Inorg. Chem. **1986**, *25*, 3048–3053

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Effects of Alcohols on Kinetics of Substitution at *cis*-Bis(pyridine)tetracarbonylmolybdenum(0)

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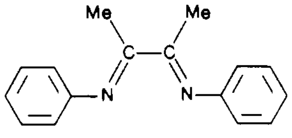
Received August 26, 1985

Kinetics of reactions between *cis*-bis(pyridine)tetracarbonylmolybdenum(0) and the diimine ligands 1,10-phenanthroline, 2,2′-bipyridyl, and 1,4-diphenyl-2,3-dimethyl-1,4-diazabutadiene are reported for solvent media toluene + 1-butanol, hexane + 2-propanol, and two microemulsions. The results in the hydrocarbon + alcohol media are discussed in terms of a three-stage mechanism involving mono- and disolvento intermediates. The use of microemulsion media for these reactions involving hydrophobic nonelectrolytes leads to only small effects on reactivity. The immediate environment of $Mo(CO)_4$(diimine) complexes in microemulsions can be probed via their strongly solvatochromic MLCT spectra.

The kinetics of reaction between *cis*-bis(pyridine)tetracarbonylmolybdenum(0) and bidentate diimine ligands LL, where LL = 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen), or the Schiff base **1** (dab), have been investigated in toluene and in 1,2-dichloroethane.[1]

$$\mathrm{Mo(CO)_4(py)_2 + LL \rightarrow Mo(CO)_4(LL) + 2py} \qquad (1)$$

Rate laws, activation parameters, and mass law retardation effects indicate the operation of a limiting dissociative (D) mechanism. In all cases the appearance of the $Mo(CO)_4(LL)$ product follows a single exponential function, corresponding to the replacement of the first pyridine ligand by one end of the incoming ligand. Subsequent chelate ring closure and concomitant loss of the second pyridine are fast.



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Over the last half-century much interest has been shown in the effects of solvent media on reactivity for a large number of organic and inorganic reactions. In most cases solvents investigated have been simply water and single nonaqueous solvents or binary mixtures, but recently a number of investigations have been concerned with more complicated media such as micellar systems and microemulsions.[2] The microheterogeneity of the latter sometimes leads to dramatic effects.[3] Thus, these tetracarbonylmolybdenum(0) derivatives can be dissolved to a remarkable extent in microemulsions containing a mole fraction of water exceeding 0.9! There can also be dramatic effects on reactivity, especially when the reaction in question involves a hydrophilic and a hydrophobic reactant. Thus, rate constants for attack of hydroxide at such organic species as methylene violet and malachite green[4] or at the hydrophobic inorganic cation $Fe(hxsb)^{2+}$, where hxsb = the hexadentate Schiff base **2**,[3] are very much greater in oil–water microemulsions than in water or in water-rich binary solvent mixtures. We wished to compare the $Fe(hxsb)^{2+}$–hydroxide reaction with an inorganic reaction involving two hydrophobic species and chose to study the molybdenum(0) substitution described in the first paragraph above. We found that microemulsion media affected not only reactivities, but also the rate law for reactions of the type shown in eq 1. Whereas in toluene reaction 1 is simply first-order,[1] in microemulsions such reactions usually have to be described by more than one exponential function. We subsequently found that such kinetic complexity was also characteristic of this type of reaction in simpler mixed-solvent media such as toluene + 1-butanol and hexane + 2-propanol.

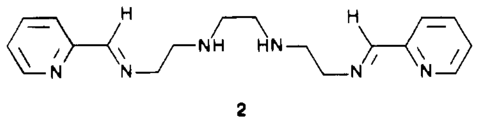

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Table I. Compositions of the Microemulsions Used in This Investigation

microemulsion I			microemulsion II		
components	wt %	mole fraction	components	wt %	mole fraction
water	4.2	0.15	water	56.5	0.91
2-propanol	42.1	0.45	1-butanol	17.4	0.068
1-hexane	53.7	0.40	toluene	4.3	0.014
			SDS[a]	8.7	0.009

[a] Sodium dodecyl sulfate.

In this paper we present our results on the kinetics of reactions of the type shown in eq 1 in mixed solvents toluene + 1-butanol and hexane + 2-propanol and in two closely related oil–alcohol–water microemulsions. We also report kinetic and equilibrium observations on solutions of $Mo(CO)_4(py)_2$ in binary solvent mixtures containing 2-propanol or 1-butanol. We suggest an appropriate mechanism that can explain the effects of the alcohols and discuss observed reactivity trends.

Experimental Section

$Mo(CO)_4(py)_2$ and diimine ligand **1** were prepared and purified as described earlier.[1] 2,2′-Bipyridyl, 1,10-phenanthroline hydrate, hexane, toluene, 2-propanol, and 1-butanol were AnalaR materials. The microemulsions were prepared by direct mixing of the components; their compositions are set out in Table I. Compositions of binary solvent mixtures are given throughout this paper in volume percentages, representing volumes before mixing.

