Galkin, Sudarikov, and Zaitsev[8] concluded that solid NH_4F–UF_4 mixtures decompose in three steps: NH_4F (10% excess NH_4F) $\xrightarrow{220\text{-}280°}$ NH_4UF_5 $\xrightarrow{320\text{-}360°}$ HUF_5 $\xrightarrow{420\text{-}450°}$ UF_4 when heated at a linear rate up to *ca.* 600°. They found percentage-weight losses which correspond very nearly to the values which we obtained for the series: $(NH_4)_2UF_6 \xrightarrow{180°} NH_4UF_5 \xrightarrow{290°} NH_4F \cdot 3UF_4 \xrightarrow{400°} UF_4$ illustrated in Fig. 1. The decomposition scheme is probably the same in both cases. We found no evidence for the existence of their suggested compound "HUF_5."

Maly, *et al.*,[7] have carried out thermogravimetric analyses on very small (mg.) quantities of products obtained by reaction of PuO_2 with NH_4HF_2. Our results suggest that the arrest which they attribute to "dark green $NH_4PuF_5 \cdot 2H_2O$" was due instead to the green compound $(NH_4)_2PuF_6$. Their decomposition curve also indicates an arrest at the weight near that of $NH_4F \cdot 3PuF_4$ that they did not point out.

The X-ray powder patterns of the 7:6 and α-1:1 phases could be indexed in the $R\bar{3}$ space group assigned to similar members of the alkali fluoride–UF_4 series. The lattice dimensions derived are: $7NH_4F \cdot 6UF_4$ and α-$NH_4F \cdot UF_4$, $a_0 = 9.55$ Å., $\alpha = 107.4°$ (hexagonal dimensions $a_0 = 15.40$, $c_0 = 10.49$ Å.); $7NH_4F \cdot 6PuF_4$ and α-$NH_4F \cdot PuF_4$, $a_0 = 9.42$ Å., $\alpha = 107.4°$ (hexagonal dimensions $a_0 = 15.18$, $c_0 = 10.36$ Å.). The preparations were too fine-grained to permit confirmation of symmetry by optical-microscopic methods.

Acknowledgments.—The authors thank G. R. Waterbury and E. G. Bosier for some chemical analyses and D. F. Bowersox for some plutonium preparations.

TABLE IV

PARTIAL X-RAY POWDER PATTERNS OF β-1:1, γ-1:1, AND 1:3 PHASES

β-NH$_4$F·UF$_4$		β-NH$_4$F·PuF$_4$		NH$_4$F·3UF$_4$		NH$_4$F·3PuF$_4$	
d_{obsd}	I^a	d_{obsd}	I^a	d_{obsd}	I^a	d_{obsd}	I^a
6.97	vs	6.95	vs	8.2	vw	8.2	vw
5.50	vw	...	...	7.9	m	7.8	m
4.55	vw	...	...	7.2	mw-b	7.2	mw-b
4.19	vw	4.10	vw	5.50	m	5.47	m
4.01	ms	3.94	ms	5.37	w	5.35	vw
3.79	m	3.74	m	4.51	mw	4.49	mw
3.66	vw	...	...	4.19	m	4.15	m
3.48	s	3.44	s-b	3.98	w	3.95	vw
3.35	vw	...	...	3.70	w	3.67	vw
3.24	ms	3.20	ms	3.63	ms	3.60	ms
3.18	mw	3.15	w	3.50	ms	3.46	ms
3.00	vw	2.99	vw	3.34	ms	3.31	ms
2.90	mw	2.86	w	3.23	ms	3.19	ms
2.71	mw	2.69	mw	3.09	mw	3.06	vw
2.62	m-b	2.61	mw-b	3.04	vw	3.00	vw
2.32	m-b	{ 2.32	m	2.89	ms	2.86	ms
		2.28	w	2.69	m	2.66	mw
2.14	w	2.13	w	2.62	mw	2.58	w
2.02	ms-b	{ 2.01	ms	2.56	m	2.54	mw
		1.985	ms	2.40	vw	2.36	vw
1.95	m	1.935	vw	2.34	mw	2.32	w
				2.25	mw-b	2.22	w-b
				2.15	mw	2.15	mw
				2.11	w	2.11	w-b
				2.08	mw	2.06	mw
				2.02	s	2.00	s
				1.995	m	1.975	m
				1.945	s	1.925	s

