

## Isorotatory Points and Racemization

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When the optical rotatory dispersion spectrum of a reacting solution is followed as a function of time, common «isorotatory» points ( $[\alpha], \lambda$ ) may be observed under a variety of circumstances. Examples are given. The case of racemization is considered in detail, where the isorotatory points occur at  $(0, \lambda)$ , and the racemization of (+) tris-*o*-phenanthrolineiron(II) perchlorate is used to illustrate the application of rotatory dispersion measurements to mechanistic studies.

## Introduction

Isosbestic points are commonly observed in solutions of reacting species, and a penetrating analysis<sup>1</sup> of their occurrence is available. A similar analysis should, in principle, be applicable to any absorption or dispersion phenomenon, depending only on the overlapping of the electronic transitions responsible. In particular, Cotton effects, the phenomena associated with optical activity in the region of electronic transitions, would be expected to show points of constant optical rotation or circular dichroism at a fixed wavelength during reactions of certain kinds. We have observed many such points, and present here some results from work on optical rotatory dispersion, where we have found, in a number of cases, points of constant optical rotation at a fixed wavelength ( $[\alpha], \lambda$ ) which we call isorotatory points. The possibility of the existence of such points has been mentioned previously, without examples; the name proposed<sup>2</sup> was «isodinetic points».

Providing that the rotatory dispersion spectra of factor and product intersect, say at  $\lambda_A, \lambda_B, \dots$ , then isorotatory points will occur at  $\lambda_A, \lambda_B, \dots$  in the following cases (where only compounds with electronic absorption bands in the appropriate region are mentioned). D and L are used as configurational labels.



This represents solvation, or intramolecular rearrangement, or redox reactions. We have mentioned some examples of this case earlier,<sup>3</sup> and as examples, isorotatory points observed during the aquation of (+) *cis*-dichloro-bisethylenediaminecobalt(III) chloride, and of (+) *cis*-chloronitrobisethylenediaminecobalt(III)

chloride are shown in Figures 1 and 2, respectively.

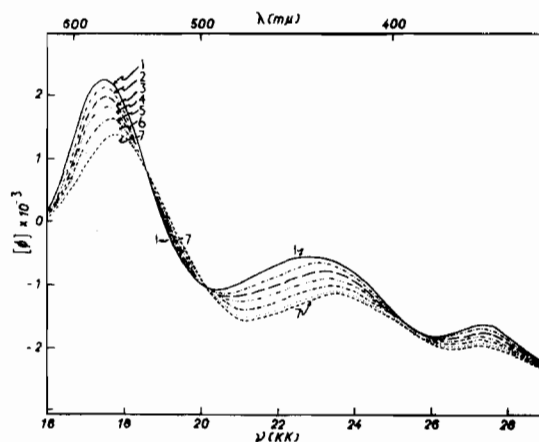


Figure 1. Isorotatory points during the aquation of (+) *cis*-[Coen<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>. The curves were obtained at the following times (rate of traverse 2kK per min.; times refer to 16 kK). 1, 2 min. 2, 15 min. 3, 30 min. 4, 45 min. 5, 61 min. 6, 75 min. 7, 91 min.

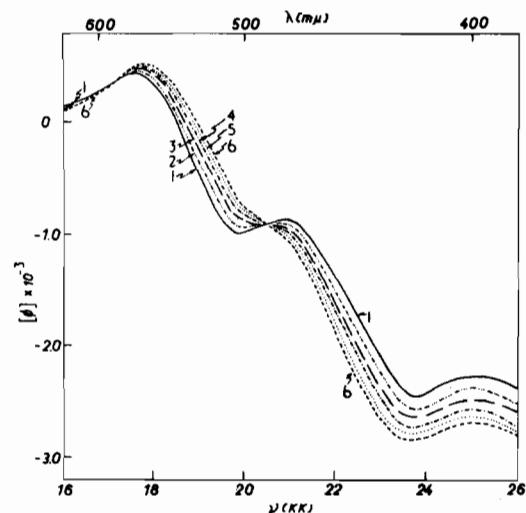
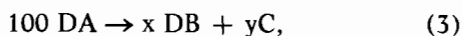


Figure 2. Isorotatory points during the aquation of (+) [Coen<sub>2</sub>(NO<sub>2</sub>)Cl]<sup>+</sup>. Curves after the following times: 1, 2.5 min. 2, 15 min. 3, 30 min. 4, 60 min. 5, 90 min. 6, 117.5 min.

