

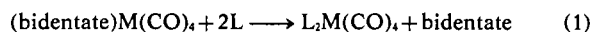
Octahedral Metal Carbonyls. XIII.¹
 Kinetics of Reactions of Metal Carbonyl
 Complexes Containing Six-Membered Chelate Rings

G. R. Dobson^{2a} and G. C. Faber^{2b}

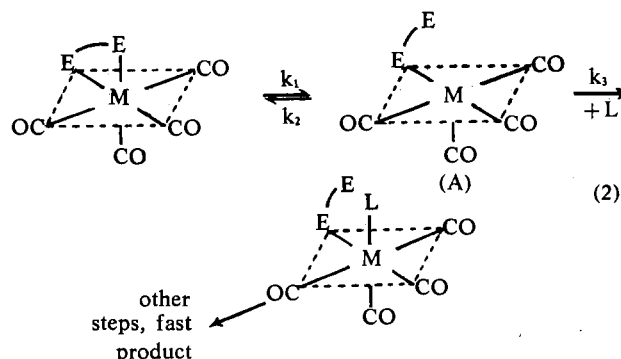
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(Bidentate)M(CO)₄ complexes (bidentate = N,N,N',N'-tetramethyl-1,3-diaminopropane and M = Cr, Mo, W; and bidentate = 2,2,8,8-tetramethyl-3,7-dithianonane (DTN) and M = W) in which the trimethylene-bridged bidentate ligands form six-membered chelate rings have been prepared, and the kinetics of the replacement of the bidentate ligands by phosphites have been investigated. The kinetic results support a mechanism quite similar to that proposed for analogous complexes containing ethylene-bridged bidentate ligands which form five-membered chelate rings, which involves reversible dissociation of one end of the bidentate ligand, followed by nucleophilic attack of the phosphite on the resulting five-coordinate intermediate, and other, rapid steps. The present data may suggest, however, a prior ligand-complex interaction which assists in the initial dissociation. Comparisons of rate data and activation energies for the tetracarbonyl tungsten complex of DTN and its ethylene-bridged analogue are interpreted as supporting a greater difficulty in return of the free end of the bidentate ligand, and higher ground state energy, for the complex containing the six-membered ring.

Where such reactions result in the exclusive replacement of the bidentate ligand,^{1,4,7,8,10}



a mechanism to be inferred in several instances involves reversible dissociation of one end of the bidentate ligand followed by nucleophilic attack of L on the resulting five-coordinate intermediate (A) and other, rapid steps to give the observed products:



For systems for which kinetic evidence has most strongly indicated this mechanism to be operative (for bidentate = N,N,N',N'-tetramethylethylenediamine, (CH₃)₂NCH₂CH₂N(CH₃)₂, tmen and M = Cr;¹⁰ bidentate = 2,2,7,7-tetramethyl-3,6-dithiaoctane, (CH₃)₃-CSCH₂CH₂SC(CH₃)₃, DTO and M = Cr, Mo, W;¹² and bidentate = 1,2-bis(diphenylarsino)ethane, (C₆H₅)₂-AsCH₂CH₂As(C₆H₅)₂, dpae and M = Cr),¹ for all of which the bidentate ligands form five-membered chelate rings with the metal, and particularly where activation parameters have been obtained,^{10,12} interesting opportunities exist for comparison of the effects of chelate ring size on reactivity.

(Bidentate)metal tetracarbonyl complexes of tmpa = N,N,N',N'-tetramethyl-1,3-diaminopropane, (CH₃)₂-NCH₂CH₂CH₂N(CH₃)₂; M = Cr, Mo, W) and DTN (DTN = 2,2,8,8-tetramethyl-3,7-dithianonane, (CH₃)₃-CSCH₂CH₂CH₂SC(CH₃)₃; M = W), in which the bidentate ligands form six-membered chelate rings have been prepared, and the kinetics of their reactions with phosphites (according to Eq. 1) have been investigated.

