

## Study of the Reactions of Hexanitrocobaltate(III) Ion with Amino Acids. IX\*. Isomerization Reactions of the Dinitrodiglycinatocobaltate(III) Ion

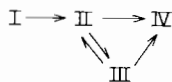
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Three of the five possible geometric isomers of dinitrodiglycinatocobaltate(III) isomerize to the stable fourth isomer by a series of first order reactions. The kinetics of the isomerization have been studied by chromatographic separation of the isomers and the data fitted with an analog computer. The results of experiments between 65° C and 95° C in neutral solution are consistent with the stoichiometric mechanism:



where I = *cis*-NO<sub>2</sub>/*cis*-N/*cis*-O, II = *trans*-NO<sub>2</sub>/*cis*-N/*cis*-O, III = *trans*-NO<sub>2</sub>/*trans*-N/*trans*-O, and IV = *cis*-NO<sub>2</sub>/*trans*-N/*cis*-O. The fifth isomer was not observed. At lower temperatures induction periods are observed, indicating a complex intimate mechanism. Some observations on the racemization of isomers I and IV are reported.

### Introduction

Four of the five possible geometric isomers of dinitrodiglycinatocobaltate(III) ion have been isolated and identified.<sup>2</sup> These are illustrated in Figure 1. Isomers I, II and III are metastable and isomerize to IV, the thermodynamically most stable isomer. The kinetics of the isomerizations have now been investigated beginning with each of the metastable isomers and a consistent stoichiometric mechanism has been established. Examination of the temperature dependence of the rate constants over a wide temperature range allows certain intimate mechanisms to be eliminated, but the observation of induction periods at lower temperatures indicates a complex mechanism.

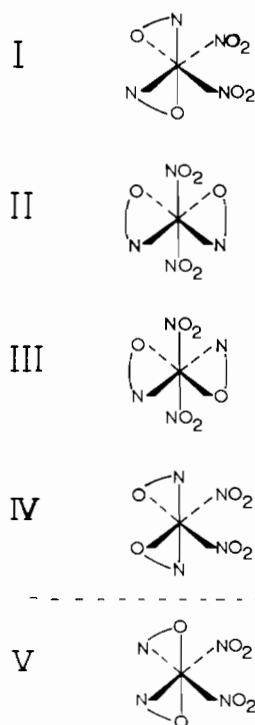


Figure 1. The five geometric isomers of dinitrodiglycinatocobaltate(III). Isomers I–IV have been isolated. Isomer V has not been observed.

### Experimental

#### Preparation of Complexes

A mixture of four isomers of sodium dinitrodiglycinatocobaltate(III) was obtained from the reaction of glycine with Na<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] at 50–60° C. The isomers were separated by fractional crystallization.<sup>2,3</sup>

Isomer I was resolved with cinchonine and the diastereomers were converted to the respective potassium salts using ion-exchange chromatography.<sup>3</sup>

\* Previous paper in this series, VIII, see ref. 1.

### Kinetics Experiments

The isomerization reactions were investigated by heating 1 ml of 0.1M solutions of a single isomer in a 5 ml flask immersed in the dark in a constant temperature bath (Thermostat Typ NBE Medingen, Dresden). At periodic intervals 1.55  $\mu$ l aliquots were transferred to 30  $\times$  4 cm Whatman No. 1 filter paper strips. These were chromatographed by the ascending method using a solvent mixture of 95 ml of dioxane and 5 ml of water containing 1 g of NaI. After 7 hours the chromatograms were dried and then developed for an additional 4.5 hours with the same solvent mixture to which 10 ml of water had been added. The chromatograms were dried in air and then immersed in a H<sub>2</sub>S saturated solution obtained by mixing 50 ml of 15% NH<sub>3</sub> with 50 ml of 96% ethanol. The chromatograms were again dried in air and the intensities of the spots developed were measured with a Beckman Model 1969 Densitometer. The R<sub>f</sub> values for the four isomers using this chromatography procedure were found in separate experiments to be: I, 0.46; II, 0.28; III, 0.15; and IV, 0.59. These control experiments demonstrated that no detectable isomerization occurred during the chromatographic separation procedure.

