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### Octahedral Metal Carbonyls. XLI: The Mechanism of the Reaction of (2,5-Dithiahexane)tetracarbonyltungsten(0) with Tri(isopropyl) Phosphite

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## SHORT COMMUNICATION

### Octahedral Metal Carbonyls. XLI: The Mechanism of the Reaction of (2,5-Dithiahexane)tetracarbonyltungsten(0) with Tri(isopropyl) Phosphite

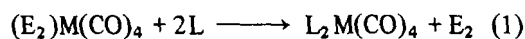
GERARD R. DOBSON† (and Honors Science 102-2, Spring Semester, 1977<sup>2</sup>)

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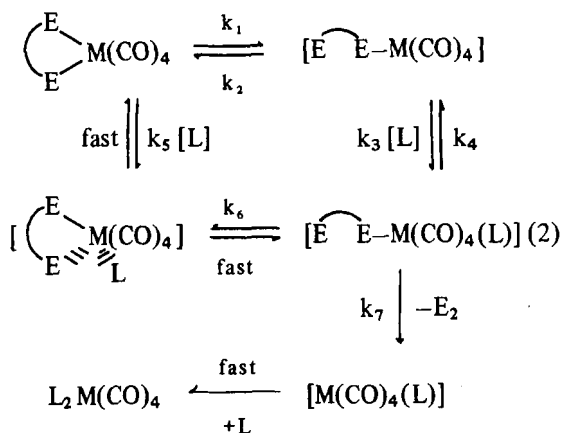
(Received May 12, 1977)

#### INTRODUCTION

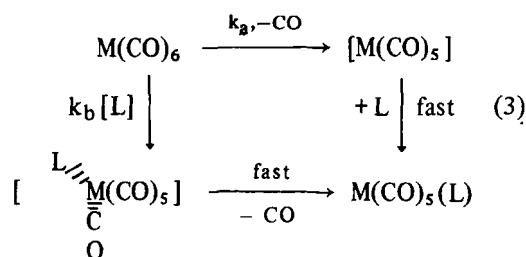
Recent rate studies of reactions of (chelating ligand)  $M(CO)_4$  complexes (chelating ligand =  $E_2$ ;  $M = Cr, Mo, W$ ) with Lewis bases ( $L$ ),



have shown that the kinetics data may be encompassed within the overall mechanism,<sup>1</sup>



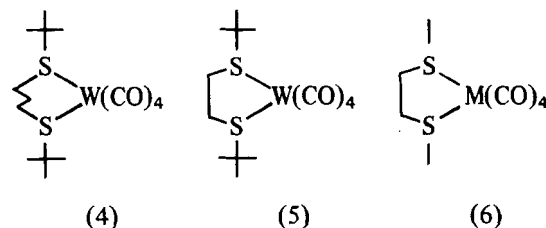
This mechanism is especially attractive in view of its analogy to the mechanism of ligand-exchange for the Group VI-B metal metal hexacarbonyls:<sup>3</sup>



However, for mechanism (2), evidence for the associative path (governed by  $k_5$ ) is limited, largely because the second-order rate law expected for that path is also consistent with a limiting form of the rate expression, governed by  $k_1 - k_4$ , for the ring-opening mechanism.

The existence of the associative path has recently been inferred for ligand-substitution reactions of  $(DTN)W(CO)_4$  (4, DTN = 2,2,8,8-tetramethyl-3,7-dithianonane) on the basis of indirect evidence,<sup>1</sup> but no such path was to be inferred for the analogous reaction of  $(DTO)W(CO)_4$  (5, DTO = 2,2,7,7-tetramethyl-3,6-dithiooctane) with Lewis bases.<sup>4</sup>

These results are of particular interest in view of an earlier study of the kinetics and mechanism of reactions of  $(DTH)M(CO)_4$  (6, DTH = 2,5-dithiahexane;  $M = Cr, Mo$ ) with Lewis bases;<sup>5</sup> it was proposed, on the basis of the observed



entropies of activation, that for  $M = Cr$  the ligand-exchange proceeded largely *via* the ring-opening path, while for  $M = Mo$ , a substantial contribution to the overall mechanism was made by the associative process.

An hypothesis stands only insofar as it enables prediction of behaviour in unstudied systems. Thus a kinetics investigation of the reaction of  $(DTH)W(CO)_4$  with a Lewis base (tri(isopropyl) phosphite) offers

the opportunity to test the validity of the mechanistic interpretations thus far placed on reactions proceeding *via* (1) both on the basis of variation in structure within complexes containing a series of closely-related bidentate ligands (4–6), and as a function of the identity of the Group VI–B metal atom (Cr, Mo, W).<sup>6</sup>

## EXPERIMENTAL

Kinetics runs in xylene solvent were carried out as described previously<sup>4–5</sup> employing a Beckman DU-2 direct-reading spectrophotometer which monitored the disappearance of an absorption in the visible spectrum (425 nm) of the substrate. Data were analyzed employing an IBM 360 Model 50 computer of the North Texas State University Computing Center. Limits of error cited (in parentheses) for values of  $k_{\text{obsd}}$ , the pseudo first-order rate constants,<sup>5</sup>  $k_5$ , the second-order rate constants, and the activation parameters, are one standard deviation. Data outside 95% confidence limits were discarded.

