

Table II. Calculated Deuterium Quadrupole Coupling Constants and Asymmetry Parameters for $[\text{Rb}-(\text{H}_2)]^+$

Rb-(H ₂), Å	H-H, Å	θ , deg ^a	η	e^2qQ/h , kHz
4.00	0.8500	0.103	0.0250	181.770
3.00	0.8492	0.378	0.0627	179.965
2.50	0.8452	1.061	0.1250	178.867
2.00	0.8386	4.665	0.3372	171.082
1.75	0.8450	12.905	0.6228	155.373
1.50	3.9545	36.733	0.0170	14.775
1.40	4.2200	32.931	0.0080	13.565
1.30	4.3840	29.974	0.0046	13.156
1.20	4.4912	27.393	0.0031	13.123
1.10	4.5582	25.019	0.0022	13.343
1.00	4.5936	22.769	0.0017	13.779
0.50	4.4346	12.003	0.0007	19.634
0.00	4.2236	0.000	0.0000	26.902

^a Angle between the H-H vector and the major axis of the electric field gradient tensor (z axis).

the orientation of the electric field gradient major axis; Figure 4 shows the evolution of the deuterium quadrupole coupling constant and asymmetry parameters. The $[\text{Rb}-(\text{H}_2)]^+$ data are summarized in Table II. The $[\text{Na}-(\text{H}_2)]^+$ system behaved similarly to $[\text{Rb}-(\text{H}_2)]^+$, differing mainly in having a shorter M-(H₂) distance in the M-H bond-breaking region.

The evolution of the minor axes of the electric field gradient tensor is not as predictable as for the major axis. For Rb-(H₂) distances of 1.75 Å and greater, q_{yy} is normal to the Rb-(H₂) plane. After the H-H bond is broken, q_{yy} lies in the Rb-(H₂) plane.

The solid-state deuterium NMR spectrum of a tungsten dihydrogen complex gives a deuterium quadrupole coupling constant of about 124 kHz,^{12c} in good agreement with the trends found herein. Due to motional averaging, the asymmetry parameter could not be obtained from the spectrum but would be expected to be non-zero.

Conclusions

Terminal Metal Hydrides. From the calculations on the alkali-metal hydrides and subsequent comparison to vibrational

stretching force constants, two general statements can be made:

1. A lower limit for the deuterium quadrupole coupling constant in organometallic hydrides is 20 kHz.

2. Metal core electrons effectively shield the deuteron from the electric field gradient generated by large nuclear charges.

Bridging Metal Hydrides. Formation of a bridging metal-hydride bond causes a reduction in the deuterium quadrupole coupling constant relative to the value found for a terminal metal-hydride bond to the same metal.

Dihydrogen Adducts. In the addition of dihydrogen to a d⁰ metal center, the major features of the electric field gradient at the hydrogen site evolve in a straightforward manner.

1. The value of the deuterium quadrupole coupling constant is reduced, with the most rapid reduction occurring as the H-H bond is being broken.

2. The orientation of the electric field gradient major axis, aligned along the H-H bond in the dihydrogen molecule, rotates toward alignment with the M-H bond as the H-H bond is broken.

3. At structures corresponding to intermediate H-H and M-H bonds, the asymmetry parameter is non-zero.

Given the occasional experimental difficulties in acquiring solid-state deuterium NMR spectra, it can be highly beneficial to the spectroscopist to optimize the instrumental parameters on the basis of estimates of the deuterium quadrupole coupling constant and the asymmetry parameter. Also, there is a clear and definitive connection between the observed solid-state deuterium NMR spectrum and structural features of the metal-hydrogen bond, making solid-state deuterium NMR spectroscopy a potentially unique and valuable asset for physical organometallic chemistry.

Acknowledgment. We thank Professor Neil Kestner for his astute comments and Bob Zinn for assistance with the Gaussian-82 program. The support of the Research Corp., the donors of the Petroleum Research Fund, administered by the American Chemical Society, the LSU Council on Research, and the LSU Center for Energy Studies is gratefully acknowledged.

