ruled out by variable-temperature measurements because the isomer distribution may be relatively insensitive to small differences in temperature.

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CHEMISTRY, INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Reaction Mechanism of Cyclopentadienyliron Tricarbonyl Cation with Cyanate Ion[1]

BY LINDA M. CHARLEY AND ROBERT J. ANGELICI*[2]

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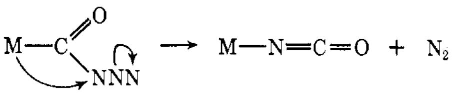
The reaction of metal carbonyl compounds with azide ion to yield isocyanato complexes was first reported[3] for $W(CO)_6$

$$W(CO)_6 + N_3^- \longrightarrow W(CO)_5(NCO)^- + N_2$$

Since that time similar reactions of $Mo(CO)_6$,[4] $Cr(CO)_6$,[4] $C_5H_5Fe(CO)_3^+$,[5] $C_5H_5Ru(CO)_3^+$,[6] and $Re(CO)_5(NH_2CH_3)^+$[7] have been carried out. Kinetic studies[4] suggest that the first step of the reaction is N_3^- attack at a carbonyl carbon atom. The resulting intermediate then rearranges with loss of N_2 to form the isocyanate product



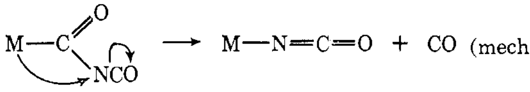
By analogy the reaction of $C_5H_5Fe(CO)_3^+$ with azide

$$C_5H_5Fe(CO)_3^+ + N_3^- \longrightarrow C_5H_5Fe(CO)_2(NCO) + N_2$$

was postulated to proceed by the same mechanism.[5] The isoelectronic cyanate ion also reacts with the cation to yield the isocyanato product. There are two possible mechanisms by which this reaction

$$C_5H_5Fe(CO)_3^+ + NCO^- \longrightarrow C_5H_5Fe(CO)_2(NCO) + CO \quad (1)$$

could occur. Mechanism A is analogous to that suggested for the azide reaction; *i.e.*, NCO^- attack occurs at the carbonyl carbon to give an intermediate which rearranges with loss of CO to give the product



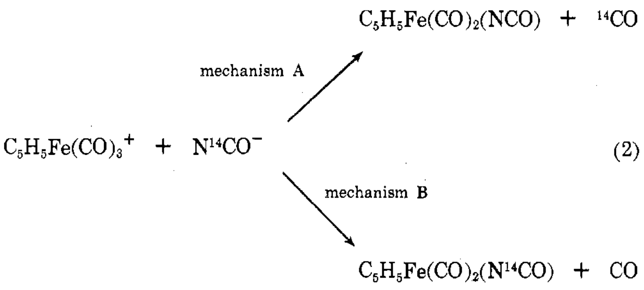
(mechanism A)

In this mechanism, it is the CO which was originally in the NCO^- ion that is evolved.

The second mechanism, B, is the simple substitution of a CO ligand by the NCO^- ligand. This might occur by direct attack of NCO^- on the metal or by dissociation of a CO group from the complex followed by rapid coordination of NCO^-. In either case it is a CO group on the metal which is evolved. Mechanism B must operate, *e.g.*, in the reactions of $C_5H_5Fe(CO)_3^+$ with Cl^-, Br^-, I^-, CN^-, and NCS^-, to give $C_5H_5Fe(CO)_2X$ accompanied by CO evolution.[5,8] In an attempt to determine whether these reactions proceeded by an associative or dissociative mechanism, the reactions with Cl^-, Br^-, and I^- were examined kinetically.[9] Unfortunately the reactions were all too fast to follow at 25° in acetone solvent.

Since NCO^- is similar to the other ions reacting by mechanism B, it appeared likely that it too would react by this general pathway. On the other hand, it is isoelectronic with N_3^- and like N_3^- has a possibility of reacting by mechanism A.