- (1) M. D. Cohen and E. Fischer, *J. Chem. Soc.*, 3044 (1962).  
 (2) O. Kling, *Acta Chem. Scand.*, 15, 229 (1961).  
 (3) K. Garbett and R. D. Gillard, *J. Chem. Soc.*, A, 204 (1966).

This represents reaction with complete inversion of optical configuration; examples of such Bailar inversions<sup>4</sup> are rare, and these more often correspond to case (4) below (isomerization accompanying inversion).



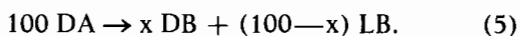
C being an inactive molecule. This case may give rise to an isotrotary point at a wavelength  $\lambda_1$ , only if

$$100[\alpha]_{A\lambda_1} = \frac{x}{100} [\alpha]_{B\lambda_1}, \text{ i.e., the product must be}$$

more strongly rotating at  $\lambda_1$  than the factor. This is quite possible, though we have not yet found an example.



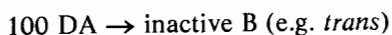
This represents a partial inversion, and is the commonly observed reaction known as Bailar inversion, which is usually accompanied by substantial *cis-trans* isomerisation, and some retention of configuration. Isotrotary points have not yet been observed for this type of reaction.



This reaction, part retention and part inversion, has not yet been observed, except in the case where  $x = 50$ , and  $A = B$ , which is racemization. When  $x = 50$ , the isotrotary points must have  $[\alpha] = 0$ , and must therefore coincide exactly with the crossing points of the optical rotatory dispersion curve of either enantiomer.

We now consider the case of racemization in detail. The mere decline of a rotation at one fixed wavelength to  $0^\circ$  does not necessarily imply racemization, but merely a change in the nature of the species present. This may be racemization, mutarotation (as in most solutions<sup>3</sup> of resolved halo complexes; many reactions of this type were thought to be racemizations by Werner, who used  $\text{Cd}_{\text{red}}$  light), or loss of optical activity with chemical change (commonly *cis-trans* isomerisation). To establish racemization, the absence of optical activity is checked at as many wavelengths as possible, and it is shown by absorption spectra or some similar means that the chemical species present remain constant.

Isotrotary points may provide a test for the presence of DA and LA only, with no other optically active species. If only DA and LA are present, the shapes of rotatory dispersion curves are exactly similar to that of the rotatory dispersion curve for a pure enantiomer. Thus, maximal rotations (« peaks »), crossing points, points of inflection, and minimum rotations (« troughs ») must occur at the same wavelengths throughout any genuine racemization. The only other case which can give similar behaviour is where



and this can of course be checked by absorption spectra.

Some of our results for the racemization of (+) tris-*o*-phenanthrolineiron(II) perchlorate are shown in Figure 3. Evidently, no other optically active species