γ-NH$_4$F·UF$_4$		γ-NH$_4$F·PuF$_4$	
d_{obsd}	I^a	d_{obsd}	I^a
4.15	m	4.10	m
3.49	s-b	3.48	s-b
2.68	mw-b	2.66	mw-b
2.08	w	2.06	w
2.02	vw	2.00	vw
1.80	vw	{ 1.81	vw
		1.77	w
...	...	1.60	vw

^{a} Intensities estimated visually; Cu Kα radiation, $\lambda = 1.5418$ Å.

CONTRIBUTION FROM THE PENNSYLVANIA STATE UNIVERSITY,
UNIVERSITY PARK, PENNSYLVANIA

The Effect of Pressure upon the Optical Activity of Crystalline Inorganic Compounds

By J. BRADY, F. DACHILLE, AND C. D. SCHMULBACH

Extreme pressures of 10,000 to 40,000 atmospheres were found to increase the rate of racemization of potassium trioxalatocobaltate(III) in the solid state. The volume of activation, ΔV^*, for the racemization process was determined experimentally and found to be -1.44 ± 0.23 and 1.80 ± 0.28 cm.^{3}/mole for two independent experiments. These data are consistent with an intramolecular mechanism. An intramolecular process that does not include metal–oxygen bond rupture and re-formation is preferred. The mechanism is discussed in terms of the possible structures for the transition state and the relationship of structure to ΔV^*. Approximate values of $4.7 \pm 1.1 \times 10^{-4}$ and $2.11 \pm 0.93 \times 10^{-4}$ hr.$^{-1}$ for the specific rate constant for racemization of $K_3[Co(C_2O_4)_3]$ at zero pressure were obtained.

Introduction

Despite the observation that the optically active salts, potassium trioxalatocobaltate(III) and potassium trioxalatochromate(III), undergo slow racemization in the solid state,[1] there has been little experimental work centered on this phenomenon and the theoretical implications arising from it. The study of isotope exchange in aqueous solution for the systems $Co(C_2O_4)_3{}^{3-}$–*$C_2O_4{}^{2-}$ [2a] and $Cr(C_2O_4)_3{}^{3-}$–*$C_2O_4{}^{2-}$ [2b] showed no interchange under conditions that lead to racemization. These results immediately suggest an intramolecular rearrangement that may or may not involve bond

(1) C. H. Johnson, *Trans. Faraday Soc.*, **31**, 1612 (1935).

(2) (a) F. A. Long, *J. Am. Chem. Soc.*, **63**, 1353 (1941); (b) F. A. Long *ibid.*, **61**, 570 (1939).

Fig. 1.—$\Delta[\alpha]_D$ *vs.* time at a constant pressure of 19,000 atm. and a constant initial specific rotation, $[\alpha_C]_D$, of $-1850°$.

rupture. That racemization in the solid state follows an intramolecular mechanism is very likely.

If racemization in the solid state proceeds through a transition state of smaller volume than either of the optically active isomers, the application of extreme pressures would be expected to accelerate the racemization process. This acceleration arises from the elevation of a greater number of reactant ions into a transition state of higher energy (and smaller volume) as the pressure increases. The purpose of these experiments was to determine what effect, if any, pressure would have on the rate of racemization of optically active inorganic salts in the solid state and to measure the volume of activation should pressure exert a rate-accelerating effect.

Experiment has shown that the application of pressures ranging from 10,000 to 40,000 atmospheres causes an increase in the racemization rate for solid potassium trioxalatocobaltate(III) and potassium trioxalatochromate(III). Typical data are given for potassium trioxalatocobaltate(III).