Kinetic runs were carried out with the apparatus described earlier,[1] in the thermostated cell compartment of a Unicam SP800 recording spectrophotometer (for preliminary repeat-scan runs in microemulsions) or in a Unicam SP1800 under computer control as described elsewhere.[3] Solvents were purged of oxygen by use of argon or of nitrogen; solutions of $Mo(CO)_4(py)_2$ were made up under argon or nitrogen. Runs were thus carried out in oxygen-free conditions, to avoid competing solvolytic oxidation, which can be significant in media containing alcohol and dissolved oxygen. Kinetics were monitored at the wavelength of maximum absorption in the visible region for the $Mo(CO)_4(LL)$ product (for LL = bpy at 490 nm; for LL = phen at 490 nm; for LL = **1** at 550 nm).[5]

[†] Technische Hochschule Darmstadt.
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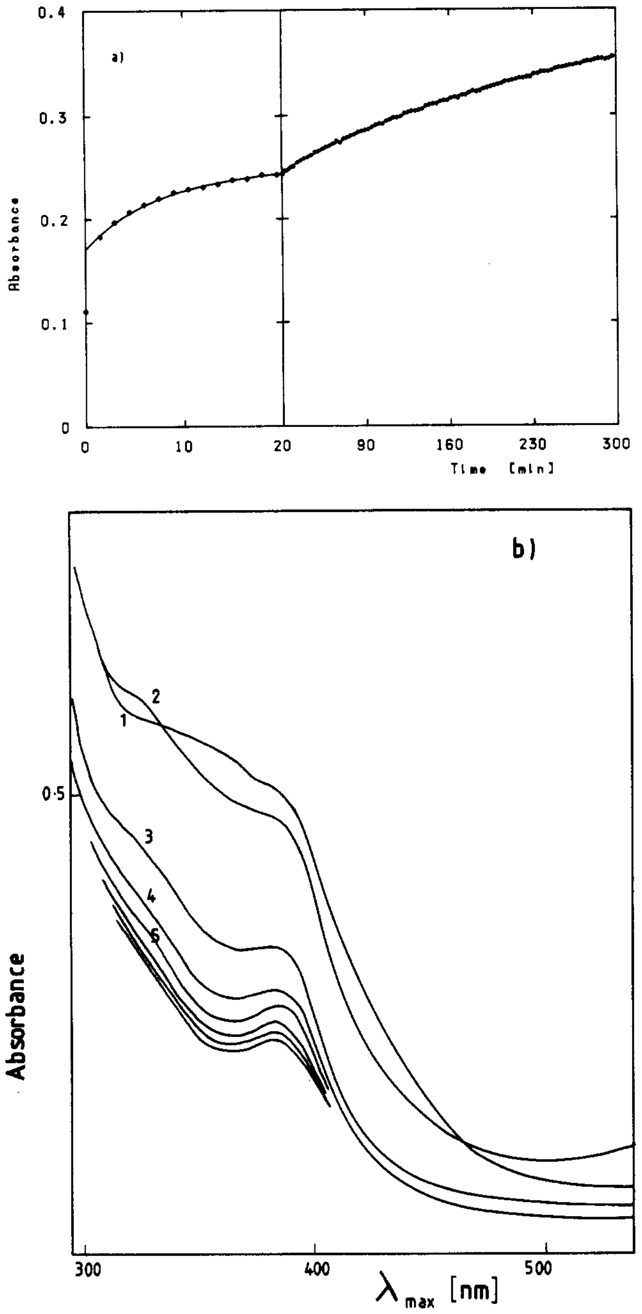

Figure 1. (a) Plot of absorbance against time for *cis*-$Mo(CO)_4(py)_2$ reacting with phen in 0.1% 1-butanol/99.9% toluene. (b) Repeat-scan spectra, numbered sequentially, for *cis*-$Mo(CO)_4(py)_2$ undergoing solvolysis in 50% 1-butanol/50% toluene.

Monitoring at the wavelength of maximum absorption of the starting material is precluded by high absorption by the incoming ligand in this region. Solvatochromic studies were carried out on the SP800 instrument, with its wavelength calibration checked against a standard didymium glass filter.

Kinetic Analysis

Some runs obeyed simple first-order kinetics over $2^1/_2$ half-lives or more. Rate constants for such runs were computed in the usual manner.[7]

Table II. Dependence of Derived Rate Constants $10^2k_1/s^{-1}$ in the $Mo(CO)_4(py)_2$ + phen Reaction on Ligand Concentration and Solvent Composition[a] in 1-BuOH + Toluene Mixtures

solvent[b]		10^3[phen]/M					
% 1-BuOH	% toluene	0.5	1.0	1.25	2.5	5.0	10.0
100		0.28	0.53	0.64	1.4	2.3	*c*
90	10	0.36	0.58	0.65	1.3	2.6	*c*
50	50	0.69	1.3		3.2	*c*	*c*
10	90	change in absorbance too small					
2	98						
0.1	99.9						
	100	no rapid initial reaction					

[a] At 298.2 K. [b] Volume percent before mixing. [c] Too fast.