The purpose of the studies reported in this note was to establish the mode of reaction. This was accomplished by carrying out reaction 1 using ^{14}C-labeled NCO^-. The ^{14}C label would be found in the evolved CO if reaction 1 proceeded by mechanism A and in the $C_5H_5Fe(CO)_2(NCO)$ if by mechanism B. (See eq 2.) The results indicate that the reaction proceeds by mechanism B.



(2)

To eliminate the possibility that $C_5H_5Fe(CO)_2(NCO)$ is formed by some entirely different pathway and then exchanges its isocyanate group with free $N^{14}CO^-$, the exchange reaction

$$C_5H_5Fe(CO)_2(NCO) + N^{14}CO^- \longrightarrow C_5H_5Fe(CO)_2(N^{14}CO) + NCO^- \quad (3)$$

was also examined. It was found that very little exchange had occurred during the time used for reaction 2.

Experimental Section

Materials.—The $[C_5H_5Fe(CO)_3]PF_6$ was synthesized as described previously.[10] Copper(I) sulfate-β-naphthol solution was prepared according to the literature.[11] The $C_5H_5Fe(CO)_2(NCO)$ was synthesized from $[C_5H_5Fe(CO)_3]PF_6$ and KNCO as described previously[5] except THF instead of acetone was used as the solvent. The $KN^{14}CO$ was used as obtained from the New England Nuclear Corp. All solvents used were reagent grade. The

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] Fellow of the Alfred P. Sloan Foundation, 1970–1972.

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[10] L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, **2**, 391 (1968).

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THF was dried over calcium hydride and distilled. All radioactive counting was done on a Beckman LS200 liquid scintillation spectrometer. The scintillation solution was prepared[12] from 946 ml of toluene, 150 ml of BBS-3-Beckman Bio-Solv-Solubilizer, and 40 ml of Liquifluor. An internal standard obtained from the National Bureau of Standards with an activity of 7.68 × 10^4 dpm/ml was used to determine the efficiency of the spectrometer.

Reaction of $[C_5H_5Fe(CO)_3]PF_6$ with $KN^{14}CO$.—A mixture of $[C_5H_5Fe(CO)_3]PF_6$ (1.03 g), KNCO (1.07 g), and $KN^{14}CO$ (0.05 mCi, 1.06 mg) in 50 ml of freshly distilled tetrahydrofuran was stirred under nitrogen for 3 hr. The CO which was liberated during this time was collected in two traps each containing 5 ml of copper(I) sulfate-β-naphthol solution, samples 3 and 4. These were connected to the reaction flask in series. The amount of solution in the traps was twice that needed[11] to absorb all of the CO liberated assuming 100% reaction of the $[C_5H_5Fe(CO)_3]PF_6$. At the end of the reaction time, the THF was removed by aspirator vacuum, and the residue was extracted with chloroform and filtered. The solid residue which remained was extracted with water and filtered, and the volume was adjusted to 50 ml (sample 1). This sample was unreacted KNCO. The volume of the chloroform solution was reduced to 5 ml, pentane was added, and the solution was cooled to $-80°$; the red precipitate of $C_5H_5Fe(CO)_2(NCO)$ and $[C_5H_5Fe(CO)_2]_2$ which formed was filtered and weighed (0.24 g). Based on the intensities of the C–O stretching absorptions and the dpm of this mixture, no more than 20 mol % was $[C_5H_5Fe(CO)_2]_2$. The solid was dissolved in acetone and the volume was adjusted to 50 ml, sample 2. The dpm for 20 μl of each of the four samples dissolved in 20 ml of scintillation solution was obtained when the 2σ statistical counting error was ±2% or at the end of 50 min. Each sample was counted four times. The background radiation was also determined for the scintillation solution by itself. The same counting procedure was repeated for each sample after the addition of 100 μl of internal standard. The number of dpm observed corrected for spectrometer efficiency and background radiation was used to calculate the total dpm of the entire volume of solution for each sample (see Results).