Registry No. $[\text{Na}-\text{H}-\text{Na}]^+$, 101985-62-0; $[\text{Na}-\text{H}_2]^+$, 109552-64-9; $[\text{Rb}-\text{H}_2]^+$, 109552-65-0; LiH, 7580-67-8; NaH, 7646-69-7; KH, 7693-26-7; RbH, 13446-75-8; CsH, 13772-47-9; deuterium, 7782-39-0.

Contribution from the Chemistry Department, University College (NSW), Australian Defence Force Academy, Campbell ACT, Australia 2600

Exchange Reactions and Microscopic Reversibility

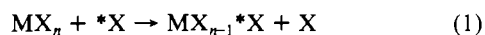
W. G. Jackson

Received July 17, 1986

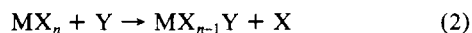
The principle of microscopic reversibility as applied to the kinetics and stereochemistry of the CO-exchange reactions of compounds of the type $\text{Mn}(\text{CO})_5\text{X}$ is reviewed, and some fundamental errors in the literature are exposed.

Introduction

The proper interpretation of the kinetics of the fundamental exchange reaction



is important in its own right, and also for the extrapolation of the results to the kinetics of the related substitution process^{1,2}



The correct application of the principle of microscopic reversibility (hereafter PMR), which is relevant to not only exchange processes but all reactions, has on occasions proved troublesome.¹

Likewise, the related principle of detailed balance (hereafter PDB)³⁻⁵ has sometimes been overlooked in correctly interpreting mechanism. Herein these principles are applied to the classic exchange reactions of $\text{Mn}(\text{CO})_5\text{X}$, processes that have received a great deal of experimental attention using ¹³CO, ¹⁴CO, or C¹⁸O as isotopic labels.⁶⁻¹² Recently¹³ we have given detailed con-

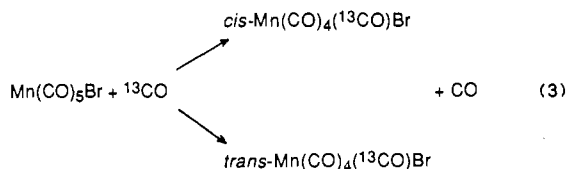
- (1) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 128-131.
 (2) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, PA, 1977; pp 378-382.

- (3) Hammes, G. G. *Principles of Chemical Kinetics*; Academic: New York, 1978; pp 14-16.
 (4) Jordan, P. C. *Chemical Kinetics and Transport*; Plenum: New York, London, 1979; pp 78-79.
 (5) Morrissey, B. W. *J. Chem. Educ.* **1975**, *52*, 296.
 (6) Wojcicki, A.; Basolo, F. *J. Am. Chem. Soc.* **1961**, *83*, 525.
 (7) Hieber, W.; Wollmann, K. *Chem. Ber.* **1962**, *95*, 1552.
 (8) Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844.
 (9) Johnson, B. F. G.; Lewis, J.; Miller, J. R.; Robinson, B. H.; Robinson, P. W.; Wojcicki, A. *J. Chem. Soc. A* **1968**, 522 and references therein.
 (10) Braterman, P. S.; Harrill, R. W.; Kaesz, H. D. *J. Am. Chem. Soc.* **1967**, *89*, 2851.

sideration to the H-exchange reactions of $(\text{NH}_3)_5\text{CoX}^{2+}$, and this has exposed some problems in the closely related CO-exchange kinetics. The PMR has been applied by others¹⁴ to the carbonyl exchange kinetics in an attempt to clarify earlier⁹ misinterpretation of the data. Unfortunately there was a fundamental error here¹⁴ that has been propagated in subsequent publications by the same group,^{11,12} and herein we remedy this situation and examine the implications. We also examine the implications of the PDB for both the IR and radiochemical data, since these are different.

