Acknowledgment is made to the Department of Science and Technology, New Delhi, for financial support. Thanks are due to Dr. J. G. Mohanty of Hyderabad University for EPR spectra.

Registry No. **1** (X = Cl), 75400-19-0; **1** (X = Br), 75400-20-3; **3** (X = Cl), 75400-21-4; **3** (X = Br), 75400-22-5.

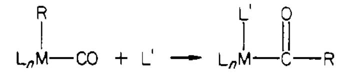
Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Acceleration of the Methyl Migration Reaction with Proton Acids

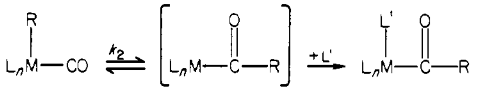
Susan Beda Butts, Thomas G. Richmond,
and Duward F. Shriver*

Received April 3, 1980

Our recent investigation of the influence of molecular Lewis acids on alkyl migration reactions in alkylmetal carbonyl complexes[1] and the known ion-pair promotion of alkyl migration[2] prompted us to study the effects of proton acids on this reaction. Many alkylmetal complexes are known to undergo an alkyl migration (CO insertion) reaction in the presence of added ligand (eq 1).[3] These reactions are thought to proceed by way of a coordinatively unsaturated acyl intermediate (eq 2). We found that strong Lewis acids (e.g., $AlCl_3$, $AlBr_3$, BF_3) induce a rapid alkyl migration in a variety of complexes, even in the absence of added ligand, to produce novel ring adducts in which one halogen atom of the acid fills the open metal coordination site.[1] Since the rate of reaction with Lewis acid (reaction 3) is much more rapid than the normal rate of formation of the intermediate I (i.e., $k_3 >> k_2$), we propose that Lewis acid lowers the activation energy by coordination with the oxygen of the CO group which is undergoing reaction (II) and thus increases the overall rate of alkyl migration. The present investigation was prompted by the thought that proton acids might function in a manner similar to the Lewis acids and thereby increase the rate of reaction 1.

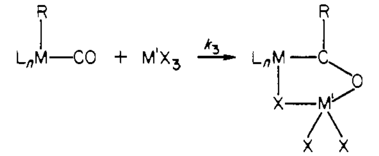


$$L_n\overset{R}{\overset{|}{M}}-CO + L' \longrightarrow L_n\overset{L'}{\overset{|}{M}}-\overset{O}{\overset{\|}{C}}-R \tag{1}$$

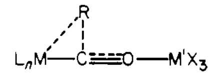


$$L_n\overset{R}{\overset{|}{M}}-CO \overset{k_2}{\rightleftharpoons} \left[L_nM-\overset{O}{\overset{\|}{C}}-R\right] \xrightarrow{+L'} L_n\overset{L'}{\overset{|}{M}}-\overset{O}{\overset{\|}{C}}-R \tag{2}$$

I



(3)



II

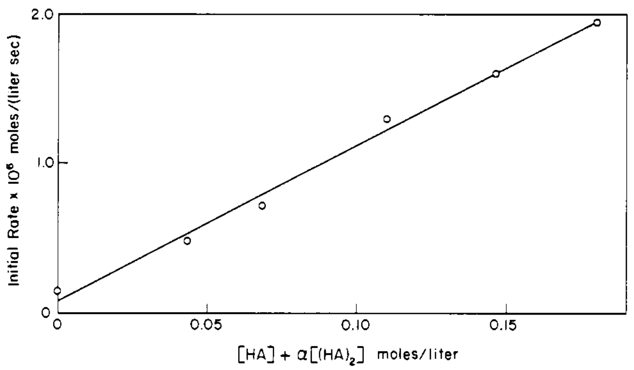
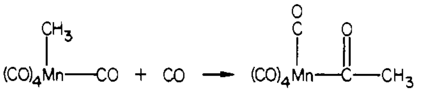


Figure 1. Intitial rate of CO uptake vs. the concentration function $[HA] + \alpha[(HA)_2]$, where the two concentration terms apply to the monomer and dimer of CCl_2HCOOH. For all experiments $[Mn(CH_3)(CO)_5] = 0.100 \pm 0.005$ mol L^{-1}, $P_{CO} = 389 \pm 7$ torr, $T = 20.0 \pm 0.1$ °C, and solvent = toluene.

