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The Effect of Pressure upon the Optical Activity of Crystalline Tris-(1,10-phenanthroline)iron(II) Perchlorate and Tris-(1,10-phenanthroline)nickel(II) Perchlorate[1]

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Pressure is shown to exert a rate-accelerating effect on the racemization of crystalline $[Fe(phen)_3](ClO_4)_2 \cdot xH_2O$ and $[Ni(phen)_3](ClO_4)_2 \cdot xH_2O$. The volumes of activation for the racemization, ΔV^*, are -0.947 ± 0.144 cm.^{3} mole^{-1} for $[Fe(phen)_3](ClO_4)_2$ and -1.10 ± 0.14 and -1.08 ± 0.22 cm.^{3} mole^{-1} for the *d* and *l* forms of $[Ni(phen)_3](ClO_4)_2$, respectively.

Introduction

Recently it has been shown that the rate of racemization of several optically active crystalline inorganic salts increases under pressure.[2] Not all optically active salts are sensitive to pressure-induced, racemization-rate increases, however. Tris(ethylenediamine)cobalt(III) iodide, for example, cannot be made to racemize at a pressure of 39,000 atm. applied for 70 hr. It is possible that racemization could be induced within this time period at higher pressures or that a time interval in excess of 70 hr. is necessary. The purpose of this work was to extend pressure studies to other inorganic salt systems. The salts $[Fe(phen)_3](ClO_4)_2 \cdot xH_2O$ and $[Ni(phen)_3](ClO_4)_2 \cdot xH_2O$ were selected because the mechanism of racemization in the solution phase differs for the two salts. Also, the rate of racemization of the iron complex is faster than the nickel complex. The possibility that the mechanism of racemization in the solid state for the two salts would be sufficiently different to cause different pressure effects was considered worthy of investigation.

From the results of a kinetic study it was concluded that the major path for racemization of the $[Fe(phen)_3]^{2+}$ ion in aqueous media was an intramolecular process.[3] A portion of the complex ions racemize by a dissociative mechanism. Basolo, Hayes, and Newmann concluded that racemization of $[Ni(phen)_3]^{2+}$ in aqueous solution occurs entirely by a dissociative mechanism, since the rates of dissociation and of racemization of the complex ion and the energy of activation for both processes are equal.[4] An exchange study with radiocarbon-labeled 1,10-phenanthroline confirmed a dissociative mechanism for racemization of $[Ni(phen)_3]^{2+}$ in neutral solution.[5]

Experimental

Preparation of *l*-$[Fe(phen)_3](ClO_4)_2 \cdot xH_2O$.—Tris-(1,10-phenanthroline)iron(II) perchlorate was prepared and resolved by the procedure of Dwyer and Gyarfas.[6] The specific rotation of this material, $[\alpha]_D$, was -1555 and $-1570°$, based on the anhydrous salt, for two separate preparations. Dwyer and Gyarfas report a value of $-1416°$ for *l*-$[Fe(phen)_3](ClO_4)_2 \cdot 3H_2O$, which is equivalent to $-1516°$ for the anhydrous salt.

Preparation and Resolution of $[Ni(phen)_3](ClO_4)_2 \cdot xH_2O$.—A partially resolved sample of *d*-$[Ni(phen)_3](ClO_4)_2$ was prepared according to the method described by Dwyer and Gyarfas.[7] This material had a specific rotation, $[\alpha]_D$, of $+1205°$. The reported values are $+1463°$[7] and $+1476°$.[8] The *l* isomer was prepared according to the procedure of Kauffman and Takahashi.[8] It possessed a specific rotation of $-1458°$ ($-1463°$[7] and $-1482°$[8] reported).

High Pressure Apparatus and Procedure.—The apparatus has been described previously.[2] The procedure for pelletizing and pressurizing samples was essentially that described earlier.[2] Pressure experiments were carried out at ambient temperature, which varied from 24 to 27°. All samples were placed in a nickel ring of 0.375-in. o.d., 0.25-in. i.d., and 0.02-in. thickness. This ring size was selected because it gave the diameter:thickness ratio for which there was no pressure gradient across the sample.[2,9]

