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Coordination Compounds of Trivalent Metals with Unsymmetrical 1,3-Diketones. III. Mechanism of Stereochemical Rearrangements[1a]

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Kinetic parameters for stereochemical rearrangements of trifluoroacetylacetonates of the trivalent metals aluminum, gallium, indium, cobalt, and rhodium were measured using F^{19} magnetic resonance spectroscopy. Coalescence of resonance lines at 103, 61.5, and $<-57°$ for the aluminum, gallium, and indium compounds, respectively, yielded approximate isomerization rate constants of 34, 38, and >36 sec.$^{-1}$, respectively. The *cis* to *trans* isomerization of the cobalt compound was studied in the temperature range 66 to 99° by following the time dependent intensities of resonance lines; an activation energy of 30.7 ± 0.6 kcal./mole and a frequency factor of exp(15.19 ± 0.37) sec.$^{-1}$ were obtained. The *cis*-rhodium compound is stable with respect to isomerization at 160–165°. The racemization of partially resolved *cis*-chromium benzoylacetonate was studied by polarimetry and was found to be accompanied by *cis* to *trans* isomerization. The results of these experiments combined with point charge ionic model calculations allow the following conclusions: (1) The trigonal twist may be eliminated for the group III compounds and for *cis*-chromium benzoylacetonate but not for *cis*-cobalt trifluoroacetylacetonate. (2) The activation energy for the trigonal twist is higher than for the rhombic twist except for metal ions which have crystal field stabilization energy. (3) The mechanism of stereochemical rearrangements in all cases studied probably proceeds by rupture of one bond to give a symmetrical five-coordinate intermediate.

Introduction

A variety of mechanisms have been suggested for the racemization of octahedral complexes containing three bidentate ligands.[2–6] A potentially fruitful approach to this problem lies in the study of complexes with unsymmetrical bidentate ligands,[7] since racemization may or may not be accompanied by *cis–trans* isomerization depending upon the mechanism of the rearrangement.

We have recently described the separation and identification of the *cis* and *trans* metal benzoylacetonates[8] and trifluoroacetylacetonates[9] (referred to throughout as $M(bzac)_3$ and $M(tfac)_3$, respectively). In this paper we explore the possible mechanisms for stereochemical rearrangement of metal tris-chelate complexes in the light of (1) kinetic data for $Cr(bzac)_3$ and $M(tfac)_3$, M = Al, Ga, In, Co, and Rh, and (2) some point charge model calculations of the expected activation energy for the various intermediates.

Experimental

Materials.—Tris(1-phenyl-1,3-butanediono)chromium(III) and the tris(1,1,1-trifluoro-2,4-pentanediono)metal(III) complexes were prepared and separated into *cis* and *trans* isomers as described previously.[8,9] Solvents were reagent grade when readily available. All solvents used in n.m.r. studies were allowed to stand over alumina with periodic shaking in order to remove any remaining polar impurities.

Fluorine Magnetic Resonance Spectra.—Fluorine magnetic resonance spectra were obtained in the temperature region −57 to +182° on a Varian Associates Model V-4300-2 high resolution spectrometer at 56.4 Mc. Chemical shifts were measured using an appropriate audiofrequency side band. In general, solutions contained 11 g. of complex in 100 ml. of deuteriochloroform or chlorobenzene. In addition, spectra of $Al(tfac)_3$ were obtained in benzene, 1,2-dichloroethane, acetonitrile, and tetramethylene sulfone (11.5 g./100 ml. except for tetramethylene sulfone where solubility limited the concentration to *ca.* 3 g. /100 ml.).

Variable temperature spectra were obtained with the aid of a Varian variable temperature n.m.r. probe accessory, Model V-4340, and a dewar probe insert, Model V-4331-THR. The sample was cooled for low temperature spectra as previously described.[9] For high temperature spectra, the 5-mm. o.d. sample tubes were sealed *ca.* 3.5 cm. above the meniscus of the sample solution. Some bubbling was encountered in deuteriochloroform solutions above 127° and in chlorobenzene solutions above 176°. Below these temperatures, satisfactory spectra could be readily obtained.

The temperature was measured, before and after running a spectrum, with a copper–constantan thermocouple which was immersed in a sample tube containing chloroform (low temperature spectra) or mineral oil (high temperature spectra). The estimated accuracy of the reported temperatures is ±1.5°.

Rate of Isomerization of *cis*-$Co(tfac)_3$.—The rate of isomerization of *cis*-$Co(tfac)_3$ was determined in chloroform solution (11.0 g./100 ml.) at 66.1, 79.1, 90.4, and 99.2°. The rate was also determined at 79.1° in a chloroform solution containing 15.7 g./100 ml. Temperatures were measured to ±0.1° with an N.B.S. calibrated thermometer. The sample solution, sealed in a 5-mm. o.d. n.m.r. tube, was suspended in the vapors of boiling hexane, benzene, 2-bromobutane, or water for an appropriate length of time. The isomerization reaction was then quenched by plunging the sample tube into Dry Ice–acetone, and the fluorine resonance spectrum was recorded in quintuplicate at −40°. At this temperature the spectrum of a mixture of the *cis* and *trans* isomers consists of a high field doublet and a low field doublet with only a small region of overlap.[10] The overlap region between the two doublets was divided by assuming that the high field doublet is symmetrical about a line perpendicular to the base line and passing through the minimum between its two components. The relative concentrations of the *cis* and *trans* isomers were determined by measuring areas under the absorption curves with a planimeter.

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[1] (a) Abstracted in part from the Ph.D. Thesis of Robert C. Fay' University of Illinois, 1962; (b) National Science Foundation Predoctoral Fellow, 1960–1962; (c) Alfred P. Sloan Foundation Fellow.

[2] A. Werner, *Ber.*, **45**, 3061 (1912).

[3] W. Thomas, *J. Chem. Soc.*, **119**, 1140 (1921).

[4] P. C. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

[5] (a) W. G. Gehman, Ph.D. Thesis, Pennsylvania State University, State College, Pa., 1954; (b) L. Seiden, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1957.

[6] J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

[7] F. Basolo, *Chem. Rev.*, **52**, 459 (1953).

[8] R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962).

[9] R. C. Fay and T. S. Piper, *ibid.*, **85**, 500 (1963).

[10] See Fig. 1, ref. 9, and discussion therein.

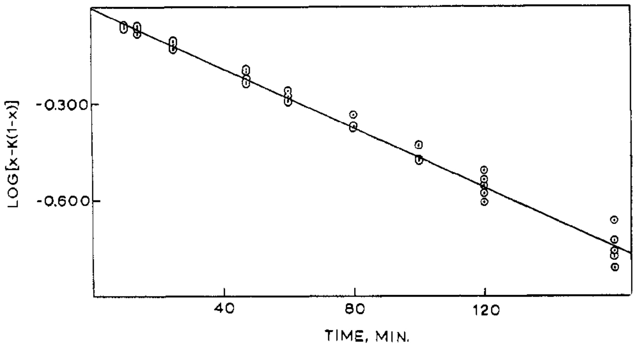

Fig. 1.—First-order rate plot for isomerization of *cis*-Co(tfac)$_3$, 15.7 g./100 ml. of chloroform at 79.1°.

