Volume 11
Number 6
June 1972

Inorganic Chemistry

Contribution from Noyes Chemical Laboratory,
University of Illinois, Urbana, Illinois 61801

Kinetics of the Exchange of Carbon-13 Monoxide with Manganese Pentacarbonyl Bromide[1]

By ALAN BERRY and THEODORE L. BROWN*

Received September 2, 1971

The exchange of ^{13}C-enriched CO with $Mn(CO)_5Br$ in hexane solution has been studied, using ir spectra in the carbonyl stretching region. The relative specific rate constants for axial and radial exchange were determined by comparing the spectra obtained in the kinetic runs with spectra for samples of $Mn(CO)_5Br$ containing statistically distributed enriched ^{13}CO. In the thermal reaction at 24° the specific rate constant for axial substitution, 1.3×10^{-5} sec^{-1}, is 0.74 times that for radial substitution. In the photochemical reaction, using 400-nm radiation at 0°, there is little or no preference for radial over axial substitution. The results rule out intramolecular exchange of axial and radial CO in $Mn(CO)_5Br$. They also suggest that the ^{13}CO exchange does not occur through a ligand migration process, with an acyl halide intermediate. The results are consistent with a CO dissociative mechanism, with a slight preference for radial CO dissociation.

The substitution of isotopically labeled CO into $Mn(CO)_5Br$ and related compounds has been the subject of considerable investigation. Following earlier work[2,3] using ^{14}CO-enriched CO which indicated a substantial difference in the rates of substitution for the radial and axial CO, infrared studies[4,5] with ^{13}CO and $C^{18}O$ showed that the rate constants for axial and radial substitution are approximately the same.[6] Considerations based on the principle of microscopic reversibility lead to the conclusion[7] that if the rates of CO dissociation from the axial and equatorial positions are in fact different, the difference must be revealed in the distribution of labeled CO in the product, unless there is an intramolecular process, rapid with respect to the dissociation rates, which results in equilibrium. More recently, attempts to synthesize a ^{13}CO-labeled $Mn(CO)_5Br$ which is relatively enriched in the radial position met with apparent failure.[8]

We set out, first, to establish, with as much quantitative precision as possible, whether ^{13}CO substitution of $Mn(CO)_5Br$ does in fact proceed with any stereochemical preference. Second, we have investigated whether any difference exists with respect to the stereochemistry when the substitution is carried out photochemically as opposed to thermally.

Experimental Section

Materials.—Manganese pentacarbonyl bromide was synthesized as described previously.[9] Reagent grade hexane (Matheson Coleman and Bell) was washed with concentrated H_2SO_4 and distilled water and passed through a silica gel column and over sodium wire. Carbon monoxide of 56% ^{13}C isotopic abundance was purchased from Merck Sharp and Dohme, in 100-cm^3 bulbs. The gas was handled on a vacuum line equipped with a Toepler pump to permit metering of the sample into bulbs fitted with vacuum-tight stopcocks. After filling with a known quantity of labeled CO and mixing with a known quantity of natural abundance CO to produce a desired degree of enrichment, in the range 8–11%, the bulbs were removed from the line and attached to the apparatus employed in the kinetic runs.

Kinetic Experiments.—The apparatus for the kinetic studies consisted of a jacketed 90-ml Pyrex cell, Figure 1. The CO atmosphere was continuously recirculated within the closed system by a variable-speed Masterflex tubing pump (Cole-Parmer Co.) at a rate of 8 cm^3/min. The reaction temperature was controlled by using a constant-temperature water bath or by a regulated flow of cold N_2 gas from a liquid N_2 reservoir. The thermal reaction was studied at several temperatures, but the most precise data were obtained at 24°. The photochemical reaction was studied at 0°, so that the thermal reaction would not interfere. All reactions were carried out in a room illuminated only with a red photographic safety bulb and under an atmosphere consisting of only CO and N_2. The radiation from a Hanovia 1000-W xenon lamp (976 C-1), passed through an interference filter with a peak transmission at 400 nm, was used in the photochemical studies.

The course of the reaction at 24° was followed over a period of 12 hr (about 40% completion); samples were withdrawn at 30-min intervals. Infrared spectral measurements were made using a Beckman IR-7 spectrophotometer, frequency-calibrated with water vapor, and using 1-mm pathlength, NaCl window sample cells. The instrument was operated at a scan speed of 10 cm^{-1}/min in the immediate region of interest, with a chart expansion of 10 cm^{-1}/in. Figure 2 illustrates a typical series of spectra taken at various times. Photochemical reactions were monitored for about 4 hr (about 60% completion), with samples being withdrawn at 15-min intervals.

