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Communications

Kinetics and Mechanism of CO_2 Insertion into a Metal–Hydride Bond. A Large Solvent Effect and an Inverse Kinetic Isotope Effect

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Summary: The results of a kinetic study of CO_2 insertion into the Re–H bond in *fac*-Re(chelate)$(CO)_3H$ (chelate is 2,2′-bipyridine or a variety of 4,4′-bpy ring-substituted derivatives) are consistent with a mechanism involving direct hydride transfer from the Re^I site to the carbon atom of CO_2 via a highly polar, charge-separated state.

A fundamental chemical step in many catalytic reduction cycles is the insertion of an unsaturated molecule into a metal–hydride bond. Often the insertion step leads to reactive intermediates which are crucial to the catalysis. Given the importance of metal–hydride insertions in processes as diverse as hydroformylation, alkene hydrogenation, the water gas shift reaction, and in Fisher–Tropsch chemistry, it is desirable to obtain information concerning the details of the insertion step using stable model systems.[1] Previous studies have addressed mechanistic details of alkene insertion[2] into metal hydrides, and the insertions of CO_2,[3] SO_2,[4] and CO[5] have been studied for selected metal–alkyl systems.

Here we report, in a preliminary fashion, the results of the first kinetics and mechanism study of CO_2 insertion into a metal–hydride bond. For the complex *fac*-Re(bpy)$(CO)_3H$[6] (bpy is 2,2′-bipyridine) we find evidence that the hydrogen is transferred to CO_2 essentially as a hydride ion, that a large solvent effect exists, and that the mechanism is characterized by a substantial, inverse (k_H/k_D) isotope effect.

The complex *fac*-Re(bpy)$(CO)_3H$ undergoes a thermally activated reaction with CO_2 in THF, acetone, CH_3CN, and other solvents to give the stable formato complex *fac*-Re(bpy)$(CO)_3OC(O)H$ quantitatively. Typical spectral changes observed in CO_2-saturated acetone solution are shown in Figure 1. They arise from the disappearance and appearance, respectively, of the low-energy $Re^I(d\pi) \rightarrow bpy(\pi^*)$ metal-to-ligand charge-transfer (MLCT) absorption bands for the hydrido and formato complexes. The inset in Figure 1 shows that the absorbance changes with time follow first-order kinetics. Pseudo-first-order rate behavior up to 7 half-lives can be observed for several solvents in which the reaction was studied.

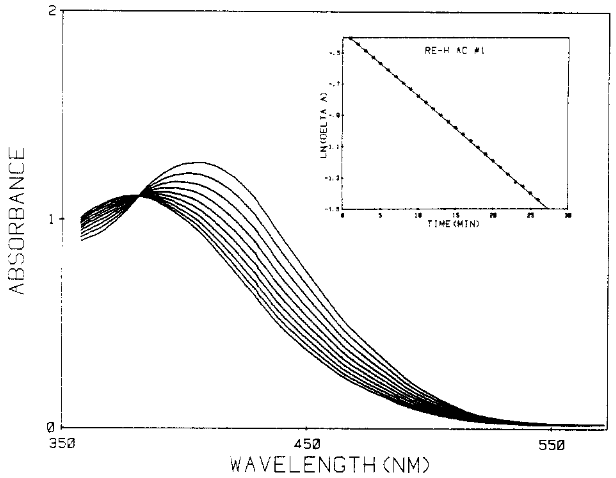

Figure 1. Spectral changes in a solution containing *fac*-Re(bpy)$(CO)_3H$ (5.5×10^{-4}M) and CO_2(0.28 M) in acetone at 2-min intervals. The inset graph shows a first-order kinetic plot over ca. 2 half-lives for data obtained under very similar conditions.