For the first-order interconversion of *cis* and *trans* isomers, we may write

$$\text{trans} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{cis}$$

where the equilibrium constant, $K_{eq} = k_1/k_{-1}$, has been determined previously[9] to be 0.245 ± 0.018 at 79.1° and 0.254 ± 0.019 at 99.2°. Calculated values (from the heat of isomerization[9]) are 0.240 at 66.1° and 0.248 at 90.4°. The rate expression

$$\log\,[x - K_{eq}(1 - x)] = \frac{-k_{-1}(1 + K_{eq})t}{2.303}$$

may be readily derived where x is the fraction of the material in the *cis* form and $(1 - x)$ is the fraction in the *trans* form. A typical plot of $\log\,[x - K_{eq}(1 - x)]$ as a function of time is presented in Fig. 1. The data were treated by least-squares analyses including all five data points at each time, *t*. The rate constants for *cis* to *trans* isomerization, k_{-1}, were determined from the slope of the best straight line.

Partial Resolution and Racemization of *cis*-Cr(bzac)$_3$.—A Pyrex column, 30 mm. o.d., equipped with a coarse glass frit and a Teflon stopcock was filled to a height of 227 cm. with 1050 g. of B & A reagent grade lactose powder. The lactose had been dried at 125° and carefully sieved to 80 mesh. The method of packing the column suggested by Collman[11] was followed. The lactose was added to the column in 30–40 g. quantities as a slurry in cyclohexane. As the lactose settled, the sides of the column were tapped vigorously with a rubber hammer. Some of the cyclohexane was allowed to drain to promote further settling. Finally, 10 lb. pressure of nitrogen was applied at the top of the column while vigorous tapping was continued. By assuming that the *cis*-Cr(bzac)$_3$ moves with the solvent front, the free volume of the column was found to be 560 cc.

After passing *ca.* 250 ml. of 1:1 benzene–hexane through the column, *cis*-Cr(bzac)$_3$ (181 mg.) in 10 ml. of benzene was placed on the column. The complex formed a narrow band 2.5 cm. wide which broadened considerably in the course of elution with 1:1 benzene–hexane. Breakthrough occurred in 23 hr., while complete elution of the compound required 31 hr. The first (18.6 mg.) and last (20.4 mg.) fractions were collected, the benzene–hexane was removed by vacuum distillation at room temperature, and rotatory dispersion curves were obtained in chloroform solution. The first fraction showed a positive Cotton effect (Fig. 2), and the last fraction exhibited a negative Cotton effect. The extremum in the dispersion curves occurs near 577 mμ. The observed rotations at 577 mμ and 27° were +0.063 and −0.065° for the first and last fractions, respectively. Molecular rotations (specific rotation × molecular weight ÷ 100) were calculated to be +550 and −520, respectively. Optical rotations were measured in a 5-cm. cell on a Rudolph recording spectropolarimeter.

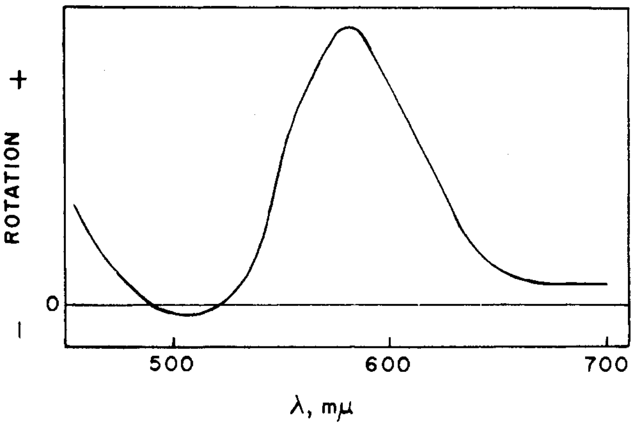

Fig. 2.—Rotatory dispersion of *cis*-Cr(bzac)$_3$, first eluted fraction from lactose.

Attempts to resolve *cis*-Co(tfac)$_3$ on the same lactose column, even using solvents as nonpolar as 5% benzene–95% hexane, were unsuccessful.

The racemization of *cis*-Cr(bzac)$_3$ was studied at 577 mμ in a 5-cm. cell to which a 12-mm. o.d. Pyrex tube had been sealed. This tube allowed the solution to be sealed off *in vacuo* at Dry Ice–acetone temperature. Little or no strain was introduced in the silica windows as a result of this treatment. The identity of the racemization product was determined by microscopy and X-ray powder patterns.

Results

Variable Temperature Fluorine N.m.r. Spectra.—The fluorine resonance spectrum of In(tfac)$_3$ in deuteriochloroform solution in the temperature region 31 to −57° showed only a single sharp resonance line. The spectra of Ga(tfac)$_3$ below 50° and Al(tfac)$_3$ below 89° in deuteriochloroform consist of four lines. The chemical shifts of the three lines at higher field relative to the line at lowest field exhibit a marked temperature dependence. The data are plotted in Fig. 3 and 4. In the region 39 to 100°, Al(tfac)$_3$ showed the same temperature dependence of the chemical shifts in chlorobenzene solution as was observed in deuteriochloroform. In the region just above 50 and 89° for the gallium and aluminum compounds, respectively, the four resonance lines merge into a single broad line which sharpens as the temperature is raised. The temperature at which the four peaks just coalesce into a single peak is 61.5° for Ga(tfac)$_3$ and 103° for Al(tfac)$_3$. N.m.r. spectra at several selected temperatures near the coalescence region are presented in Fig. 5.

The n.m.r. spectrum of a mixture of *cis*- and *trans*-Co(tfac)$_3$ in chlorobenzene showed strong temperature dependence in the region −41 to +83°, similar to that of the aluminum and gallium compounds. The resonance lines were very much broader, however, and they began to merge as the chemical shifts between the four lines decreased with increasing temperature. At 94° only a single broad peak could be distinguished; this peak, however, did not sharpen as the temperature was raised. At 182° the line width was still *ca.* 10 c.p.s.

The spectrum of *trans*-Rh(tfac)$_3$ in chlorobenzene

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(11) J. P. Collman, R. P. Blair, R. L. Marshall, and L. Slade, *Inorg. Chem.*, **2**, 576 (1963).