---

[1] This research was supported by Grant GP-6396X from The National Science Foundation.

[2] A. Wojcicki and F. Basolo, *J. Amer. Chem. Soc.*, **83**, 525 (1961).

[3] W. Hieber and K. Wollman, *Chem. Ber.*, **95**, 1552 (1962).

[4] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc.*, **89**, 2344 (1967).

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

[6] Although in one of these reports[5] rate constants for both axial and radial substitution were reported, the experimental procedures and data analysis described did not admit of accurate determination of the relative rates.

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

[8] P. W. Robinson, M. A. Cohen, and A. Wojcicki, *ibid.*, **10**, 2081 (1971).

[9] R. B. King, "Organometallic Syntheses," Academic Press, New York, N. Y., 1965, p 174.

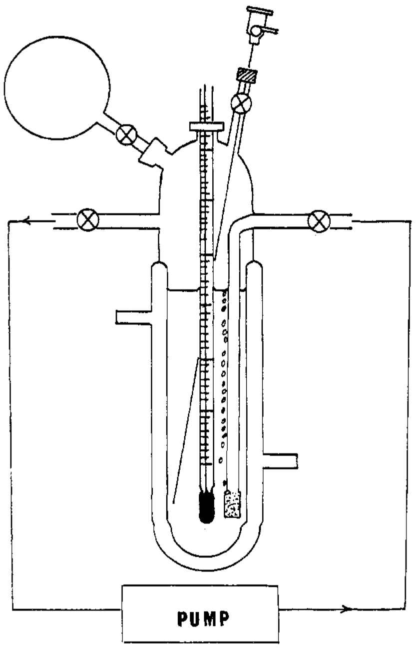

Figure 1.—Apparatus for conducting the ^{13}CO-exchange reaction. Samples for ir analysis were withdrawn through the stainless steel needle, equipped with a valve. The needle enters through a serum cap and open stopcock.

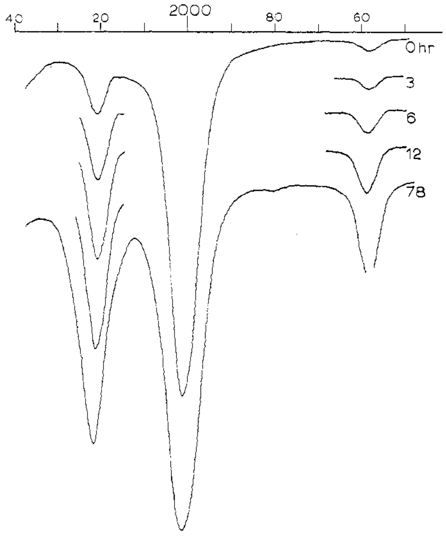

Figure 2.—Infrared spectra in the carbonyl stretching region for $Mn(CO)_5Br$ + ^{13}CO. The bands at 1958 and 2021 cm^{-1} represent ^{13}CO substitution in the axial and radial positions, respectively.

Treatment of Data

A series of $Mn(CO)_5Br$ samples of known isotopic ^{13}CO content was prepared by allowing a known weight of $Mn(CO)_5Br$ to remain in contact with a known mass of CO of known initial enrichment, for several half-lives, until it could be assumed that complete equilibration of the ^{13}CO label between axial and equatorial positions had been effected. The relative quantities of CO and $Mn(CO)_5Br$ were chosen so that final ^{13}CO contents at each position ranged from the 1.1% which characterizes the natural abundance to about 8 or 9%. The relative abundances of the bands due to axial and radial substitution in these samples provided reference points for evaluating the spectra from the kinetic runs. The spectra obtained during the kinetic runs were compared with reference spectra containing the same extent of ^{13}CO enrichment, as determined by comparing the absorbance at 1958 cm^{-1}, due to axial ^{13}CO with the 2001-cm^{-1} band due to the nonisotopically labeled molecule. The ratio of the absorbances due to radial and axial ^{13}CO substitution in the kinetic runs, $R = A_{2021}/A_{1958}$, was divided by the same ratio R', measured from the spectra of reference compounds. A deviation from 1 for R/R' thus provides a direct indication of a nonstatistical distribution of ^{13}CO in the product of the exchange reaction. Figure 3 depicts the manner in which R/R' varies as a function of time in typical thermal and photochemical reactions.