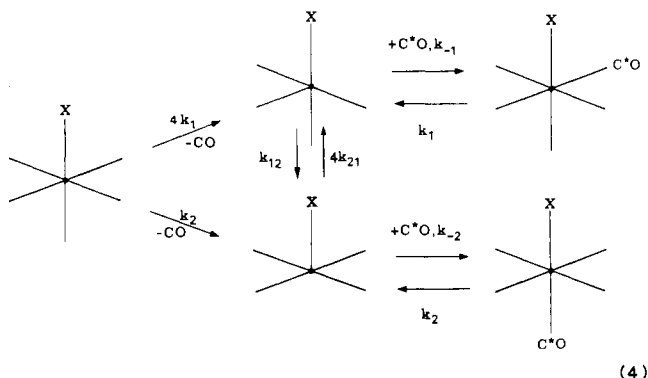
Results and Discussion

The experimental facts for the kinetics and steric course for the reaction typified as



have conjured both controversy and misinterpretation, although it is agreed that the kinetics require a limiting dissociative mechanism involving at least one coordinatively unsaturated intermediate.^{1-12,14} It now seems¹² that there is a pronounced preference for the loss of CO cis to X, ending a long debate not only over the interpretation of the data but also over the validity of the facts.

The argument that the CO group cis to X is more labile than that trans in compounds such as $\text{Mn}(\text{CO})_5\text{X}$ has run full circle, since very early Johnson et al.⁹ believed this was so. By use of the IR technique it was deduced that the substitution reaction (3) led to comparable amounts of *cis*- and *trans*- $\text{Mn}(\text{CO})_4(\text{*CO})\text{X}$. Ostensibly to accommodate this fact while retaining the idea of selective (*cis*) CO loss from the parent molecule(s), Johnson et al.⁹ invoked stereomobility in the $\text{Mn}(\text{CO})_4\text{X}$ intermediate:



Thus with $k_1 \gg k_2$ ¹⁵ they claimed that the *trans*-labeled product arose via rearrangement (k_{12}) of the first-formed intermediate prior to C^*O addition. Subsequently, it was asserted by Brown¹⁴ that this proposition violated the PMR. Brown stated that, irrespective of the modes of equilibration in the five-coordinate state, axial/equatorial addition of (labeled) CO *must*, by the PMR, display the identical degree of preference to dissociation of the *trans* or *cis* CO in $\text{Mn}(\text{CO})_5\text{X}$.¹² Stated formally¹

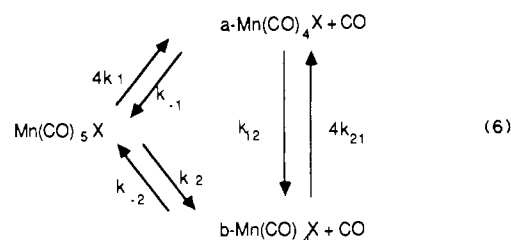
$$4k_1/k_2 = k_{-1}/k_{-2} \quad (5)$$

The explicit reasoning whereby (5)¹ was obtained was not given.¹⁴ We now show that this relationship is unreasonable on

- (11) Berry, A.; Brown, T. L. *Inorg. Chem.* **1972**, *11*, 1165.
 (12) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.
 (13) Jackson, W. G. *Inorg. Chim. Acta* **1987**, *131*, 105.
 (14) Brown, T. L. *Inorg. Chem.* **1968**, *7*, 2673.
 (15) We depart from the earlier nomenclature systems.^{1,11,12,14} Our k_1 and k_2 represent the intrinsic specific exchange rates for a CO group *cis* and *trans* to X in $\text{Mn}(\text{CO})_5\text{X}$, respectively. The present and earlier¹ rate constants are related as follows: $4k_1 = k_d^c$, $k_2 = k_d^t$, $k_{-1} = k_c^c$, $k_{-2} = k_c^t$, $k_{12} = k_a$, $4k_{21} = k_{ic}$. None of the results in this article depend upon our inclusion of statistical factors in the rate constant definitions, qualitatively or quantitatively.

thermodynamic grounds and that it is *not* required by the PMR.