*(2,5-Dithiahexane)tetracarbonyltungsten(0)* Ten grams of tungsten hexacarbonyl (Pressure Chemical), 25 ml of 2,5-dithiahexane (Aldrich) and 150 ml of mesitylene were heated at reflux under nitrogen for 90 min. The mixture was then cooled and filtered with suction to afford a black residue. This residue was extracted with several portions of hot chloroform/decolorizing charcoal. The filtered chloroform extracts were placed in a freezer and the resulting ochre precipitate of impure  $(\text{DTH})\text{W}(\text{CO})_4$  was collected. Recrystallization from hot chloroform/decolorizing charcoal afforded bright yellow microcrystals of the product, which was identified through its characteristic carbonyl stretching spectrum.<sup>7</sup>

The reaction product was found to be exclusively the *trans*- $\{\text{P}[\text{OCH}(\text{CH}_3)_2]_3\}_2\text{W}(\text{CO})_4$  complex, as determined through comparison of the carbonyl stretching spectrum of reaction solutions at infinite time to that of the known product.<sup>8</sup>

## RESULTS AND DISCUSSION

Rate data at three temperatures for reaction of  $(\text{DTH})\text{W}(\text{CO})_4$  in xylene with tri(isopropyl) phosphite are presented in the Table. The Figure illustrates plots of  $k_{\text{obsd}}$  vs.  $[\text{P}(\text{OCH}(\text{CH}_3)_2)_3]$ .

A least-squares analysis of the plots of  $k_{\text{obsd}}$  vs.  $[\text{L}]$  confirms that the plots are non-linear for

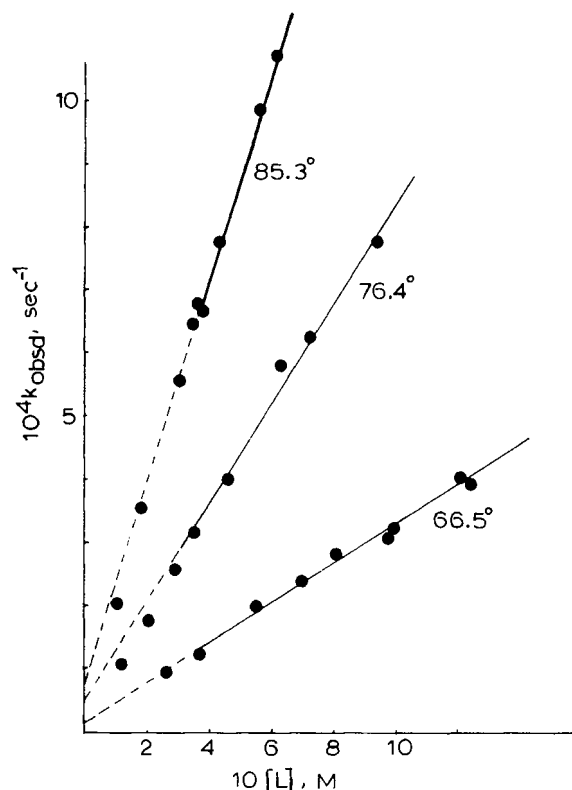


FIGURE 1 Plots of  $k_{\text{obsd}}$  vs.  $[\text{L}]$  for reaction of  $(\text{DTH})\text{W}(\text{CO})_4$  with tri(isopropyl) phosphite in xylene at various temperatures.

$[\text{L}] < 0.35\text{M}$ , exhibiting curvature toward the origin (Figure).<sup>9</sup> Above  $[\text{L}] = 0.35\text{M}$ , however, the randomness of deviations of individual values of  $k_{\text{obsd}}$  from the best least-squares line indicate the plots to be linear. These observations are qualitatively in agreement with those expected on the basis of mechanism (2). Assuming  $k_6$  to be negligible,<sup>10</sup> the applicable steady-state rate law in terms of  $k_{\text{obsd}}$  is,<sup>4</sup>

$$k_{\text{obsd}} = k_5 [\text{L}] + k_1 k_3 k_7 [\text{L}] / (k_2 (k_4 + k_7) + k_3 k_7 [\text{L}]) \quad (7)$$

For this rate law, as  $[\text{L}]$  approaches zero, the value of  $k_{\text{obsd}}$  should also approach zero, while at high  $[\text{L}]$ , assuming  $k_3 k_7 \gg k_2 (k_4 + k_7)$ , Eq. (7) becomes,

$$k_{\text{obsd}} = k_5 [\text{L}] + k_1, \quad (8)$$

and thus the  $k_{\text{obsd}}$  plots should become linear, with positive intercepts, as is observed.<sup>11</sup> The magnitudes of the intercepts (*ca.* 5% of  $k_5$ ) preclude their quantitative evaluation, but the slopes,  $k_5$  (Eq. 8),

