

and for $\text{Al}(\text{acac})_2(\text{DMF})_2^+$, along with data for other metal acetylacetonates suspected of having either exclusively *cis* or *trans* structures in solution, which also indicate that factors other than electric field effects are important in determining ring proton shifts.

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Carbon Monoxide Exchange Reaction of *o*-Phenanthrolinechromium Tetracarbonyl

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Early carbon monoxide exchange studies of the compounds $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)^{1,2} were interpreted as indicating that the four equatorial carbonyl groups exchanged at a much faster rate than did the axial group. More recently infrared techniques have been employed to examine the rate of ^{13}CO or C^{18}O incorporation into $\text{Mn}(\text{CO})_5\text{X}$ compounds.^{3,4} Under these conditions no significant difference in the rate constants for equatorial and axial substitution was detected, and mechanisms based on the equivalence of these rate constants have been postulated.⁴ However, Brown⁵ has questioned the validity of these mechanisms and suggested that intermolecular exchange at the axial and equatorial positions may occur at different rates but that equilibration, either by a nondissociative twist mechanism or by halide exchange *via* an acyl halide intermediate, may offer an alternate explanation for the observed similarity of the rate constants.

In continuing our examination of the possibility of different exchange rates for stereochemically different CO ligands in substituted carbonyl compounds, we have examined the exchange reaction of $\text{Cr}(\text{CO})_4$ -*o*-phen) with C^{18}O . Evidence is presented that the rate constants for exchange of the axial and equatorial⁶ CO groups are significantly different.

Experimental Section

$\text{Cr}(\text{CO})_4$ (*o*-phen) was prepared and purified by the literature method.⁷ 1,2-Dichloroethane was dried by refluxing over P_2O_5 and was freshly distilled before use. C^{18}O was supplied by Miles Laboratory, Inc., Elkhart, Ind.

(1) A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

(2) W. Hieber and K. Wollmann, *Chem. Ber.*, **95**, 1552 (1962).

(3) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

(4) B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson, and A. Wojcicki, *J. Chem. Soc., A*, 522 (1968).

(5) T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968).

(6) The 1,10-phenanthroline ligand is assumed to be in the equatorial plane. The two CO ligands *trans* to the amine are the equatorial CO groups. The two mutually *trans* CO groups are in the axial positions.

(7) R. J. Angelici and J. R. Graham, *Inorg. Chem.*, **6**, 988 (1967).

The apparatus used for the exchange experiments was essentially the same as has been previously described.⁸ All exchange reactions were carried out in 1,2-dichloroethane. Under an atmosphere of carbon monoxide, the decomposition of the substrate at the temperature of the experiments was effectively zero. A large number of other solvents were tested but poor solubility or rapid decomposition of the substrate precluded their use.

The infrared spectrum of $\text{Cr}(\text{CO})_4$ (*o*-phen) exhibits four C—O stretching absorptions. They have been assigned⁹ as 2008 cm^{-1} (a_1 , axial CO), 1907 cm^{-1} (b_1 , axial CO), 1883 cm^{-1} (a_1 , equatorial CO), and 1831 cm^{-1} (b_2 , equatorial CO). Upon substitution with C^{18}O new bands were observed at 1986, 1888, 1875, and 1822 cm^{-1} . Spectra before and after exchange are shown in Figure 1. Since there was no overlap with bands due to the isotopically substituted products, the intensities of the bands at 2008 and 1831 cm^{-1} were measured as they decreased with increasing substitution. The extinction coefficients of these two bands were measured for solutions from 1.0×10^{-4} to 5.0×10^{-3} *M* (the maximum concentration range). Beer's law was confirmed and the effective molar extinction coefficient for the axial a_1 band was found to be 1.8×10^3 l. $\text{mol}^{-1} \text{cm}^{-1}$ and for the equatorial b_2 , 3.1×10^3 l. $\text{mol}^{-1} \text{cm}^{-1}$. The solubility of carbon monoxide in 1,2-dichloroethane was measured by a tensimetric technique.¹⁰