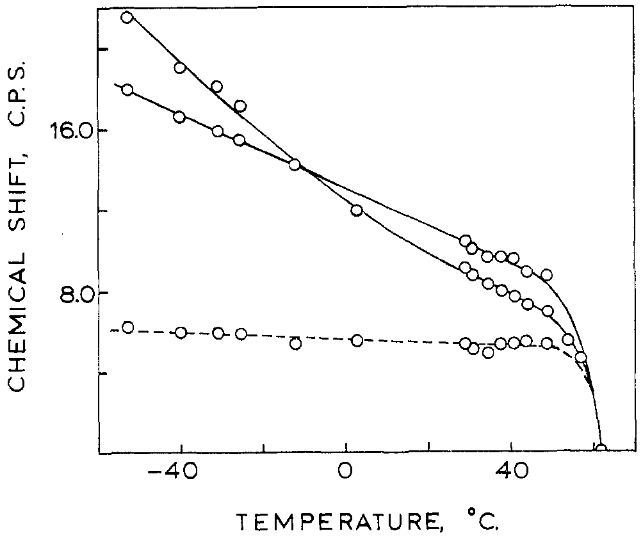

Fig. 3.—Temperature variation of fluorine chemical shifts for an equilibrium mixture of *cis-* and *trans*-$Ga(tfac)_3$ [11 g. of $Ga(tfac)_3$/100 ml. of $CDCl_3$]. Chemical shifts of the *cis* isomer, – – – –, and the two high field resonances of the *trans* isomer, ———, are plotted relative to the resonance of the *trans* isomer which occurs at lowest field.

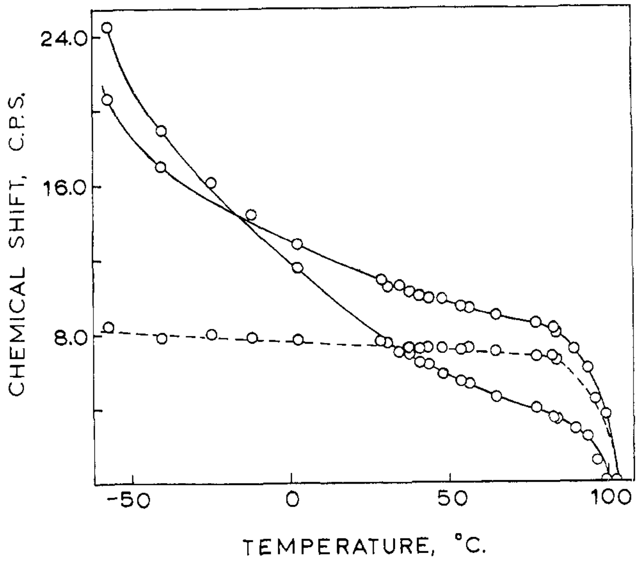

Fig. 4.—Temperature variation of fluorine chemical shifts for an equilibrium mixture of *cis-* and *trans*-$Al(tfac)_3$ [11.5 g. of $Al(tfac)_3$/100 ml. of $CDCl_3$]. Chemical shifts of the *cis* isomer, – – – –, and the two high field resonances of the *trans* isomer, ———, are plotted relative to the resonance of the *trans* isomer which occurs at lowest field.

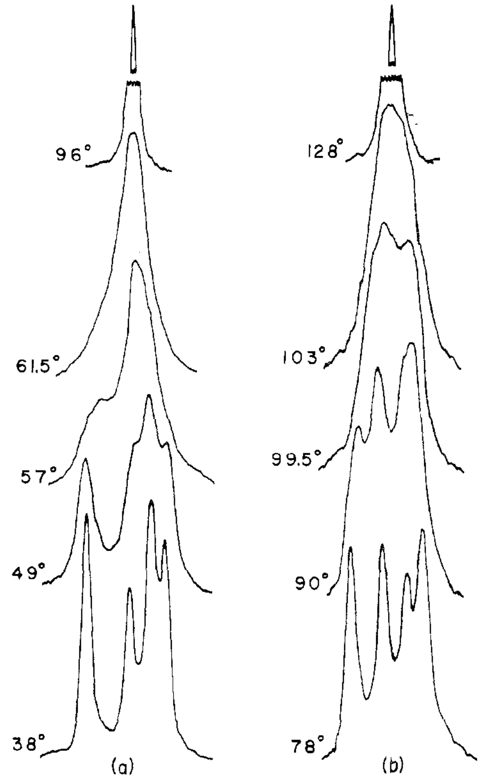

Fig. 5.—Fluorine resonance spectra of (a) $Ga(tfac)_3$ and (b) $Al(tfac)_3$ at several temperatures near the coalescence region.

Table I

Coalescence of Resonance Lines for $Al(tfac)_3$ in Various Solvents

Solvent	Dielectric constant[a]	Coalescence temp., °C.	ΔF^*, kcal./mole
Benzene[b]	2.13	97.5 ± 2	19.3
Deuteriochloroform[b]	3.82	103 ± 2	19.6
Chlorobenzene[c]	4.73	97.5 ± 2	19.4
1,2-Dichloroethane[b]	8.5	90 ± 2	19.2
Acetonitrile[b]	28.6	71 ± 2	18.3
Tetramethylene sulfone[d]	39.4	75.5 ± 3	18.0

[a] Extrapolated from data in International Critical Tables, Vol. 6, pp. 83–89, except for tetramethylene sulfone. Value for tetramethylene sulfone was extrapolated from the data of B. D. Coleman and R. M. Fuoss, *J. Am. Chem. Soc.*, **77**, 5472 (1955), and R. L. Burwell, Jr., and C. H. Langford, *ibid.*, **81**, 3799 (1959). [b] 11.5 g./100 ml. solvent. [c] 10 g./100 ml. [d] *ca.* 3 g./100 ml.

was found to consist of three sharp lines in the region 31 to 182°. The chemical shifts (Fig. 6) exhibit the same general temperature dependence as found for the aluminum and gallium compounds in chloroform. There is no suggestion of coalescence even at 182°, nor does there appear a resonance line due to the *cis* isomer. The extreme stability of $Rh(tfac)_3$ with respect to isomerization was further shown by the fact that the *cis* isomer gave no resonance lines characteristic of the *trans* isomer after heating for 52.5 hr. at 160–165° (11 g./100 ml. of chlorobenzene). Some decomposition to give a brown precipitate was observed after 38 hr., but no *cis–trans* isomerization.

The coalescence of the four resonance lines of $Al(tfac)_3$ was investigated in several solvents of different dielectric constant. The frequency separation between the lines in the various solvents was very similar, although somewhat smaller for 1,2-dichloroethane and acetonitrile. The Eyring equation[12] was assumed to hold, and the free energies of activation, ΔF^*, were then calculated from the estimated frequency separations and coalescence temperatures. The results are presented in Table I.

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(12) S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 190.