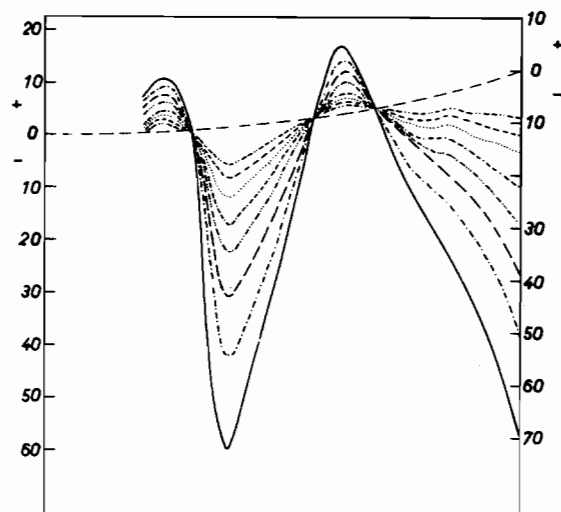
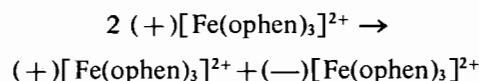


Figure 3. Experimental rotatory dispersion spectra during the racemization of (+)  $[\text{Fe}(\text{phen})_3]^{2+}$  ( $10^{-4} \text{ M}$  in water; 1 cm. cell). Curves were obtained at 10 min. intervals (rate of traverse  $2 \text{ kK. min.}^{-1}$ ).

than the factor and its enantiomer intervenes, since the isotrotary points all have  $[\alpha] = 0$ , and we are dealing with a genuine racemization. From measurements<sup>5</sup> of absorption spectra under the same conditions, no isomerization or solvation occurs, so that the reaction is



In studying rates of reactions of optically active complexes, visual polarimetry at a single wavelength (usually  $\text{Na}_D$  or  $\text{Hg}_{5461}$ ) has always been employed. However, the most suitable wavelength for readings, whether visual or automatic, is one where rotation is high relative to optical density. [A further complication in visual polarimetry concerns the varying sensitivity of the eye to small changes of illumination at differing wavelengths.] A preliminary inspection of the optical rotatory dispersion curve establishes suitable wavelengths, and those used in this work have high ratios of optical rotation to optical density. The use of optical rotation measurements relative to the more commonly employed absorption spectra gives results of high precision.

Our results for the racemization of (+) tris-*o*-phenanthrolineiron(II) perchlorate in water at  $20.0^\circ$  are shown in Table I, with the results obtained in earlier work,<sup>5</sup> using optical rotations at one wavelength only. The point was then made that the use of the  $\text{Na}_D$  line in visual determinations gave data of rather limited accuracy. Our results for solutions containing acids are also given in Table I, together with results obtained<sup>5</sup>

(5) F. Basolo, J. C. Hayes and H. M. Neumann, *J. Amer. Chem. Soc.*, 76, 3807 (1954).

(4) K. Garbett and R. D. Gillard, *J. Chem. Soc.*, 6084 (1965).

**Table I.** Racemization of tris-*o*-phenanthrolineiron(II) perchlorate

Solvent	Temp.	k (min. <sup>-1</sup> × 10 <sup>2</sup> )	Ref.
H <sub>2</sub> O	0.0	0.05	a
H <sub>2</sub> O	16.0	0.4	b
H <sub>2</sub> O	20.0	2.74	c
H <sub>2</sub> O	24.7	4.0	b
0.1M HCl	20.0	2.64	c
»	25.0	3.4	b
1M HCl	15.9	0.99	d
»	20.0	2.4	c
»	24.8	4.0	d
»	30.9	12.2	d

<sup>a</sup> L. Seiden, F. Basolo and H. M. Neumann, *J. Amer. Chem. Soc.*, **81**, 3809 (1959). <sup>b</sup> N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 1325 (1954). <sup>c</sup> This work. <sup>d</sup> Ref. 5.

by visual polarimetry under the same conditions. The complicated acid dependence<sup>6</sup> of rates of dissociation of certain complexes of iron(II) is well known. However, using the values for rate of dissociation given by earlier workers,<sup>5</sup> it is quite clear that rate of racemization ( $k_r = 2.74 \times 10^{-2}$  at 20°) is much greater than the rate of dissociation ( $k_d = 0.4 \times 10^{-2}$  at 20°).