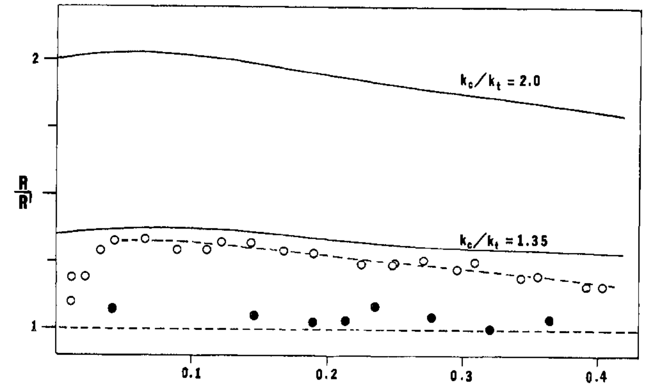

Figure 3.—Variation in R/R' based on observed spectra with fractional completion of reaction in the thermal (○) and photochemical (●) reactions of $Mn(CO)_5Br$ with ^{13}CO. The solid lines represent calculated R/R' values based on various assumed ratios k_c/k_t, as indicated. The experimental data begin from R/R' = 1 at zero time because the reactant contains ~1% natural abundance ^{13}CO, statistically distributed. This was not included in the computer calculations.

It is evident from Figure 3 that the thermal reaction does not occur with statistical distribution of ^{13}CO in the axial and radial positions but rather that substitution in the radial position is faster. The same degree of preference for the radial position was seen in the thermal reaction at temperatures as low as 0°. In the photochemical process, on the other hand, the substitution appears to be essentially statistical. There remains the problem of interpreting these qualitative conclusions more quantitatively and satisfactorily interpreting the variation in R/R' as a function of time. To this end, two different kinetic schemes were evaluated.

Figure 4 shows a kinetic scheme for the incorporation

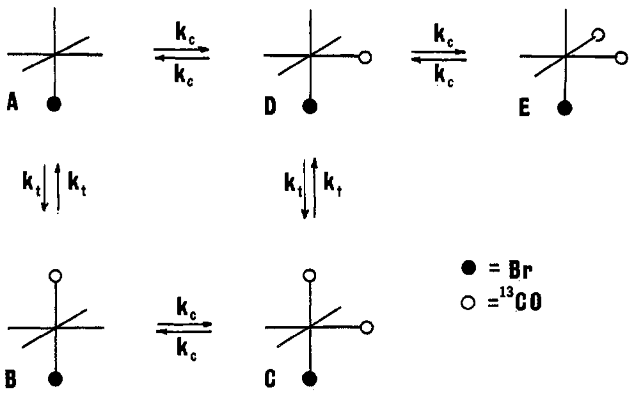

Figure 4.—Model kinetic scheme, including disubstitution, for ^{13}CO exchange with $Mn(CO)_5Br$.

of ^{13}CO into Mn(CO)$_5$Br, which allows for disubstitution. This scheme does not allow for direct interconversion of D and B nor for several other possible direct interconversions involving the disubstituted species E and C. Species D and B can interconvert in this scheme, however, through re-formation of A. The differential equations corresponding to this model are

$$\mathrm{d}A/\mathrm{d}t = -4k_cfA - k_tfA + k_c(1-f)D + k_t(1-f)B$$

$$\mathrm{d}B/\mathrm{d}t = -4k_cfB - k_t(1-f)B + k_tfA + k_c(1-f)C$$

$$\mathrm{d}C/\mathrm{d}t = -k_c(1-f)C - k_t(1-f)C + 4k_cfB + k_tfD$$

$$\mathrm{d}D/\mathrm{d}t = -k_c(1-f)D - k_tfD - 3k_cfD + 4k_cfA + k_t(1-f)C + 2k_c(1-f)E$$

$$\mathrm{d}E/\mathrm{d}t = -2k_c(1-f)E + 3k_cfD$$

The A, B, etc., refer to the concentrations of the species indicated in Figure 4, and f represents the fractional abundance of ^{13}CO in the CO atmosphere. This system of coupled differential equations was solved using an EAI Model 580 analog hybrid computer, with an 1130 Variplotter recorder output. The time dependences of the relative concentrations of all five species were obtained as a function of various assumed values for k_c/k_t, the ratio of specific rate constants for radial and axial substitution.