However, the majority of runs deviated significantly or dramatically from a simple first-order pattern. Almost all such runs could be fitted by a pair of exponential functions, though in some runs the first step was so rapid that it could not be monitored. In one case (reaction in 0.1% 1-butanol in toluene) reaction 1 proceeded in three kinetically distinct steps, an initial very fast absorbance jump followed by two exponential processes. Figure 1a illustrates results obtained in 0.1% 1-butanol in toluene, clearly showing these three stages. Figure 1b shows successive spectra for *cis*-$Mo(CO)_4(py)_2$ dissolved in 50% 1-butanol in toluene, indicating the two kinetic stages for reaction of this compound in alcohol-containing mixed solvents even in the absence of added phen, bpy, or dab.

Whenever possible, time constants for the two-exponential kinetic runs were computed from the variation of absorbance (A) at the wavelength of maximum absorption of the $Mo(CO)_4(LL)$ product by using an expression of the form

$$A = a_1 \exp(-k_1t) + a_2 \exp(-k_2t) + A_\infty \qquad (2)$$

In a few cases the second stage was so slow that it was necessary to replace the second term by a term linear in t:

$$A = a_1 \exp(-k_1t) + mt + a_3 \qquad (3)$$

Fitting the absorbance–time data to eq 3 gives the faster rate constant, k_1 and the slope, m, from which the slower rate constant, k_2, is derived by $k_2 = m/(A_\infty - a_3)$. Due to the slight (and unavoidable) variation in the initial concentration of $Mo(CO)_4(py)_2$ between experiments, an average value of A_∞ had to be used to calculate k_2. In fact, such a situation is only one of several where it is not possible to compute two time (rate) constants with precision. One loses one of the two terms not only if the reaction stage in question is too fast or too slow, but also if the amplitudes (a_1 and a_2 in eq 2) are too disparate or if k_1 and k_2 are too similar.

Results

1-Butanol + Toluene. We discuss the kinetic results in this series of mixed solvents first, both since we have studied this system most fully and since there is the direct relation to earlier kinetic work in pure toluene. Under various conditions either one or two exponential functions were needed to fit the absorbance–time data (three exponentials for 0.1% 1-butanol; vide supra). We use subscripts 1, 2, and 3 to denote the three stages, with subscripts S, L, and D for solvent-assisted, ligand-assisted, and dissociative pathways. The dependences of derived first-order rate constants on incoming ligand concentration are detailed in Tables II–IV for k_1–k_3, respectively. These dependences are illustrated in Figure 2, which shows that the rate constants for the three stages may be represented by

$$k_1 = k_{1L}[\text{phen}]$$

$$k_2 = k_{2S} + k_{2L}[\text{phen}]$$

$$k_3 = k_D$$

with k_3 independent of concentration of added ligand. Values of

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(5) These wavelengths refer to toluene solutions. For λ_{max} (ν_{max}) in other solvents, see reports of the solvatochromic behavior of complexes of this type in ref 6.

(6) Bock, H.; tom Dieck, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 520; *Chem. Ber.* **1967**, *100*, 228. Saito, H.; Fujita, J.; Saito, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 863. Tom Dieck, H.; Renk, I. W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 793. Renk, I. W.; tom Dieck, H. *Chem. Ber.* **1972**, *105*, 1403, 1419. Walther, D. *Z. Anorg. Allg. Chem.* **1973**, *396*, 46. Burgess, J. *J. Organomet. Chem.* **1969**, *19*, 218. Burgess, J.; Chambers, J. G.; Haines, R. I. *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 145.

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Scheme I

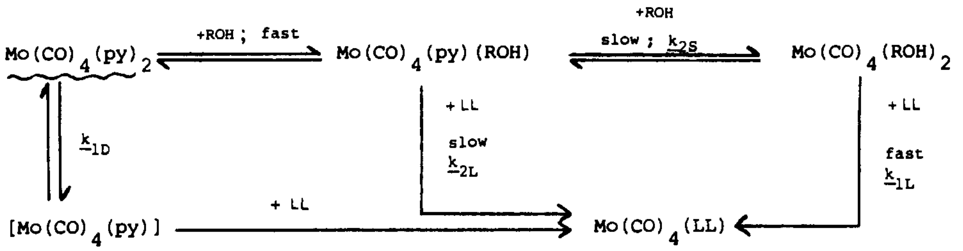

Table III. Dependence of Derived Rate Constants $10^4k_2/s^{-1}$ in the $Mo(CO)_4(py)_2$ + phen Reaction on Ligand Concentration and Solvent Composition[a]

solvent[b]		10^3[phen]/M								
% 1-BuOH	% toluene	0.5	1.0	1.25	2.0	2.5	5.0	10.0	13.0	14.0
100			9.3			11.2	13.5	18.1		
90	10	4.4	4.3	4.6		6.2	6.8		11.9	
50	50	4.2	4.4			4.4	5.0	5.2		
10	90		2.7		2.8	2.7	2.7	2.6		2.5
2	98	1.6	2.1			2.2	2.5	2.7		
0.1	99.9	0.26	0.30			0.34	0.38	0.65		

[a] At 298.2 K. [b] Volume percent before mixing.

