thereby ruling out the possibility of a HP analogue being the endproduct. Furthermore, HP under several denaturing circumstances did not show an ESR spectrum similar to those of 3-Fe proteins. This strongly indicates that the new compound described in this work is indeed a 3-Fe cluster. It also implies that ESR spectra of iron–sulfur clusters are not easily changed by the surroundings as is often assumed. We therefore believe that the first ESR spectrum reported for a synthetic 3-Fe cluster was the one published by Cammack et al.,[51] whereas the spectra shown by Christou et al.[52] most probably were neither those of a HP nor those of a 3-Fe cluster.

The kinetics justify the expectation that even higher conversions of 4-Fe to 3-Fe could be attained. Alternatively the 3-Fe cluster might be produced from a HP analogue in a controlled-degradation reaction. Isolation and elucidation of the structure then come within reach.

Acknowledgment. We gratefully acknowledge the cooperation of Drs. K. K. Rao and M. K. Johnson and thank Drs. P. H. M. Budzelaar and E. Münck for helpful discussions. This study was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO) and by National Science Foundation Grant No. NSF/DMB8306964.

Registry No. $(NMe_4)_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$, 52678-92-9; $K_3[Fe(CN)_6]$, 13746-66-2; $(NBu_4)_2[Fe_4S_4(SPh)_4]$, 52586-83-1.

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(51) Cammack, R.; Christou, G. *Hydrogenases: Their Catalytic Activity, Structure, and Function*; Schlegel, H. G., Schneider, K., Eds.; Erich Goltze: Göttingen, BRD, 1978; pp 45–56.

(52) Christou, G.; Garner, C. D.; Drew, M. G. B.; Cammack, R. *J. Chem. Soc., Dalton Trans.* **1981**, 1550.

Notes

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Studies on the Alkylation of Vitamin B_{12s} and Related Systems Revisited: Novel Features of Oxidative-Addition Reactions

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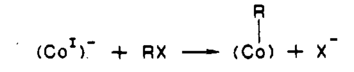
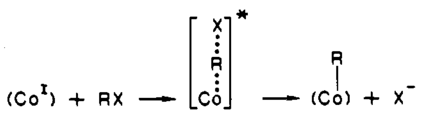
Vitamin B_{12} is a Co(III) complex of the corrin moiety. It is the only vitamin known to contain a metal center. Its chemistry[1,2] is so fascinating and challenging that there seems to be unabated constant interest in this vitamin and its derivatives to workers of various disciplines of chemistry since its isolation in 1948 (for a comprehensive study, see ref 1; a few selected aspects are covered in ref 2). This vitamin can exist in three different oxidation states—the Co(I) variety is known as B_{12s}. Alkylation of vitamin B_{12s} (schematically represented by reaction 1) gives rise to a



$$(Co^{I})^{-} + RX \longrightarrow \underset{\textbf{1}}{(\overset{R}{\overset{|}{Co}})} + X^{-} \qquad (1)$$

Co(III) species with a metal–carbon bond through an oxidative reaction mechanism.[3a] It may be mentioned in this connection that coenzyme B_{12}, which has such a metal–carbon bond, and methylcobalamin (R = CH_3 in **1** of eq 1), which is a substrate in the methionine biosynthesis are nature's only organometallic compounds known to date.[3a]

Extensive studies carried out by Schrauzer and co-workers[4] led to the earlier conclusion that reaction 1, which is reversible,[5] proceeds through an S_N2 mechanism (eq 2). Later observation of inversion of configuration at the reacting carbon center by Jensen et al.[6] supported this view. However, they seemed to have missed the electron-transfer component of such reactions, and "attempts to demonstrate the expected inversion of configuraion at carbon resulting from these oxidative additions led to"[7] such erroneous conclusions.[7-9] Herein we reanalyze the data of Schrauzer and co-workers[4] to obtain certain interesting features of the alkylation reaction and the oxidative additions, in general.