TABLE I  
Rate data for reaction of (2,5-dithiahexane)tetracarbonyltungsten with tri(isopropyl) phosphite in xylene

(T, °C)	L, [M]	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$	(T, °C)	L, [M]	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$
(66.5°)	0.2670	0.944(17)	(85.3°)	0.1030	2.00(2)
	0.3727	1.226(22)		0.1895	3.55(4)
	0.5533	1.898(12)		0.3042	5.55(3)
	0.7002	2.40(5)		0.3535	6.47(6)
	0.8119	2.84(1)		0.3632	6.79(7)
	0.9763	3.09(5)		0.3792	6.66(2)
	0.9949	3.25(4)		0.4362	7.75(4)
	1.212	4.08(5)		0.5674	9.87(8)
	1.251	3.95(7)		0.6182	10.73(7)
	(76.4°)	0.1219		1.056(10)	
0.2037		1.75(1)			
0.2908		2.56(3)			
0.3505		3.15(7)			
0.4624		4.01(5)			
0.6330		5.81(6)			
0.7270		6.24(3)			
0.9418		7.75(5)			

Values of rate constants at various temperatures

T, °C	$10^4 k_1 (\text{sec}^{-1})$	$10^4 k_5 (\text{M}^{-1} \text{sec}^{-1})$
66.5	0.14(13)	3.15(12)
76.4	0.48(33)	7.89(23)
85.3	0.77(26)	16.05(14)

$$\Delta H_s^\ddagger = 20.3(9) \text{ kcal/mole}; \Delta S_s^\ddagger = 15.4(25) \text{ cal/deg-mole}$$

afford activation parameters quite consistent with expectations in that a highly negative entropy of activation is observed (Table I), to be anticipated for an associative mechanism, in which more bond-making than bond-breaking accompanies formation of the transition state. Thus the evidence is strongly suggestive of a predominantly associative process, *i.e.*, one largely governed by  $k_5$  (Eq. 2). These results are also consistent with the overall mechanism (2), based both on expected results for W relative to Cr and Mo for the (DTH)M(CO)<sub>4</sub> series<sup>5</sup> and on the nature of DTH compared to other bidentate chelating ligands (4,5) thus far investigated.<sup>1,4</sup>

a) *The metal atom.* Based upon atomic size, which in several studies has been inferred to exert a crucial influence on mechanism in octahedral metal carbonyls and derivatives,<sup>12</sup> it is to be expected that (DTH)W(CO)<sub>4</sub> should react by a mechanism similar to that observed for (DTH)Mo(CO)<sub>4</sub>, since the covalent radii for Mo(0) and W(0) should be virtually identical;<sup>13</sup> data have supported a largely associative mechanism for action of (DTH)Mo(CO)<sub>4</sub> with phosphines and phosphites.<sup>5</sup>

b) *The nature of the chelating ligand.* Comparison of kinetics results for (DTO)W(CO)<sub>4</sub> with those for (DTH)W(CO)<sub>4</sub> are instructive. It is to be anticipated that the ring-opening path will be less important for the latter than for the former, since it is observed in several systems that ring-reclosure is inhibited by the presence of bulky substituents on sulfur.<sup>1,4,14</sup> Further, those bulky substituents should inhibit reaction *via* an associative path. Thus on both grounds the associative path is to be favoured for (DTH)W(CO)<sub>4</sub> as compared to (DTO)W(CO)<sub>4</sub>, as is to be inferred from the rate data. It is interesting to note that reaction of (DTN)W(CO)<sub>4</sub> with Lewis bases evidently proceeds to a larger degree *via* an associative path than does that of (DTO)W(CO)<sub>4</sub>.<sup>1,4</sup> This observation may in part be due to the weaker W-S bonds expected in the six than the five-membered chelate ring complex; there is significant evidence that the "associative" path in fact involves significant bond-breaking.<sup>15</sup>

The results provide strong additional support for the accessibility of an associative path, probably concerted, in these systems.

## ACKNOWLEDGEMENT

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9. The curvature is especially evident at 85.3°, at which more data for lower concentrations were taken and for which a dissociative path with a higher enthalpy of activation and more positive entropy of activation would be expected to be more competitive with a largely associative path. *Vide infra*.
10. The form of the observed rate behaviour does not permit determination of the accessibility of the path governed by  $k_6$ ; in other systems in which the bidentate ligand forms a five-membered chelate ring this path is not observed. See, *e.g.*, Ref. 4.
11. It can be shown for proposed rate law (7) where  $k_3 k_7 [L] - k_2 (k_4 + k_7)$  (at low [L]) that a plot of  $[L]/k_{obsd} - k_5 [L]$  vs [L] should be linear, with slope  $1/k_4$ . This relationship is well-obeyed at 85.3°.
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