Table IV. Dependence of Derived Rate Constants $10^4k_3/s^{-1}$ in the $Mo(CO)_4(py)_2$ + phen Reaction on Ligand Concentration[a]

solvent[b]			10^3[LL]/M						
% 1-BuOH	% toluene	LL[c]	0.5	1.0	1.5	2.0	2.5	5.0	10.0
0.1	99.9	phen	25	25			25	29	26
	100	phen		24	24	24		25	26
		bpy	23	24		24	25	25	
		dab	20			22	21	22	

[a] This pathway not observed when % 1-BuOH > 0.1. [b] Volume percent before mixing. [c] Incoming ligand.

k_{1L}, k_{2S}, k_{2L}, and k_D are collected together in Table V. This table also indicates under which conditions rate constants could not be calculated and under which conditions certain steps or pathways were not detected (cf. end of Kinetic Analysis section above).

It proved impossible to obtain an estimate for the first stage in the solvolysis of *cis*-$Mo(CO)_4(py)_2$ in 1-butanol in the absence of added diimine, as the compound dissolves with difficulty and much too slowly. However, repeat-scan spectra run immediately after mixing a saturated solution of *cis*-$Mo(CO)_4(py)_2$ in toluene with an equal volume of 1-butanol (cf. Figure 1b) indicate a rate constant of about 2×10^{-3} s^{-1} for loss of the first pyridine. The rate constant for the loss of the second pyridine under these conditions is smaller by a factor of approximately 5. Lack of an accurate value for the first step precludes an accurate estimate for the second step as they are similar enough in magnitude for them to be significantly coupled. Addition of pyridine after solvolysis had finished (split cell) resulted in reversal of the solvolysis.

2-Propanol + 1-Hexane. We have, in our more restricted investigation in these mixtures, not encountered any three-step processes. Nonetheless, we would expect that at least in a certain, perhaps very restricted, composition range such processes might be found. The dependences of rate constants on incoming ligand concentration are detailed in Tables VI and VIII; the pattern for k_1 is depicted in Figure 3. They correspond to

$$k_1 = k_{1L}[\text{phen}]$$

$$k_2 = k_{2S}$$

Table VII contains some entries for bpy as an entering group, to show that k_2 is independent of the nature as well as of the concentration of the incoming ligand. Kinetics in pure hexane had perforce to be monitored with dab (**1**) as incoming ligand, as both bpy and phen proved too sparingly soluble. In pure hexane, as in toluene, only one step is observed, whose rate constant is 2.1×10^{-5} s^{-1} at 298.2 K.

Microemulsions. Kinetic results are given in Table IX. Under most conditions the absorbance–time data are satisfactorily fitted by a two-exponential function, though for phen as incoming ligand in microemulsion II the fast step makes too small a contribution for its time constant to be determined with any accuracy. It was not possible to obtain kinetic data for dab (**1**) as incoming ligand, since $Mo(CO)_4$(dab) undergoes solvolytic decomposition at an appreciable rate in these microemulsions.

Neither step in these reactions in microemulsions has a rate constant that varies significantly with the amount of phen or bpy in the system. Indeed, the rate constants also differ remarkably little between the two microemulsions. Kinetic runs on microemulsions containing the molybdenum compound but no added diimine showed rate constants of 160×10^{-4} and 1.4×10^{-4} s^{-1} for microemulsion I and ca. 2.3×10^{-4} s^{-1} for microemulsion II.

Charge-Transfer Spectra. The charge-transfer spectrum of *cis*-$Mo(CO)_4(py)_2$ is affected to only a very small extent by a change in solvent, but the products $Mo(CO)_4$(LL) with LL = bpy, phen, or dab exhibit strong solvatochromism.[5,6,8] Frequencies

Table V. Summary of Rate Constants for the $Mo(CO)_4(py)_2$ + phen Reaction in 1-Butanol + Toluene Solvent Mixtures

solvent[a]		1st step	2nd step		3rd step
% 1-BuOH	% toluene	$k_{1L}/M^{-1}\ s^{-1}$	$10^4k_{2S}/s^{-1}$	$10^2k_{2L}/M^{-1}\ s^{-1}$	$10^4k_D/s^{-1}$
100		5.1 ± 0.3	8.6 ± 0.2	9.6 ± 0.4	*c*
90	10	5.2 ± 0.1	4.0 ± 0.3	6.0 ± 1.2	*c*
50	50	12.8 ± 0.4	4.2 ± 0.1	1.2 ± 0.2	*c*
10	90	*b*	2.70 ± 0.03	*c*	*c*
2	98	*b*	1.90 ± 0.15	0.9 ± 0.3	*c*
0.1	99.9	*b*	0.24 ± 0.03	0.38 ± 0.05	26 ± 1
	100	*c*	*c*	*c*	24.8 ± 0.5

[a] Volume percent before mixing. [b] Not calculable with acceptable accuracy. [c] Not observed.