The dependence of the observed first-order rate constants on CO_2 concentration was determined in THF and CH_3CN solution over a concentration range which varied by 2 orders of magnitude. A first-order dependence of k_{obsd} on $[CO_2]$ was found in both solvents. In THF where the solubility of CO_2 is known, the second-order rate constant was found to be $(1.97 \pm 0.07) \times 10^{-4}$ M^{-1} s^{-1}. Over the entire concentration range the kinetics were consistent with the simple second-order rate law $-d[Re]/dt = k_i[Re][CO_2]$. Kinetics studies using *fac*-Re(bpy)$(CO)_3D$ revealed an inverse k_H/k_D isotope effect of $(k_H/k_D) = 0.58 \pm 0.03$ for THF, $(k_H/k_D) = 0.55 \pm 0.11$ for acetone, and $(k_H/k_D) = 0.52 \pm 0.05$ for CH_3CN.

Unlike previously studied alkene[2a] and SO_2[4b,c] insertions, we find a dramatic solvent effect for CO_2 insertion, which as shown in Table I, can lead to rate variations of several orders of magnitude. The results of the solvent-dependent studies are shown in Table I for two pure solvents and for three solvent mixtures where the CO_2 concentration is known or can be estimated. From the data, k_i increases with the static dielectric constant of the medium (D_s).

The temperature dependence of k_i for *fac*-Re(bpy)$(CO)_3D$ was obtained from kinetic runs over the temperature range 4–39 °C in THF solution. From an Eyring plot of $\ln(k_i/T)$ vs. T^{-1}, the activation parameters were found to be $\Delta H^{\ddagger} = 12.8 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = -33.0 \pm 6.9$ eu.

Synthesis of the series of complexes *fac*-Re(4,4′-X_2-2,2′-bpy)$(CO)_3H$ (X = Cl, Me, *t*-Bu, or OMe) by a modification of the published procedure[6] for the parent hydride has allowed an assessment of the rate variation with

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(1) See, for example: (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980. (b) And, the entire volume of: *Adv. Organomet. Chem.* **1979**, Vol. 17.

(2) (a) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670–2682. (b) Halpern, J.; Okamoto, T.; Zakchariev, A. *J. Mol. Catal.* **1976**, *2*, 65–68. (c) Poe, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 7771–7772. (d) Clark, H. C.; Jablonski, C.; Halpern, J.; Mantovani, A.; Weil, T. A. *Inorg. Chem.* **1974**, *13*, 1543–1541. (e) Halpern, J.; Okamoto, T. *Inorg. Chim. Acta* **1984**, *89*, L53–L54.

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Table I. Rate Constant Variation with Solvent (24.8 ± 0.3 °C) for *fac*-Re(bpy)(CO)$_3$H

solv	[CO$_2$], M	k_{obsd} s^{-1}	k_i, M^{-1} s^{-1}	D_s	$(D_s - 1)/(2D_s + 1)$
tetrahydrofuran (THF)	0.33[a]	(6.50 ± 0.23) × 10^{-5}	(1.97 ± 0.07) × 10^{-4}	7.32	0.404
1/7 Ac/THF	0.32[a]	(9.73 ± 0.04) × 10^{-5}	(3.04 ± 0.11) × 10^{-4}	9.1[b]	0.422
1/2 Ac/THF	0.30[b]	(1.84 ± 0.07) × 10^{-4}	(6.13 ± 0.23) × 10^{-4}	12.1[b]	0.440
acetone (Ac)	0.28[a]	(7.05 ± 0.27) × 10^{-4}	(2.52 ± 0.05) × 10^{-3}	20.7	0.465
dimethylformamide	0.23[c]	(2.21 ± 0.09) × 10^{-3}	(9.67 ± 0.39) × 10^{-3}	36.7	0.480
acetonitrile	0.14[d]	(7.62 ± 0.14) × 10^{-3}	(5.44 ± 0.10) × 10^{-2}	36.1	0.480

[a] See: *Chem. Abstr.* **1900**, *55*, 3175h–i, 3176a–g. [b] Estimated based on the properties of the pure solvents and the mole fraction composition of the solution. [c] "Solubilities of Inorganic and Organic Compounds"; Stephen, H., Stephen, T., Eds.; MacMillan: New York, 1963; Vol. 1, Part 2, p 1063. [d] Quoted in: Pearce, D. J.; Pletcher, D. *J. Electroanal. Chem.* **1986**, 317–330.