$$(Co^{I}) + RX \longrightarrow \left[\begin{matrix} X \\ \vdots \\ R \\ \vdots \\ Co \end{matrix}\right]^{*} \longrightarrow (\overset{R}{\overset{|}{Co}}) + X^{-} \qquad (2)$$

Table I. Variation of the Rate Constants of the Alkylation of Tributylphosphine–Cobaloxime$_s$ with Alkyl Halides (RX)[a]

R group	$\sigma^{*\,b}$	log *k*		
		Cl	Br	I
$-CH_3$ (**1**)	0.000	−0.070	2.340	3.360
$-C_2H_5$ (**2**)	−0.100	−2.046	0.204	
$-CH_2CH_2CH_3$ (**3**)	−0.115	−2.201	0.174	
$-CH(CH_3)_2$ (**4**)	−0.190	−3.495	−0.959	0.505
$-CH_2CH_2CH_2CH_3$ (**5**)	−0.130	−2.137		
$-CH(CH_3)CH_2CH_3$ (**6**)	−0.210			−0.086
$-CH_2CH(CH_3)_2$ (**7**)	−0.125	−3.110	−0.553	0.924
$-CH(CH_3)CH{=}CH_2$ (**8**)		0.778		
$-CH_2C_6H_5$ (**9**)	0.215	2.640	4.280	
$-CH(CH_3)C_6H_5$ (**10**)	0.110	0.360		
$-CH(C_6H_5)_2$ (**11**)	0.405	0.000		
$-CH_2CN$ (**12**)	1.300	3.204		
$-CH_2CONH_2$ (**13**)	0.600	1.146		

[a] Meanings of the symbols used are same as in the text. Rate data are taken from ref 4. [b] In case of $-CH_2CONH_2$ σ^* has been calculated from the σ_I data (0.27) given in Table 16 of: Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119. The formula $\sigma_I(X) = 0.45\sigma^*$ $(-CH_2X)$ of Taft (Taft, R. W.; Lewis, I. C. *J. Am. Chem. Soc.* **1958**, *80*, 2436) was used. Others are taken from ref 13.

[†] An FIP fellow.

(1) Dolphin, D., Ed. *B_{12}*; Wiley-Interscience: New York, 1982; Vol. 1 and 2.

(2) Stevens, R. V.; Chang, J. H.; Lapalme, R.; Schow, S.; Schlageter, M. G.; Shapiro, R.; Weller, H. N. *J. Am. Chem. Soc.* **1983**, *105*, 7719. Scheffold, R.; Orlinski, R. *J. Am. Chem. Soc.* **1983**, *105*, 7200. Jorim, E.; Schweiger, A.; Gunthard, Hs. H. *J. Am. Chem. Soc.* **1983**, *105*, 4277. Balasubramanian, P. S.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 824. Halpern, J.; Kim, S. H.; Leung, T. W. *J. Am. Chem. Soc.* **1984**, *106*, 8317. Parker, W. O., Jr.; Bresciani-Pahor, N.; Zangrando, E.; Randacio, L.; Marzilli, L. G. *Inorg. Chem.* **1985**, *24*, 3908. Christianson, D. W.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1985**, *107*, 2682. Halpern, J. *Science* (Washington, D.C.) **1985**, *227*, 869. Baldwin, D. A.; Betterton, E. A.; Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1985**, 1613.

(3) (a) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983; pp 878–880. (b) *Ibid.* pp 137–160.

(4) Schrauzer, G. N.; Deutsch, E.; Windgassen, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 2441. Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341.

(5) Stadlbauer, E. A.; Holland, R. J.; Lamm, F. P.; Schrauzer, G. N. *Bioinorg. Chem.* **1974**, *4*, 67.

(6) Jensen, F. R.; Madan, V.; Buchanan, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 1414.