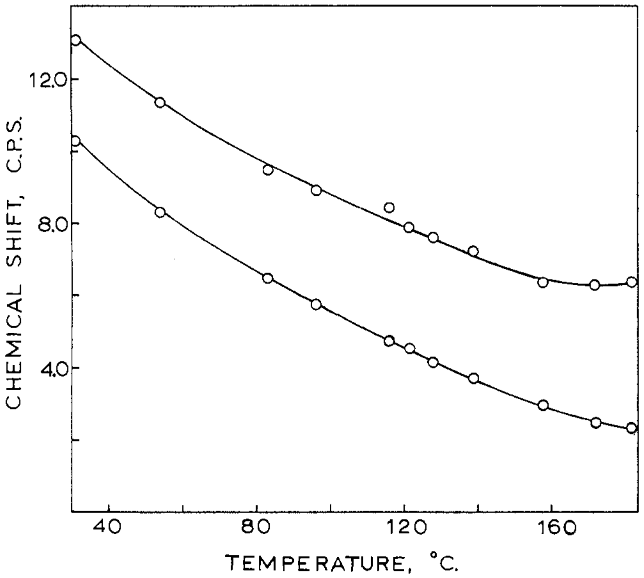

Fig. 6.—Temperature variation of fluorine chemical shifts for *trans*-Rh(tfac)$_3$, 11 g./100 ml. of chlorobenzene. Chemical shifts of the two resonances which occur at high field are plotted relative to the resonance at low field.

TABLE II

RATE OF ISOMERIZATION OF Co(tfac)$_3$ IN CHLOROFORM SOLUTION

Concn., g./100 ml.	Temp., °C.	$k_{-1} \times 10^4$, sec.$^{-1}$	$k_1 \times 10^4$, sec.$^{-1}$
11.0	66.1	0.247 ± 0.010	0.059 ± 0.005
11.0	79.1	1.52 ± 0.04	0.37 ± 0.03
15.7	79.1	1.44 ± 0.04	0.35 ± 0.03
11.0	90.4	5.20 ± 0.16	1.3 ± 0.1
11.0	99.2	14.5 ± 0.5	3.7 ± 0.3

The fluorine resonance spectrum of a mixture of In(tfac)$_3$ (11.6 mg., 0.020 mmole) and trifluoroacetylacetone (15.5 μl., 0.124 mmole) in 0.25 ml. of chloroform was found to consist at 31° of two sharp lines. The first line was found at +165.4 c.p.s. relative to *cis*-Rh(tfac)$_3$ (11.3 g./100 ml. of CHCl$_3$ in a sealed 1.5-mm. o.d. capillary tube); the second, twice as intense as the first, was observed at +218.4 c.p.s. Similarly, two resonance lines were observed for Al(tfac)$_3$ in the presence of excess trifluoroacetylacetone in the temperature region 103 to 133°.

Isomerization of *cis*-Co(tfac)$_3$.—Kinetic data for the isomerization of *cis*-Co(tfac)$_3$ are presented in Table II. Rate constants for the reverse reaction, calculated from the equilibrium constants, are also included. Errors are estimated at the 95% confidence level. The isomerization follows first-order kinetics as shown by Fig. 1 and also by the fact that nearly the same value was obtained for the rate constant at two different concentrations. A plot of log k_{-1} *vs.* $1/T$ (Fig. 7) gives an Arrhenius activation energy of 30.7 ± 0.6 kcal./mole and a frequency factor of exp(15.19 ± 0.37) sec.$^{-1}$. Estimates of error for the activation energy and the frequency factor are one standard deviation. Assuming that the Eyring equation holds, a positive entropy of activation of 8.6 ± 1.7 cal./deg. mole was calculated.

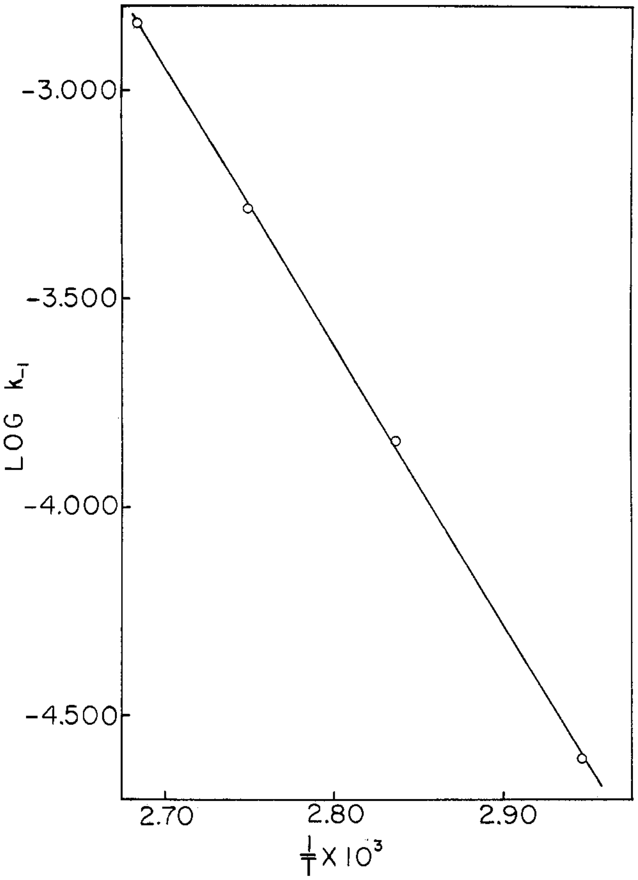

Fig. 7.—Arrhenius plot for isomerization of *cis*-Co(tfac)$_3$.

Racemization and Isomerization of *cis*-Cr(bzac)$_3$.—*cis*-Cr(bzac)$_3$ was found to be optically stable in chloroform solution at temperatures up to 51.4°. No losses in optical activity were observed after 61 hr. at 26.5°, 19 hr. at 42.5°, nor after 16 hr. at 51.4°. At 95.5° in 1,1,2,2-tetrachloroethane the rate constant for inversion[13] was found to be 0.0023 ± 0.0002 min.$^{-1}$, and at 105.0° in the same solvent the rate constant was estimated to be 0.009 ± 0.002 min.$^{-1}$. The most important observation is that at both of these temperatures racemization was accompanied by *cis–trans* isomerization. Although no quantitative analytical method exists for measuring the rate of isomerization in this case, microscopic evaluation of the relative amounts of *cis* and *trans* isomers in the racemized product indicated that the rate of isomerization must be approximately the same as the rate of racemization.

Discussion

Fluorine Resonance Spectra.—The coalescence of n.m.r. signals due to rapid exchange of nuclei between two magnetically nonequivalent sites has been observed in both organic and inorganic systems.[14] The characteristic spectra show the gradual merging of two sharp resonance lines into a single broad line which

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[13] This is the rate at which the optical isomers are interconverted and one-half times the rate of loss of optical activity.

[14] See, for example (a) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); (b) G. Claeson, G. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4357 (1961); (c) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *ibid.*, **84**, 386 (1962); (d) E. L. Muetterties and W. D. Phillips, *ibid.*, **79**, 322 (1957); (e) C. R. McCoy and A. L. Allred, *ibid.*, **84**, 912 (1962).