After the samples had been placed under pressure for the desired length of time, they were removed and the optical activity was measured on water solutions in the conventional manner. A Rudolph Model 80 high precision polarimeter fitted with a No. 200 photoelectric attachment was used for this purpose. Due to the rapid rate of racemization and the limited solubility of $[Fe(phen)_3](ClO_4)_2$ in water, normal polarimetry techniques could not be used. It was necessary to take readings of the optical rotation at timed intervals. A least-squares line through a plot of $\ln \alpha_{obsd}$ *vs.* time data was extrapolated to zero time to obtain the correct value for α_{obsd}. Standard deviations for α_{obsd} were computed from the least-squares, best straight line.[10] For control pellets the standard deviations in α_{obsd} were generally less than 1% while for sample pellets the values were in the range of ± 1-2%. The concentration of the $[Fe(phen)_3]^{2+}$ ion was then determined spectrophotometrically. A Beckman Model DU spectrophotometer was used for this purpose. A calibration curve for the determination of $[Fe(phen)_3]^{2+}$ was made according to the procedure outlined by Sandell.[11] This calibration curve gave an extinction coefficient of 11,400 at 508 mμ. Errors in the determination of concentration were estimated to be $\pm 2\%$. The errors in specific rotation given in Table I represent estimated

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[1] Abstracted in part from the Master's thesis of Marvin E. Bunch, The Pennsylvania State University, 1963.

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[6] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 263 (1949).

[7] F. P. Dwyer and E. C. Gyarfas, *ibid.*, **83**, 232 (1949).

[8] G. B. Kauffman and L. T. Takahashi, *J. Chem. Educ.*, **39**, 481 (1962).

[9] M. Myers, F. Dachille, and R. Roy, Technical Report No. 16, Contract No. Nonr-656(20), College of Mineral Industries, The Pennsylvania State University, University Park, Pa.

[10] Y. Beers, "Introduction to the Theory of Error," 2nd Ed., Addison-Wesley Publishing Co., Inc., Reading, Mass., 1957, p. 40.

[11] E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 541.

TABLE I

DATA FOR VOLUME OF ACTIVATION OF $[Fe(phen)_3](ClO_4)_2$

$[\alpha]_D$ control, deg.	$[\alpha]_D$ sample,[a] deg.	$\Delta[\alpha]_D$,[b] deg.	Pressure, atm. × 10^{-3}	$\ln\ln\left(\frac{[\alpha]_{D_0}}{[\alpha]_D}\right)^{1/2}$
−1560 ± 109[c]	−944 ± 39	−625	47.62	−1.369
−1608 ± 58	−873 ± 40	−696	47.62	−1.226
−1476 ± 48[c]	−986 ± 40	−583	47.62	−1.458
−1597 ± 46	−1073 ± 35	−496	40.82	−1.659
−1542 ± 48	−1188 ± 38	−381	40.82	−1.970
−1594 ± 47	−1224 ± 45	−345	34.01	−2.084
−1585 ± 45	−1291 ± 46	−278	27.21	−2.324
−1541 ± 48	−1352 ± 40	−217	27.21	−2.594
−1539 ± 51	−1259 ± 39	−310	20.41	−2.204
−1564 ± 46	−1316 ± 40	−253	13.60	−2.428
−1564 ± 47	−1423 ± 34	−146	13.60	−3.013

[a] Samples kept under pressure for 24 hr. [b] Based on the average of nine control values = 1569°. [c] Not included in average control value.

error limits which include the computed standard deviations in α_{obsd}. (Deviations in the polarimeter tube length are considered negligible.) The tris-(1,10-phenanthroline)nickel(II) salt racemizes very slowly in a solution 50% by volume of acetone and water. Optical rotations could therefore be read directly without resorting to an extrapolation technique. The individual values for $[\alpha]_D$ in Tables II and III are average values for a set of eight readings on a single sample. The standard deviations for α_{obsd} ranged from ±0.2 to 0.5%. The errors estimated for $[\alpha]_D$ were ±1%.

TABLE II

DATA FOR VOLUME OF ACTIVATION OF $[Ni(phen)_3](ClO_4)_2$

$[\alpha]_D$ control, deg.	$[\alpha]_D$ sample,[a] deg.	$\Delta[\alpha]_D$,[b] deg.	Pressure, atm. × 10^{-3}	$\ln\ln\left(\frac{[\alpha]_{D_0}}{[\alpha]_D}\right)^{1/2}$
1197	1000	−205	47.62	−2.373
1207	1042	−163	40.82	−2.622
1205	1074	−131	36.29	−2.855
1215	1095	−110	34.01	−3.039
1204	1139	−66	27.21	−3.570
1218	1163	−42	22.24	−4.032
1184	1122	−83	20.41	−3.333
1208	1143	−62	19.06	−3.634
1210	1154	−51	13.60	−3.834
1178	1169	−36	6.35	−4.189

[a] Samples under pressure for 22 hr. [b] Based on an average of ten control values = 1205°.