The racemization kinetics were studied at the Na<sub>D</sub> line using a Perkin Elmer 141 MC Digital Polarimeter with a reproducibility of  $\pm 0.002^\circ$ . Measurements were made on 0.35 ml of a 0.1M solution in a thermostatted cuvette (2 mm pathlength) at 5 minute intervals.

### Data Analysis

An Electronics Associates TR-20 Analog Computer and an X-Y recorder were used to analyse the kinetics data for the higher temperature experiments between 65 and 95°C. Concentration vs time curves for each isomer were generated by the computer for an assumed mechanism for each of the three different initial conditions, depending on whether isomer I, II or III was present exclusively at the beginning of the experiment. These curves were compared visually with the three sets of curves obtained from the experimental data for these initial conditions. The relative values of the rate constants were then adjusted on the computer to give the best fit simultaneously for the three independent experiments at a given temperature. The relative rate constants so obtained were finally normalized by comparison with the first order rate of disappearance of isomer I at each temperature. The rate constants are

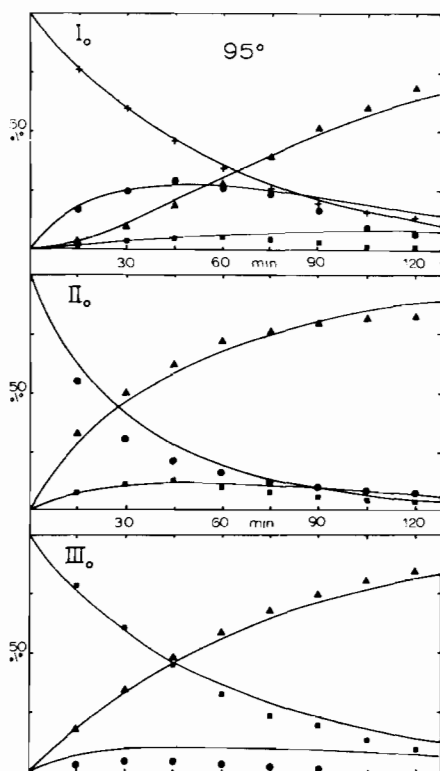


Figure 2. The concentration-time dependence of the isomerization reactions at 95°C. The points denote the experimental amounts of isomers I(+), II(●), III(■) and IV(▲). The lines represent the analog computer solutions using the relative rate constants given in Table I.

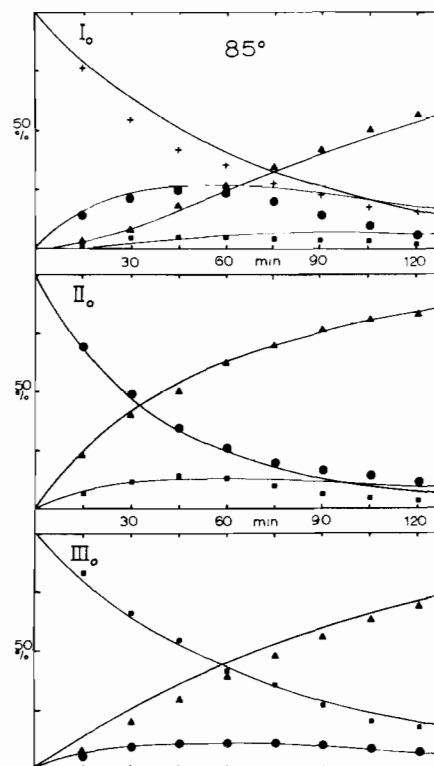


Figure 3. The isomerization reactions at 85°C. Details as in Figure 2.

believed to be accurate to within  $\pm 20\%$ . The accuracy of the chromatographic data, in particular the mass balance which generally varies between 90 and 100%, does not justify more sophisticated procedures for fitting the data.

## Results

### Higher Temperature Isomerizations

The experimental results of the three isomerization studies beginning with isomers I, II or III at each of four temperatures from 95 to 65°C are presented in Figures 2–5. Several qualitative observations can be made from these data: (i) Isomerization of I results in the formation of II and III before complete conversion to IV; (ii) Isomerizations of II and III do not involve formation of detectable amounts of I; (iii) Isomerization of II results in some formation of III before complete conversion to IV; (iv) Isomerization of III results in some formation of II before complete conversion to IV.

From these observations it is possible, without further analysis, to eliminate (1) as a possible reaction

mechanism, since such a mechanism is inconsistent with observation (iv) above.