Experimental

Potassium Trioxalatocobaltate(III), $K_3[Co(C_2O_4)_3]\cdot2.6H_2O$.[3]—This compound was prepared according to the method described by Bailar and Jones.[4] Resolution was accomplished using the procedure described by Johnson and Mead[5] with strychnine sulfate as the resolving agent. The diastereomer was cleaved with potassium iodide. The highest specific rotation, $[\alpha]_D$, of samples resolved in this manner was $-2130°$. The more recently reported value of $[\alpha]_D$ $\pm4050°$ for the pure optically active material[6] indicates incomplete resolution of samples used in these experiments. The magnitude of the pressure effect on changes in

(3) The value 2.6 for the waters of hydration represents an average for the samples used in these experiments. Our value is larger than the value of 2 reported by Johnson and Mead.[5]

(4) J. C. Bailar, Jr., and E. M. Jones, *Inorg. Syn.*, **1**, 35 (1939).

(5) C. H. Johnson and A. Mead, *Trans. Faraday Soc.*, **29**, 626 (1933).

(6) F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, **60**, 1331 (1956).

optical activity made it unnecessary to resort to materials of highest optical purity.

High Pressure Apparatus and Procedure.—A modified Bridgman opposed anvil high pressure apparatus was used in these experiments.[7] This type apparatus is capable of applying "hydrostatic" pressures of up to 180,000 atmospheres on samples as large as 30 mg. using 50-ton presses.

Experiments were carried out at ambient temperatures ranging from 24 to 28°, a factor which contributed in some degree to the scatter of data. The slow application of pressure to the samples over several minutes allowed for the dissipation of any heat that was generated as the pistons did work on the sample. That undesirable heat effects due to pressurization were of no consequence was demonstrated experimentally. If heat generation during pressurization had caused a large increase in temperature of the sample, it would be reasonable to expect immediate and rapid racemization during the initial stages of each run followed by slower rates as the heat of the sample was dissipated. Failure to note any measurable change in optical activity for samples subjected to 40,000 atmospheres pressure for short periods of 5 min. to 1 hr. eliminates the possibility that any initial temperature increases due to pressurization caused extensive racemization. Any generated heat was rapidly dissipated to the massive metal heat-sink surrounding the sample.

Samples of solid optically active complex were pressed into wafers at low pressures of approximately 60,000 lb./in.[2]. This operation was shown to have no effect on the optical activity of the samples. The wafer, encased in a nickel ring 0.01 in. thick, then was placed between sheets of platinum–10% rhodium foil and subjected to pressures of up to 40,000 atmospheres for varying periods of time. After removal of the samples from the pressure apparatus, the optical rotation was measured in water solution in the conventional manner using a Rudolph Model No. 80 high precision polarimeter fitted with a No. 200 photoelectric attachment. Based on a large number of measurements of rotation of sucrose, the deviation in specific rotation for any *single* measurement never exceeded $\pm0.6\%$. For potassium trioxalatocobaltate(III) the deviation for a *single* sample did not exceed $\pm1.5\%$ of the mean rotation obtained from five samples. The specific rotation of the pressurized sample was compared to that of a control which had not been subjected to pressure. The error in specific rotation of samples for which data are given is estimated to be $\pm15°$, giving an error of $\pm30°$ for $\Delta[\alpha]_D$.

Results

The data plotted in Fig. 1 show the rate of racemization under pressure is demonstrably greater than at 1 atmosphere. The change in specific rotation of the pressurized sample is recorded in terms of $\Delta[\alpha]_D$, a

Table I

EFFECT OF PRESSURE ON OPTICAL ACTIVITY OF l-$K_3[Co(C_2O_4)_3]\cdot 2.6H_2O^a$

Pressure, atm.	$[\alpha_S]_D$ sample	$[\alpha_C]_D$ control	$\Delta[\alpha]_D$	$\ln\ln([\alpha_C]_D/[\alpha_S]_D)^{1/2}$
12,200	-1517	-1560	-43	-4.270
16,300	-1389	-1504	-115	-3.225
20,400	-1461	-1565	-104	-3.370
24,200	-1403	-1570	-167	-2.878
27,200	-1446	-1558	-112	-3.289
30,600	-1322	-1532	-210	-2.608
35,400	-1354	-1558	-204	-2.657
35,400	-1367	-1570	-203	-2.670
38,800	-1220	-1537	-317	-2.159
38,800	-1316	-1583	-267	-2.382

^{a} Time under pressure of 22.0 hr. and initial specific rotation are held constant.