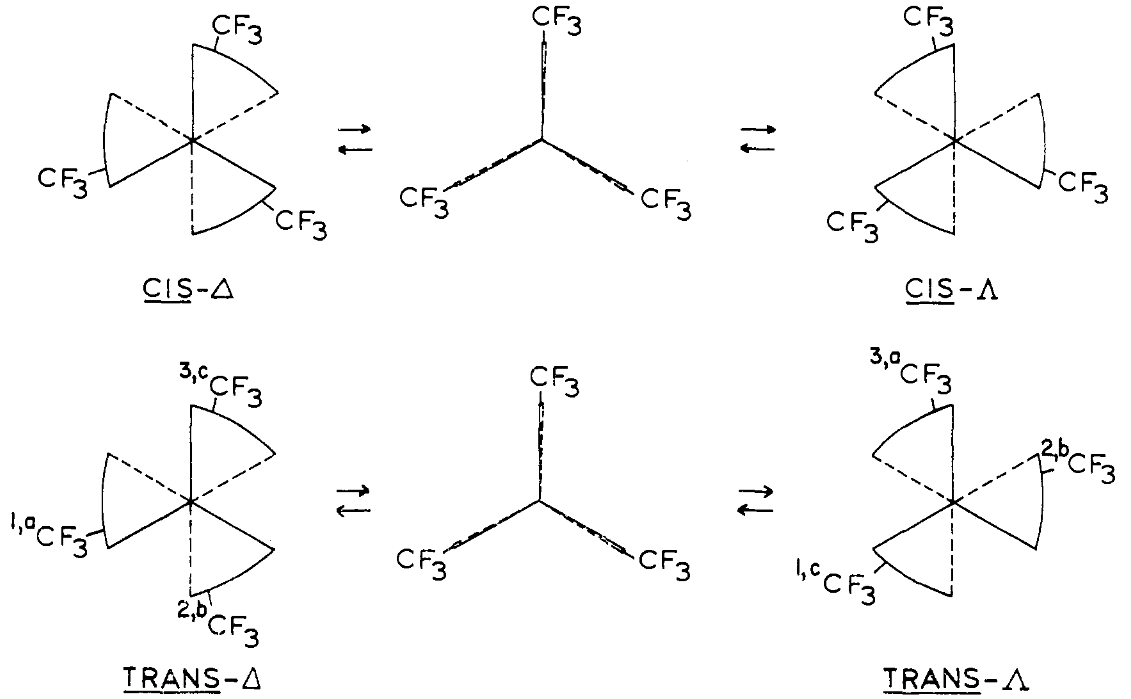

Fig. 8.—Racemization of *cis* and *trans* metal trifluoroacetylacetonates by thet rigonal twist mechanism. The absolute configuration of the optical isomers is indicated by Δ and Λ. Numbers label trifluoromethyl groups, and letters indicate environments.

eventually sharpens as the temperature is raised. The spectra of $Al(tfac)_3$ and $Ga(tfac)_3$ reported here exhibit these same characteristics, and therefore the coalescence of the four resonance lines is attributed to rapid exchange of trifluoromethyl groups between the four possible nonequivalent sites of the *cis* and *trans* isomers. This exchange may be viewed as a very rapid racemization and isomerization.

For exchange between two equally populated sites, Gutowsky and Holm[14a] have shown that at the temperature of coalescence the rate constant for exchange is given by $\delta\omega/2\sqrt{2}$ where $\delta\omega$ is the frequency separation in radians/sec. between the two lines in the absence of exchange. We have not attempted a detailed treatment of the coalescence herein observed. Mathematical difficulties are formidable, and moreover one would have to know the details of the mechanism of exchange, which may proceed stepwise. An additional barrier to a precise treatment is the temperature dependence of the chemical shifts in the absence of exchange, probably due to interaction of the complexes with the solvent. It is reasonable to assume, however, that, in the present case also, the rate constant for exchange is of the same order of magnitude as the frequency separation between the lines in the absence of exchange. We have extrapolated the chemical shift dependence in the absence of exchange to the coalescence temperature and have taken the frequency separation, $\delta\omega$, as the average separation in radians/sec. between the low field *trans* resonance and the three resonances at higher field. Setting the rate constant at the coalescence temperature equal to $\delta\omega$, we obtain rate constants of 34 sec.$^{-1}$ at 103° for $Al(tfac)_3$ and 38 sec.$^{-1}$ at 61.5° for $Ga(tfac)_3$. Since $In(tfac)_3$ gives a single sharp line at −57°, a lower limit of *ca.* 36 sec.$^{-1}$ may be assigned for the rate constant at −57° by assuming that $\delta\omega$ is the same as for the aluminum and gallium compounds. These rate constants may be in error by an order of magnitude, but this propagates an error of only 2 kcal./mole or less in the activation energies.

The free energies of activation at the coalescence temperatures, ΔF^*, were calculated directly from the rate constants using the Eyring expression

$$k = \frac{RT}{Nh}e^{-\Delta F^*/RT}$$

and making the usual assumption that the transmission coefficient is unity. The activation energies may be calculated from the Arrhenius equation by assuming a reasonable value for the frequency factor, A. We have assumed that A for the exchange of trifluoromethyl groups in the aluminum, gallium, and indium compounds is the same as A for the *cis* to *trans* isomerization of $Co(tfac)_3$, *viz.*, exp(15.19 ± 0.37). The results for the rates and energies of activation determined from the coalescence behavior of the aluminum, gallium, and indium compounds are presented in Table III along with similar data for the *cis* to *trans* isomerization of the cobalt and rhodium compounds. The limits on the data for the rhodium compound are derived from the fact that no *cis–trans* isomerization was observed after 52.5 hr. at 160–165°, from which we infer that the half-time for isomerization must be greater than 210 hr. The same frequency factor was assumed as found for $Co(tfac)_3$.

The data for the group III complexes are of particular interest since, because of lability, activation energies for the racemization and isomerization of group III complexes are not generally available. The energies are of reasonable magnitude, and the order of activa-

TABLE III

KINETIC DATA FOR EXCHANGE OF CHELATE RINGS IN METAL TRIFLUOROACETYLACETONATES

Compound	Coalescence temp., °C.	k, sec.$^{-1a}$	ΔF^*, kcal./mole^{a,b}	ΔE^*, kcal./mole^{b}
In(tfac)$_3$	<-57	>36	$<11.0 \pm 1.0$	$<13.5 \pm 1.1$
Ga(tfac)$_3$	61.5	38	17.2 ± 1.5	20.8 ± 1.6
Al(tfac)$_3$	103	34	19.6 ± 1.7	23.5 ± 1.8
Co(tfac)$_3$	>182	1.45×10^{-3}	26.80 ± 0.03	30.7 ± 0.6
Rh(tfac)$_3$	>182	$<9.2 \times 10^{-7}$	>37.9	>42.4

[a] Data for the aluminum and gallium compounds refer to the coalescence temperatures. Data for the indium, cobalt, and rhodium compounds refer to −57, 99.2, and 163°, respectively. [b] The reported errors for the group III complexes were estimated assuming a one order of magnitude error in the rate constants.

tion energies, In < Ga < Al < Co < Rh, is in agreement with qualitative estimates for the relative bond energies in this series.