The scheme shown in (4), save for the isotopic tagging, amounts to the following cyclic equilibrium system:

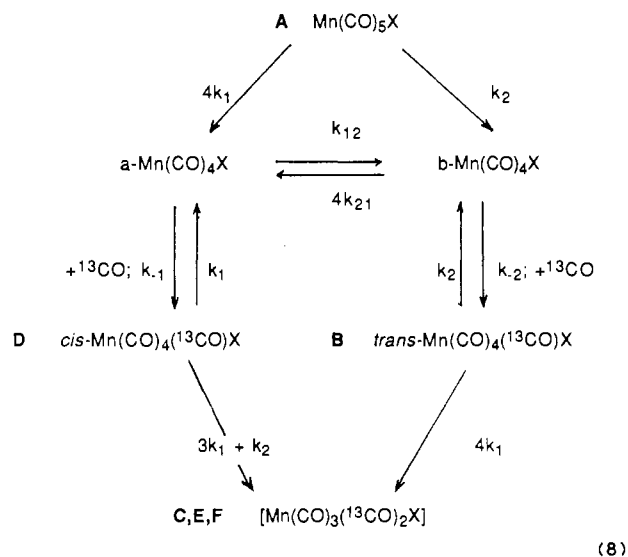


The equilibrium equivalent of the PMR, the PDB,³⁻⁵ requires that only five of the six rate constants in (6) be independent. For such a system, the equilibrium a-/b- $\text{Mn}(\text{CO})_4\text{X}$ distribution is defined¹ by either $4k_{21}/k_{12}$ or $4k_1k_{-2}/k_2k_{-1}$. Hence, the relationship between the specific rates

$$k_{21}/k_{12} = (k_1/k_2)(k_{-2}/k_{-1}) \quad (7)$$

must hold, irrespective of whether the intermediates are at actual equilibrium. Substitution of "Brown's condition" (5) into (7) leads immediately to the conclusion $4k_{21}/k_{12} = 1$; i.e., the constant for equilibrium between the chemically distinct $\text{Mn}(\text{CO})_4\text{X}$ intermediates is unity, and they must therefore be equal in energy. Of course this cannot be generally true. It follows that (5) and (7) are incompatible, and thus, given that (7) is correct, (5) cannot be. Therefore there can be no imposed condition on the relative magnitudes of k_{-1}/k_{-2} and k_1/k_2 as expressed in this equation.

In subsequent publications,^{11,12} the belief that the steric course of CO exchange was independent of the question of intermediate rearrangement was again expressed, although in a modified form. Specifically, it was stated that the distribution of labeled CO in the *initially* forming monoisotopically substituted species D and B (eq 8) was independent of the question of a fluxional or non-



fluxional five-coordinate intermediate.¹¹ Again, as shown ahead, this is *not* correct.

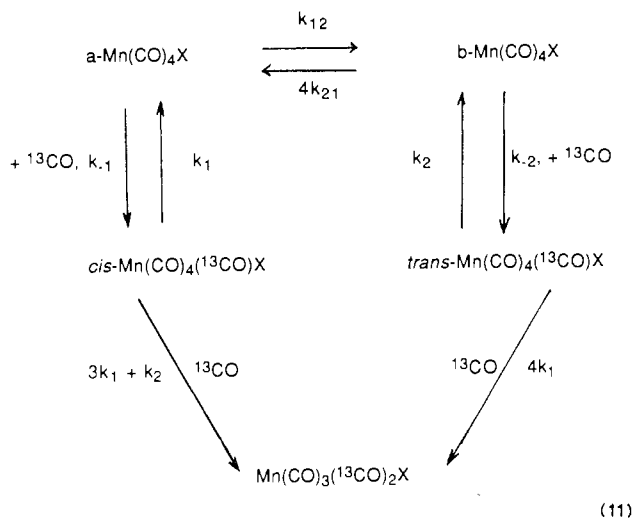
Consider first the case of rigid (nonfluxional) intermediates, i.e. $k_{12}, k_{21} = 0$. A straightforward kinetic analysis gives the time dependences (9) and (10) for the isomeric monoisotopic substi-

$$[\text{cis-Mn}(\text{CO})_4({}^{13}\text{CO})\text{X}] = 4R_0[e^{-(3k_1+k_2)t} - e^{-(4k_1+k_2)t}] \quad (9)$$

$$[\text{trans-Mn}(\text{CO})_4({}^{13}\text{CO})\text{X}] = R_0[e^{-4k_1t} - e^{-(4k_1+k_2)t}] \quad (10)$$

tution products. From (9) and (10) it is obvious that the *cis/trans* product ratio is time dependent, but since $e^x \rightarrow 1 + x$ for small x , it can be seen that this ratio approaches $4k_1/k_2$ as t approaches zero. If k_1 were equal to k_2 the ratio would exactly reflect $4k_1/k_2$ at all times. However, it now seems¹² that k_1 is substantially larger than k_2 , and therefore with time the observed *cis/trans* ratio quickly departs from $4k_1/k_2$.