(7) F. Dachille and R. Roy, *Z. Krist.*, **111**, 451 (1959); F. Dachille and R. Roy in R. H. Wentorf, Jr., Ed., "Modern Very High Pressure Techniques," Butterworths Press, Washington, D. C., 1962, Chapter 9.
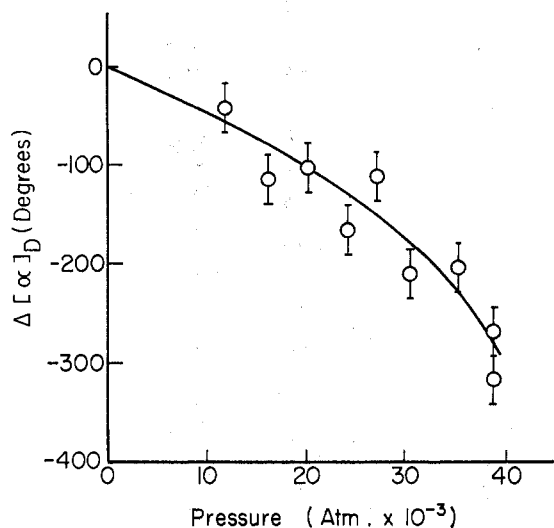
Fig. 2.—$\Delta[\alpha]_D$ *vs.* pressure at a constant time under pressure for 22.0 hr. and at constant initial specific rotation, $[\alpha_C]_D$.

value which is obtained by subtracting the absolute value of the specific rotation of the control sample, $[\alpha_C]_D$ from the absolute value of the specific rotation of a sample subjected to pressure, $[\alpha_S]_D$. Negative values for $\Delta[\alpha]_D$ indicate increased racemization rates under pressure. The *extent* of racemization for samples of fixed initial specific rotation, which had been subjected to pressures for a constant period of time, was definitely increased with an increase in pressure. The data are given in Table 1 and plotted in Fig. 2.

Discussion

It is unquestionable from these data that an increase in pressure increases the rate of racemization of optically active potassium trioxalatocobaltate(III). Furthermore, since increasing the pressure increases the rate of racemization, it may be concluded that the volume of activation is negative. The volume of activation, ΔV^*, is related to the variation of the specific rate constant with pressure by the relationship

$$\frac{d \ln k}{d p} = \frac{-\Delta V^{*8}}{RT} \tag{1}$$

The scatter of data at short time intervals does not permit the determination of specific rate constants nor of the reaction order by standard techniques. More recent experiments using improved methods indicate the reaction is first order with respect to the complex anion. It is possible to relate the change in the observed specific rotation with respect to pressure and the volume of activation and thus permit the calculation of an experimental value of ΔV^* without having to determine specific rate constants at various pressures. It has been established that racemization of potassium trioxalatocobaltate in aqueous media is first order with respect to the complex anion.[9]

If first-order kinetics is assumed for racemization in the solid state as well, the relationship

$$\ln \frac{[\alpha]_{D_0}}{[\alpha]_D} = k't = 2kt \tag{2}$$

(8) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).
(9) E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937 (1939).
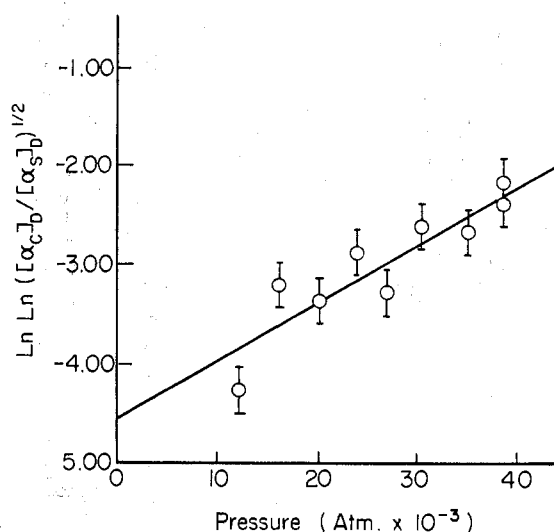
Fig. 3.—ln ln $([\alpha_C]_D/[\alpha_S]_D)^{1/2}$ *vs.* pressure for samples of constant initial optical activity and constant time under pressure.