The broad resonance lines observed for Co(tfac)$_3$ at slightly elevated temperatures which do not sharpen with increasing temperature are not characteristic of exchange. Kinetic data in the range 66.1 to 99.2° indicate that coalescence is not expected until *ca.* 219°. The broadening is probably due to a small amount of decomposition to give a Co(II)-containing species.[15]

Mechanism of Rearrangements.—We turn now to a consideration of the mechanism of these stereochemical rearrangements. The dissociation mechanism

$$\mathrm{M(tfac)_3} \rightleftharpoons \mathrm{M(tfac)_2^+} + \mathrm{tfac^-}$$

which was first suggested by Thomas[3] for the racemization of the metal trisoxalates, may be regarded *ab initio* as a rather unlikely mechanism for the exchange of ligands for a complex of zero charge in a medium of low dielectric constant. If we preserve the 90° O–M–O bond angles within a given chelate ring[16] in the four-coordinate intermediate, the best electrostatic disposition of the four oxygen ligands has D_{2d} symmetry. A point charge model calculation was performed for the aluminum compound assuming D_{2d} symmetry for the cation, an aluminum–oxygen distance of 1.85 Å.,[17] and that interactions of the resulting large ions with the chloroform solvent may be neglected. The result for the activation energy in kcal./mole is $1077q - 1124q^2$ where q is the number of electronic charges on each oxygen ligand. For a charge of 0.5 the calculated activation energy is 258 kcal./mole. The effective charge on the ligands is probably somewhat greater than 0.5 since the neglected lone pair permanent dipole moments and the induced dipole moments of the oxygen atoms will contribute to the effective q. Even if q is set equal to 0.9 an activation energy of 59 kcal. is obtained. Inclusion of ion pair interactions does not reduce this value by more than *ca.* 7 kcal./mole. These energies are much larger than the experimental value of 23.5 kcal./mole.

Further evidence for rejecting the dissociation mechanism is found in the fluorine resonance spectra of In(tfac)$_3$ and Al(tfac)$_3$ above the coalescence temperatures in the presence of excess trifluoroacetylacetone. A dissociation mechanism predicts the coalescence of the trifluoroacetylacetone resonance with the resonance due to the complex near 130° for Al(tfac)$_3$ and at less than −39° for In(tfac)$_3$. In contrast, the spectra observed reveal two sharp resonance lines at 133 and +31° for the aluminum and indium compounds, respectively.

An intramolecular twisting mechanism has been suggested independently by Gehman,[5a] Seiden,[5b] and Bailar[6] in which racemization is achieved by twisting three of the ligands through an angle of 120° about the C_3 or pseudo-C_3 axis of the octahedron (see Fig. 8). We shall refer to this mechanism as the trigonal twist after the symmetry of the ligand field in the transition state. The transition state assumed by Bailar is a trigonal prism in which all of the bond angles are equal to 81°10′. For this model the increase in ligand–ligand repulsion relative to the octahedron was calculated to be $0.194 \cdot q^2/R$. There is also a contribution to the activation energy due to strain which is introduced in the chelate rings upon decreasing the bond angles. Since the latter energy is not readily evaluated, it is best to calculate the activation energy for a trigonal prism in which the 90° O–M–O bond angles within a given chelate ring have been preserved. For this model, for complexes of ions which do not have crystal field stabilization energy, the only contribution to the activation energy is the increase in ligand–ligand repulsion; an activation energy of $0.242q^2/R$ results. Assuming again that R is 1.85 Å. for Al(tfac)$_3$, the calculated activation energy is $43.4q^2$ kcal./mole. Although this activation energy is near the experimental value for certain choices of q, it will be shown below that the rhombic twist mechanism provides a lower energy path for all values of q.

It will be noted (Fig. 8) that the trigonal twist interconverts optical antipodes[18] but fails to interconvert *cis* and *trans* isomers. Since the racemization of *cis*-Cr(bzac)$_3$ was accompanied by isomerization, the trigonal twist may be eliminated as the lowest energy path for racemization. It will also be noted that the

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(15) Irreversible decomposition of metal diketone chelates has been described in a recent series of papers by Arnett and co-workers. See E. M. Arnett and M. A. Mendelsohn, *J. Am. Chem. Soc.*, **84**, 3824 (1962), and earlier papers cited therein.

(16) The O–M–O bond angle in metal trisacetylacetonates has been found to be nearly 90°. See R. B. Roof, *Acta Cryst.*, **9**, 781 (1956); V. M. Padmanabhan, *Proc. Indian Acad. Sci.*, **47A**, 329 (1958); E. A. Shugam and L. M. Shkolinikova, *Dokl. Akad. Nauk SSSR*, **133**, 386 (1960).

(17) The iron–oxygen distance in iron(III) acetylacetonate is 1.95 Å. (R. B. Roof, ref. 16) and the ionic radius of Al(III) is 0.10 Å. less than that of Fe(III) [V. M. Goldschmidt, *Ber.*, **60**, 1263 (1927)].

(18) T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961). This note explains the Δ and Λ notation.