Attempts were made to fit mechanism (2) to the data. These were unsuccessful



for it was impossible to account for the more rapid formation of IV than III in the experiments in which II is the starting material (see, for example, Figure 2b).

The data were fitted satisfactorily using mechanism (3).



The solid curves in Figures 2–5 represent the analog computer results for this mechanism using the relative rate constants given in Table I. It should be noted that the same set of five rate constants is used to fit the data simultaneously for the three individual experi-

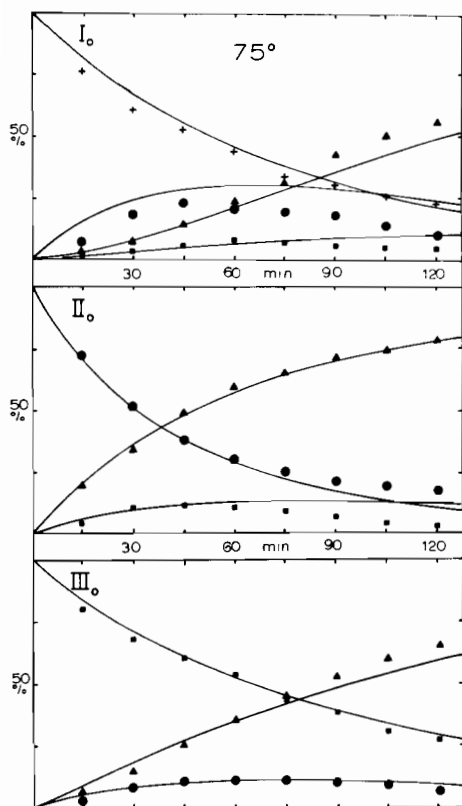


Figure 4. The isomerization reactions at 75°C. Details as in Figure 2.

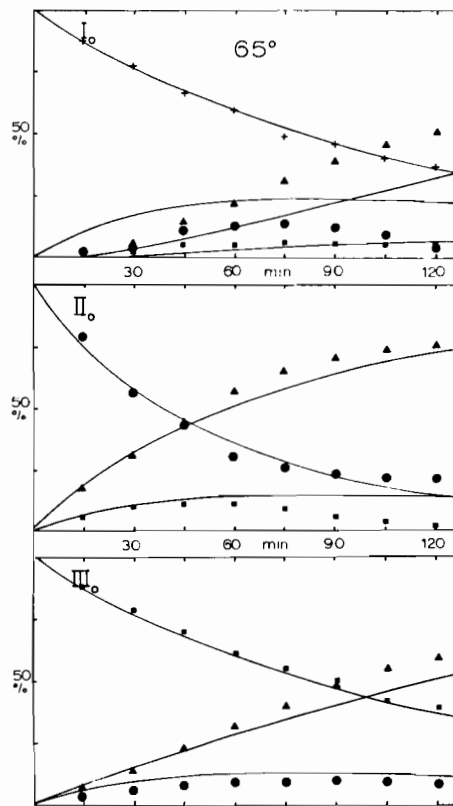


Figure 5. The isomerization reactions at 65°C. Details as in Figure 2.

TABLE I. First-Order Rate Constants for Mechanism 3 Obtained from Analog Computer Simulation and the Absolute Values of  $k_1$ .

$^{\circ}\text{C}$	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$	$(10^4 \text{ sec}^{-1})$
95	3.0	1.5	1.2	3.7	2.1	
85	2.5	1.3	1.0	3.1	1.5	
75	2.1	1.0	0.85	2.4	1.0	
65	1.5	0.93	0.86	2.2	0.79	

ments at a given temperature, beginning with isomers I, II or III.

We can now make further observations about the analog simulation of the experimental data: (v) The assumed mechanism and rate constants account qualitatively for the observed data at 75, 85 and 95 $^{\circ}\text{C}$ ; (vi) The quantitative fit to the data is poorest near the end of the two hour reaction period. This might be attributed to some decomposition of the complex at the high temperatures employed, but the mass balance remains between 90 and 100% and shows no trend toward larger deviations as time increases; (vii) The fit to the data at 65 $^{\circ}\text{C}$  for the experiment beginning with I is very poor, although the results for the experiments beginning with II and with III are reasonable good; (viii) The disappearance of I at each temperature is approximately first-order. This permits calculation of  $k_1$  values directly from the experimental data. From these, values of the other rate constants are calculated from the relative first order rate constants obtained from the analog simulation; (ix) The temperature dependence of the rate constants is very small, with no rate constant changing by more than a factor of three between 65 and 95 $^{\circ}\text{C}$ . From the experimental values of  $k_1$ , the apparent enthalpy and entropy of activation are 3.9 kcal mol $^{-1}$  and -62 e.u. at 75 $^{\circ}\text{C}$  respectively.