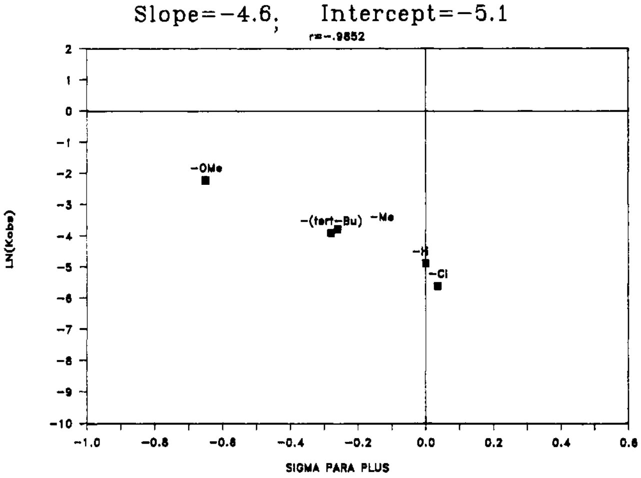
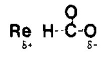


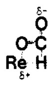
Figure 2. Effect on the insertion rate of substituents at the 4,4′-positions of the bpy ligand (see text).

changes in the electron density at the metal. In Figure 2 is shown the linear relation that exists between σ_p^+ and ln k_{obsd}[7a] for data obtained in CO$_2$-saturated THF solution. It is clear from these data that electron-releasing substituent groups facilitate insertion.

Since the kinetics of the reaction are cleanly second order with no sign of an intermediate and the addition of trapping agents like PPh$_3$ or NEt$_3$ has no effect[8] on the insertion rate, dissociative mechanisms are not likely. Consequently, the above data are best interpreted in terms of an associative hydride-transfer process where the transition state or intermediate is either linear (a) or cyclic (b) in form as shown below.



a



b

The charge-separated state is also consistent with the observed isotope effect although there are several possible explanations. Inverse deuterium isotope effects have been shown[2a,9] to arise in cases of a rapid pre-equilibrium followed by a rate-determining hydrogen-transfer step.[10] However, a kinetically indistinguishable origin could be in a transition state in which C–H bond formation is nearly complete at the expense of the Re–H bond. For such a case the zero point energy difference between the transition state and ground state could be larger for the deuterio than the protio complex since the quantum spacing for the ν(CH) normal mode is greater than the spacing for ν(ReH).

The dramatic solvent effect provides evidence that a rather large degree of charge separation is present during hydride transfer. As shown in Table I the ln k_i values increase as the dipole solvation function $(D_s - 1)/(2D_s + 1)$, behavior which can be interpreted by means of a simple thermodynamic cycle in terms of solvation of a dipolar transition state or intermediate at the expense of a relatively nonpolar ground state. Further support for a highly polar hydride-transfer process comes from the ordering and magnitude of the substituent effects, at the bpy ligand and the large negative value for ρ (−4.6) which is consistent with a buildup of positive charge at the Re^I site in the transition state.[7b]

The results of our study are also consistent with evidence from a number of synthetic and mechanistic studies that suggest that a common insertion mechanism for both metal hydrides and metal alkyls exists involving direct attack of

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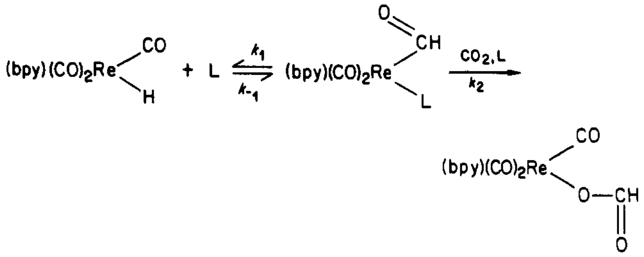
(7) (a) Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley: New York, 1972; pp 152–155. (b) Chapman, N. B.; Shorter, J., Eds. "Advances in Linear Free Energy Relationships"; Plenum Press: London, 1972.