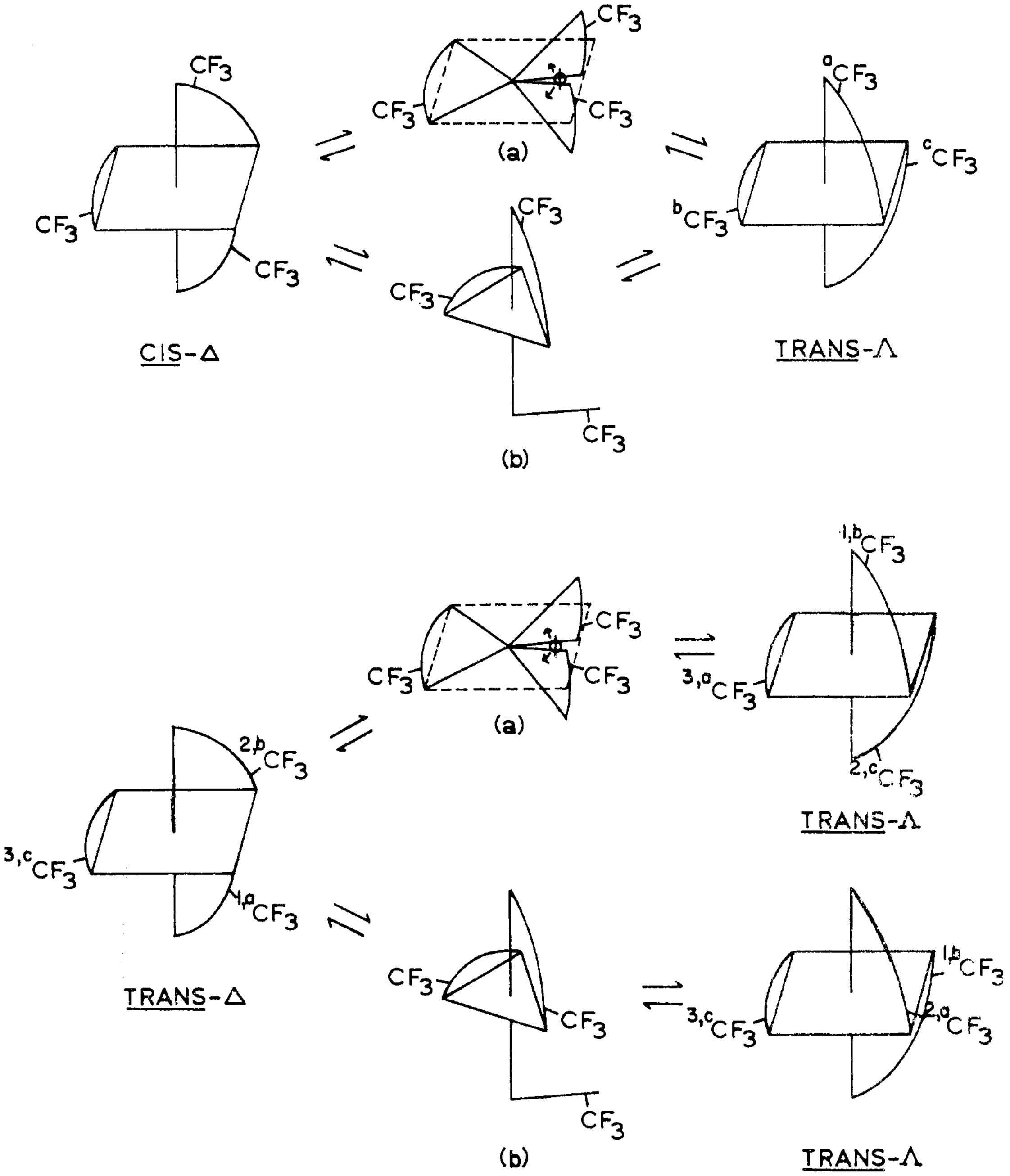

Fig. 9.—Stereochemical rearrangements by (a) the rhombic twist mechanism and (b) the bond rupture mechanism. Numbers label trifluoromethyl groups and letters indicate environments.

trigonal twist interchanges the environments of trifluoromethyl groups 1 and 3 but leaves the environments of trifluoromethyl group 2 and the trifluoromethyl groups of the *cis* isomer unaffected. The trigonal twist, therefore, predicts the coalescence of two *trans* isomer lines in the n.m.r. spectra while the other two lines should remain sharp. Since the high temperature spectra of $Al(tfac)_3$ and $Ga(tfac)_3$ (Fig. 5) reveal the coalescence of all four resonance lines, the trigonal twist may again be eliminated as the lowest energy path for the exchange. Our experiments do not allow elimination of the trigonal twist in the case of $Co(tfac)_3$.

The rhombic twist mechanism suggested by Ray and Dutt[4] and the bond rupture mechanism proposed by Werner[2] will be considered together because both can give simultaneous racemization, isomerization, and exchange of all four trifluoromethyl groups. The two mechanisms are pictured in Fig. 9. In the rhombic twist mechanism, two of the chelate rings move through an angle of 90° in opposite directions about axes which pass through the metal ion perpendicular to their own planes, while the third chelate ring remains essentially unchanged. The ligand field in the transition state has pseudorhombic symmetry, hence the name, rhombic twist. The mechanism proposed by Werner involves momentary rupture of one bond to give a five-coordinate intermediate with eventual re-formation of the bond to give the other optical isomer. The intermediate which will be considered here is a trigonal bipyramid in which the dangling ligand occupies an axial position.

This is only one possible intermediate which can form once a metal–oxygen bond has been ruptured. In addition to trigonal bipyramidal intermediates, square pyramidal intermediates are possible if one allows migration of a bound oxygen ligand to the vacant coordination position. It is also possible to have an intermediate in which the vacated octahedral position is occupied by a solvent molecule.

Both mechanisms (Fig. 9) always convert a *cis*-Δ isomer to a *trans*-Λ isomer; a *trans*-Δ isomer, however, may be converted to a *cis*-Λ or a *trans*-Λ isomer depending upon which two chelate rings are rotated in the rhombic twist mechanism or which bond is broken in the bond rupture mechanism. The interconversion of right- and left-handed *trans* molecules leads to interchange of the environments of three trifluoromethyl groups by the rhombic twist mechanism and two trifluoromethyl groups by the bond rupture mechanism. The interconversion of *cis* and *trans* isomers, of course, leads to exchange of all four trifluoromethyl groups. Since both mechanisms provide a path for the exchange of the four trifluoromethyl groups in one or more steps, both are consistent with the coalescence of four resonance lines observed in the n.m.r. spectra. If exchange proceeds *via* a five-coordinate intermediate, the intermediate must be very short-lived since its n.m.r. spectrum is not observed.

The order of activation energies, In < Ga < Al < Co < Rh, is consistent with either mechanism. If the mechanism involves bond rupture, one would predict increasing activation energy with decreasing radius of the metal ion within group III and greater activation energies for the compounds of the transition elements because of the larger effective nuclear charge of ions with electronic configuration d^6. For the group III complexes, the twist mechanisms predict the same result since increases in ligand–ligand repulsion upon going to the transition state are inversely proportional to the metal–ligand distance.

Some point charge model calculations were carried out in an attempt to distinguish between the two mechanisms. The rhombic twist transition state suggested by Ray and Dutt has 90° O–M–O bond angles in the chelate rings and an angle ϕ of 90° between the planes of the two rings which are undergoing rotation (see Fig. 9). We have calculated the increase in ligand–ligand repulsion energy for this transition state relative to the octahedron and have obtained the rather large value of $0.286q^2/R$. It is obvious, however, that the suggested transition state is not the configuration of lowest energy. The activation energy may be decreased by allowing the angle ϕ to increase as the two rings rotate. In general, the ligand–ligand repulsion energy may be expressed in terms of ϕ by the relation

$$V = q^2/R\{3/\sqrt{2} + 4[2 + \cos(\phi/2) - \sin(\phi/2)]^{-1/2} + \\ 4[2 + \cos(\phi/2) + \sin(\phi/2)]^{-1/2} + \\ 2[1 - \cos\phi]^{-1/2} + 2[3 - \cos\phi]^{-1/2}\}$$

This function minus the ligand–ligand repulsion of the octahedral configuration $(9.985q^2/R)$ is plotted in Fig. 10 and the minimum, *viz.*, $0.144\ q^2/R$, is obtained for ϕ equal to 115°. The rhombic twist, therefore, provides a lower energy path for stereochemical rearrangements than the trigonal twist for all values of q and R for complexes of ions which do not have crystal field stabilization energy. The calculated rhombic twist activation energies agree with the experimental values for the following values of q: $Al(tfac)_3$, 0.95; $Ga(tfac)_3$, 0.91; $In(tfac)_3$, ≤ 0.79.