#### Lower Temperature Isomerizations

The very low apparent enthalpy of activation indicates that the isomerization should proceed measurably at room temperature within a few hours. Incubation of isomer I at 20 $^{\circ}\text{C}$  for 78 hours and at 35 $^{\circ}\text{C}$  for 10 hours, however, resulted in no detectable isomerization.

Experiments at intermediate temperatures between 45 and 60 $^{\circ}\text{C}$  revealed an induction period for the isomerization of I which decreases as the temperature increases. The results are presented in Figure 6. Furthermore, once initiated the rate of the isomerization in this temperature range displays a much greater temperature dependence than in the higher temperature range between 65 and 95 $^{\circ}\text{C}$ . This is illustrated in Figure 7. The existence of this reaction with a larger temperature dependence may account for the poor fit of the data at 65 $^{\circ}\text{C}$  using mechanism (3).

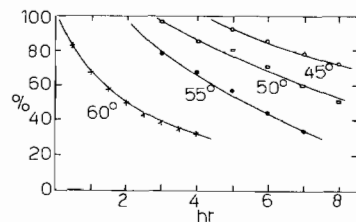


Figure 6. The time dependence of the isomerization of I showing induction periods which increase with decreasing temperature.

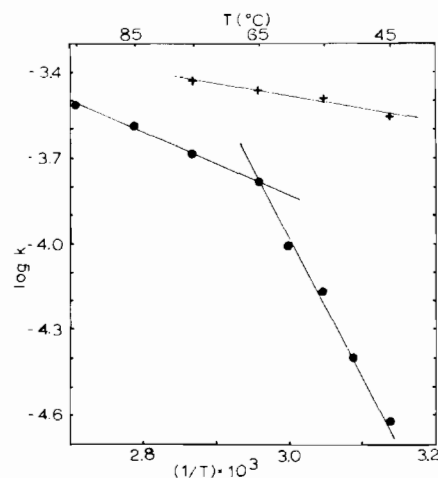


Figure 7. The temperature dependence of the rate of isomerization (●) and of the rate of racemization (+) of isomer I.

The following blank experiments on the isomerization of I were performed in attempts to determine the cause of the induction period, but in none of these were the induction period or the rate of isomerization affected: (i) addition of charcoal at 50 $^{\circ}$  and 65 $^{\circ}\text{C}$ ; (ii) addition of 0.1M NaNO $_2$  at 75 $^{\circ}\text{C}$ ; (iii) addition of 2.5  $\times 10^{-3}$ M cobaltous chloride at 50 $^{\circ}\text{C}$ ; (iv) addition of 2.5  $\times 10^{-3}$ M cobaltous chloride, 5.0  $\times 10^{-3}$ M glycine, and 5.0  $\times 10^{-3}$ M sodium nitrite at 50 $^{\circ}\text{C}$ ; (v) maintenance of a nitrogen atmosphere.

#### Racemization of Isomer I

According to mechanism (3) proposed above, the isomerization of I, which possesses *cis* nitro ligands, proceeds by formation of II, which possesses *trans*-nitro ligands. Consequently, the isomerization of optically active I should be accompanied by loss of optical activity. The rate constant for racemization should equal  $k_1$  if no inversion of I occurs without isomerization.

The racemization of a solution of I was studied at four temperatures between 45 $^{\circ}$  and 75 $^{\circ}\text{C}$  under the

same conditions as used for the isomerization experiments. The rates of racemization were found to be first-order and no induction periods were observed. The results are presented in Figure 7. At 75° and 65° C the rates of racemization are somewhat greater than those of isomerization, but at 55° and 45° C the rates of racemization are considerably greater than the lower temperature isomerization process. The apparent enthalpy of activation for racemization is 2.6 kcal mol<sup>-1</sup>.