Now consider the case of rapid equilibrium between the intermediates shown in the previous scheme. With $k_{12}, k_{21} \gg k_{-1}, k_{-2}$, the simplified scheme (11) is appropriate, and if one takes



account of the PDB condition (7), the time dependences for the monoisotopic products are as shown in (12) and (13), where R_0

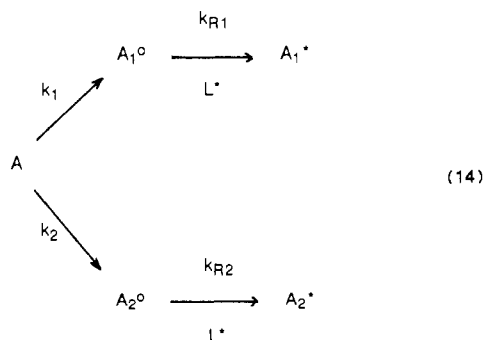
$$[\text{cis-Mn(CO)}_4(\text{}^{13}\text{CO})\text{X}] = [4k_1(4k_1 + k_2)R_0 / (4k_1^2 + k_2^2)] [e^{-\lambda_1 t} - e^{-\lambda_2 t}] \quad (12)$$

$$[\text{trans-Mn(CO)}_4(\text{}^{13}\text{CO})\text{X}] = k_2(4k_1 + k_2)R_0 / (4k_1^2 + k_2^2) [e^{-\lambda_1 t} - e^{-\lambda_2 t}] \quad (13)$$

is the initial concentration of $\text{Mn(CO)}_5\text{X}$, $\lambda_1 = 4k_1(3k_1 + 2k_2) / (4k_1 + 2k_2)$, and $\lambda_2 = 4k_1 + k_2$. This leads to the simple result $[\text{cis}] / [\text{trans}] = 4k_1 / k_2$, independent of time.

In summary, these considerations show that the possibility of equilibration between the intermediates *does* affect the steric course of CO exchange, contrary to belief of Brown et al.^{4,11,12} We have shown that the relative specific rates of generation of the intermediates ($4k_1/k_2$) mirror the stereochemistry of the dissociative process *only when intermediate equilibration is very rapid*. Otherwise this relationship is approximate only and becomes more approximate as time advances.

A proof for the opposite case has been given,¹¹ moreover one which is reported to be general, and it must be challenged. For an exchange process occurring via two intermediates¹⁶ that may interconvert (eq 14) a free energy profile was presented. While



not mentioned explicitly, the PMR was accommodated in this scheme; our equation (7) expressed in terms of products of rate constants is of course equivalent to an equation expressing sums and differences of the appropriate free energies. However, in order to show that the relative rates of formation of the isomeric (labeled) products, $R = k_{R1}[A_1^\circ] / k_{R2}[A_2^\circ]$ where k_{R1}, k_{R2} are

(16) A reviewer suggested that a single trigonal-bipyramidal intermediate could still accommodate the facts. While this might be so, we note that the PDB here imposes no special restrictions unless it is fluxional. A fluxional intermediate still requires the consideration of two such species (equatorial and axial X), and the implications of the PDB are identical with the case of two square-pyramidal intermediates.

equivalent to our k_{-1}, k_{-2} , respectively, were equal to the relative rates of formation of the intermediates, it was assumed "that the intermediates are in thermodynamic equilibrium with the ground state reactant, in consonance with the postulates of absolute rate theory". Clearly this statement confuses intermediates and transition states. Also, the substitution of $[A_1^\circ] / [A_2^\circ]$ by $e^{\Delta G_{12} / RT}$, in their expression for R , is equivalent to regarding A_1° and A_2° in equilibrium with each other. This could only be justified if the A_1° / A_2° interconversion rates (governed by the barriers G_1^* and $(G_1^* - \Delta G_{12})$ in the published¹¹ diagram) were much greater than their decay by any other process, such as the uptake of labeled CO to produce isomerically distinct labeled products. The proof therefore lacks generality, despite the claim to the contrary, since it implicitly assumes a rapid rate of equilibration between the intermediates.