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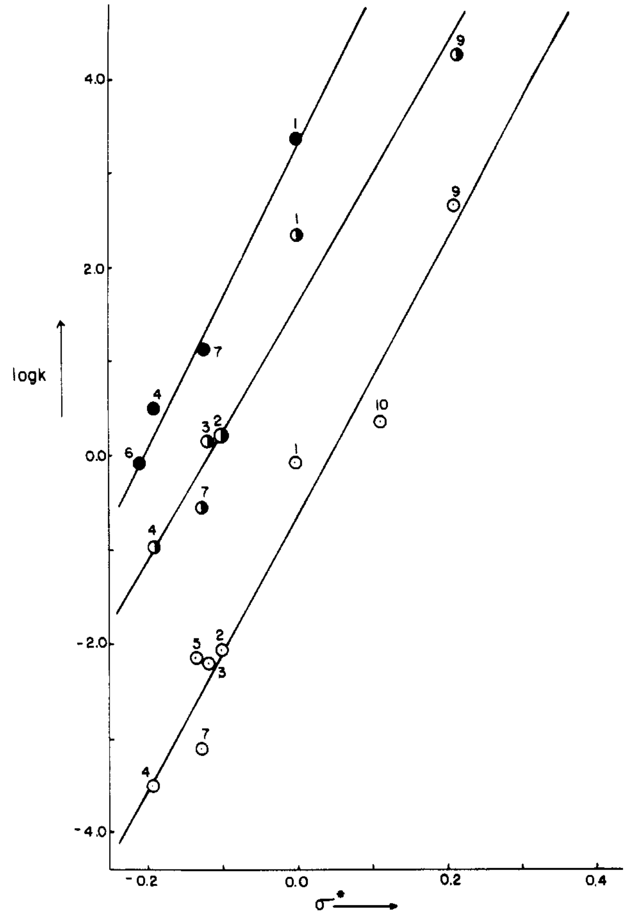

Figure 1. Plot of σ^* vs. log k for tributylphosphine–cobaloxime$_s$ with various RX: (○) X = Cl; (◑) X = Br; (●) X = I. The identification numbers are explained in Table I.

On inspection of the rate data[4] (Table I) for the alkylation of tributylphosphine–cobaloxime$_s$,[10] a considerably good model of vitamin B_{12s}, it is revealed that the rate systematically increases with the increase in electron-withdrawing power of the alkyl chain. Consequently a relation is sought between log k and σ^*, Taft's polar substituent constants. The results are encouraging. Satisfactorily linear correlations are obtained separately for chloride, bromide, and iodide (Figure 1). What is really interesting is that the slopes in the three cases are very close to each other (Cl, 14.51; Br, 13.56; I, 15.76). Since σ^* serves as an index of the inductive effect exerted by an alkyl group,[11-14] we find that the transition state is lowered with the decrease in the electron-releasing character of a group—a result in consonance with the general notion of oxidative-addition reactions.[7,9] The general rate behavior thus can be represented by eq 3. In eq 3 the slope ρ, as will be

$$\log k = \log k_0 + \rho\sigma^* \qquad (3)$$

seen in a later section, characterizes the nucleophile, and k_0 refers to the situation where σ^* is zero.

Table II. Variation of the Rate Constants of the Alkylation of Tributylphosphine–Cobaloxime$_s$ with Charge on Chlorine in Alkyl Chlorides (RCl)[a]

R group[b]	a	$2b$[c]	δ_{Cl}	log k
1	7.37	3.24	−0.138	−0.071
2	7.40	1.85	−0.150	−2.046
3	7.41	1.30	−0.156	−2.201
4	7.41	1.30	−0.156	−3.495
5	7.41	1.00	−0.160	−2.137
7	7.41	1.00	−0.160	−3.113
8	7.60[d]	1.19[d]	−0.142	0.778
9	7.40	4.31	−0.122	2.643
10	7.82	0.77	−0.129	0.362
11	7.99	0.55	−0.117	0.000
12	9.16[d]	2.75[d]	−0.016	3.204
13	8.71[d]	1.19[d]	−0.054	1.146