Results and Discussion

As a model system we studied the reaction of $(CO)_5Mn(CH_3)$ and CO in the presence of a variety of proton acids (eq 4). Kinetic data for these experiments are summarized in Table I. The observed enhancement of reaction rate caused by haloacetic acids increases with the strength of the acid. The strongest of these haloacetic acids, CF_3COOH, also caused significant $Mn-CH_3$ bond cleavage with resultant CH_4 formation. Thus, the greater rate enhancement caused by the stronger acid is offset by this detrimental cleavage. In the extreme case of the strong mineral acid HBr, the cleavage reaction is completely dominant. Formation of $BrMn(CO)_5$ and CH_4 occurs rapidly, and no alkyl migration is observed. Such acid cleavage reactions are well documented in the literature.[5]



$$(CO)_4\overset{CH_3}{\overset{|}{Mn}}-CO + CO \longrightarrow (CO)_4\overset{\overset{O}{\overset{\|}{C}}}{\overset{|}{Mn}}-\overset{O}{\overset{\|}{C}}-CH_3 \tag{4}$$

The initial rate of reaction with CO was determined at 20 °C for several concentrations of CCl_2HCOOH.[6] These data show a nonlinear dependence on nominal acid concentration, and a linear dependence of rate on acid monomer concentration, but, for the latter case, the extrapolated intercept at zero acid concentration indicates a negative rate, which is physically unacceptable. A satisfactory fit to all of the data, including the reaction in the absence of acid, is obtained by assuming that both the acid monomer and acid dimer accelerate the reaction according to eq 5. This equation contains

$$\text{initial rate} = \{k_u + k_1[HA] + k_2[(HA)_2]\}[Mn(CO)_5(CH_3)]P_{CO} \tag{5}$$

a term for the uncatalyzed reaction, k_u, the rate constant for the acid monomer path, k_1, and the corresponding term for the acid dimer path, k_2. Concentrations of the monomer and dimer were calculated by using the dimer formation constant determined by Steigman and Conkright ($K_D = 27.1$ M^{-1} in benzene at 25 °C; the ±1.9 error in this value probably exceeds the difference between K_D at 25 °C and that at 20 °C).[7,8] The

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(1) S. B. Butts, E. M. Holt, S. H. Strauss, N. W. Alcock, R. E. Stimson, and D. F. Shriver, *J. Am. Chem. Soc.*, **101**, 5864-5866 (1979).

(2) J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 4766 (1978).

(3) A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87-145 (1973); F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, **16**, 299-311 (1977).

(4) Z. Rappaport, "Handbook of Tables for Organic Compound Identification,", CRC Press, Cleveland, Ohio, 1967.

(5) (a) R. W. Johnson and R. G. Pearson, *Inorg. Chem.*, **10**, 2091-2095 (1971); (b) E. L. Muetterties and P. L. Watson, *J. Am. Chem. Soc.*, **98**, 4665-4667 (1976); (c) A. E. Stevens and J. L. Beauchamp, *ibid.*, **101**, 245-246 (1979); (d) P. L. Watson and R. G. Bergman, *ibid.*, **101**, 2055-2062 (1979); (e) A. Dawson, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653-3666 (1962); (f) W. N. Rogers and M. C. Bard, *J. Organomet. Chem.*, **182**, C65-C68 (1979).

(6) Dichloroacetic acid was studied because it caused the greatest rate enhancment without any detectable $Mn-CH_3$ bond cleavage.