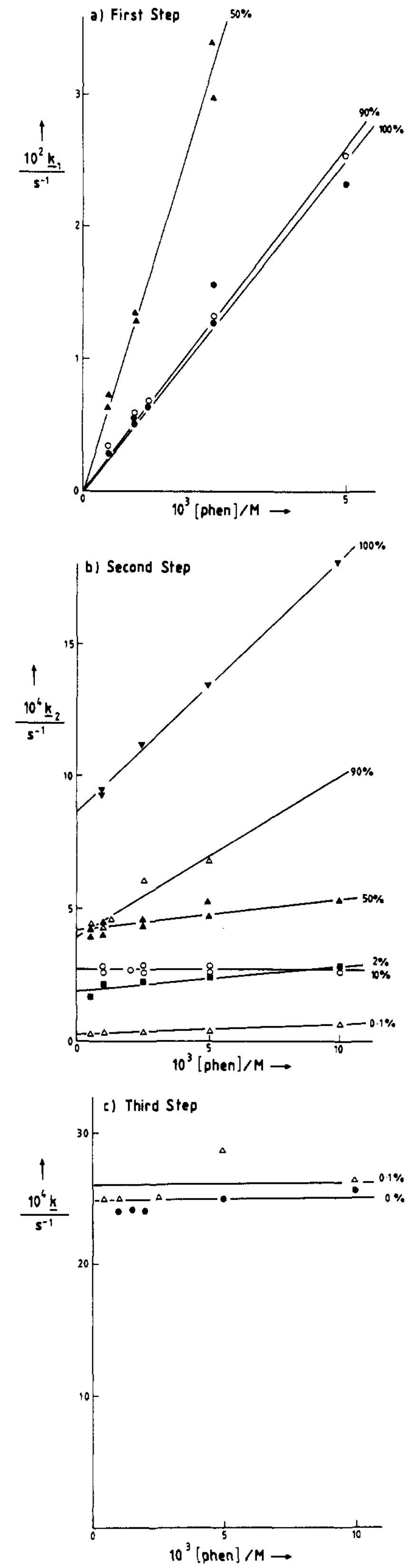

Figure 2. Plots of observed first-order rate constants against phen concentration for the various stages in its reaction with *cis*-$Mo(CO)_4(py)_2$ in 1-butanol (percentage specified)/toluene.

Table VI. Dependence of Derived Rate Constants $10^2k_1/s^{-1}$ in the $Mo(CO)_4(py)_2$ + phen Reaction on Ligand Concentration and Solvent Composition[a] in 2-Propanol + 1-Hexane Mixtures

solvent[b]		10^3[phen]/M				
% 2-PrOH	% 1-hexane	0.5	1.0	1.25	2.5	5.0
100		0.43	0.81	0.96	2.1	4.4
90	10	0.39	0.84	1.05	1.8	3.4
50	50	0.66	1.4		2.7	*c*
10	90	change in absorbance too small				

[a] At 298.2 K. [b] Volume percent before mixing. [c] Too fast.

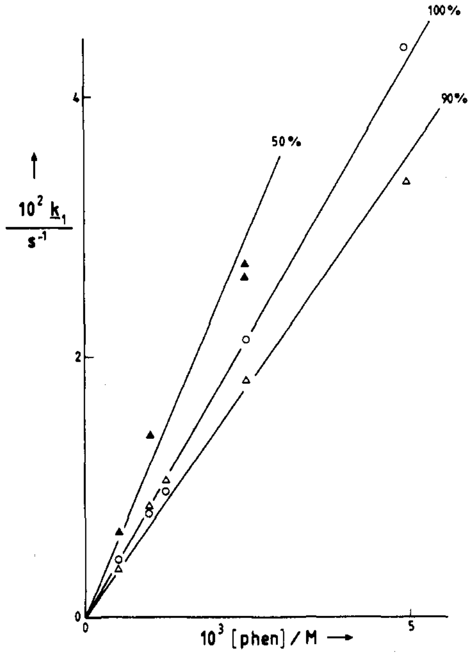

Figure 3. Dependence of k_{obsd} on phen concentration for the first stage of its reaction with *cis*-$Mo(CO)_4(py)_2$ in 2-propanol (percentage specified)/hexane.

of maximum absorption, ν_{max}, for these three compounds are 20 880, 21 190, and 18 320 cm^{-1} in microemulsion I and in 33% 1-hexane/67% 2-propanol (cf. 17 920 and 18 450 cm^{-1} for $Mo(CO)_4(dab)$ in 1-hexane and in 2-propanol, respectively), suggesting a solvation shell containing on average these two components in a ratio close to 2:1 for this type of compound in microemulsion I. In microemulsion II $Mo(CO)_4(phen)$ has ν_{max} = 21 150 cm^{-1}. Comparison of this value with ν_{max} = 21 300 cm^{-1} in 1-butanol, 20 300 cm^{-1} in toluene, and 21 510 cm^{-1} in toluene saturated with water indicates an important solvating role for water here. By implication, water may also play a significant role in determining the reactivity of *cis*-$Mo(CO)_4(py)_2$.