On the basis of Kaesz and coworkers' analysis[4] of the ir spectra in the CO stretching region of ^{13}CO-labeled Mn(CO)$_5$Br, we can assume that species C, D, and E contribute to the absorption due to radial substitution, whereas species B and C contribute to the absorption due to axial substitution. The relative absorbances at the respective frequencies due to each species depend on the product of concentration and extinction coefficient. Thus we can write

$$R = \frac{\epsilon^{r}{}_{d}D + \epsilon^{r}{}_{c}C + \epsilon^{r}{}_{e}E}{\epsilon^{a}{}_{b}B + \epsilon^{a}{}_{c}C}$$

The extinction coefficients of the bands due to the disubstituted species are probably very similar to those for the monosubstituted compounds at the peak heights of the bands, but these may be shifted a few reciprocal centimeters from the maxima which characterize the monosubstituted compounds. On this account the extinction coefficients of the bands due to disubstitution may be less at 2021 and 1958 cm^{-1} than for the monosubstituted species. We have nevertheless chosen to assume that they are the same, because this places an upper limit on the value which the calculated R can attain for a given ratio k_c/k_t and thus leads to the most conservative interpretation of the experimental data. It should be emphasized that the contributions of the disubstituted products are very small, especially in the early stages of the reaction, so that the kinetic analysis is not critically dependent on their inclusion, let alone on what assumption is made regarding their relative extinction coefficients at the measurement frequencies.

With these assumptions

$$R = \frac{\epsilon^{r}{}_{d}(D + C + E)}{\epsilon^{a}{}_{b}(B + C)}$$

The theoretical value for R', the ratio of absorbances for the thermally equilibrated samples, is of the form

$$R' = \frac{\epsilon^{r}{}_{d}(D + C + E)_{\mathrm{equil}}}{\epsilon^{a}{}_{b}(B + C)_{\mathrm{equil}}}$$

The relative concentrations of all the species at equilibrium are calculated from simple statistical considerations. We then obtain

$$(R/R')_{\mathrm{calcd}} = \frac{(D + C + E)/(B + C)}{\{(D + C + E)/(B + C)\}_{\mathrm{equil}}}$$

In this expression, the value used for R' is that appropriate to the extent of overall ^{13}CO incorporation at each point in the calculation. Thus, from the calculated concentrations of the various species as a function of time (the analog computer output) we generate a calculated R/R' as a function of time for a given ratio k_c/k_t. Figure 3 shows two calculated curves and for comparison a set of data obtained from the thermal reaction. The agreement between the theoretical and experimental curves is quite satisfactory. The results indicate that the maximum value attained by R/R' is a good measure of the ratio of k_c/k_t.

The kinetic scheme depicted in Figure 4 is possibly deficient in not providing for a direct interconversion between several of the labeled species, most especially between D and B. Such an interconversion might occur in the following way. Suppose that any one of the ^{12}CO groups dissociates from D, leading to a five-coordinate species, Mn(CO)$_3$(^{13}CO)Br, and suppose further that this species is capable of intramolecular exchange among the CO groups in the short time it exists before combining with a ^{12}CO to form Mn(CO)$_4$(^{13}CO)Br. The labeled CO might then appear at either the axial or radial position. If it appears at the radial position, the net effect is no reaction. If it appears at the axial position, the net effect is a direct conversion of D into B. Unfortunately all the possible interconversions could not be accommodated on the analog computer when all five species shown in Figure 4 were included. It is, however, possible to test effectively the importance of such interconversion by considering only the monosubstituted species. Figure 5 shows the kinetic scheme in which the interconversion described above is explicitly included. For the particular process described, k_i has the value $k_c(3k_c + k_t)/4(k_c + k_t)$. Using this scheme and the procedure described above, we have calculated R/R' for $k_c/k_t = 1.35$, both with and without the direct interconversion. The results are shown in Figure 6 along with the experimental data. It is evident that the direct interconversion *via* the process described leads to a better agreement with experiment at longer times, in the sense that the decrease in R/R' with time is more realistically produced. This

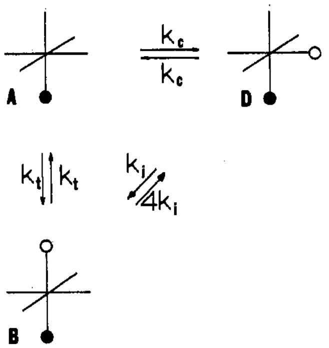

Figure 5.—Model kinetic scheme, involving only monosubstitution, for ^{13}CO exchange with Mn(CO)$_5$Br.