Reaction of $[C_5H_5Fe(CO)_2(NCO)]$ with $KN^{14}CO$.—A mixture of $[C_5H_5Fe(CO)_2(NCO)]$ (0.35 g), KNCO (1.06 g), and $KN^{14}CO$ in 50 ml of freshly distilled tetrahydrofuran was treated in the same manner as in the previous reaction except no traps for CO were used. The counting procedure used previously was repeated for this reaction.

Results and Discussion

The reaction (eq 2) of cyclopentadienyliron tricarbonyl cation with ^{14}C-labeled isocyanate ion was carried out as described in the Experimental Section. In addition to $C_5H_5Fe(CO)_2(NCO)$ and CO, a reduction product, $[C_5H_5Fe(CO)_2]_2$, is also formed in smaller amounts. The other products of this side reaction have not been identified, but even if they did contain some of the ^{14}C, their concentrations were low enough so as not to alter the final conclusions.

If reaction 2 proceeded entirely by mechanism A with an attack of NCO^- on a carbonyl carbon atom, all of the ^{14}C consumed in the reaction would be released as ^{14}CO and therefore could be detected in the carbon monoxide trap solutions, samples 3 and 4. However, if the reaction proceeded entirely by mechanism B with direct displacement of a carbonyl group by the isocyanate ligand, all of the ^{14}C consumed in the reaction would remain in the isocyanate complex product. If the reaction proceeded by a combination of mechanisms A and B, the percentage occurring by mechanism B could be calculated by the expression

$$\frac{\text{activity in complex}}{\text{activity in complex} + \text{activity in CO traps}} \times 100 \tag{4}$$

The activity of each sample was calculated as follows. First, the efficiency, D, of the spectrometer was calculated from the expressions

$$A - B = C \tag{5}$$

$$\frac{C}{7.68 \times 10^3} = D \tag{6}$$

where A is the average observed dpm of a 20-μl sample plus background with internal standard, B is the average observed dpm of a 20-μl sample plus background without internal standard, C is the average observed dpm of the standard, D is the efficiency of the spectrometer, and 7.68 × 10^3 is the known activity of the standard. Knowing D, the actual activity of each sample plus background was calculated (eq 7). E is the average

$$\frac{B}{D} = E \tag{7}$$

dpm of a 20-μl sample plus background. Correction for background activity gave the sample activity, F. In eq 8 F is the average dpm of a 20-μl sample. The activ-

$$E - \left(\begin{matrix}\text{average dpm of background} \\ \text{corrected for efficiency}\end{matrix}\right) = F \tag{8}$$

ity of the total sample solution is then

$$F\left(\frac{\text{volume of solution (ml)}}{2 \times 10^{-2}\ \text{ml}}\right) = \text{dpm of total solution}$$

These activities in dpm are listed in Table I.

TABLE I

TOTAL ACTIVITY IN DPM FOR EACH OF THE SAMPLES

Sample no.	Reaction 2	Reaction 3	Sample no.	Reaction 2	Reaction 3
1[a]	8.205×10^7	5.927×10^7	3[c]	4.0×10^3	...
2[b]	5.091×10^6	4.686×10^5	4[d]	2.1×10^3	...

[a] Unreacted $KN^{14}CO$. [b] $C_5H_5Fe(CO)_2(NCO)$, plus some $[C_5H_5Fe(CO)_2]_2$. [c] First CO trap. [d] Second CO trap.

The results clearly indicate that the vast majority of ^{14}C is in the $C_5H_5Fe(CO)_2(NCO)$ rather than the evolved CO. Using expression 4 and activities of samples 2–4, it can be said that greater than 99% of the reaction proceeds by mechanism B, and very little if any occurs by mechanism A.

To eliminate the possibility that $C_5H_5Fe(CO)_2(NCO)$ formed by some route other than A or B and then exchanged its isocyanato ligand with free $N^{14}CO^-$, the extent of exchange according to eq 3 over the 3-hr period used in reaction 2 was determined. The values for this reaction found in Table I were calculated in the same manner as those for reaction 2.