(8) Addition of PPh$_3$ (0.19 M) to a ca. 4.5 × 10^{-4} M solution of *fac*-Re(bpy)(CO)$_3$D in CH$_3$CN, which was saturated by a CO$_2$–N$_2$ gas mixture 32.0% in CO$_2$, gave a pseudo-first-order rate constant for insertion of (1.58 ± 0.11) × 10^{-2} s^{-1}. This value compares with k_{obsd} = (1.49 ± 0.09) × 10^{-2} s^{-1} in the absence of PPh$_3$ and of k_{obsd} = (1.46 ± 0.10) × 10^{-2} s^{-1} under the same conditions but with 0.19 M added NEt$_3$.

(9) Melander, L.; Saunders, W. H., Jr., "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980.

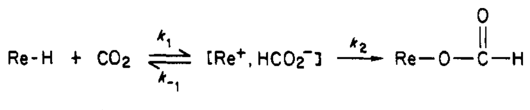
(10) (a) The interesting possibility exists of a formyl mechanism:



where L could be an added ligand or the solvent. The rate law in this case is

$$V = \frac{k_1k_2[\mathrm{Re}][\mathrm{CO_2}]}{k_{-1} + k_2[\mathrm{L}]}$$

When $k_{-1} \gg k_2$[L], a simple second-order equation obtains, $V = k_i$[Re][CO$_2$], and $k_i = k_1k_2/k_{-1}$ is predicted. Although an inverse isotope effect could arise for this mechanism, added PPh$_3$ had no effect on the kinetics[8] and the mechanism is inconsistent with the observed substituent effect in that electron-donating groups should stabilize the carbonyl precursor relative to the electron rich formyl intermediate. (b) An ionic mechanism was suggested by a reviewer:



$$\mathrm{Re{-}H} + \mathrm{CO_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Re^+}, \mathrm{HCO_2^-}] \xrightarrow{k_2} \mathrm{Re{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}$$

$$-\mathrm{d[Re]}/\mathrm{d}t = k_{eq}(k_2 + k_3[\mathrm{L}])[\mathrm{ReH}][\mathrm{CO_2}]$$

Although possible, the mechanism seems unlikely since we would have expected to have observed *fac*-Re(bpy)(CO)$_3$(CH$_3$CN)$^+$ or, in the presence of added PPh$_3$, *fac*-Re(bpy)(CO)$_3$(PPh$_3$)$^+$ as products. Both cations are known are stable under the conditions of the kinetic experiments.

(11) Böttcher, C. J. F. "Theory of Electric Polarization"; Elesevier: New York, 1952.

the hydride or alkyl ligand at the CO_2 carbon atom.[3,12-14] The few examples in which dissociative mechanisms appear are found for complexes with enhanced ligand lability or where the metal-ligand bond is cleaved photochemically prior to the insertion step.[15,16]

Acknowledgment. We wish to acknowledge the Gas Research Institute for generous funding.

Registry No. *fac*-Re(bpy)$(CO)_3H$, 94241-40-4; *fac*-Re(bpy)$(CO)_3C(O)H$, 100229-21-8; *fac*-Re(4,4′-Cl_2-2,2′-bpy)$(CO)_3H$, 100229-22-9; *fac*-Re(4,4′-Me_2-2,2′-bpy)$(CO)_3H$, 100229-23-0; *fac*-Re(4,4′-*t*-Bu_2-2,2′-bpy)$(CO)_3H$, 100229-24-1; *fac*-Re(4,4′-OMe_2-2,2′-bpy)$(CO)_3H$, 100229-25-2; D_2, 7782-39-0; CO_2, 124-38-9.

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The Electronic Structure of a Methylated Polysilane Chain: Trans H-$(SiMe_2)_5$-H

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Summary: CNDO/2(S + DES CI) computations on trans H-$(SiMe_2)_5$-H are shown to yield energies and transition intensities which parallel experiment. The nature of the levels contributing to excitation is discussed.