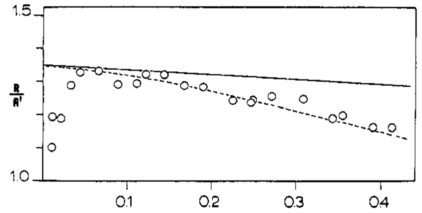

Figure 6.—Comparison of calculated R/R' curves with experimental results, represented by the data points, for ^{13}CO exchange with $Mn(CO)_5Br$, employing the model kinetic scheme shown in Figure 5, with (broken line) and without (solid line) provision for direct interconversion of B and D. In both cases $k_c/k_t = 1.35$. The solid line is essentially superimposable on the line for $k_c/k_t = 1.35$ in Figure 3, indicating that provision for disubstitution has a negligible effect on the results.

result suggests that the five-coordinate intermediate produced by dissociation of CO does exist for a sufficiently long time to undergo intramolecular scrambling of the remaining CO groups. A similar conclusion about the intermediate in dissociation of the amine ligand from $Mo(CO)_5NHC_5H_{10}$ was reported recently[10] on the basis of rather different evidence.

As a further test of the kinetic scheme, we assumed a value of 20 for k_c/k_t and assumed that there is an intramolecular process which could make k_i of comparable magnitude with k_c. One such process is a twist about a pseudo-threefold axis between the axial and two radial CO groups.[7] Values of k_i ranging from $0.5k_c$ to $4.0k_c$ were tried. The purpose of the exercise was to determine whether such a rapid intramolecular process might not produce low apparent values of R/R', even though the ratios k_c/k_t were high. In all cases, however, the calculated R/R' curves did not remotely resemble the experimental results.

Finally, by following the absorbance changes in the 1958-cm^{-1} band to completion of the reaction, it was possible to calculate a value of 1.3×10^{-5} sec^{-1} for k_t, the first-order rate constant for substitution at the axial position, at 24°. The thermal reaction was also studied at 0°. The same relative values were found for axial and radial exchange, and the value for k_t was determined to be $(1.5\text{–}1.6) \times 10^{-7}$ sec^{-1}. The two values for k_t give us a rough estimate of 28 kcal/mol for the activation energy.

Discussion

The reaction under study in this work is

$$Mn(CO)_5Br + {}^{13}CO \longrightarrow Mn(CO)_4({}^{13}CO)Br \qquad (1)$$

The reaction is studied in hexane solution, in a closed system consisting of an atmosphere of CO, continuously bubbled through the solution to ensure saturation and to ensure that the isotopic composition of CO in the solution remains in equilibrium with that in the gas reservoir during the reaction. The total quantity of gaseous CO employed was in considerable molar excess with respect to the quantity of $Mn(CO)_5Br$, which meant that the isotopic composition of the gas changed only slightly during the portion of the reaction actually studied.

The presence of CO in the solution also served to suppress the dimerization reaction

$$2Mn(CO)_5Br \rightleftharpoons Mn_2(CO)_8Br_2 + 2CO \qquad (2)$$

which occurs[11] in the absence of added CO. The kinetics of this reaction have been studied.[12] Although several questions with respect to the equilibrium between parent compound and dimer remain, it seems most likely that dimer is formed *via* the same dissociative step which leads to ^{13}CO incorporation. When the dimer is present in only small concentrations, therefore, it cannot significantly influence the observed kinetics regardless of how rapidly it may undergo ^{13}CO exchange.[13] The necessity of maintaining a substantial concentration of CO to suppress the dimerization reaction meant that we could not determine the rate law for reaction 1. The substitution of $Mn(CO)_5Br$ by other ligands has, however, been studied;[12,14] the rate was found to be first order in $Mn(CO)_5Br$ and zero order in substituting ligand

$$\text{rate} = k_1[Mn(CO)_5Br] \qquad (3)$$

We assume that the same rate expression applies to the ^{13}CO substitution. The results of a very substantial body of kinetic studies indicate[15,16] that CO as a substituting ligand follows the behavior observed for other ligands such as phosphines, etc. Angelici and Basolo[14] observed a rate constant for substitution of $Mn(CO)_5Br$ by $As(C_6H_5)_3$ in cyclohexane of about 5.5×10^{-5} sec^{-1}, after correction to 24°. In terms of the rate constants we have been discussing this should be $4k_c + k_t$. Our data correspond to a value of about 8×10^{-5} sec^{-1} for this sum, in reasonable agreement with the earlier result. The rough estimate of 28 kcal/mol which we obtain for the Arrhenius energy is also in good agreement with Angelici and Basolo's value of 30 kcal/mol, with chloroform as solvent.