Carbon Monoxide Exchange Calculations.—The reaction sequence to be studied is shown in Figure 2. Let C_{ij} represent the concentration of each particular species, where i refers to the number of equatorial CO groups that have been substituted by C^{18}O , and similarly j is the number of axial CO groups that have become labeled. It was assumed and verified under the conditions of the experiments that

$$C_{02} + C_{12} + C_{22} = C_{20} + C_{21} + C_{22} = 0 \quad (1)$$

In order to treat the data, the simplification was made that coupling between *cis* CO groups is negligible. Then if we let $C_{00} + C_{10} = x$ and $C_{00} + C_{01} = y$, the intensity of the axial a_1 band is proportional to x and that of the equatorial b_2 band is proportional to y . Now if we consider a system containing a mol of $\text{Cr}(\text{CO})_4$ (*o*-phen) and b mol of free CO, it can be shown¹¹ that

$$\frac{-dx}{dt} = R_{ax} \left[\frac{z}{b} \frac{2x}{2a} - \frac{b - za - x}{b} \frac{x}{2a} \right] \quad (2)$$

$$\frac{-dy}{dt} = R_{eq} \left[\frac{z}{b} \frac{2y}{2a} - \frac{b - za - y}{b} \frac{y}{2a} \right] \quad (3)$$

where z is the concentration of C^{18}O at time t , and R_{ax} and R_{eq} are the gross rates of exchange at the axial and equatorial positions, respectively. From an examination of mass balance

$$z = d - C_{01} - C_{10} - 2C_{11} \quad (4)$$

where d is the concentration of C^{18}O at time $t = 0$. Substituting for C_{01} and C_{10} , the term C_{11} cancels, and thus

$$z = d - 2a + x + y \quad (5)$$

Hence for a first-order reaction

$$\frac{-dx}{dt} = \frac{k_{ax}}{2b} [a(d - 2a - b) + (d - a + b)x + ay + xy + x^2] \quad (6)$$

$$\frac{-dy}{dt} = \frac{k_{eq}}{2b} [a(d - 2a - b) + (d - a - b)y + ax + xy + y^2] \quad (7)$$

(8) J. P. Day, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **90**, 6927 (1968).

(9) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

(10) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, p 58.

(11) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, New York, N. Y., 1961, p 192.

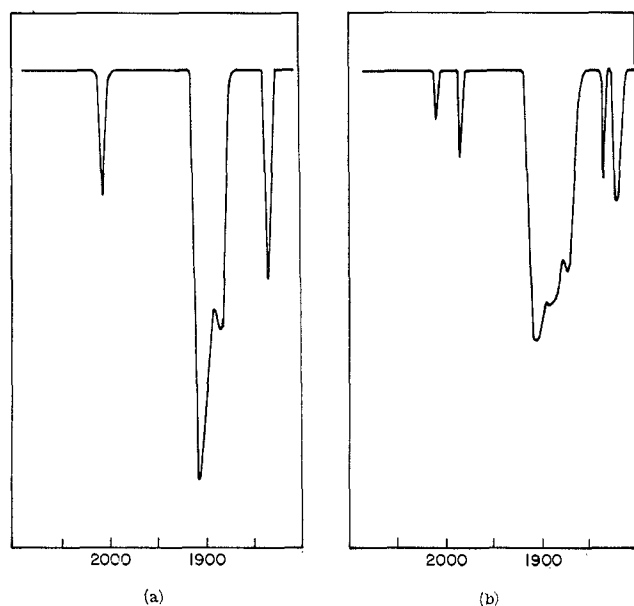


Figure 1.—Infrared spectrum of $\text{Cr}(\text{CO})_4(o\text{-phen})$ in the C—O stretching region: (a) before exchange; (b) after exchange.