Electronically saturated aryl- and alkyl-substituted silane chains and their cyclic counterparts have been found to exhibit a wide range of properties generally associated with π-electron frameworks.[1] Of interest is elucidation of the nature of the strong and conformationally dependent electronic absorption observed in the near UV for longer chain systems.[2-5] Although several computational efforts have addressed silane chain ground-state conformational properties,[6] the nature of the lower lying excited states is not well understood.

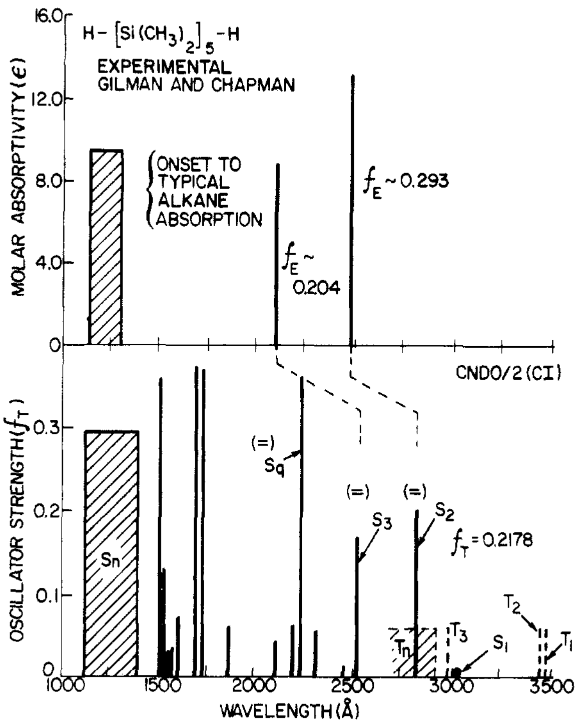

Figure 1. Comparison of the experimental[9] and calculated silane chain absorption spectrum. The experimental oscillator strengths were estimated from the molar absorptivities[9] in accord with the approximately of H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules* (Academic: New York 1967), p 9, assuming $(\Delta\bar{\nu})_{1/2} = 5.0 \times 10^3$ cm^{-1}. Polarizations relative to the long chain axis are given in parenthesis. T_n denontes a dense manifold of triplets at $\sim S_2$, suggesting efficient intersystem crossing. For comparison to typical alkane absorption, see Robin.[5c]

This communication reports the results of semiempirical CNDO/2(S + DES Cl) computations[7] on the ground and selected singlet and triplet excited-state properties of trans H-$(SiMe_2)_5$-H using an Si 3s, 3p, C 2s, 2p + H1s minimal basis set.[8] Si-Si bond stabilization due to methyl substitution is discussed and attributed in part to ionic bonding enhancements.

Figure 1 compares the computational results with the optical absorptions.[9] Although S_2 and S_3 are considerably below the observed transition energies, their separation and relative oscillator strengths reflect the experimental splitting and intensity pattern. Furthermore, the calculated intense transition ~0.6 eV above S_3 (S_9 in Figure 1) is in accord with expectations based on the spectra of closely related system.[1b,5c] The lower lying Cl wave functions have dominant singly excited components in-

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[8] The molecular geometry was approximated (C_{2v}) using Si-Si and Si-H bond lengths of 2.280 and 1.430 Å, respectively, with slightly distorted tetrahedral Si-Si-Si bond angles of 120°—see (a)-(c) below for *optimized* Si-Si-Si bond angles near 120°; Si-C and C-H bond lenghs of 1.850 and 1.119 Å, respectively, with C-Si-C and Si-Si-C bond angles of 120° and standard tetrahedron bond angles for the methyl groups. (a) Dewar, M. J. S.; Lo, D. H.; Ramdsen, C. A. *J. Am. Chem. Soc.* **1975**, *97* 1311-1318. (b) Teramae, H,; Yamabe, T.; Imamura, A., Theoret. Chim. Acta **1983**, *64*, 1-12. (c) Takeda, K.; Matsumoto, N.; Fukuchi, M., *Phys. Rev. B: Condens. Matter* **1984**, 30, 5871-5876.

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