### Experimental Section

Optical rotatory dispersion spectra were obtained using a Bendix «Polarmatic 62» spectropolarimeter.

**Complexes.** Active chloro-complexes were prepared as earlier described.<sup>3</sup> Tris-*o*-phenanthrolineiron(II) perchlorate was resolved (via its (+) antimonyltartrate) by a published method.<sup>7</sup>

**Kinetic experiments.** Solutions of the iron complex were generally  $10^{-4}M$ , and measurements were at 20°. Curves of the type of Figure 3 were obtained, and rotation readings were taken at several frequencies.  $k_r$  was obtained from the slope of  $\log [\alpha]_t$  plotted against time. The values of  $k$  obtained from results at differing frequencies agreed well; for example, in water, values of  $k$  were obtained from readings at 19, 19.3, 20, 28, 29, 30 and 31 kK; the extreme values (min.<sup>-1</sup>) were  $2.67 \times 10^{-2}$  and  $2.83 \times 10^{-2}$ , and the mean value was  $2.72 \times 10^{-2}$ .

### Discussion

Examples of inversion of optical configuration in octahedral complexes are few and far between, and these are usually associated with reactions such as isomerization. Any intramolecular racemization reaction

necessarily involves a Bailar inversion, and for this reason, the few examples known require authentication. The present work confirms that the racemization of the tris-*o*-phenanthrolineiron(II) cation is authentically intramolecular.

The Bailar twist mechanism<sup>8</sup> for intramolecular racemization is shown (viewed down the 3-fold axis) in Figure 4. In the case of the majority of bidentate ligands, non-bonding interactions serve to destabilize the trigonal prismatic form (B of Figure 4, the symmetrical

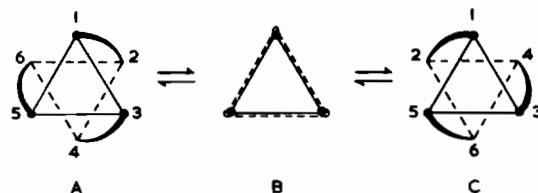


Figure 4. The Bailar twist mechanism for intramolecular racemization of a tris-chelate complex.

intermediate) relative to the octahedral form. The energy of such non-bonded interactions could give a rough measure of the activation energy required to form the symmetrical intermediate, and hence racemization. We suggest that the Bailar twist mechanism applies to the racemization of trisphenanthrolineiron(II) cations, the symmetrical intermediate being rather less unstable in this case than is usually true. The effect of pressure on the rate of racemization of solid tris-*o*-phenanthrolineiron(II) perchlorate was interpreted<sup>9</sup> in terms of an intramolecular Bailar twist mechanism.

A trigonal prismatic hexacoordinate complex (cf. B of Figure 4) has recently been characterized.<sup>10</sup> Possibly, therefore, in the case of  $\pi$ -bonding ligands where marked delocalization of electronic charge occurs into orbitals of the ligand with aromatic character, intramolecular racemization may occur more readily than in tris-complexes of  $\sigma$ -bonding ligands like ethylenediamine. A second cause of low-energy pathways to intramolecular racemization would be steric compression in the octahedral complex [A of Figure 3] which becomes smaller in the transition state symmetrical complex. Experiments are under way to check this second possibility.

It seems likely that, if resolvable octahedral tris-maleonitriledithiolato-complexes are made, they will racemize very readily by an intramolecular mechanism.

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(8) J. C. Bailar, *J. Inorg. Nuclear Chem.*, **8**, 165 (1958).

(9) C. D. Schmulbach, F. Dacheille and M. E. Bunch, *Inorg. Chem.*, **3**, 808 (1964).

(10) R. Eisenberg and J. A. Ibers, *Amer. Chem. Soc.*, **87**, 3778 (1965).

(6) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 736 (1950).

(7) F. P. Dwyer and E. C. Gyrfas, *J. Proc. Roy. Soc.*, New South Wales, **85**, 135 (1951).