The more recent papers^{11,12} admit that the kinetics of CO exchange, as probed by the IR technique, are contingent upon the fluxionality of the five-coordinate intermediate, in accordance with our view. Yet paradoxically the (incorrect) view persists in these same papers that the steric course of CO exchange must *initially* reflect the relative cis and trans dissociation rates, and that the departure from this agreement arises only from a *subsequent* process, namely rapid scrambling in a five-coordinate $\text{Mn(CO)}_3(\text{}^{13}\text{CO})\text{X}$ intermediate formed by rate-determining loss of any of the four ^{12}CO groups from $\text{Mn(CO)}_4(\text{}^{13}\text{CO})\text{X}$, followed by rearrangement and then recombination with ^{12}CO . This argument is misleading and irrelevant. We have shown that the question of fluxionality affects the rate laws for exchange as probed by using pure ^{13}CO , and it must also do so when isotopically dilute CO is used. The process referred to above as "subsequent" vanishes when operating at low complex concentrations in pure ^{13}CO .

Because a fluxional intermediate *does* affect the relationship between the observed steric course and relative rates of cis- and trans-CO dissociation, the original mechanism of Johnson et al.⁹ cannot be immediately discounted in principle. However, in practice it is not a viable proposition since, as we have shown, the observed cis/trans product ratio is equal to or greater than k_1/k_2 and quite inconsistent with the proposal $k_1 \gg k_2$ and a product ratio of ca. 1.

The time dependence of ^{14}C incorporation into $\text{Mn(CO)}_5\text{X}$ was studied long ago by standard radiochemical techniques.^{6,7} Experimentally this is straightforward, and not subject to the difficulties associated with the IR technique discussed in detail elsewhere.^{11,12} The radiotracer ^{14}C work showed clearly that four (cis) CO groups exchanged rapidly and one (trans) slowly, and the conclusion $k_1 \gg k_2$ seems inescapable. This is consistent with the most recent work of Brown et al.,^{11,12} but it remains reasonable to ask what effect a fluxional intermediate would have on the interpretation of the early ^{14}C work, since the two techniques measure different things and the implications for a pair of rapidly rearranging intermediates likewise could be different.

For convenience consider the case of fully labeled $\text{Mn(CO)}_5\text{X}$ in exchange with natural-abundance CO. The activity measurement of course does not distinguish cis from trans isotopic isomers, nor molecules containing different numbers of ^{14}CO . Indeed, the sum of all the radioactive complex species is measured, each suitably weighted according to the number of ^{14}CO ligands. Elsewhere¹³ we have considered the kinetics of H exchange in $(\text{NH}_3)_5\text{CoX}^{n+}$ species, where there are direct analogies to the system here, and the α and β as defined there have similar significance. Given α is the fraction of label in cis sites and β is the corresponding trans fraction, then $(\alpha + \beta)$ is directly proportional to what is measured in the radiotracer experiments (A/A_0) .¹⁷ The expressions for the time dependences for α and β separately, and hence their sum, have been worked out¹³ for conditions where the intermediate is both nonfluxional and fluxional and where account is taken of the requirements of the PDB. For the case of nonfluxional intermediates, the expression is simply

(17) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; pp 285-286.

$$A/A_0 = \alpha + \beta = e^{-k_1 t} + e^{-k_2 t} \quad (15)$$

Thus the activity does *not* decay by a simple first-order process, unless k_1 and k_2 are very different (which they seem to be), and this was the circumstance originally considered.^{6,7} However, a *different* sum of two exponentials applies if the intermediate is fluxional. The exponents are complicated functions of both k_1 and k_2 ,¹⁸ but for example, when $k_1 \gg k_2$ the expression is

$$A/A_0 = \alpha + \beta = (-2/13)e^{-4k_1 t} + (28/13)e^{-3k_1 t/4} \quad (16)$$