Discussion

The equilibrium and kinetic properties of *cis*-$Mo(CO)_4(py)_2$ in the alcohol + hydrocarbon solvent mixtures demonstrate the importance of the role played by the alcohol in the mechanism of substitution at this complex. The course of reaction in alcohol + hydrocarbon mixtures is clearly more complicated than the simple D substitution established for reaction with diimine ligands in toluene.[1] To account for all the observations reported in this paper, we propose the mechanism shown in Scheme I, in which the terms "fast" and "slow" refer to the rates at which the solvolysis equilibria are established. A simpler mechanism consisting of two linked, consecutive D processes involving an intermediate $Mo(CO)_4(py)(N\frown N)$ containing monodentate phen (bpy; dab) explains nearly all our observations but is not consistent with the three-step process established for reaction in 0.1% 1-butanol or with the solvolysis behavior of *cis*-$Mo(CO)_4(py)_2$ in the absence of added diimine ligand.

The (approximate) rate constants for replacement of the first and second pyridine ligands from *cis*-$Mo(CO)_4(py)_2$ were derived from the solvolysis experiments (vide supra). The relation between the half-lives for these two reactions and the time needed to make

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Table VII. Dependence of Derived Rate Constants $10^4k_2/\mathrm{s}^{-1}$ in the $Mo(CO)_4(py)_2$ + phen Reaction on Ligand Nature[a] and Concentration and on Solvent Composition[b] in 2-Propanol + 1-Hexane Mixtures

solvent[c]		10^3[phen]/M											
% 2-PrOH	% 1-hexane	0.5	1.0	1.25	2.0	2.5	5.0	7.0	10.0	20.0	23.0	67.0	130
100		4.3	4.5	4.3		5.9					4.6	3.9 B, 4.6	4.4 B
90	10	1.3		6.1		7.1							4.3 B
50	50	6.1	6.7			6.8	5.6		5.5				
10	90	2.4	4.4		5.5	4.8		3.5		3.5			

[a] At 298.2 K. [b] Incoming ligand is phen unless otherwise stated (B = bpy). [c] Volume percent before mixing.

Table VIII. Summary of Rate Constants for the $Mo(CO)_4(py)_2$ + phen Reaction in 2-Propanol + Hexane Solvent Mixtures

solvent[a]				
% 2-PrOH	% 1-hexane	1st step k_{1L}/M^{-1} s^{-1}	2nd step $10^4k_{2S}/\mathrm{s}^{-1}$	3rd step $10^4k_D/\mathrm{s}^{-1}$
100		8.4	40	*c*
90	10	7.1	50–60	*c*
50	50	11.5	60	*c*
10	90	*b*	40–50	*c*
	100	*c*	*c*	0.21

[a] Volume percent before mixing. [b] Not calculable with acceptable accuracy. [c] Not observed.

Table IX. Kinetic Results $10^4k/\mathrm{s}^{-1}$ for the Reaction of $Mo(CO)_4(py)_2$ with phen and bpy in Microemulsions[a]

Microemulsion I

		10^3[LL]/M		
		7.0	24.0	70.0
1st step	LL = phen	140	128	126
	LL = bpy	193	173	167
2nd step	LL = phen	3.7	3.7	3.6
	LL = bpy	3.7	3.7	3.8

Microemulsion II

		10^3[LL]/M			
		7.7	27.0	59.0	77.0
1st step[b]	LL = bpy			178	
2nd step	LL = phen	4.1	4.0		4.0
	LL = bpy			4.3	

[a] At 298.2 K. [b] First step too small for LL = phen.

up, purge, and thermally equilibrate the *cis*-$Mo(CO)_4(py)_2$ solutions used in the kinetic investigations of the reactions with diimines means that the molybdenum solution contains $Mo(CO)_4(py)_2$, $Mo(CO)_4(py)(ROH)$, and at least some $Mo(CO)_4(ROH)_2$ at the start of each kinetic run. An initial very fast reaction (k_{1L}[phen]; Table II) derives from reaction of this bis(ROH) complex with the added diimine; the amplitude of this step increases as the length of time taken to prepare and equilibrate the molybdenum solution increases. Subsequent reaction via $Mo(CO)_4(ROH)_2$ is rate-controlled by solvolysis of $Mo(CO)_4(py)(ROH)$ and is thus quite slow. It is this solvolysis and parallel direct attack by the incoming diimine at the mono(ROH) species that gives the $k_{2S} + k_{2L}$[phen] rate law established above (Table III). Only in pure toluene or pure hexane or in the presence of *very* little alcohol (e.g. 0.1% 1-butanol in toluene) is the slow D step not involving solvento intermediates observed. In the 0.1% 1-butanol case there is apparently just the right balance between rate constants for the amplitudes of the three pathways to be roughly equal (all >20% of the reaction) and thus for three kinetic stages to be observable. As soon as more alcohol is present the direct D path becomes negligible, overshadowed by the solvolytic paths through $Mo(CO)_4(py)(ROH)$.