To minimize the number of assumptions necessary in reducing the infrared spectral data to relative rate constants, we have based our analysis of the data as much as possible on reference spectra for ^{13}CO-enriched samples of $Mn(CO)_5Br$ known to be completely equilibrated. On the basis of these results, we can therefore stipulate precisely the ratio of absorbances of the 2021- and 1958-cm^{-1} bands, Figure 2, due respectively to radial and axial ^{13}CO substitution. Comparison of spectra for the reacting system with reference spectra tells whether the substitution is proceeding with different rate constants for the axial and radial substitutions. If the specific rate constants are the same, clearly the spectra will be identical with reference spectra corresponding to the same overall degree of isotopic labeling. If, on the other hand, radial substitution proceeds more rapidly than axial, the 2021-cm^{-1} band will exhibit an absorbance relative to the 1958-cm^{-1} band in excess of that shown in the reference spectra. In this sense, the spectra can give us a quite sensitive answer to the question of whether the substitution is strictly statistical. If it is not statistical, however, the quantitative degree to which it is not can be ascertained only by careful measurements of absorp-

---

[10] D. J. Darensbourg, M. Y. Darensbourg, and R. J. Denenberg, *J. Amer. Chem. Soc.*, **93**, 2807 (1971).

[11] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

[12] F. Zingales, M. Graziani, F. Faraone, and U. Belluco, *Inorg. Chim. Acta*, **1**, 172 (1967).

[13] G. Cetini, O. Gambino, G. A. Vaglio, and R. P. Ferrari, *Inorg. Chem.*, **8**, 1371 (1969), invoked the dimerization reaction for $Re(CO)_5X$ to account for a higher rate of ^{13}CO exchange at lower CO concentrations. On the assumption that dimer formation is rate controlled by CO dissociation from $Re(CO)_5X$, however, the explanation fails.

[14] R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, **84**, 2495 (1962).

[15] R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

[16] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 578.

tions including corrections for overlap and by comparisons with similarly analyzed reference spectra. The manner in which this has been done is detailed in the Experimental Section. The important point is that we have proceeded in the most empirical manner possible, placing maximum reliance on comparisons with reference spectra, to avoid all unnecessary assumptions about extinction coefficients, etc.

The quantity R/R' is a measure of the degree to which the substitution deviates from statistical. It represents the relative degree of radial ^{13}CO enrichment at any stage in the reaction, as compared with an equilibrated reference sample possessing the same extent of enrichment in the axial position. If there is a difference in the specific rates for axial and radial substitution, R deviates from 1 in the early stages of the reaction, but with the passage of time it must approach 1, as both axial and radial positions become completley equilibrated with respect to the CO present. From the results shown in Figure 3 and reproduced in other runs, it can be said that the radial substitution rate is faster by a factor of about 1.35 than the axial rate. In the photochemical process, on the other hand, the axial and radial substitution rates appear to be the same within experimental error. The photochemical process is more difficult to study quantitatively, because Mn(CO)$_5$Br decomposes to a significant extent under the irradiation conditions, to produce a brown insoluble material, even though the solution contains a large molar excess of CO. Nevertheless, it is quite apparent from the spectra that the relative axial to radial substitution rate is different in the photochemical and thermal reactions. *This result suggests that the intermediates in the two reactions are not identical.* Possibly the Mn(CO)$_4$Br intermediate in the photochemical reaction is formed in an excited state of sufficiently long lifetime to persist during the interval before reaction with a CO.

The observation of different radial and axial substitution rates in the thermal reaction requires that any intramolecular exchange of axial and radial CO in Mn(CO)$_5$Br at room temperature be slow with respect to the overall rate of exchange with ^{13}CO.

The fact that the specific rate constant for radial exchange is larger than for axial rules out the formation of an acyl halide intermediate as an important pathway for the ^{13}CO exchange. Assuming that such an intermediate would be formed *via* ligand migration and under the influence of attacking ligand, axial substitution and *total* radial exchange rates should be in the ratio 1:2, as observed for CH$_3$Mn(CO)$_5$.[17] In terms of specific rate constants, this would mean that $k_c = 0.5k_t$, whereas k_c is observed to be $1.35k_t$. The present results are consistent with a mechanism involving dissociation of CO from Mn(CO)$_5$Br to form a five-coordinate intermediate which is probably fluxional in the short time before it encounters a CO to form product. In terms of the principle of microscopic reversibility, the slightly faster rate of radial exchange reflects a slightly lower free energy of activation for dissociation of a radial CO.[18,19] It should be emphasized that fluxional behavior or lack of it in the five-coordinate intermediate can have no effect whatever on the distribution of labeled CO in *initially* forming species D and B.[7] The proof of this is outlined in the Appendix. Once ^{13}CO is incorporated in the molecule, however, it may be intramolecularly exchanged between axial and radial positions upon dissociation of one of the other CO groups, as described above. The present results suggest that the five-coordinate intermediate, whatever its symmetry, is fluxional.