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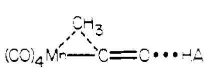
Table I. Rate of Reaction between $(CO)_5Mn(CH_3)$ and CO in the Presence of Proton Acids[a]

acid	pK_a[b]	acid concn,[c] mol L^{-1}	$10^6 \times$ initial rate, mol L^{-1} s^{-1}	rate enhancement factor[d]	% M-R bond cleavage[e]
			0.18[f]	1	h
$CClH_2COOH$	2.86	0.404	0.44	2.4	h
CCl_2HCOOH	1.29	0.404	1.3	7.2	h
CF_3COOH	0.23	0.44	1.7[g]	9.4	20
HBr		0.082			100

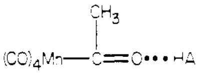
[a] All experiments were performed under the following conditions: $[(CO)_5Mn(CH_3)] = 0.100 \pm 0.005$ mol L^{-1}; $P_{CO} = 374 \pm 22$ torr; $T = 20.0 \pm 0.1$ °C; solvent = toluene. [b] Values from ref 4. [c] Calculated on the basis of the total number of moles of HA. [d] Defined as the ratio of the rate in the presence of acid to rate in the absence of acid. [e] Estimated by IR. [f] The rate of reaction of $(CO)_5Mn(CH_3)$ in the absence of acid. [g] This value is not corrected for CH_4 production. [h] No CH_4 detected.

rate constant k_1 and the ratio for the two acid catalyzed paths, $\alpha = k_2/k_1$, were varied to fit the data. As shown in Figure 1 an acceptable correlation ($R = 0.994$) was obtained for $\alpha = 0.20$, $k_1 = 2.6 \times 10^{-8}$ L mol^{-1} torr^{-1} s^{-1}, and $k_1 = 2.8 \times 10^{-9}$ torr^{-1} s^{-1}. The latter rate constant is in reasonable agreement with the value of k_u determined in the absence of acid (4.3×10^{-9} torr^{-1} s^{-1}). It should be noted that a variation of α by ±0.05 will give equally acceptable fits. The greater catalytic activity of the monomer over the dimer acid which is indicated by the observed value of α is physically reasonable.

The main monomer-promoted path is consistent with stabilization of the transition state by coordination with acid monomer (III).[9] Although we observed no direct spectroscopic evidence for III or the corresponding coordinatively unsaturated intermediate (IV), the coordinatively saturated product does clearly form an adduct with acid (V). Mixtures of $(CO)_5Mn(C(O)CH_3)$ with excess CCl_2HCOOH or CF_3COOH exhibit strong bands at 1591 and 1581 cm^{-1}, respectively, in addition to the acetyl ν_{CO} of the parent complex $(CO)_5Mn(C(O)CH_3)$. We attribute the new bands to an acetyl acid adduct (probably having the formula indicated in V) which is in equilibrium with the parent acetyl complex. The assignment of these new bands to structure V is consistent with the change in frequency of the acetyl band observed on coordination with various acids. The very stable adducts, $(CO)_5Mn(C(OMX_3)CH_3)$, formed with the strong Lewis acids $AlBr_3$ and $AlCl_3$ exhibit an acetyl ν_{CO} at ca. 1480 cm^{-1}.[1] A weakly hydrogen-bonded adduct such as V should have an acetyl ν_{CO} somewhere between that of a strongly bound adduct (1483 cm^{-1}) and the parent complex (1653 cm^{-1}). A fully protonated acetyl complex (e.g., $(\eta^5\text{-}C_5H_5)(CO)_2Fe(C(OH)CH_3)^+$) behaves like a hydroxycarbene and exhibits a ν_{OH} at 1652 cm^{-1} rather than an acetyl ν_{CO}.[10]

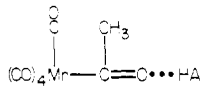


III



$(CO)_4Mn{-}\overset{\overset{\large CH_3}{|}}{C}{=}O\cdots HA$

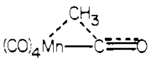
IV



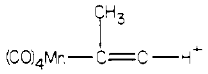
$(CO)_4\overset{\overset{\large OC}{|}}{Mn}{-}\overset{\overset{\large CH_3}{|}}{C}{=}O\cdots HA$