Introduction

A number of kinetic investigations of (bidentate)-metal tetracarbonyls (metal = Cr, Mo, W) in their reactions with Lewis bases (L) have been reported.^{1,3-12}

- (1) Part XII: D. R. Powers, G. C. Faber and G. R. Dobson, *J. Inorg. Nucl. Chem.*, **31**, 2970 (1969).
- (2) a) To whom correspondence should be addressed, at Department of Chemistry, North Texas State University, Denton, Texas 76203. b) N. D. E. A. Predoctoral Fellow, 1967-1969.
- (3) For recent reviews of metal carbonyl kinetics see, a) D. A. Brown, *Inorg. Chim. Acta Reviews*, **1**, 35 (1967); b) W. Strohmeier, *Fortschr. Chem. Forsch.*, **10**, 306 (1968); c) R. I. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968); d) H. Werner, *Angew. Chem. Intern. Ed.*, **7**, 950 (1968).
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Experimental Section

General. Infrared spectra were obtained through use of a Beckman IR-12 infrared spectrophotometer in chloroform solvent except as noted. Chemical analyses and molecular weight determinations were performed by Midwest Microlab, Inc., Indianapolis, Indiana. All chemical reactions were carried out, and all manipulations were performed under a nitrogen atmosphere.

Preparative. (Tmpa)Cr(CO)₄: A mixture of 3.0 g of Cr(CO)₆ and 20 ml of tmpa (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin) was refluxed for eight hours. The reaction solution was then cooled and filtered, and the collected product was recrystallized from tmpa. The complex was found to be unstable, decomposing readily under nitrogen at room temperature. Successive scans of its carbonyl stretching spectrum ($\nu_{\text{CO}} = 2025$ (w), 1890 (vs), 1875 (s), 1835 (s) cm^{-1} , Perkin Elmer Model 237B infrared spectrophotometer)¹³ in solution showed rapid decomposition of (tmpa)Cr(CO)₄, with attendant growth of bands attributable to Cr(CO)₆ and a mono-substituted product. Reaction of (tmpa)Cr(CO)₄ with triethyl phosphite in hydrocarbon solvent at 0° was complete within seconds after mixing.

(Tmpa)Mo(CO)₄: A mixture of 2.0 g of Mo(CO)₆ and 20 ml of tmpa were refluxed for five hours. The reaction solution was cooled, and the crude product was collected by suction filtration. Bright yellow crystals were obtained by recrystallization from toluene. Carbonyl stretching frequencies: 2019 (w), 1896 (vs), 1873 (s) and 1823 (m) cm^{-1} . (Tmpa)Mo(CO)₄ decomposes rapidly in solution at room temperature, as indicated by the growth of a band attributable to Mo(CO)₆ during the recording of successive spectra.

(Tmpa)W(CO)₄: A mixture of 2.0 g of W(CO)₆ and 20 ml of tmpa was refluxed for six hours. The reaction solution was then cooled and filtered, and the crude product was collected, and was recrystallized from 50-50 toluene-hexane to give bright yellow crystals. Carbonyl stretching frequencies: 2011 (w), 1883 (vs), 1864 (s) and 1816 (s) cm^{-1} . *Anal.* Calc'd for C₁₁H₁₈N₂O₃W: C, 30.98; H, 4.22. Found: C, 31.73; H, 3.95. Molecular weight (determined osmotically in acetone): Calc'd. 426; Found: 418.

DTN: DTN was prepared by a method similar to that of Federov and Savel'eva.¹⁴ Sodium (one mole, 23 g) was allowed to react with 500 ml of absolute ethanol in a one liter, three-necked flask equipped with a mechanical stirrer, dropping funnel, reflux condenser and nitrogen inlet. After the sodium had dissolved, *t*-butyl mercaptan (one mole, 90 g) was slowly added to the reaction solution, which was then stirred for approximately two hours. 1,3-dibromopropane (0.5 mole, 101 g) was then added dropwise, under ice cooling, and the resulting

mixture was then stirred for an additional hour at room temperature. After filtration to remove precipitated NaBr, the solvent was removed from the filtrate *in vacuo*, and the residue was distilled under nitrogen at reduced pressure (bp, 120°/4.4 mm). The yield was 40 g, or 32% of theory. *Anal.* Calc'd for C₁₁H₂₄S₂: C, 59.52; H, 10.99. Found: C, 59.98, H, 11.13. ¹H NMR spectrum (Varian Associates A-60 A spectrometer, neat, TMS standard): (CH₃)₃C-, singlet, τ 8.70; S-CH₂-C, triplet, τ 7.40, J = 7 Hz; C-CH₂-C, triplet, τ 8.22, J = 7 Hz.