TABLE III

DATA FOR VOLUME OF ACTIVATION OF $[Ni(phen)_3](ClO_4)_2$

$[\alpha]_D$ control, deg.	$[\alpha]_D$ sample,[a] deg.	$\Delta[\alpha]_D$,[b] deg.	Pressure, atm. × 10^{-3}	$\ln\ln\left(\frac{[\alpha]_{D_0}}{[\alpha]_D}\right)^{1/2}$
−1461	−1305	−153	48.38	−2.893
−1454	−1288	−170	48.38	−2.781
−1444	−1296	−162	41.12	−2.832
−1484	−1323	−135	40.82	−3.024
−1462	−1357	−101	27.21	−3.327
−1444	−1396	−62	23.13	−3.829
−1454	−1409	−49	19.06	−4.069
−1452	−1414	−44	13.60	−4.178
−1452	−1463	0	6.35	Undefined

[a] Samples under pressure for 22 hr. [b] Based on the average of ten controls = −1458°.

Results

The observed changes in specific rotation are reported in terms of $\Delta[\alpha]_D$. This quantity has been defined as the absolute value of the specific rotation of the sample less the absolute value of the specific rotation of the control.[2] Values of $\Delta[\alpha]_D$ are thus always negative if pressure has caused racemization. Values of $\Delta[\alpha]_D$ are given in Table I for $[Fe(phen)_3](ClO_4)_2$ and in Tables II and III for $[Ni(phen)_3](ClO_4)_2$. The values for the volume of activation, ΔV^*, were determined by applying the equation[2]

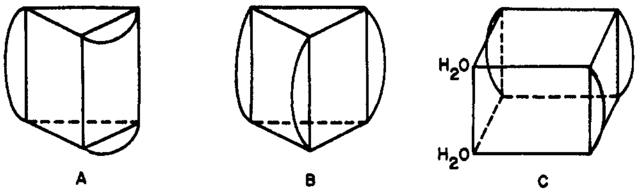

Figure 1.

$$\frac{d \ln \ln ([\alpha]_{D_0}/[\alpha]_D)^{1/2}}{dp} = \frac{-\Delta V^*}{RT} \qquad (1)$$

The notation $[\alpha]_{D_0}$ is equal to the specific rotation of the sample at time zero and $[\alpha]_D$ is the specific rotation at time *t*. The values for $[\alpha]_D$ (sample) and $[\alpha]_D$ (control) can be substituted for $[\alpha]_D$ and $[\alpha]_{D_0}$, respectively. According to eq. 1, a plot of $\ln \ln ([\alpha]_{D_0}/[\alpha]_D)^{1/2}$ *vs.* pressure, p, should give a straight line of slope $-\Delta V^*/RT$. A least-squares treatment of the data given in Tables I–III gave for ΔV^* a value of −0.947 ± 0.144 cm.^{3} mole^{-1} for $[Fe(phen)_3](ClO_4)_2$, and −1.10 ± 0.14 and −1.08 ± 0.22 cm.^{3} mole^{-1} for $[Ni(phen)_3](ClO_4)_2$.

Discussion

It is evident that pressure exerts a rate-accelerating effect on the solid state racemization of both salts. The negative values for ΔV^* also indicate that either a unimolecular, intramolecular rearrangement or a bimolecular reaction is involved in the racemization process for both complexes.[12] A mechanism involving complete dissociation of the 1,10-phenanthroline ligand is considered very unlikely, since the dissociation process would involve the stretching of bonds and thus manifest itself in a positive volume of activation. Several models have been proposed for the activated complex in a racemization process which do not involve complete dissociation of a ligand.[2] Of these the trigonal prismatic structures A and B shown in Fig. 1 (models D and E, respectively, in ref. 2) are considered most likely for the activated complex. Model C must be considered as a possible structure for the activated complex since the dependence of the racemization rate on the degree of hydration was not measured. All three structures are compatible with a negative volume of activation. Arguments leading to the selection of these models are the same as those already given in ref. 2.