Appendix

Let a species A be capable of undergoing a reactive process (*e.g.*, dissociation of a CO) along two distinct pathways to form intermediates A$_1$° or A$_2$°

$$A \xrightarrow{k_1} A_1^\circ$$

$$A \xrightarrow{k_2} A_2^\circ$$

We assume that A$_1$° possesses a lower free energy than A$_2$° and that the free energy barrier for interconversion of A$_1$° to A$_2$° is $G_i^{\ddagger}$. A$_1$° and A$_2$° are assumed to undergo processes which convert them into A$_1$* or A$_2$*, respectively. These processes might, for example, consist of combination with ^{13}CO. A schematic free energy diagram for the system is shown in Figure 7. We do not specify whether $G_i^{\ddagger}$ or ΔG_{12} is large or small. A large value for $G_i^{\ddagger}$ corresponds to the case in which the intermediates do not interconvert (nonfluxional). A small $G_i^{\ddagger}$, conversely, corresponds to a case in which the intermediates are rapidly interconverting. The free energies of the intermediates may differ considerably or may be the same, as in the limiting case in which only one intermediate exists ($G_i^{\ddagger} = 0$, $\Delta G_{12} = 0$).

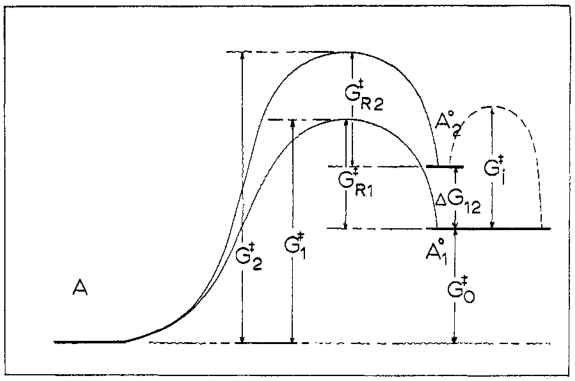

Figure 7.—Schematic free energy diagram for formation of intermediates capable of leading to distinct products A$_1$* and A$_2$*.

The rate of formation of A$_1$* is of the form $\mathrm{d}A_1^*/\mathrm{d}t = k_{R1}[A_1^\circ][L^*]$, where [L*] represents the concentration of labeled species. A similar expression applies to the formation of A$_2$*. We are interested in the ratio of these rates

$$R = \frac{\mathrm{d}A_1^*/\mathrm{d}t}{\mathrm{d}A_2^*/\mathrm{d}t} = \frac{k_{R1}[A_1^\circ]}{k_{R2}[A_2^\circ]}$$

But if we assume that the intermediates are in thermodynamic equilibrium with the ground-state reactant,

---

[17] K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967).

[18] The slight preference for radial CO dissociation is consistent with the results of molecular orbital calculations for Mn(CO)$_5$X compounds.[19] The nature of the CO dissociation process is so poorly understood at present, however, that correlations with ground-state properties cannot be made with much confidence.

[19] R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, **9**, 1053 (1970).

in consonance with the postulates of absolute reaction rate theory, we have

$$R = \frac{k_{\mathrm{R1}}}{k_{\mathrm{R2}}} e^{\Delta G_{12}/kT} = \frac{e^{-G_{\mathrm{R1}}^{\ddagger}/kT}}{e^{-G_{\mathrm{R2}}^{\ddagger}/kT} e^{-\Delta G_{12}/kT}}$$

Multiplying top and bottom by $e^{-G_0^{\ddagger}/kT}$ gives us

$$R = \frac{e^{-G_{\mathrm{R1}}^{\ddagger}/kT} e^{-G_0^{\ddagger}/kT}}{e^{-G_{\mathrm{R2}}^{\ddagger}/kT} e^{-\Delta G_{12}/kT} e^{-G_0^{\ddagger}/kT}} = \frac{k_1}{k_2}$$

Thus the relative rates of formation of the experimentally distinct products (in our case, stereospecifically labeled as axial or radial) are determined *only* by the relative rates of formation of the intermediates.

In particular, it does not depend on whether the intermediates are a single species or two distinct species. It also does not depend on whether the intermediates are capable of rapid interconversion in the event they are distinct, nor does it matter whether they have the same or different free energies.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Kinetic Study of the Oxygen Exchange of Sodium Bicarbonate and Carbonatopentaamminecobalt(III)[1]

BY D. J. FRANCIS[2] AND R. B. JORDAN*

Received September 15, 1971

The kinetics of oxygen-18 exchange between water and the carbonate species obtained by dissolving $NaHCO_3$ in water and by dissolving $(NH_3)_5CoCO_3^+$ in water have been measured. Both systems were studied in the pH range 7.2–8.5 at 20, 26, and 30° at an ionic strength of 1 *M* ($NaClO_4$). The results of this study confirm a previous proposal that the rate of exchange in the complexed system is controlled by the hydration rate of carbon dioxide.