Using the expressions

$$\frac{\text{mol of } C_5H_5Fe(CO)_2NCO \times \text{total activity}}{\text{mol of } [C_5H_5Fe(CO)_2NCO + KNCO + KN^{14}CO]} = \text{activity for 100\% exchange}$$

$$\frac{\text{actual activity found}}{\text{activity for 100\% exchange}} \times 100 = \text{percentage exchange}$$

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[12] "Beckman Supplies for Nuclear Instrumentation," Bulletin 81-B, 1969–1970, p 13.

a 14% exchange of isocyanate ligand was calculated to have taken place at the end of the 3-hr period. Hence a maximum of 14% of the $C_5H_5Fe(CO)_2(N^{14}CO)$ formed in reaction 2 could have resulted from ligand exchange. The conclusion remains that mechanism B is the predominant and perhaps the only mechanism for reaction 2.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTH FLORIDA, TAMPA, FLORIDA 33620

An Improved Procedure for the Resolution of the Bis(oxalato)ethylenediaminecobaltate(III) Ion

BY JAY H. WORRELL

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Because the optically active forms of the bis(oxalato)-ethylenediamine cobaltate(III) ion have been and will continue to be excellent resolving agents for many cationic cobalt(III) complexes, it is only proper that a detailed resolution procedure be developed to afford both enantiomorphic forms in useful quantities.

Dwyer, Reid, and Garvan have reported a general method for the resolution of $Co(en)(ox)_2^-$. In their resolution procedure,[1] they failed to indicate such necessary data as volumes, yields, and the details of their fractional crystallization schemes. Although their directions allow one intuitively skilled in the art to obtain an undisclosed quantity of one optically active antipode, the method used to obtain the other optically active form is complicated by the incorrect use of *d* and *l* rotational designations. The preparation of materials used in the resolution as well as the resolution itself is a formidable time-consuming task. This author feels the following experimental details with a view toward clarification will enable future investigators to conserve time and energy in the resolution of the bis(oxalato)ethylenediaminecobaltate(III) ion.

Experimental Section

Reagent Properties.—Racemic sodium and calcium bis(oxalato)-ethylenediaminecobaltate(III) were prepared by the method given by Dwyer, Reid, and Garvan.[1] The yields obtained were consistently 50% less than stated.

trans-Dichlorobis(ethylenediamine)cobalt(III) chloride was prepared by the method given by Bailar.[2]

cis-Dinitrobis(ethylenediamine)cobalt(III) nitrite was prepared by dissolving *trans*-$[Co(en)_2Cl_2]Cl$ (20 g) in 50 ml of water which was then warmed to 40–50° with stirring. To this solution was added potassium nitrite (22 g) dissolved in 50 ml of water. The solution was filtered and placed in an ice bath. Yellow *cis*-$[Co(en)_2(NO_2)_2]NO_2$ precipitated as the side of the beaker was scratched with a glass rod. The product (12 g) was collected by filtration, washed with ethanol and ether, and air dried.

An alternate method has been developed by Harbulak and Albinak.[3]

The *cis*-$[Co(en)_2(NO_2)_2]NO_2$ was resolved by the method developed by Dwyer and Garvan[4] using a fourfold increase in reagent quantities.

Optical Rotations.—Optical rotations were determined using a Rudolph high-precision photoelectric polarimeter equipped with a mercury arc lamp and a Beckman monochrometer. The instrument zero was determined before and after each measurement using the same 10-cm cell and solvent as employed for the sample. All rotations are an average of at least six sets of readings and are accurate to within 1% unless otherwise indicated. Samples were weighed using a Sartorius MPRS electromicrobalance.

Analyses.—Microanalyses were obtained from Galbraith Laboratories, Knoxville, Tenn.