The rate constants were obtained from the data by a curve-fitting technique. Using the known starting conditions (*a*, *b*, *d*) and trial values for k_{ax} and k_{eq} , eq 5 and 6 were solved using a numerical integration method (Runge-Kutta¹²). The trial values were varied to produce optimum agreement between the observed and calculated concentrations of the designated species. An example of the calculated and experimental data for both the axial and equatorial species is shown in Figure 3.

Calculations were carried out on the Northwestern University CDC 6400 computer. A modified form of library program NUC-0062 was used for the numerical integration of differential equations by the Runge-Kutta method.

Results and Discussion

The results collected in Table I show that the ex-

TABLE I
AXIAL AND EQUATORIAL RATE CONSTANTS FOR THE
EXCHANGE OF $\text{Cr}(\text{CO})_4(o\text{-phen})$ WITH C^{18}O

$10^3[\text{Cr}(\text{CO})_4(o\text{-phen})]$, M	$10^3[\text{C}^{18}\text{O}]$, M	Temp, °C	$10^4 k_{\text{ax}}$, ^a sec ⁻¹	$10^4 k_{\text{eq}}$, sec ⁻¹
1.00	1.55	51.3	4.3	1.1
1.14	3.35	51.3	4.6	1.3
1.82	2.10	50.6	3.7	1.2
1.06	4.00	50.6	4.2	1.5
2.53	3.10	43.6	1.5	0.75
2.30	2.80	43.6	1.3	0.44
1.45	1.57	36.8	0.59	...

^a For k_{ax} , $\Delta H^* = 26.9 \pm 1.3$ kcal mol⁻¹ and $\Delta S^* = 9.0 \pm 4.0$ cal deg⁻¹ mol⁻¹. ^b Values for substitution from ref 7 are $\Delta H^* = 26.4 \pm 0.8$ kcal mol⁻¹ and $\Delta S^* = 7.0 \pm 2.6$ cal deg⁻¹ mol⁻¹.

change reactions follow a first-order law with respect to the complex irrespective of the C^{18}O concentration. The rate constants for exchange of the axial CO ligands compare very closely with those obtained by Angelici⁷ for the substitution of $\text{Cr}(\text{CO})_4(o\text{-phen})$ with the bicyclic phosphite ligand $\text{P}(\text{OCH}_2)_3\text{CCH}_3$; the product of this reaction was of the type $\text{Cr}(\text{CO})_3\text{L}(o\text{-phen})$ with the phosphite ligand replacing an axial CO. Also,

(12) S. D. Conte, "Elementary Numerical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 223.

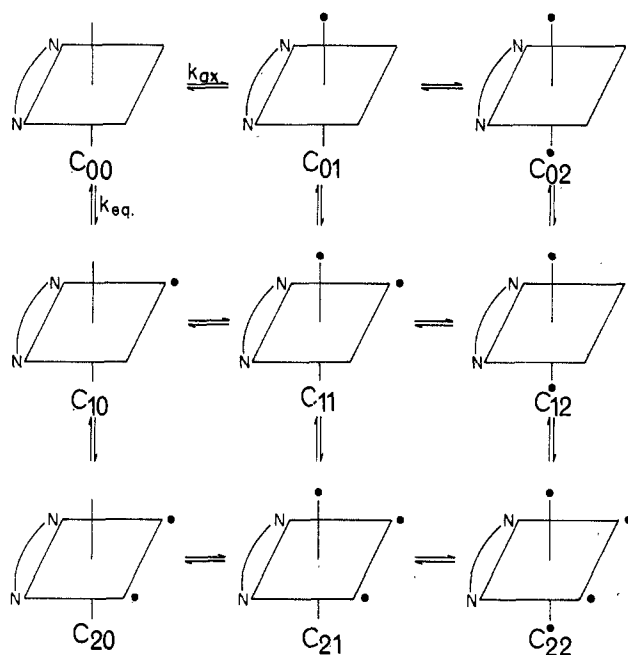


Figure 2.—Possible species produced during substitution reaction: ● = C^{18}O ; only the species C_{00} , C_{01} , C_{10} , and C_{11} were detected in this experiment and hence included in the treatment of the data.