[a] Meanings of the symbols are the same as in the text. Rate data are taken from ref 4. [b] The boldfaced numerals represent the groups as shown in Table I. [c] What is "b" in Huheey's work is "$2b$" here because of the factor of 2 incorporated in the denominator of the definition of hardness (see ref 17). The values are taken from ref 15 unless otherwise mentioned. [d] This work; calculated by Huheey's method.[15]

Table III. Variation of log k_0 with Halides for Tributylphosphine–Cobaloxime$_s$ and Vitamin B_{12s}

		log k_0[b]	
leaving group	hardness[a]	tributylphosphine–cobaloxime$_s$	vitamin B_{12s}
Cl	4.70	−0.651	0.701
Br	4.24	1.626	3.032
I	3.70	3.244	4.531[c]

[a] The data are taken from ref 20. [b] Obtained from Figures 1 and 4 unless otherwise mentioned. [c] Experimental log k obtained for CH_3I.

Table IV. Variation of the Rate Constants of the Alkylation of Vitamin B_{12s} with Halides (RX)[a]

		log k		
R group[b]	σ^*[c]	Cl	Br	I
1	0.000	0.699	3.204	4.531
2	−0.100	−1.328	1.491	
3	−0.115	−1.432	1.146	
4	−0.190		0.255	2.362
5	−0.130	−1.553		
7	−0.125	−2.387	0.322	

[a] Meanings of the symbols are same as in the text. Rate data are taken from ref 4. [b] The boldfaced numerals represent the alkyl groups as shown in Table I. [c] Values are taken from ref 13.

To have a look at the above correlation from the halogen side, we have calculated the group charge on R and the charge on chlorine (δ_{Cl}) in various alkyl chlorides employed for the study.[4] The charge calculations (Table II) are done by Huheey's method,[15] which has been shown recently by Jardine et al.[16] to produce results comparable to those of ab initio calculations in many cases. Though the method faces problem regarding the isomeric groups,[17-22] it seems to serve our purpose quite well.[23] A rather

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(7) For a brief review on this aspect, see: Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 310. This paper deals with similar alkylation reactions of a four-coordinate isoelectronic Rh(I) macrocyclic complex.

(8) Two related works are: (a) Eberson, L. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 533. (b) Lund, T.; Lund, H. *Tetrahedron Lett.* **1986**, *27*, 95.

(9) For an introduction to "oxidative additions" in general, see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; 4th ed.; Wiley-Interscience: New York, 1980; pp 1237–1243.

(10) It is a bis(dimethylglyoximato) complex of Co(I) with one of the axial positions occupied by tributylphosphine.

(11) There has been considerable debate on the actual nature of σ^*. There are workers who plead for abandoning it. However, it has been felt that it actually expresses the electronic effect with some component of the steric effect also.[12] We choose to stick to what has been stated in the text because of the following three reaons—(i) Huheey has obtained[13] an excellent linear correlation of group charge on R in RCOOEt with σ^*, (ii) it is a fact that Taft's σ_I scale is based on σ^* through the equation $\sigma_I(X) = 0.45\ \sigma^*(CH_2X)$, and (iii) Levitt and Widing have shown[14] correspondence between Taft's σ_I parameter and a structural parameter "s" characterizing the effect of R on gas-phase ionization potentials of 25 series of alkyl compounds RX.

(12) Shorter, J. *Correlation Analysis of Organic Reactivity*; Chemometric Research Studies Series. 4; Research Studies: Chicester, 1982.

(13) Huheey, J. E. *J. Org. Chem.* **1966**, *31*, 2365.

(14) Levitt, L. S.; Widing, H. F. *Prog. Phys. Org. Chem.* **1976**, *12*, 119.

(15) Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284; **1966**, *70*, 2086.

(16) Jardine, W. K.; Langler, R. F.; MacGregor, J. A. *Can. J. Chem.* **1982**, *60*, 2069.