Some semiquantitative support for Scheme I can be obtained by comparison of k_{2S} values with estimated rate constants obtained from solvolysis runs from which diimines were absent. Thus, the rate constant for loss of the pyridine from $Mo(CO)_4(py)(1\text{-BuOH})$ in 50% 1-butanol + toluene, 4×10^{-4} s^{-1}, compares very well with k_{2S} in this solvent mixture (4.2×10^{-4} s^{-1}). Similarly, $k_{2S} = 4 \times 10^{-3}$ s^{-1} in pure 2-propanol (Table VIII) compares favorably with the analogous solvolysis rate constant of approximately 5×10^{-3} s^{-1}. Agreement is not quite so close in the case of the microemulsions, but solvolysis rates in the presence and absence of added diimine are of comparable orders of magnitude (they differ by factors of around 2).

We now consider the relatively small effects of solvent on reactivity for the various pathways delineated above (Scheme I). The rate constant for the D path (k_3 or k_D) for reaction of *cis*-$Mo(CO)_4(py)_2$ with phen, bpy, or dab in toluene is affected only very slightly by the addition of 0.1% 1-butanol (Table V), despite the enormous effect of small amounts of alcohol on the balance between various reaction pathways. However, direct D substitution in 1-hexane takes place some 100 times slower than in toluene. This difference can presumably be attributed to the less favorable solvation of the leaving group by hexane. Both the thermodynamic excess functions for mixing of pyridine with hexane and with toluene[9] and the much greater solubility of 2,2′-bipyridyl (here taken as a model for two pyridine molecules) in toluene than in hexane support this idea. However, it is important to bear in mind that pyridine as a leaving group may have rather different solvation characteristics than free pyridine, since the nitrogen's lone pair is in the former case still interacting significantly with the metal center and therefore relatively unavailable for interaction with solvent.[10] The rate constant for pyridine loss from $Mo(CO)_4(py)_2$ in toluene containing 0.1% 1-butanol is essentially the same as that in pure toluene, but pyridine loss is around 8 times faster in the microemulsions (Table IX).

There are three clear trends in other rate constants with solvent composition, but interpretation is rendered difficult by the impossibility of making unequivocal mechanistic assignments. The rate constants for the reactions $Mo(CO)_4(py)(ROH) \rightarrow Mo(CO)_4(ROH)_2$, viz. k_{2S}, increase as the proportion of ROH in the solvent medium increases, from 1.4×10^{-4} s^{-1} in microemulsion I through 2.3×10^{-4} s^{-1} in microemulsion II, 4×10^{-4} s^{-1} in 50% 1-butanol/50% toluene, 8.6×10^{-4} s^{-1} in 1-butanol, to about 40×10^{-4} s^{-1} in 2-propanol/hexane and 2-propanol. This modest reactivity variation may be attributed to small changes in solvation of the leaving pyridine in a D mechanism. Comparison with $Mo(CO)_4(py)_2$ reactivity would then indicate a marked drop in rate constant for pyridine loss from $Mo(CO)_4(py)(ROH)$ on going from the media listed above to pure hexane, apparently the one medium in this study that is reluctant to solvate pyridine. Unfortunately, the determination of k_{obsd} for $Mo(CO)_4(py)(ROH)$ solvolysis in pure hexane is technically unfeasible.

Second-order rate constants for reaction of $Mo(CO)_4(py)(1\text{-BuOH})$ with 1,10-phenanthroline, k_{2L}, show a similar solvent dependence to k_{2S}. In both cases there is a roughly 30-fold decrease in reactivity as the 1-butanol content drops from 100 to 0.1% (in toluene). No comment on k_{2L} in 2-propanol/hexane is possible, since any reaction by this pathway is obscured by the faster solvolytic (k_{2S}) path. The rate constant k_{2L} could arise either from solvent vs. incoming ligand competition (discrimination) in a D mechanism or from associative attack by the 1,10-

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phenanthroline at the molybdenum. Either way solvation of the pyridine and the 1,10-phenanthroline will affect reactivities. What may provide a clue as to the mechanism operative is the observation that solvent effects on reactivity of $Mo(CO)_4(ROH)_2$ and of $Mo(CO)_4(py)(ROH)$, k_{2L} and k_{1L}, respectively, act in opposite directions. The modest increase in k_{1L} as the proportion of 1-butanol decreases (Table V) may be attributable to the corresponding increase in the chemical potential of the incoming ligand as its solvation decreases somewhat, with consequent increase in rate constant for associative attack. Thus, here we have associative displacement of ROH from $Mo(CO)_4(ROH)_2$ in contrast to dissociative loss of py from $Mo(CO)_4(py)(ROH)$, as indubitably from $Mo(CO)_4(py)_2$.