applies, where k' is the rate constant for change in optical rotation, k, the rate constant for the disappearance of d or l ions, $[\alpha]_{D_0}$, the specific rotation at time zero and $[\alpha]_D$, the specific rotation at time t. Taking the logarithm of both sides of eq. 2 and differentiating with respect to pressure, holding t constant, gives

$$\frac{d \ln \ln \left(\frac{[\alpha]_{D_0}}{[\alpha]_D}\right)^{1/2}}{d p} = \frac{d \ln k}{d p} \tag{3}$$

Combining eq. 1 and 3 yields

$$\frac{d \ln \ln \left(\frac{[\alpha]_{D_0}}{[\alpha]_D}\right)^{1/2}}{d p} = \frac{-\Delta V^*}{RT} \tag{4}$$

Thus, for a first-order reaction, a plot of ln ln $([\alpha]_{D_0}/[\alpha]_D)^{1/2}$ *vs.* pressure would give a straight line, the slope of which is $-\Delta V^*/RT$. Such a plot is given in Fig. 3 for the data recorded in Table I. A least-squares treatment was applied to the data to give a value for ΔV^* of -1.44 ± 0.23 cm.^{3}/mole. Similar treatment to a second series of data gave the value 1.80 ± 0.28 cm.^{3}/mole for ΔV^*.

Several possible transition states are possible for intramolecular racemization of octahedral complexes as shown in Fig. 4.[10] Models A and B are not considered likely since bond stretching, which would precede bond rupture, would be suppressed at high pressures and would result in decreased rates of racemization.

Davies[11] suggested that intramolecular racemization probably results from a process of expansion which gives rise to an increase in the interatomic distance between the donor and the metal atom. The transition state thus would be more ionic in character and might well rearrange prior to returning to the stable state. Such an expansion in metal–ligand bond distance does not preclude a decrease in volume of the anion. A simple

(10) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 271–274.
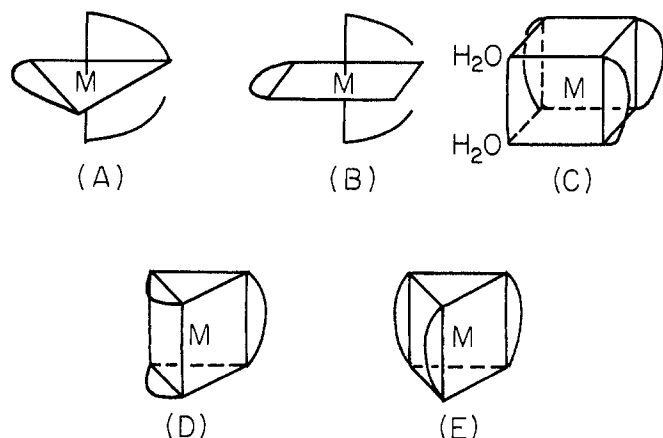(11) N. R. Davies, *Rev. Pure Appl. Chem.*, **4**, 66 (1954).

Fig. 4.—Possible transition states for intramolecular racemization of octahedral complexes.

computation shows that there is a volume decrease of about 8% in the transition from an octahedral to a trigonal prismatic structure, if one assumes that the oxygen–oxygen distance for the bonded oxygen atoms on the oxalate ligands remains constant. At the same time there is an increase in the metal–oxygen distance of about 8%. Models D and E, which involve unimolecular, intramolecular rearrangements, are consistent with the observed negative sign for ΔV^*.[12] The magnitude of the experimentally derived value for ΔV^* is considered to be larger than the true value because there is some experimental evidence to indicate that the actual pressures on the samples in these experiments are greater than the calculated load pressures. This would cause a decrease in slope for the line plotted in Fig. 3 and a reduced value for ΔV^*.