(18) The exact expressions are as follows:¹³

$$\alpha = [k_1(k_1 - k_2)/(13k_1^2 + 6k_1k_2 + k_2^2)] \exp(-4k_1 t) + [(4k_1 + k_2)(3k_1 + k_2)/(13k_1^2 + 6k_1k_2 + k_2^2)] \exp(-3k_1 t/4 + 2k_2 t/(4k_1 + k_2))$$

$$\beta = [(3k_1 + k_2)(k_2 - k_1)/(13k_1^2 + 6k_1k_2 + k_2^2)] \exp(-4k_1 t + k_2 t) + [4k_1(4k_1 + k_2)/(13k_1^2 + 6k_1k_2 + k_2^2)] \exp(-k_1(3k_1 + 2k_2)t/(4k_1 + k_2))$$

Here the loss of radiolabel is governed essentially by the dominant second term, and all five CO groups would be *observed* to exchange with the same specific rate. Provided $k_1 > k_2$,¹³ then irrespective of the relative magnitudes of k_1 and k_2 , the two exponents for the case of a fluxional intermediate never differ greatly.^{13,18}

Clearly the kinetics are affected by the question of a fluxional intermediate, and the facts^{6,7} indicate that the intermediate is rigid since two very different specific exchange rates are observed. This is inconsistent with the conclusions of Brown et al.,^{11,12} drawn from the less clear-cut IR data, and it must be concluded that the problem of the lifetime of the intermediate remains unresolved. What is now clear, however, is that its lifetime does affect the rate laws for exchange, whether studied by the IR technique or by standard radiotracer methods, and it has been possible using the PMR to derive the exact rate laws for the two sets of circumstances.

Registry No. CO, 630-08-0.

Contribution from the Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019

Acid-Induced Aquation of (Trifluoromethyl)cobaloximes with Aromatic Nitrogenous Axial Ligands

Kenneth L. Brown* and Te-Fang Yang

Received February 10, 1987

(Trifluoromethyl)(ligand)cobaloximes, $\text{CF}_3\text{Co}(\text{D}_2\text{H}_2)\text{L}$ (L = pyridine, 1-methylimidazole, and 1,5,6-trimethylbenzimidazole), have been prepared and characterized by ^1H and ^{19}F NMR spectroscopy. The kinetics of axial ligand dissociation from the pyridine complex have been studied as a function of acidity in sulfuric acid/water mixtures. The first equatorial oxime protonation is found to increase the rate of pyridine dissociation by 3 orders of magnitude while the second equatorial oxime protonation increased the rate of pyridine dissociation only 10-fold. A complete analysis of the relative free energies of all of the ground and transition states involved shows that the extraordinary effect of the first equatorial oxime protonation on the kinetics of pyridine dissociation is due to a significant stabilization of the transition state by this protonation. It is postulated that the transition states for ligand dissociation from the cationic complexes are substantially stabilized by intramolecular proton transfer from the protonated, equatorial oxime functionalities to the departing axial ligand. Kinetic measurements of the rate of axial ligand dissociation from the 1-methylimidazole complex in sulfuric acid/water mixtures suggest, but do not prove, that this ligand dissociation is specific-acid catalyzed via preequilibrium protonation of the axial ligand at N-1.

Introduction

Many studies of the kinetics and mechanism of axial ligand substitution in cobaloximes have appeared.¹⁻³³ However, the effect

of equatorial oxime protonation³⁴⁻³⁸ on such processes has never been investigated. Organocobaloximes have been shown to un-