V

The enhancement of the rate of alkyl migration caused by proton acids is significantly less than that caused by strong Lewis acids. Molecular orbital calculations carried out by Berke and Hoffmann indicate that coordination with a proton should stabilize the transition state (VI) and acyl intermediate (VII) of reaction 2 by 3 and 14 kcal/mol, respectively.[11] The Arrhenius equation predicts that a decrease of 3 kcal/mol in activation energy will increase reaction rate by 2 orders of magnitude. We do not achieve this degree of acceleration, presumably, because strong proton acids could not be studied owing a very rapid metal–alkyl bond cleavage. The weaker acids, which did not cleave Mn–C bonds, increase the rate of alkyl migration by 1 order of magnitude or less.



VI



$(CO)_4Mn{-}\overset{\overset{\large CH_3}{|}}{C}{=}O{-}H^+$

VII

Experimental Section

$Mn(CH_3)(CO)_5$ was prepared by a modification of the literature method and purified by sublimation.[12] Trifluoroacetic acid (MCB) and CCl_2HCOOH (MCB) were vacuum distilled immediately before use. Chloroacetic acid (Aldrich) was crystallized twice from dry toluene. Hydrogen bromide (Matheson) was purified by removing noncondensable gases. Carbon monoxide (Matheson CP grade) was used as received. Toluene was distilled under N_2 from sodium benzophenone ketyl immediately before use. All materials were handled and transferred under a N_2 atmosphere.

Rates of CO uptake were measured in a simple, grease-free tensimeter.[13] Approximately 10 mL of a 0.10 M toluene solution of $(CO)_5Mn(CH_3)$ with the desired acid concentration was prepared in a 50 mL flask which was then attached to the manometer, degassed, and thermostated at 20.0 ± 0.1 °C. Excess CO, which was saturated with toluene vapor, was admitted to the tensimeter to give a CO pressure of 389 ± 7 torr. The solution was stirred vigorously with a magnetic stirrer, and pressure and time readings were recorded at appropriate intervals. The initial rate of reaction was calculated from the slope of the plot of moles of CO gas (determined by *PVT* calculation) vs. time for the first 10% of reaction (based on $(CO)_5Mn(CH_3)$). Experimental error in the rates is ca. ±10%.

After the collection of kinetic data (at least 30% completion) the noncondensable gases above the reaction mixture were checked for the presence of CH_4 by IR. The amount of CH_4 was determined on the basis of the intensity of the 3010 cm^{-1} band. The lower limit of detection for CH_4 is 0.05 torr which corresponds to ca. 0.6% yield of CH_4 based on $Mn(CH_3)(CO)_5$.

In the case of HBr no detectable alkyl migration occurred. Hydrogen bromide was condensed into the reaction flask containing frozen $Mn(CN)_3(CO)_5$ solution, and gas (presumably CH_4) evolution began as soon as the solution thawed. Carbon monoxide was added quickly, but gas evolution continued, and a yellow precipitate formed. The

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(7) J. Steigman and W. Cronkright, *Spectrochim. Acta, Part A*, **26A**, 1805 (1970).

(8) K_D is also solvent dependent, but the difference between benzene and toluene should be small and therefore not substantially affect our results. Our interpretation of the kinetic data is relatively insensitive to the specific value of K_D and the plot shown in Figure 1 remains linear even if K_D is varied by ±100%.

(9) F. Calderazzo and F. A. Cotton (*Inorg. Chem.*, **1**, 30–36 (1962)) found that the rate of reaction between $(CO)_5Mn(CH_3)$ and CO is faster in solvents with higher dielectric constants. Such an effect cannot explain the rate enhancement in the acid-catalyzed systems since the acid dielectric constants increase in the order $CF_3COOH < CCl_2HCOOH < CClH_2COOH$ (R. C. Weast, Ed., "Handbook of Chemistry and Physics", 53rd ed., The Chemical Rubber Company, Cleveland, Ohio, 1972–1973).