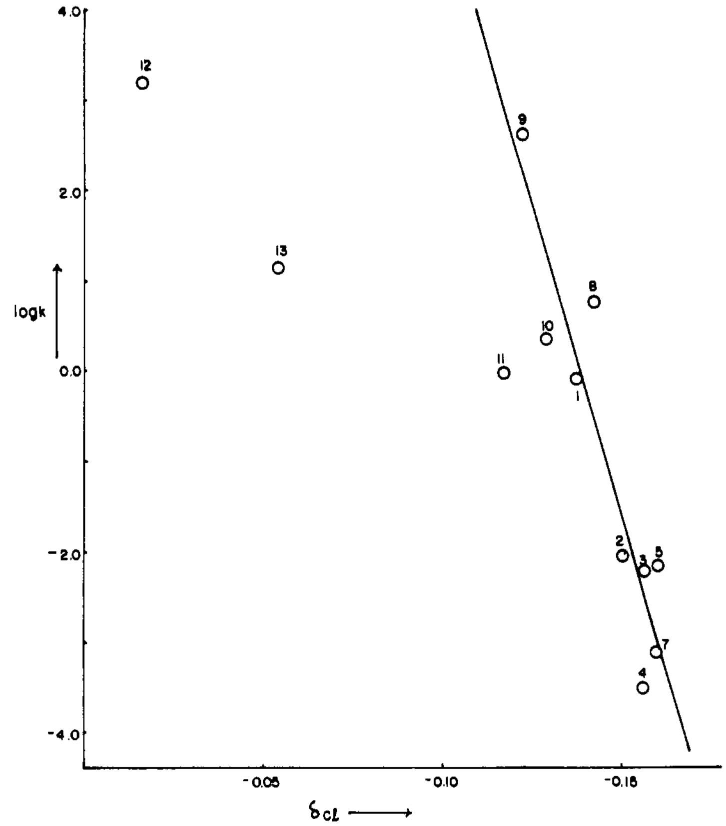

Figure 2. Variation of log k with δ_{Cl} in various RCl for tributylphosphine–cobaloxime$_s$. The identification numbers are illustrated in Table I. The points corresponding to **11**, **12**, and **13** are not used for the least-squares fitting.

peculiar result emerges (Figure 2). We observe that smaller the amount of negative charge on the halogen, the easier its depature as chloride anion. This would mean that presence of electron-withdrawing groups like $-CN$ and $-CONH_2$ at the α-carbon should make the reaction very fast in the case of the model B_{12s} complex. But, in reality, we find that the reactions are retarded. Since these are polar groups, solvation of the transition state would be better in the polar medium used for the study (0.1 M NaOH in methanol).[3] The point is the effect should have been reversed.[24] Though the reason(s) for such retardation is (are) not clear at present, we might suspect some kind of ambivalence of the electronic factor—the factor that increases the rate of the reaction is also acting against it. Another possibility is that a prior coordination, e.g., Co–NC~, may give rise to a wrong geometry for the reaction.[25] Nevertheless, we can summarize our observations by saying while weakly withdrawing groups (like $-C_6H_5$, or, $-CH{=}CH_2$ etc.) increase the rate of the reaction, presence of a strong electron-withdrawing group decreases the rate.