The kinetics of the exchange of carbon-14-labeled carbonate ion and carbonatopentaamminecobalt(III) has been studied by Stranks[3] and by Lapidus and Harris.[4] The results were interpreted assuming that the rate-controlling equilibrium was

$$(NH_3)_5CoCO_3H^{2+} + H_2O \rightleftarrows (NH_3)_5CoOH_2^{3+} + HCO_3^- \quad (1)$$

This interpretation has been reexamined recently by Dasgupta and Harris[5] by using the rate and equilibrium data which are now available for reaction 1, and it was found that the rate of reaction 1 was about 66 times greater than the observed exchange rate. It was suggested then by Dasgupta and Harris that the rate-controlling reaction involves hydration of CO_2, according to the reactions

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \quad (2)$$

$$CO_2 + OH^- \rightleftarrows HCO_3^- \quad (3)$$

By using the known rate constants for these reactions Dasgupta and Harris compared calculated exchange rates to those measured by Stranks. The calculated and observed rates agreed well at the higher pH values but the experimental rate appears to increase more rapidly with increasing acidity than predicted by the CO_2 hydration rate. It was suggested[5] that the original pH measurements may be in error. The only alternative would be that the pentaamminecobalt(III) species catalyzes the hydration of CO_2.

In order to test the CO_2 hydration mechanism, the rate of oxygen-18 exchange of $(NH_3)_5CoCO_3^+$ and of uncomplexed carbonate species has been measured under the same conditions in this work. If the same CO_2 hydration step is rate controlling in both systems, then the same rate constants should describe the oxygen-18 exchange in both.

Experimental Section

Reagents.—The preparation and characterization of the carbonatopentaamminecobalt(III) nitrate have been described previously.[6] Reagent grade sodium bicarbonate, 70% perchloric acid, sodium perchlorate, and 2-amino-2-(hydroxymethyl)-1,3-propanediol (THM) were used as supplied. The oxygen-18-enriched water, initially 1.58 atom % oxygen-18, was obtained from Bio-Rad Laboratories. This water was used as supplied and was recovered for reuse by vacuum distillation, followed by distillation from alkaline potassium permanganate at atmospheric pressure in an all-glass apparatus. Deionized water of normal isotopic content also was distilled from alkaline permanganate.

Exchange Kinetics.—For each kinetic run an isotopically enriched solution and an unenriched buffer solution were prepared by dissolving 0.17 g of THM in 5 ml of either oxygen-18-enriched water or unenriched water. Each solution was titrated to the required pH with 1.0 *M* $HClO_4$ and then diluted to volume (10 ml) with either enriched or unenriched water.

For the carbonate exchange studies the reaction solution was prepared by dissolving 1.08 g of $NaClO_4$ and a weighed sample (about 0.015 g) of $NaHCO_3$ in 1 ml of unenriched buffer solution in a 10-ml volumetric flask.[7] This solution and the appropriate enriched buffer solution were equilibrated at the required temperature before diluting the sample to volume with enriched buffer solution. At appropriate times 0.8-ml samples of the reaction solution were syringed into a nitrogen bubbler containing 0.5 ml of 70% $HClO_4$. The CO_2 evolved was dried and collected as described elsewhere.[8]

---

[1] Financial support from the National Research Council of Canada is gratefully acknowledged.

[2] This work represents part of the dissertation of D. J. Francis presented to the Faculty of Graduate Studies of the University of Alberta in partial fulfillment of the requirements for the Ph.D. degree.

[3] D. R. Stranks, *Trans. Faraday Soc.*, **51**, 505 (1955).

[4] G. Lapidus and G. M. Harris, *J. Amer. Chem. Soc.*, **85**, 1223 (1963).

[5] T. P. Dasgupta and G. M. Harris, *ibid.*, **90**, 6360 (1968).

[6] D. J. Francis and R. B. Jordan, *ibid.*, **89**, 5591 (1967).

[7] The contribution of the buffer to the ionic strength actually changes with pH so that the ionic strength of the reactant solution varied from 1.0 *M* at pH 7 to 0.89 *M* at pH 9.

[8] D. J. Francis and R. B. Jordan, *Inorg. Chem.*, **11**, 461 (1972).