(10) M. L. H. Green and C. R. Hurley, *J. Organomet. Chem.*, **10**, 188–190 (1967).

(11) H. Berke and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 7224–7236 (1978).

(12) R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, 1965, pp 147–148.

(13) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, 1969, pp 58–61.

precipitate was identified as $MnBr(CO)_5$ by IR spectroscopy, and no $Mn(C(O)CH_3)(CO)_5$ could be detected in the solution.

Acknowledgment. This work was supported by a grant from the National Science Foundation. We appreciate help from R. E. Stimson for exploratory work.

Registry No. $(CO)_5Mn(CH_3)$, 13601-24-6; CO, 630-08-0; $CClH_2COOH$, 79-11-8; CCl_2HCOOH, 79-43-6; CF_3COOH, 76-05-1; HBr, 10035-10-6.

Contribution from the Departments of Chemistry,
Clemson University, Clemson, South Carolina 29631,
and Kansas State University, Manhattan, Kansas 66506

Direct Evidence for Rearrangement of Five-Coordinate Excited-State Fragments Generated from Ligand Field Photodissociation in d^6 Complexes of Rhodium(III)

Stephen F. Clark and John D. Petersen*

Received July 7, 1980

Recently, Vanquickenborne and Ceulemans[1] have used an "additive point ligand model" to explain stereochemical changes during photosubstitution reactions of d^6 complexes. Their conclusion is that the stereochemical changes that sometimes occur during the photochemical experiment are a result of rearrangement of a five-coordinate, triplet fragment which results directly from ligand loss out of the lowest triplet, ligand field excited state of the six-coordinate reactant. The five-coordinate fragment $[ML_4X]^q$ displays a thermodynamic preference for the X ligand to appear apical or basal in the square-pyramidal intermediate depending on whether $e_\sigma(L)$ is greater than or less than $e_\sigma(X)$, respectively. This thermodynamic preference, which has been observed experimentally for rhodium(III) amine complexes by our group[2] and others,[3,4] pertains only to the spin triplet and not the lower energy singlet configuration. If correct, this model is very important in deducing the mechanism of d^6 photosubstitution reactions. The presence of the five-coordinate triplet fragment not only implies a photodissociative primary process but also indicates that the reaction is occurring from an electronic excited state and not a high vibrational level in the ground-state manifold.

We have extended the theoretical work of Vanquickenborne and Ceulemans[1] to cases in which $e_\sigma(X) > e_\sigma(L)$ and have observed experimentally[5] the predicted trans to cis photoaquation reaction for *trans*-$Co(en)_2(CN)Y^{n+}$ ($Y = Cl, H_2O$) complexes. However, in a number of studies, photolysis of *cis*- and *trans*-$Rh(en)_2(NH_3)X^{2+}$ complexes (X = Cl,[2a] Br,[2b] I[2c]) leads to $Rh(en)_2(NH_3)(H_2O)^{3+}$ with stereoretention whenever the photolabilized ligand is X. The five-coordinate fragment which is formed, $[Rh(en)_2(NH_3)^{3+}]^*$, should not show much of a thermodynamic preference for NH_3 apical or basal ($e_\sigma(NH_3) \simeq e_\sigma(en)$), so that a cis/trans product mixture and not stereoretention should have resulted if the racemization is controlled by the thermodynamics of the square-pyramidal $[ML_4X]^q$ fragments. We have proposed[2] that the lack of rearrangement of the apical and basal $[Rh(en)_2(NH_3)^{3+}]^*$ fragments is due to a kinetic control of the rearrangement in that the barrier to NH_3 apical ↔ basal rearrangement is too large to be competitive to intersystem crossing (triplet → singlet) of the five-coordinate fragment. Since this premise is very important in assessing the applicability and correctness of the Vanquickenborne model,[1] we report here the 25 and 50 °C photochemistry of *cis*- and *trans*-$Rh(en)_2(NH_3)(H_2O)^{3+}$.