(DTN)W(CO)₄: Tungsten hexacarbonyl (3.0 g) and 2.0 g of DTN were dissolved in 350 ml of *n*-hexane, and the solution was irradiated for 1.5 hr employing a Hanovia 450 watt immersion ultraviolet lamp. During the course of the irradiation, crystals of the product separated. After cooling of the reaction mixture in a freezer, the crude product was collected through suction filtration. Yellow crystals were obtained through recrystallization from toluene-hexane. Carbonyl stretching frequencies: 2019 (w), 1902 (vs), 1883 (s), 1848 (s) cm^{-1} . *Anal.* Calc'd for C₁₅H₂₄O₄S₂W: C, 34.89; H, 4.69; M.W., 516. Found: C, 35.12; H, 4.52; M.W. (osmometrically in CHCl₃), 350.

Purification of Reagents. Pidcock, Smith and Taylor have reported phosphate impurities in phosphite ligands to catalyze certain substitution reactions of metal carbonyls.¹⁵ Such ligands must therefore be rigorously purified, and used as soon as possible after purification. All phosphite ligands employed in this investigation were distilled over sodium, and then repeatedly fractionated under nitrogen or under high vacuum until shown to be free of volatile impurities by gas chromatographic analysis. They were then stored under nitrogen until used. Reagent grade xylene (Fisher) was used as obtained.

Determination of Rates. Reactions of (tmpa)W(CO)₄ and (DTN)W(CO)₄ with various phosphites were monitored at 425 nm on a Beckman DU-2 direct reading spectrophotometer under pseudo first order reaction conditions (at least a 20-fold excess of phosphite) in xylene. The absorbances of ligand-solvent blanks, which differed from A_∞ values by less than 1% of the A_∞ values were subtracted from all measurements. Plots of $\ln(A_t - A_{\infty})$ vs. *t* were linear to at least two half lives. Further details with regard to the determination of the reaction rates have been given.⁹

Rates of reaction of (tmpa)Mo(CO)₄ with triethyl phosphite were determined at 430 nm on a Beckman DU spectrophotometer fitted with a constant temperature cell assembly which regulated the temperature to $\pm 0.5^\circ$. Reactants were mixed at temperatures below that of the kinetic runs (15.0°), were placed in a 1 cm cuvette, and were allowed to equilibrate, after which time data were taken. Plots of $\ln(A_t - A_{\infty})$ vs. *t* were linear to at least two half lives.

Least squares analyses were performed on all data. Limits of error given are one standard deviation.

(13) Relative band intensities: s = strong; M = medium; w = weak; v = very.

(14) B. P. Federov and I. S. Savel'eva, *Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk*, 225 (1950).

(15) A. Pidcock, J. D. Smith and B. W. Taylor, *Inorg. Nucl. Chem. Letters*, 4, 467 (1968).

Product Identification. The reaction products, $L_2M(CO)_4$, were those reported in previous kinetic investigations,^{9,10,12} as determined through their carbonyl stretching spectra.

Table I. Rates of Reaction of $(Tmpa)M(CO)_4$ ($M = Mo, W$) and $(DTN)W(CO)_4$ with Phosphites in Xylene Reaction