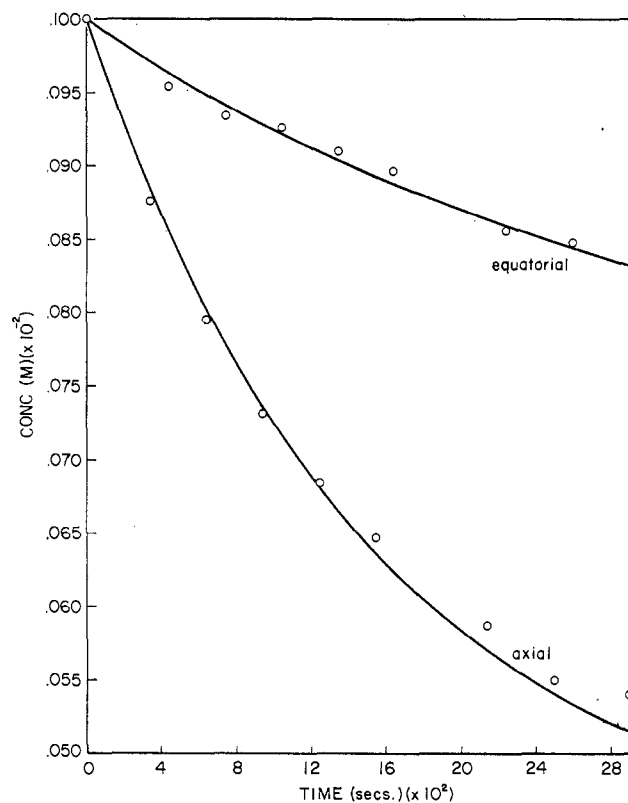


Figure 3.—Demonstration of curve fitting. The calculated curves which gave the best fit are shown as solid lines; the experimental data are shown as points.

the enthalpy and entropy of activation are very similar, as would be expected if exchange and substitution involve the same $\text{S}_{\text{N}}1$ process.

An examination of the data in Table I and Figure 2 clearly shows that the rate of exchange of the equatorial

CO groups is significantly smaller than that of the axial ligands. The equatorial rate constant could not be calculated with any greater certainty than $\pm 50\%$, and this precluded the evaluation of activation parameters for the equatorial exchange.¹³ However, within this limit of accuracy, the rate constants for exchange at the axial positions exceed the equatorial rate constants by a factor of approximately 4.

On the basis of the observed first-order rate law and the activation parameters for exchange of the axial CO groups, it is concluded that exchange at both the equatorial and axial positions occurs by a dissociative mechanism. The possibility of a mechanism involving opening of the chelate ring was recognized, but such a mechanism is not consistent with the observed zero order of the reaction with respect to CO concentration. Moreover, no $\text{Cr}(\text{CO})_6$ was detected during the course of the reaction.

The difference in the axial and equatorial rate constants is insufficiently large to allow an unequivocal interpretation of the energy differences involved. However, on the assumption that the ΔS^* term is similar for exchange at axial and equatorial positions, the larger rate constant for the axial exchange reaction may be related to a smaller chromium-carbon bond energy.

The σ -bonding effect of the *o*-phenanthroline on the CO groups is expected to be largely isotropic. This is confirmed by the fact that both the axial and the equatorial CO groups undergo exchange more readily in the *o*-phenanthroline-substituted compound compared with the parent hexacarbonyl.¹⁴ Such a *trans* effect due to σ bonding as may exist for the amine ligand would lead to labilization of the equatorial CO groups over the axial ligands, in direct contrast to the observed results. The explanation of the different rate constants would appear to lie in the fact that the π^* orbitals of the axial CO groups compete for the same set of metal *d* orbitals, whereas the equatorial CO groups are *trans* to an essentially non- π -bonding ligand. Hence, the Cr-CO bonding to the equatorial CO groups is expected to have a greater degree of π character. This is in accord with the infrared spectrum of the compound, in which the symmetric and asymmetric C-O stretching vibrations occur at higher frequencies for the axial than for the equatorial CO groups.