Resolution Procedure.—Silver oxalate (3.5 g) was prepared from an aqueous solution of oxalic acid and silver nitrite and collected by filtration. The solid silver oxalate was added to $(+)_{546}$-$[Co(en)_2(NO_2)_2]Br$ (8.25 g, 1.9×10^{-2} mol, $[\alpha]_{546}$ +110 ± 10°) in 300 ml of water at 55°, shaken vigorously for 3 min, and filtered. Racemic $Ca[Co(en)(ox)_2]_2$ (7.05 g, 1.2×10^{-2} mol) was added to the orange-yellow filtrate and the solution was stirred mechanically for 30 min at 50–55°. The calcium oxalate which formed was quickly filtered off and racemic $Na[Co(en)(ox)_2]$ (6.93 g, 2.0×10^{-2} mol) dissolved in 150 ml of water at 50° was added to the red-brown filtrate. The mixture was rapidly stirred and the temperature was maintained at 50–55° for 20 min. The red-brown diastereoisomer of $(+)_{546}$-$[Co(en)_2(NO_2)_2]$-$(+)_{546}$-$[Co(en)(ox)_2]$ (5.0 g) was collected by rapid filtration at 50°, washed with ethanol, and dried *in vacuo* at 25°. An aqueous solution containing 21.4 mg/100 ml gave α +0.212 whence we have $[\alpha]_{546}$ +991 ± 15°. *Anal.* Calcd for $(+)_{546}$-$[Co(C_4H_{16}N_4)(NO_2)_2]$-$(+)_{546}$-$[Co(C_2H_8N_2)(C_4O_8)]$: C, 21.21; H, 4.24; N, 19.79. Found: C, 21.33; H, 4.31; N, 19.90.

The filtrate was transferred to a graduated 500-ml beaker and treated as indicated in the flow sheet. By cooling the filtrate to 35°, a second fraction of red-brown solid (0.55 g, $[\alpha]_{546}$ −292 ± 10°) was collected. The filtrate was stirred and heated to 45°, and the solvent was evaporated under a stream of air until the volume was 200 ml. The volume was measured with the stirring apparatus turned off. The solution was filtered giving 0.35 g of solid with $[\alpha]_{546}$ −875 ± 12°. Again the volume was reduced at 45° under an air stream to 125 ml. The mixture was filtered yielding 3.75 g of red-brown solid with $[\alpha]_{546}$ −880 ± 16°. The third and fourth fractions contained $(+)_{546}$-$[Co(en)_2(NO_2)_2]$-$(-)_{546}$-$[Co(en)(ox)_2]$. A portion of the diastereoisomer was recrystallized from hot ethanol–water solution, collected by filtration, washed with ethanol and ether, and dried *in vacuo* at 25°. An aqueous solution containing 26.86 mg/100 ml gave α −0.237 whence we have $[\alpha]_{546}$ −890 ± 15°.

Nine additional fractions of diastereoisomer and starting material were obtained as the volume was slowly reduced to 35 ml; however, the rotations were not sufficient to warrant recovery of optically pure $Co(en)(ox)_2^-$. The resolving agent present in these latter fractions was recovered as the iodide by grinding the solid with sodium iodide in a water slurry followed by filtration. Ethanol was added to the purple-red filtrate and $Na[Co(en)(ox)_2]$ precipitated. It could be purified by recrystallization from water–ethanol. *Anal.* Calcd for $(+)_{546}$-$[Co(C_4H_{16}N_4)(NO_2)_2]$-$(-)_{546}$-$[Co(C_2H_8N_2)(C_4O_8)]$: C, 21.21; H, 4.24; N, 19.79. Found: C, 21.15; H, 4.14; N, 19.99.

The diastereoisomers were broken up and the resolved complex was recovered as the sodium salt as indicated below. The first fraction (5.0 g) of $(+)_{546}$-$[Co(en)_2(NO_2)_2]$-$(+)_{546}$-$[Co(en)(ox)_2]$ was ground with 30 ml of warm (35–40°) water containing 6.0 g of sodium iodide. The solution was cooled and the insoluble yellow $(+)_{546}$-$[Co(en)(NO_2)_2]I$ was collected by filtration. Absolute ethanol (15 ml) was added to the purple-red filtrate and the solution was cooled in the refrigerator for 6 hr. The first

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