Temperature	[L], M	$10^4 k_{obsd}$ (sec^{-1})	
$(tmpa)Mo(CO)_4 + P(OC_2H_5)_3$ 15.0°	0.2163	6.84	
	0.2954	8.95	
	0.5045	13.4	
	0.6616	17.2	
	1.0764	24.3	
$(tmpa)W(CO)_4 + P(OC_2H_5)_3$ 25.0°	0.1820	0.316	
	0.2175	0.356	
	0.5184	0.528	
	0.9726	0.620	
	33.6°	0.2017	1.22
		0.2453	1.39
		0.5376	2.20
	43.0°	1.1079	2.78
		0.1183	2.76
		0.1942	4.03
		0.2653	5.12
		0.4902	8.02
0.9807	10.6		
$(tmpa)W(CO)_4 + P[OCH(CH_3)_2]_3$ 43.0°	0.1247	1.69	
	0.1778	2.63	
	0.2978	4.03	
	0.4691	6.03	
	0.8546	11.2	
$(DTN)W(CO)_4 + P(OC_2H_5)_3$ 54.6°	0.3643	2.55	
	0.5087	2.88	
	0.6164	3.00	
	0.9519	3.31	
	61.9°	0.1135	3.75
		0.2331	5.58
		0.5296	7.51
	66.5°	0.7585	8.30
		1.0285	8.58
		1.5790	9.18
		0.2107	9.80
		0.3416	11.7
72.4°	0.4567	13.1	
	0.5906	14.1	
	0.1491	15.2	
	0.2883	22.2	
	0.4305	25.9	
$(DTN)W(CO)_4 + P[OCH(CH_3)_2]_3$ 66.5°	0.5770	27.5	
	0.9408	30.0	
	0.2350	8.53	
	0.2523	9.00	
	0.4011	12.7	
$(DTN)W(CO)_4 + P(OC_2H_5)_3$ 66.5°	0.4739	13.5	
	0.8352	18.7	
	0.9023	19.9	
	0.1183	5.67	
	0.2203	9.39	
	0.2711	11.0	
$(DTN)W(CO)_4 + P(OCH_3)_3$ 66.5°	0.3690	13.4	
	0.5276	16.7	
	0.5648	17.4	
	0.2044	6.79	
	0.2678	7.08	
	0.6924	8.13	

Results and Discussion

Reactions of $(tmen)M(CO)_4$ and $(tmpa)M(CO)_4$, and of $(DTO)M(CO)_4$ and $(DTN)M(CO)_4$ ($M = Cr, Mo, W$) were studied qualitatively to select those systems which would permit kinetic investigations of $(bidentate)M(CO)_4$ complexes differing only in chelate ring size. It was found that only the $(DTO)W(CO)_4$ vs. $(DTN)W(CO)_4$ comparison could be made. Both $(tmen)Mo(CO)_4$ and $(tmen)W(CO)_4$ were found to react with phosphites to give carbonyl as well as bidentate ligand replacement;¹⁶ these systems would be expected to yield ambiguous kinetic results. The instability of $(tmpa)Cr(CO)_4$ and its extreme reactivity toward phosphites (see Experimental Section) precluded its kinetic investigation so as to allow a comparison between it and the already-reported $(tmen)Cr(CO)_4$ system.¹⁰ In view of the limited stability in solution of $(tmpa)Cr(CO)_4$ and $(tmpa)Mo(CO)_4$, no attempt was made to prepare the analogous DTN complexes.

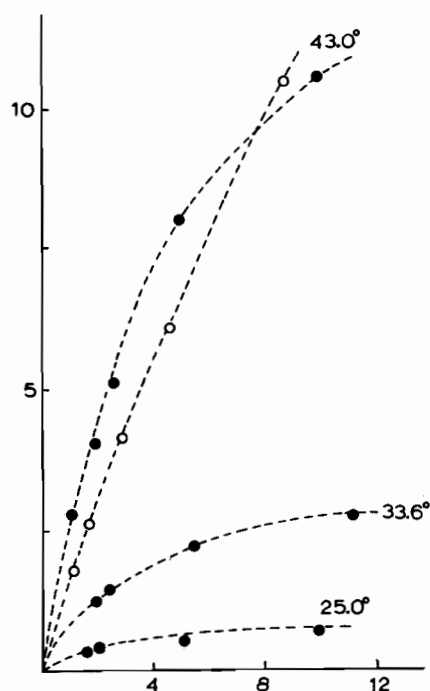


Figure 1. Plots of k_{obsd} vs. $[L]$ for Reaction of $(Tmpa)W(CO)_4$ with Phosphites in Xylene at Various Temperatures. ●: triethyl phosphite; ○: triisopropyl phosphite. Ordinate: $10^4 k_{obsd}$ (sec^{-1}); Abscissa: $10[L]$ ($mole\ liter^{-1}$).