It is difficult to make a direct reactivity comparison for the rapid (k_1) step between the binary mixtures and the microemulsions, since the former show a first-order dependence on the concentration of the incoming ligand and the microemulsions a zero-order dependence. However, the k_{obsd} values for the microemulsions (Table IX) correspond to k_{obsd} for binary mixtures where incoming ligand concentrations are of the order of 5×10^{-3} M. This comparison may be giving a clue as to the effective concentration of phen or bpy in those regions of the microemulsions in close proximity to the molybdenum species. Indeed, it turns out that the small medium effects on reactivities, the probable inequivalence of second-order terms in mixed solvents and in microemulsions, and the lack of a probe for the possible effect of water on the charge-transfer spectra make comparisons of kinetic and spectroscopic results for the present compounds and reactions rather fruitless. Rather than conduct further investigations in this particular area, we feel it would be better to switch attention to other systems where greater contrasts between reactants, in terms of charges and hydrophobic or hydrophilic natures, would give greater reactivity contrasts. It would also be advantageous to use a substrate whose reactions were less complicated than those in Scheme I. In particular, a single leaving group would be desirable.

Solvolysis and substitution at *cis*-$Mo(CO)_4(py)_2$ have now been shown to follow an interesting and complicated pattern, with a rich diversity of reaction pathways. The kinetic situation in these alcohol-containing solvent media contrasts with the simple patterns encountered when, as has been usually the case, "innocent" solvents such as toluene or dichloromethane have been used. Our study of alcohol-containing solvents opens up new reaction pathways, involving a variety of reactive intermediates and new aspects of organometallic reactivity and mechanisms.

Acknowledgment. We are grateful to the Royal Society, Deutsche Forschungsgemeinschaft, Verband der Chemischen Industrie, and NATO (Grant No. 450/82) for support of this research. We thank Elke Hilms for carrying out some of the kinetic experiments.

Registry No. *cis*-$Mo(CO)_4(py)_2$, 16742-99-7; phen, 66-71-7; bpy, 366-18-7; dab, 5393-49-7; BuOH, 71-36-3; *i*-PrOH, 67-63-0.

Contribution from the Chemistry Department, University of Pretoria, Pretoria 0002, South Africa,
and National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria 0001, South Africa

π-Arene Complexes. 3.[1] End-to-End Bridging Thiocarbonyl Complexes. Crystal and Molecular Structure of $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$

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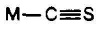
Received December 12, 1985

The dinuclear complexes $(\eta^6\text{-}C_6H_5R)(CO)_2CrCSCr(CO)_5$ (R = OMe, Me) and $(\eta^6\text{-}C_6H_3Me_3)(CO)_2CrCSCr(CO)_5$ containing a thiocarbonyl bridged in an end-to-end manner (via C and S) have been synthesized from the π-arene thiocarbonyl complexes and $Cr(CO)_5THF$. The X-ray structure of $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ (A) has been determined by single-crystal X-ray diffraction. Crystals of A ($Cr_2C_{15}H_8O_7S$) are triclinic, space group $P\bar{1}$, with a = 7.395 (1) Å, b = 10.373 (3) Å, c = 12.057 (1) Å, α = 77.72 (2)°, β = 79.91 (1)°, γ = 75.69 (2)°, and Z = 2. Although the Cr–C–S linkage is linear (angle 177.3 (3)°), the C–S–Cr linkage deviates greatly from linearity. The lowering of the C–S bond order on coordination through the sulfur atom is suggested by a C–S bond length of 1.604 (5) Å and $\nu(C{\equiv}S)$ absorption bands in the infrared region approximately 75 cm^{-1} lower than those observed for the parent thiocarbonyl complexes. The very long S–Cr distance of 2.486 (2) Å is indicative of a weak bond that is easily broken in polar solvents.

Introduction

Thiocarbonyl ligands have been found to coordinate to transition metals in different ways, and possible arrangements are shown (A–G).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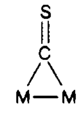
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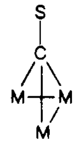
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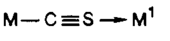
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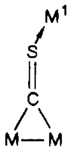
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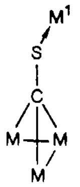
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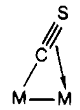
G

A large number of transition-metal complexes with terminal and doubly bridged thiocarbonyls (A, B)[2,3] are known, and complexes with an additional coordination through the sulfur (D, E)[4,5] have also been reported. The complex $\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ is an example of a complex with a triply bridged thiocarbonyl (C) and $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]Cr(CO)_5$ the corresponding end-to-end-bonded compound (F).[6] To our knowledge no examples of complexes with thiocarbonyl ligands bonded sideways, as in arrangement G, exist.

It is known that the electrophilic character of the carbon of a thiocarbonyl is markedly greater compared to that of a carbonyl carbon and the sulfur is more basic than the oxygen.[7] Thiocarbonyl ligands therefore exhibit a much wider range of reactions toward nucleophiles and Lewis acids.[8,9] This explains why the

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