- (1) Hague, D. N.; Halpern, J. *Inorg. Chem.* **1967**, *6*, 2059-2063.
- (2) Tsiang, H. G.; Wilmarth, W. K. *Inorg. Chem.* **1968**, *7*, 2535-2542.
- (3) Birk, J. P.; Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1968**, *90*, 6959-6963.
- (4) Costa, G.; Tauzher, G.; Puxeddu, A. *Inorg. Chim. Acta* **1969**, *3*, 41-44.
- (5) Ludwick, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1969**, *91*, 5188-5189.
- (6) Crumbliss, A. L.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1970**, *92*, 2593-2594.
- (7) Sakurai, T.; Fox, J. P.; Ingraham, L. L. *Inorg. Chem.* **1971**, *10*, 1105-1106.
- (8) Brown, T. L.; Ludwick, L. M.; Stewart, R. S. *J. Am. Chem. Soc.* **1972**, *94*, 384-388.
- (9) Herlinger, A. W.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *94*, 388-393.
- (10) Brown, K. L.; Kallen, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 1894-1901.
- (11) Brown, K. L.; Chernoff, D.; Keljo, D. J.; Kallen, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 6697-6704.
- (12) Earley, J. E.; Zimmerman, J. G. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 687-688.
- (13) Guschl, R. J.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2815-2819.
- (14) Courtright, R. L.; Drago, R. S.; Nusz, J. A.; Nozari, M. S. *Inorg. Chem.* **1973**, *12*, 2809-2815.
- (15) Trogler, W. C.; Stewart, R. C.; Marzilli, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 3697-3699.
- (16) Guschl, R. J.; Stewart, R. S.; Brown, T. L. *Inorg. Chem.* **1974**, *13*, 417-422.
- (17) Espenson, J. H.; Russell, R. *Inorg. Chem.* **1974**, *13*, 7-11.
- (18) Jensen, F. R.; Kiskis, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 5820-5825. However, see ref 22.
- (19) Brown, K. L.; Lyles, D.; Pencovici, M.; Kallen, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 7338-7346.
- (20) Seibles, L.; Deutsch, E. *Inorg. Chem.* **1977**, *16*, 2273-2278.

- (21) Brown, K. L.; Autrey, A. W. *Inorg. Chem.* **1978**, *17*, 111-119.
- (22) Stewart, R. C.; Marzilli, L. G. *J. Am. Chem. Soc.* **1978**, *100*, 817-822.
- (23) Toscano, P. J.; Marzilli, L. G. *Inorg. Chem.* **1979**, *18*, 421-424.
- (24) Lawrence, G. A.; Surachiltanout, S. *Inorg. Chim. Acta* **1980**, *44*, L61-L62.
- (25) Bresciani-Pahor, N.; Randaccio, L.; Toscano, P. G.; Sandercock, A. C.; Marzilli, L. G. *J. Chem. Soc., Dalton Trans.* **1982**, 129-134.
- (26) Dreos-Garlatti, R.; Tauzher, G.; Costa, G. *Inorg. Chim. Acta* **1983**, *70*, 83-86.
- (27) Dreos-Garlatti, R.; Tauzher, G.; Costa, G. *Inorg. Chim. Acta* **1983**, *71*, 9-13.
- (28) Dreos-Garlatti, R.; Tauzher, G.; Costa, G. *Inorg. Chim. Acta* **1984**, *82*, 197-200.
- (29) Randaccio, L.; Bresciani-Pahor, N.; Orbell, J. D.; Calligaris, M.; Summers, M. F.; Snyder, B.; Toscano, P. J.; Marzilli, L. G. *Organometallics* **1985**, *4*, 469-478.
- (30) Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E.; Toscano, P. J. *Inorg. Chim. Acta* **1985**, *96*, 193-198.
- (31) Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E.; Summers, M. F.; Ramsden, J. H.; Marzilli, P. A.; Marzilli, L. G. *Organometallics* **1985**, *4*, 2086-2090.
- (32) Bresciani-Pahor, N.; Forcolin, M.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, P. J. *Coord. Chem. Rev.* **1985**, *63*, 1-125.
- (33) Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L.; Charland, J. P.; Marzilli, L. G. *Organometallics* **1986**, *5*, 1938-1944.
- (34) Adin, A.; Espenson, J. H. *J. Chem. Soc., Chem. Commun.* **1971**, 653-654.
- (35) Abley, P.; Dockal, E. R.; Halpern, J. *J. Am. Chem. Soc.* **1972**, *95*, 3166-3170.
- (36) Crumbliss, A. L.; Bowman, J. T.; Gaus, P. L.; McPhail, A. T. *J. Chem. Soc., Chem. Commun.* **1973**, 415-416.
- (37) Crumbliss, A. L.; Gaus, P. L. *Inorg. Chem.* **1975**, *14*, 486-490.
- (38) Brown, K. L.; Lu, L.-Y. *Inorg. Chem.* **1981**, *20*, 4178-4183.