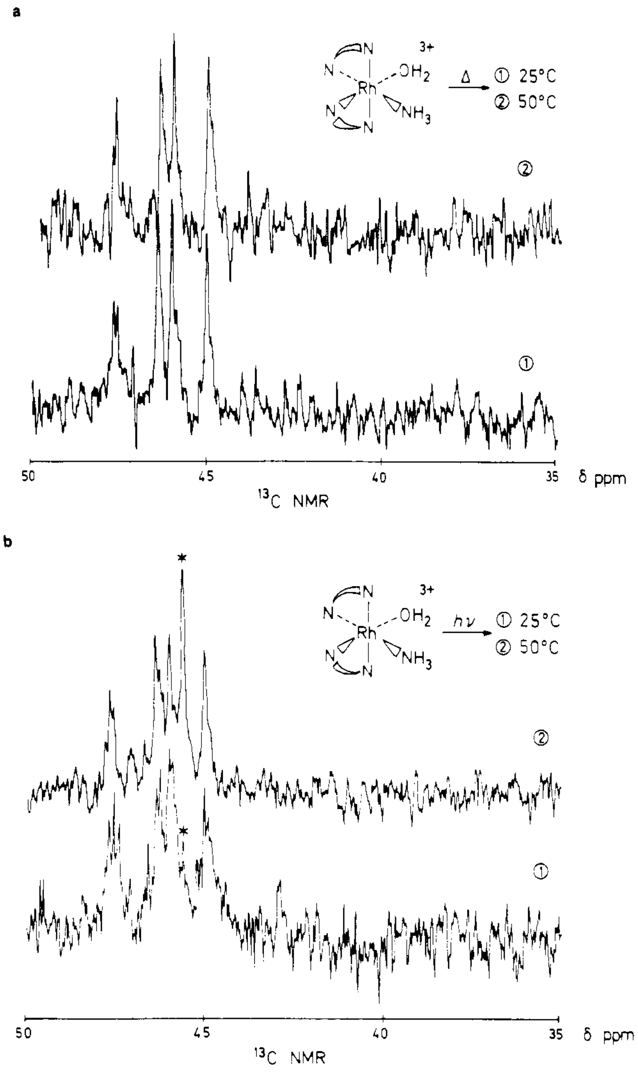

Figure 1. Proton-decoupled ^{13}C NMR spectra: (a) thermal reaction of *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ at 25 °C; (b) photochemical reaction of *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ at 25 and 50 °C with * denoting trans isomer.

Experimental Section

Materials and Syntheses. The *cis*- and *trans*-$[Rh(en)_2(NH_3)(H_2O)](ClO_4)_3$ complexes were prepared from $RhCl_3$ by previously described procedures.[2a] All reagents used in compound preparation were analytic reagent grade and used without further purification. Solvent water, used in both compound preparation and photolysis studies, was redistilled from alkaline permanganate in all glass apparatus.

Photolysis and Dark Control Reactions. All photolysis and dark control solutions were approximately 10^{-3} M in complex in pH 3.5 aqueous $HClO_4$. For photolysis solutions, the irradiation wavelength of 313 nm was used on a previously described apparatus.[6] Both photo and dark control experiments were run at both 25 and 50 °C for *cis*- and *trans*-$Rh(en)_2(NH_3)(H_2O)^{3+}$. Photolyses were carried out at 50 °C until changes were minimal in the electronic spectra (8 h for the trans complex, 5 h for the cis). All other experiments—all dark

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* To whom correspondence should be addressed at Clemson University.

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(2) (a) Petersen, J. D.; Jakse, F. P. *Inorg. Chem.* **1979**, *18*, 1818. (b) Clark, S. F.; Petersen, J. D. *Ibid.* **1979**, *18*, 3394. (c) Clark, S. F.; Petersen, J. D. *Ibid.* **1980**, *19*, 2917.
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(6) Figard, J. E.; Petersen, J. D. *Inorg. Chem.* **1978**, *17*, 1059.

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