In one experiment the rate of isomerization at 45° C was examined using a sample of the optically resolved complex employed in the racemization studies. An induction period was observed and the rate constant for the isomerization was the same as that obtained previously using an unresolved sample of isomer I.

## Discussion

The stereochemical course of the isomerization of the *cis*(NO<sub>2</sub>)-*cis*(N)-*cis*(O) isomer I of Co(gly)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub><sup>-</sup> to the thermodynamically more stable *cis*(NO<sub>2</sub>)-*trans*(N)-*cis*(O) isomer IV appears to be adequately represented by mechanism (3) at the higher temperatures. Consistent results are obtained in three independent experiments beginning with pure samples of isomers I, II or III between 75 and 95° C. There is no appreciable decomposition of the complex and almost quantitative formation of isomer IV is observed.

The intimate mechanism of the isomerizations remains obscure. Ignoring for the moment the observation of an induction period and the complex temperature dependence of the reactions, at least two possible mechanisms can be eliminated by consideration of the higher temperature data alone.

The very low activation enthalpy of approximately 4 kcal mol<sup>-1</sup> observed in the higher temperature region appears to eliminate a simple dissociative mechanism typical of cobalt(III) substitution reactions. These generally display activation energies of at least 20 kcal mol<sup>-1</sup>.<sup>4</sup> Similarly, more complex mechanisms based on substitution reactions at cobalt(III) appear improbable. One such mechanism might involve the one-ended dissociation of the glycine ligand with formation of an aquo intermediate, perhaps in equilibrium with the original complex. In such a mechanism the rate-determining step could be ring closure accompanied by stereochemical rearrangement. Since the activation process for this step would require the dissociation of a water molecule from cobalt(III), a higher enthalpy of activation is expected.

An intramolecular mechanism without bond rupture, the trigonal twist mechanism, might account for the low enthalpy and the highly negative entropy of activation.<sup>5</sup> Examination of the possible isomerizations by this mechanism, considering the constraints imposed

by the chelate rings, leads to the following scheme of possible interconversions. These do not correspond to the observed stereochemical changes (4).



Insofar as the identification of the isomers is correct, (these have been made using X-ray crystallography,<sup>6</sup> p.m.r. and electronic spectra,<sup>2,7</sup> and the optical resolution of the two *cis*-isomers,<sup>2,8</sup>) the trigonal twist mechanism can be excluded as a general mechanism for the isomerization reactions.

The observation of an induction period at lower temperatures and the biphasic temperature dependence of the reaction confirm that the mechanism is complex. One possible explanation is that the isomerization is catalysed by cobalt(II) complexes which are stereochemically labile.<sup>9</sup> The hypothesis of cobalt(II) catalysis is consistent with the possible amounts of cobalt(II) which could be formed by the decomposition of the cobalt(III) complexes. Since the mass balance during the course of the isomerization is maintained, this corresponds to a concentration of less than 5 × 10<sup>-3</sup> M. Consequently, if electron transfer with cobalt(II) is the rate-limiting step in the isomerization, or faster, the lower limit of the rate constant for electron transfer is about 2 × 10<sup>-2</sup> M<sup>-1</sup> sec<sup>-1</sup>. However, a number of blank experiments designed to demonstrate cobalt(II) catalysis had no effect on the induction period or the rate of isomerization of I.

The observed temperature dependence of the isomerization suggests that at lower temperatures a catalyst is formed or an inhibitor is consumed in a slow reaction with a high activation enthalpy. At higher temperatures this is not rate determining and the isomerization proceeds with a very small apparent activation energy.

The observation that racemization of I is much faster than isomerization at 55° and 45° C is remarkable. This indicates that racemization can occur by a separate inversion mechanism without accompanying isomerization. This conclusion is confirmed by the fact that an identical sample of I was found to racemize without significant isomerization.

The very low enthalpy of activation together with a large negative entropy of activation suggests the possibility of a twist mechanism for the racemization reaction. This hypothesis is supported by the observation<sup>10</sup> that racemization of IV occurs with an activation energy of approximately 30 kcal mol<sup>-1</sup>. Examination of the stereochemistry of the two isomers reveals that I can racemize by a trigonal twist whereas inversion of IV by a twist mechanism is not possible.

### Acknowledgements

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