It is interesting to note that the volume of activation for $[Ni(phen)_3](ClO_4)_2$ measured for a sample with an initial specific rotation of $[\alpha]_D$ 1205° was −1.10 cm.^{3}

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(12) See E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959).

mole^{-1}. This is in very good agreement with the value of -1.08 obtained for the optically pure sample with an initial specific rotation of $-1458°$. The close agreement of the two values for ΔV^* is experimental proof that the value of ΔV^* does not depend upon the initial rotation of the sample.[2]

The relationship

$$\ln \ln ([\alpha]_{D_0}/[\alpha]_D)^{1/2}{}_{p=0} = \ln k_{p=0} + \ln t \qquad (2)$$

has been used to obtain a value for the specific rate constant for the disappearance of *d* or *l* ion at zero pressure, $k_{p=0}$, for a sample under pressure for time t.[2] The value for $\ln \ln ([\alpha]_{D_0}/[\alpha]_D)^{1/2}{}_{p=0}$ is a value obtained from a linear extrapolation of the $\ln \ln ([\alpha]_{D_0}/[\alpha]_D)^{1/2}$ *vs.* p data to zero pressure. Equation 2 is valid only if the value of ΔV^* is constant over the entire pressure range. The rate constant for racemization (change in optical activity), k', is double the rate constant for the disappearance of *d* or *l* ions, k. The rate constants for racemization, k', obtained from our data are $3.10 \pm 0.65 \times 10^{-3}$ hr.$^{-1}$ for $[Fe(phen)_3](ClO_4)_2$ and $9.70 \pm 1.70 \times 10^{-4}$ and $6.82 \pm 2.13 \times 10^{-4}$ hr.$^{-1}$ for $[Ni(phen)_3](ClO_4)_2$. These correspond to half-lives of racemization of 9.3 ± 2.0 days, 29.8 ± 5.2 days, and 42.3 ± 13.2 days, respectively. An inspection of the half-lives calculated from the rate constants shows that the compounds, especially the iron complex, should racemize very rapidly at 1 atm. pressure in the solid state. In fact, the iron complex used in the pressure studies was used for a period of 4 months with no noticeable change in the $[\alpha]_D$ of the control samples, although the calculated half-life for racemization is approximately 10 days. One explanation for this discrepancy would be that the volume of activation changes rapidly toward more negative values as the pressure approaches atmospheric pressure. This would produce a smaller value for the racemization rate constant and a corresponding increase in the half-life. A rapid increase in the value of ΔV^* as the applied pressure approaches atmospheric pressure has been observed in solution.[13]

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The Dimesitylenevanadium(I) Cation

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Hexacarbonylvanadium oxidizes dimesitylenevanadium(0) to the $[V(C_6H_3(CH_3)_3)_2]^+$ cation, the compound $[V(C_6H_3(CH_3)_3)_2][V(CO)_6]$ (I) being formed. The corresponding iodide $[V(C_6H_3(CH_3)_3)_2]I$ (II) can be prepared by a metathetical reaction of I with LiI in tetrahydrofuran. Dimesitylenevanadium(0), characterized here for the first time, was obtained by the reaction of VCl_3 with mesitylene and aluminum in the presence of aluminum halides, followed by treatment with aqueous alkali. A reinvestigation of this reaction has shown that in the first stage, the aluminum reduces V(III) to the dimesitylenevanadium(I) cation; the iodide (II) was in fact isolated from the first stage products by the metathetical reaction mentioned above. The dimesitylenevanadium(I) iodide in the presence of water yields dimesitylenevanadium(0) predominantly by the disproportionation reactions below.

$$2V(I) \longrightarrow V(0) + V(II) \quad \text{(neutral medium)}$$

$$3V(I) \longrightarrow 2V(0) + V(III) \quad \text{(alkaline medium)}$$

Introduction

Diarene–metal complexes of formula $M(arene)_2$ (M = V, Cr, Mo, W) can be synthesized by a two-stage reaction, the first stage of which consists of treating the anhydrous metal halide with aluminum and aluminum chloride in the presence of aromatic hydrocarbons.[1,2]

Fischer and co-workers postulated the formation of the cations $[M(arene)_2]^+$ during this stage, the zerovalent complexes being formed in a second stage carried out in the presence of water. Dibenzenechromium[3] was obtained by using an alkaline solution of dithionite, whereas a simple treatment with an aqueous alkaline solution gave dibenzenevanadium,[4] dibenzenemolybdenum, and dibenzenetungsten.[5] In the latter three cases disproportionation reactions with simultaneous formation of the zerovalent complex and of the uncomplexed metal in its highest oxidation state were reported.

However, the presence of the cations $[Cr(arene)_2]^+$ and $[V(arene)_2]^+$ in the pre-"hydrolytic" mixtures of the reactions on $CrCl_3$ and VCl_4 was later questioned

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