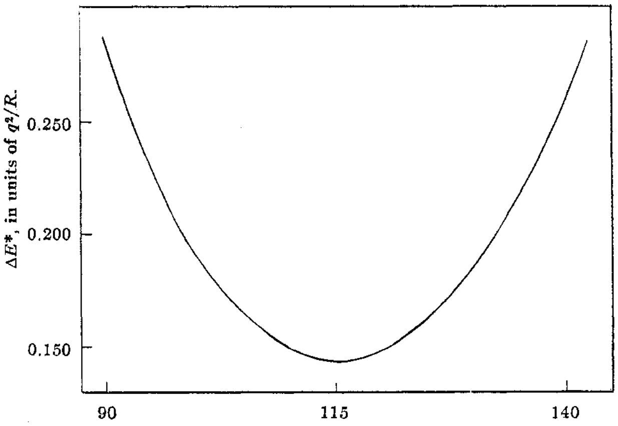

Fig. 10.—Activation energy for the rhombic twist mechanism as a function of the angle ϕ.

For complexes of ions which do have crystal field stabilization energy, it is a remarkable fact that the stabilization energy may actually favor the intermediate of the trigonal twist over the octahedron. Calculations based on approximate radial crystal field parameters for chromium(III)[19] indicate that this stabilization energy may amount to about 11 kcal./mole for chromium(III). Similar calculations for cobalt(III) (assuming $\rho_4 = 12{,}000$ cm.$^{-1}$, $\rho_2 = 18{,}000$ to 24,000 cm.$^{-1}$) suggest that the crystal field stabilization energy may favor the trigonal prism by 21 to 30 kcal./mole. It is common to take the crystal field stabilization energy as indicative of the most stable geometrical configuration. This argument neglects both the primary bonding forces and the ligand–ligand repulsion energy; it clearly fails for cobalt complexes. However, this observation suggests that if stable trigonal prismatic cobalt complexes were to be isolated, they might well involve ligands with a strong field and low mutual repulsions. We do not know the change in crystal field stabilization energy on going to the rhombic intermediate; all previous experience with such calculations suggests that there will be a loss of stabilization energy. It is conceivable then that the crystal field stabilization energy might in some cases offset the mutual repulsions of the ligands, thus promoting the trigonal over the rhombic twist in cases where there is no bond rupture.

Point charge model calculations were performed for a pseudotrigonal bipyramidal intermediate having 90° O–M–O bond angles in both chelate rings and the dangling ligand in an axial position. Two models

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(19) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **36**, 3330 (1962).

were selected. In the first, a charge of q was assumed on all six oxygen atoms and interactions of the charge on the dangling oxygen atom with the rest of the complex and the deuteriochloroform solvent were neglected. The result for the activation energy was $[3q - 3.452 \cdot q^2]/R$. For the group III complexes, this model gives agreement with the experimental activation energies for values of q near 0.83; it is somewhat unrealistic, however, since the charge on the unbound end of the dangling ligand is expected to shift in large part to the end which is bound to the metal ion.

In the second model, a charge of $2q$ was assumed to reside on the bound oxygen atom of the dangling ligand and a charge of q was assigned, as usual, to the other bound oxygen atoms. The ligand–ligand repulsion energy could be readily evaluated, but attempted molecular orbital calculations of loss of delocalization energy in the dangling ligand proved to be sufficiently sensitive to the choice of resonance integrals so as to be useless.

In view of these difficulties encountered in calculating the expected activation energy for the trigonal bipyramidal intermediate, it is not possible to predict whether the bond rupture or the rhombic twist mechanism has the lower activation energy. However, two pieces of experimental evidence may be cited in favor of the bond rupture mechanism for certain of the rearrangements observed in the present work.

The first of these concerns the magnitude of the frequency factor. Ray and Dutt[4] found an unusually low frequency factor of exp(4.16) sec^{-1} for the inversion of the tris(biguanidinium)cobalt(III) cation. The low frequency factor was interpreted as indicative of a relatively long time interval needed to get the activation energy into the appropriate vibrational modes for the rather improbable twisting motion, with a consequent increase in the chance of deactivation. The high frequency factor of exp(15.19 ± 0.37) sec.^{-1} which is reported here for the *cis–trans* isomerization of Co(tfac)_3 is not consistent with the rhombic twist mechanism.

Second, the coalescence temperature for trifluoromethyl group exchange in Al(tfac)_3 and the free energy of activation for the exchange (at the coalescence temperature) were found to decrease, in general, with increasing dielectric constant of the solvent (see Table I). The decrease in ΔF^* is probably[20] due to a decrease in ΔH^* as a result of greater charge separation and greater solvation of the transition state. Since the expected dipole moments of the rhombic twist intermediates are less than that of the *cis* isomer and comparable to that of the *trans* isomer, the rhombic twist mechanism predicts less charge separation in the transition state; the bond rupture mechanism, on the other hand, predicts greater solvation in the transition state due to the presence of the partially charged dangling carbonyl group.

Having demonstrated that twisting mechanisms may be definitely eliminated in certain cases, it is of interest to list factors which may favor such mechanisms. Intramolecular twisting mechanisms are most likely to occur with (1) cationic complexes, (2) complexes which contain rigid bidentate or polydentate ligands, (3) complexes of ions which have crystal field stabilization energy (trigonal twist favored), and (4) rearrangements which occur in the gas phase or in solvents of low dielectric constant. The importance of twisting mechanisms for ions containing rigid bidentate ligands, for example Fe(phen)_3^{2+} and Fe(bipy)_3^{2+}, has been demonstrated by Basolo.[21] More recently, Busch[22] has accounted for the racemization of Co(EDTA)^- in acid solution in terms of the trigonal twist mechanism. The importance of bond rupture mechanisms for anionic complexes, for example $\text{Cr(C}_2\text{O}_4)_3^{3-}$, has been indicated by the results of Hamm[23] and particularly Llewellyn and Odell.[24]

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[20] The difference in ΔF^* of 1.6 kcal./mole upon going from deuteriochloroform (ΔF^* = 19.6 kcal./mole at 103°) to tetramethylene sulfone (ΔF^* = 18.0 kcal./mole at 75.5°) can be attributed entirely to the temperature difference if ΔS^* is very large and negative (*ca.* −58 e.u.). This possibility is regarded unlikely in view of the positive ΔS^* of 8.6 e.u. obtained for isomerization of *cis*-Co(tfac)_3.

[21] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 3807 (1954).

[22] D. W. Cooke, Y. A. Im, and D. H. Busch, *Inorg. Chem.*, **1**, 13 (1962).

[23] R. E. Hamm, R. Kollrack, G. L. Welch, and R. H. Perkins, *J. Am. Chem. Soc.*, **83**, 340 (1961).

[24] D. R. Llewellyn and L. Odell, *Proc. Australian At. Energy Symp.*, 623 (1958).