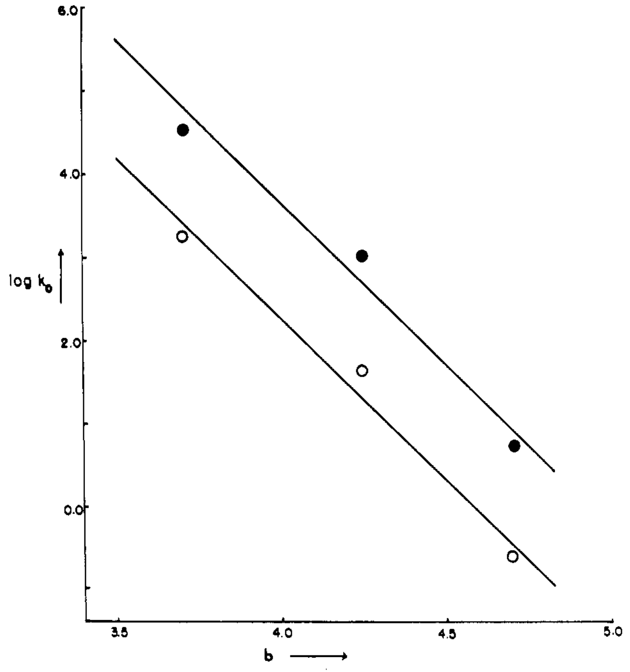

Figure 3. Plot of log k_0 vs. b (hardness) of X: (○) tributylphosphine–cobaloxime$_s$; (●) vitamin B_{12s}.

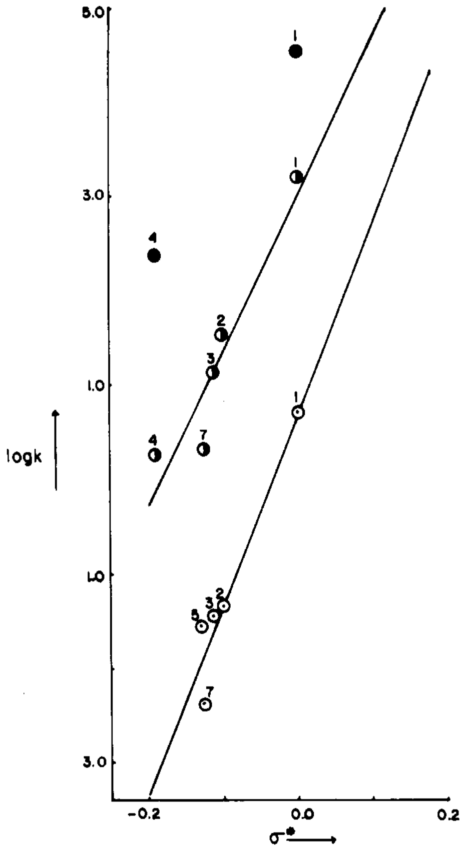

Figure 4. Plot of log k vs. σ for vitamin B_{12s} with various RX: (○) X = Cl; (◑) X = Br; (●) X = I. For group identification, see Table I.

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(17) Actually, the method fails to distinguish between the isomeric groups. To overcome this problem, Huheey has suggested 80% equalization of electronegativity.[15] The percentage is definitely ad hoc. Moreover, that equalization of electronegativities of atoms is achieved throughout a molecule is now well established.[18,19] However, since the method developed by Huheey based on electronegativity equalization[15] is tested by Jardine et al.,[16] we have adopted it for our purpose. In this method, δ_R, charge on the group R in RX is given by $\delta_R = (a_X - a_R)/2(b_X + b_R)$ where "a" is the valence state electronegativity of the neutral group or atom ($a = (I' + A')/2$), "b" is the valence-state hardness of the group or atom ($b = (I' - A')/2$),[20,21] and I' and A' are valence-state ionization potential and electron affinity (note that the conventional definitions[20,21] have been extended to valence state). This formulation uses the notion that the electronegativity χ of a group or an atom in the valence state can be expressed as a function of its charge δ by the equation[3b,21] $\chi = a + 2b\delta$. It should be mentioned here that this equation is an approximation.[22]

(18) Sanderson, R. T. *Polar Covalence*; Academic: New York, 1983.

(19) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.

(20) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(21) Gazquez, J. L.; Ortiz, E. *J. Chem. Phys.* **1984**, *81*, 2741.

(22) Nalewajski, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 944.

(23) The trends observed in Figures 1 and 2 are parallel.