These results are in accord with the data provided by the recent studies of carbon monoxide exchange with $\text{Mn}(\text{CO})_5\text{X}$,^{3,4} which showed the similarity of exchange rates of CO groups *trans* and *cis* to a halide ligand. In this case, more accurate techniques may be required

(13) The low solubility of carbon monoxide in the solvent, combined with the factor that there are four unlabeled CO groups on each molecule which can be released by exchange with the free C^{18}O , makes more accurate determination of the equatorial rate constants very difficult. The apparent equilibrium distribution of the labeled molecule throughout the various species is defined by

$$4C_0 \frac{(4a + b - d)^4}{4a + b} + \frac{4C_1}{2} \frac{(4a + b - d)^3}{4a + b} \frac{d}{4a + b}$$

For a typical run, only 25% of the starting complex was converted to labeled species.

(14) G. Cetini and O. Gambino, *Atti Accad. Sci. Torino, Classe Sci. Fis. Mat. Nat.*, **97**, 1197 (1963).

to detect what is now expected to be only a small difference in the rate of exchange of axial and equatorial CO groups.

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The Stability of Chromyl Fluoride

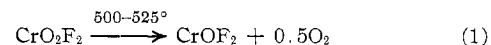
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Little is known about the stability of chromyl fluoride. von Wartenberg² first studied its stability toward heat and light and more recently Englebrecht and Grosse³ found CrO_2F_2 to polymerize with light. von Wartenberg found CrO_2F_2 to polymerize readily with ultraviolet irradiation. The polymer was described as being dirty white and melting around 200° . No data seem to be available on the thermal stability of CrO_2F_2 .

Results and Discussion

CrO_2F_2 when heated to 500° decomposed quantitatively according to the equation



Chromium oxide difluoride (CrOF_2) is a brown-black solid (brown when in a finely divided state) and is insoluble in water, in acids (HCl, HF, HNO_3), in bases (NH_4OH , NaOH, KOH), and in common organic solvents. CrOF_2 is stable at $\sim 1600^\circ$ *in vacuo*, but in a nickel crucible at atmospheric pressure and at $\sim 1600^\circ$ it is converted to Cr_2O_3 and presumably NiF_2 .

TABLE I
POWDER SPECTRUM FOR CrOF_2

<i>d</i> , Å	Intensity	<i>d</i> , Å	Intensity	<i>d</i> , Å	Intensity
6.32	s	2.27	w	1.760	vw
5.84	s	2.11	vw	1.745	vw
3.75	s	2.07	vw	1.713	w
3.66	m	2.01	vw	1.620	w
3.24	vw	1.984	vw	1.587	w
3.17	vs	1.949	w	1.546	vw
3.06	w	1.882	w	1.528	w
2.93	w	1.831	m	1.458	w
2.42	vw	1.791	w	1.417	w
2.30	w				

The X-ray powder photograph (see Table I for *d* spacings) did not correspond to CrO , CrO_2 , Cr_2O_3 , Cr_3O_4 , Cr_2O_5 , Cr_3O_8 , CrF_3 , CrF_2 , $\text{CrF}_3 \cdot 3\text{H}_2\text{O}$, FeF_2 ,

(1) To whom correspondence should be addressed.

(2) H. von Wartenberg, *Z. Anorg. Allgem. Chem.*, **247**, 135 (1941).

(3) A. Englebrecht and A. V. Grosse, *J. Am. Chem. Soc.*, **74**, 5262 (1952).