An intramolecular rearrangement *via* transition states D and E would involve no rupture of the metal–ligand bonds. Such a mechanism has been proposed independently by three investigators.[13–15]

The possibility that waters of hydration would participate in racemization to generate a transition state shown as model C remains a possibility and may not be excluded in view of the negative value for ΔV^*. Experiments establishing the order of racemization with respect to water would be extremely valuable in selecting models for the transition state.

The intercept obtained by extrapolation of the least-squares line in Fig. 3 also yields valuable information. The integrated form of eq. 4 is

$$\ln \ln \left(\frac{[\alpha]_{D_0}}{[\alpha]_D} \right)^{1/2} = \frac{-p\Delta V^*}{RT} + C \qquad (5)$$

where C is the constant of integration. As $p \to 0$, eq. 5 becomes

$$\left[\ln \ln \left(\frac{[\alpha]_{D_0}}{[\alpha]_D} \right)^{1/2} \right]_{p=0} = C \qquad (6)$$

in which the intercept, C, equals $\ln k_{p=0} + \ln t$ as can be readily ascertained from inspection of eq. 1. By making the assumption that ΔV^* is invariant with pressure, an assumption that is not entirely justified over a wide pressure range, it is possible to obtain a value for $k_{p=0}$ of $4.7 \pm 1.1 \times 10^{-4}$ hr.$^{-1}$. A second set of data gave the value $2.11 \pm 0.93 \times 10^{-4}$ hr.$^{-1}$ for $k_{p=0}$, a value within experimental error of that for which data are given.

If the logarithmic expression for eq. 1 is differentiated with respect to $1/T$ instead of p, there results an equation

$$\frac{d \ln \ln \left(\frac{[\alpha]_{D_0}}{[\alpha]_D} \right)^{1/2}}{d(1/T)} = \frac{d \ln k}{d(1/T)} = \frac{-E_a}{R} \qquad (7)$$

Experiments will soon be undertaken to determine the energy of activation for the racemization of solid potassium trioxalatocobaltate(III) using this method.

It should be made clear that the experimentally determined value $[\alpha_C]_D$ may be substituted for the term $[\alpha]_{D_0}$, and the experimentally determined value $[\alpha_S]_D$ may be substituted for $[\alpha]_D$, making it possible to express the above equations in terms of quantities measured experimentally.

Preliminary studies have shown that the rate of racemization of potassium trioxalatochromate(III) dihydrate also increases under pressure while samples of tris-(ethylenediamine)-cobalt(III) iodide could not be racemized at pressures of 39,000 atmospheres applied for 70 hr. The effect of pressure is being extended to other inorganic systems. Refined measurements will soon allow evaluation of E_a for solid state racemization of potassium trioxalatocobaltate(III). Future studies will be devoted to a more detailed investigation of this system in order to provide more data for establishing a mechanism and the configuration of the transition state.

There is a need in high pressure experimentation for methods of internal calibration of pressure on the sample system. Changes in electrical resistance of metals going through transitions at definite pressures have been used in this respect.[16] The change in refractive indices of glasses with pressure has been suggested.[17] Optical rotation measurements can be made with great accuracy so that if the pressure effect on an optically active coordination compound is found to be quenchable and reproducible under different time and temperature conditions, this compound may be used as an internal pressure calibrant.

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

(13) J. C. Bailar, Jr., International Conference on Coördination Chemistry, Rome, September, 1957.

(14) W. G. Gehman, Doctoral Thesis, The Pennsylvania State University, University Park, Pa., 1954.

(15) L. Seiden, Doctoral Thesis, Northwestern University, Evanston, Ill., 1957.

(16) M. Meyers, F. Dachille, and R. Roy, Proceedings, Symposium on High Pressure Measurements, American Society of Mechanical Engineers, November, 1962, New York, N. Y.

(17) R. Roy and H. M. Cohen, *Nature*, **190**, 798 (1961).