(24) The steric effects encountered in $NCCH_2X$ and NH_2COCH_2X in the trigonal-bipyramidal transition state can be at most comparable to those in ethyl and n-propyl halides, respectively. Since the data obtained in ethyl and n-propyl chlorides are quite in order (Figures 1 and 2), the large negative deviations observed in these two cases cannot be the simple consequence of steric effects.

(25) We are grateful to one of the reviewers for pointing out this possibility.

For a particular RX, the rates uniformly follow the order Cl < Br < I. We have attempted to rationalize it in Figure 3 where the experimental hardnesses of Cl, Br, and I (Table III) are plotted against the respective values of log k_0. Though it has been pointed out very recently that in the neutral ground-state electronegativity of an atom is proportional to its hardness,[26] we have chosen to use the hardness parameter to obtain an understandable physical picture: the less hard or more polarizable a group is, the lower the activation energy or the better the leaving group ability.

Similar trends are observed for vitamin B_{12s} also (Tables III and IV; Figures 3 and 4). The ρ values obtained from Figure 4 for Cl and Br are comparable −20.22 and 16.49 respectively. In Figure 3 the slopes of the lines in the two cases are almost same (3.83 ± 0.04). These results only corroborate the earlier notion[4] that the kinetics of alkylation of the model complex and the vitamin B_{12s} are similar in a semiquantitative manner. We find the ρ_{av} value obtained from Figure 1 (14.61) is slightly less than that obtained in Figure 4 (18.35). This may be correlated with the difference in the nucleophilicities of the two systems[4]—vitamin B_{12s} being a stronger nucleophile than the model system.[27]

In conclusion, we feel that the various features revealed here should be the general features of any oxidative-addition reaction. However, detailed theoretical calculations on model oxidative-addition reactions can help explore the real meaning of the present correlations.

Acknowledgment. The authors are indebted to Prof. J. Halpern for helpful advice regarding the manuscript. Thanks are also due to Prof. A. Chakravorty of IACS, Calcutta 700 032, India, for his kind interest. We thank reviewers for their constructive criticisms—especially the one who pointed out ref 7, 8, and 25.

Note Added in Proof. The values of *a* and *b* (Table II, Table III, and Figure 3) are in electronvolts.

Registry No. Vitamin B_{12s}, 18534-66-2; tributylphosphine–cobaloxime$_s$, 18475-26-8.

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(26) Nalewajski, R. F. *J. Phys. Chem.* **1985**, *89*, 2831. Yang, W.; Lee, C.; Ghosh, S. K. *J. Phys. Chem.* **1985**, *89*, 5412. Datta, D. *J. Phys. Chem.* **1986**, *90*, 4216.

(27) It should be mentioned in this context that the nucleophilicity of cobaloxime$_s$ depends[4] on its axial base, which is tributylphosphine in the chosen model system.[10]

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Electrochemical Study of Thermodynamics and Kinetics of the Cis–Trans Isomerization of Dicarbonylbis[1,2-bis(diphenylphosphino)ethane]molybdenum and -tungsten Complexes and Their Cations

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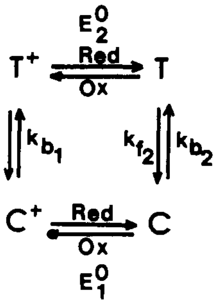
Received February 18, 1986

Certain organometallic complexes can exist in two different forms, either because of a configurational change (e.g. cis–trans or *fac-mer* isomerization) or because of a ligand exchange. When the oxidation state of the metal can vary, the situation can be described[1-6] by using the square scheme first proposed by Jacq[7] or variants thereof.[6] An example relative to a cis–trans isomerization and definition of the equilibrium constants are given in Figure 1.



$$K_1 = ([C^+]/[T^+])_{equil} = k_{f1}/k_{b1}$$

$$K_2 = ([C]/[T])_{equil} = k_{f2}/k_{b2}$$

Figure 1. The square scheme with definition of equilibrium constants. E°_1 and E°_2 are the standard potentials, E°_1 being more positive than E°_2.

