	...	0.25 *M* $CuCl_2$[a]	5.56	5.16
1 *M* KCl	5.88	6.60			

[a] Ionic strength adjusted with KCl to 1.25.

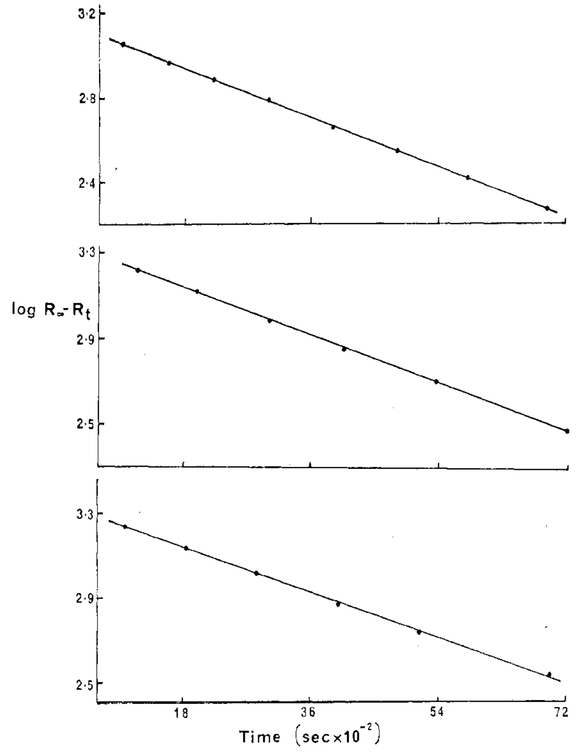

Figure 3.—Typical oxygen-18 exchange rate plots for 1 *M* HCl solutions at 40° and unit ionic stength: $Cr(ox)(bipy)_2^+$, upper plot; $Cr(ox)(phen)_2^+$, middle plot; $Cr(ox)(en)_2^+$, lower plot.

Discussion

The data of Table III fit an oxygen exchange rate law of the form rate = $k'[H^+][complex]$. There is virtually no exchange in the absence of acid. The good agreement between the calculated and observed 46/44 mass ratio values (Table IV) together with the linear plots of Figure 3 shows that both carbonyl and carboxyl oxygens exchange at the same rate, a result found previously for the anions $Cr(ox)_2bipy^-$ and $Cr(ox)_2phen^-$.[2] Therefore, in all examples of chromium(III) complexes that have so far been studied a uniform picture emerges with respect to their oxalate oxygen exchange reactions. Changing the overall charge on the complex has very little effect on the rate parameters which may be seen by comparing results in Table V with those given in part I of this study. For the cationic complexes, in particular, the exchange rates are essentially identical. Though the aromatic amine and ethylenediamine ligands differ most obviously in their back-bonding ability, this leads to no changes in the acid lability of the chromium–oxygen bond. Possible mechanisms of oxygen exchange involve chelate ring opening or carbonyl–carboxyl oxygen interchange and have been discussed fully elsewhere.[2]

Although the racemization of $Cr(ox)(phen)_2^+$ shows little acid dependence, by contrast $Cr(ox)(bipy)_2^+$ and $Cr(ox)(en)_2^+$ are both markedly affected (Figure 2). The absorption spectral studies (Figure 1) show that hydrolysis is a major complication for $Cr(ox)(en)_2^+$, which displays optical inactivation rather than a true racemization. The loss of optical activity observed for solutions of $Cr(ox)(en)_2^+$ in the absence of acid is contrary to the findings of Bushra and Johnson[5] but we have not investigated this reaction further.

As with corresponding studies on the anionic complexes no meaningful comparison of racemization and oxygen-18 data can be made since the rate expressions for the two processes are certainly different.[2] For example, there is no oxygen-18 exchange at zero acidities whereas racemization takes place under these conditions (Figure 2). However for $Cr(ox)(bipy)_2^+$ and $Cr(ox)(phen)_2^+$ certain possible mechanisms of racemization can be eliminated. Thus there is no spectral evidence for complete loss of the aromatic amine ligand. A prediction of the spectral changes accompanying stepwise oxalate ligand hydrolysis is made difficult by the proximity of oxalate and water in the spectrochemical series. Both $Cr(H_2O)_2(phen)_2^{3+}$ and $Cr(H_2O)_2(bipy)_2^{3+}$ have been described[8] and show absorption maxima about 7 mμ lower than for the corresponding oxalato species so that a movement to shorter wavelengths would be anticipated. This is not observed. Therefore in solutions up to 1 *M* in acid racemization appears to proceed by some form of intramolecular mechanism. These have been thoroughly discussed by Basolo and Pearson.[10] The acid dependence of the rates (Figure 2) suggests that for each complex more than one pathway contributes to racemization, for example, an intramolecular twist mechanism and a mechanism requiring half-bonded species. Though $Cr(ox)(bipy)_2^+$ and $Cr(ox)(phen)_2^+$ both show an initial rate decrease when the medium is changed from 1 *M* KCl to dilute HCl, it is only the bipyridine complex that shows a rate increase at increasing acidity. In this context it seems significant that other cationic bipyridine complexes studied to date have shown acid-accelerated racemization rates.[11,12] To explain such acid dependence the participation of half-bonded bipyridine ligands has been suggested. However failure to detect free bipyridine either spectrally or chemically (using iron(II)) in this work leads to an alternative suggestion that acid-dependent racemization of $Cr(ox)(bipy)_2^+$ arises indirectly. For example, a possible mechanism for the acid-catalyzed oxygen-18 exchange involves oxalate ring opening. Though this would be common to both $Cr(ox)(bipy)_2^+$ and $Cr(ox)(phen)_2^+$, acid dependence would be confined to $Cr(ox)(bipy)_2^+$ if it alone was able to racemize at the half-bonded oxalate stage. The greater flexibility of the bipyridine ligand may well permit a twist racemization pathway not available to the rigid phenanthroline ligand.

Both cations and anions showed specific effects on the racemization of $Cr(ox)(bipy)_2^+$ and $Cr(ox)(phen)_2^+$ (Table VI). The dipolar nature of these complexes could be expected to facilitate interactions with either type of counterion. The overall positive charge and the presence of several peripheral hydrogen atoms should favor anion interactions whereas the oxalate ligand provides a center for cation effects.

Acknowledgments.—We wish to thank the CSIRO for award of a studentship (to N. K. M.) and the ARGC for a grant for purchase of a mass spectrometer.

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