A general theory of the square scheme has been developed by Jacq[7] in the case of the potentiostatic stationary method on a rotating disk electrode, but it is too complex to be used practically. When the electrochemical reactions can be considered at equilibrium, which is generally the case for organometallic compounds, the situation becomes simpler, but even then the mathematical resolution of the problem remains difficult. A partial solution was given by Bond and Oldham[8] for the potentiostatic method on an immobile planar electrode, and simulations have been made by Evans,[9] but these methods do not allow a complete analysis of the results to be carried out. The equilibrium constants can be determined only when the equilibria do not lie too far in one direction, e.g. by using spectroscopic[6b] or voltammetric[2h] methods. The analysis of the square scheme is thus often restricted to the measurement of the rate constants k_{f2} and k_{f1}.

In a recent publication,[10] we have shown that the system can be completely analyzed; i.e., the equilibrium and rate constants can be determined by using electrochemical methods. When the ratio of the rate constants of the chemical reactions to the sweep

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(1) (a) Rieke, R. D.; Kojima, H.; Ofele, D. *J. Am. Chem. Soc.* **1976**, *98*, 6735. (b) Pilloni, G.; Zotti, G.; Corvaja, C.; Martelli, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *91*, 385. (c) Rader, R. A.; McMillin, D. R. *Inorg. Chem.* **1979**, *18*, 546. (d) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 3407.

(2) (a) Bond, A. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *50*, 285. (b) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 274. (c) Bond, A. M.; Cotton, R.; McCormick, M. J. *Inorg. Chem.* **1977**, *16*, 155. (d) Bond, A. M.; Grabaric, B. S.; Grabaric, Z. *Inorg. Chem.* **1978**, *17*, 103. (e) Bond, A. M.; Darensbourg, D. J.; Mocellin, E.; Stewart, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 6827. (f) Bond, A. M.; Carr, S. W.; Colton, R. *Inorg. Chem.* **1984**, *23*, 2343. (g) Bond, A. M.; Carr, S. W.; Colton, R. *Organometallics* **1984**, *3*, 541. (h) Bond, A. M.; Colton, R.; Kevekordes, J. E. *Inorg. Chem.* **1986**, *25*, 749.

(3) Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617.

(4) Bond, A. M.; Grabaric, B. S.; Jackowski, J. J. *Inorg. Chem.* **1978**, *17*, 2153.

(5) (a) Mugnier, Y.; Moïse, C.; Laviron, E. *J. Organomet. Chem.* **1981**, *204*, 61; *Nouv. J. Chim.* **1982**, *6*, 197. (b) Fakhr, A.; Mugnier, Y.; Broussier, R.; Gautheron, B.; Laviron, E. *J. Organomet. Chem.* **1983**, *255*, C8.

(6) (a) Faure, D.; Lexa, D.; Savéant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *140*, 269, 285, 297. (b) Lexa, D.; Reutien, P.; Savéant, J. M.; Xu, F. *J. Electroanal. Chem.* **1985**, *191*, 253. (c) Lexa, D.; Savéant, J. M. *Acc. Chem. Res.* **1983**, *16*, 235. (d) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323.

(7) Jacq, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *29*, 149.

(8) Bond, A. M.; Oldham, K. B. *J. Phys. Chem.* **1983**, *87*, 2492.

(9) (a) Olsen, B. A.; Evans, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 839. (b) Neta, P.; Evans, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 7041. (c) Evans, D. H.; Busch, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 5057. (d) Olsen, B. A.; Evans, D. H. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *136*, 139. (e) Evans, D. H.; Xie, N. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *133*, 367; *J. Am. Chem. Soc.* **1983**, *105*, 315. (f) Matsue, T.; Evans, D. H.; Agranat, I. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *163*, 137.

(10) Laviron, E.; Roullier, L. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *186*, 1.

0020-1669/87/1326-0332$01.50/0