Both $(tmpa)W(CO)_4$ and $(DTN)W(CO)_4$ react with phosphites according to Eq. 1. Pseudo first order rate (k_{obsd}) data for their reactions in xylene solvent are given in Table I. Plots of k_{obsd} vs. $[L]$ reactions of $(tmpa)W(CO)_4$ with triethyl- and tri(isopropyl) phosphite, and of $(DTN)W(CO)_4$ with triethyl phosphite at various temperatures are shown in Figures 1 and 2. The observed decreased dependence of rate on $[L]$ at high $[L]$ is characteristic of mechanism(2)

(16) G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, 1, 287 (1967).

for which, employing a steady-state approximation on the intermediate 2-A the rate law,

$$\text{rate} = \frac{k_1 k_3 [E_2 W(CO)_4] [L]}{k_2 + k_3 [L]} \quad (3)$$

is obtained. Rearrangement of this expression in terms of k_{obsd} gives

$$1/k_{\text{obsd}} = 1/k_1 + k_2/k_1 k_3 [L] \quad (4)$$

and thus plots of $1/k_{\text{obsd}}$ vs. $1/[L]$ are expected to be linear, with y-intercept $1/k_1$ and slope $k_2/k_1 k_3$.

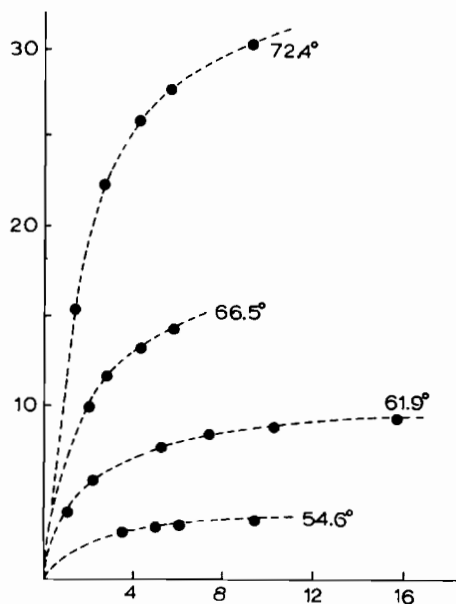


Figure 2. Plots of k_{obsd} vs. $[L]$ for Reaction of (DTN)- $W(CO)_4$ with Triethyl Phosphite in Xylene at Various Temperatures. Ordinate: $10^4 k_{\text{obsd}}$ (sec^{-1}); Abscissa: $10[L]$ (mole liter^{-1}).

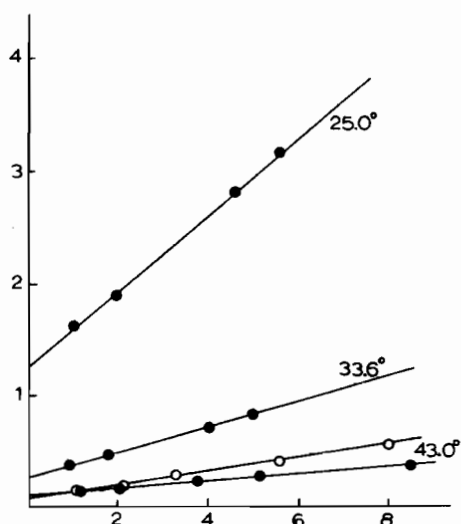


Figure 3. Plots of $1/k_{\text{obsd}}$ vs. $1/[L]$ for Reaction of (Tmpa)- $W(CO)_4$ with Phosphites in Xylene at Various Temperatures. ●: triethyl phosphites; ○: triisopropyl phosphite. Ordinate: $10^{-4}(1/k_{\text{obsd}})$ (sec); Abscissa: $1/[L]$ (liter mole^{-1}).

The reciprocal plots corresponding to the k_{obsd} vs. $[L]$ data presented graphically in Figures 1 and 2 are shown in Figures 3 and 4. Their linearity strongly suggests mechanism (2) to be operative. Further, k_2/k_3 values for reactions of these (bidentate) $W(CO)_4$ complexes with phosphites at a given temperature (Table II) vary with the steric nature of the phosphite ligand in a manner which closely corresponds to the variation of reaction rate with ligand steric nature observed for (2,5-dithiahexane) $Cr(CO)_4$, for which the reversible dissociation mechanism is also favored.⁹

Examination of the reciprocal plots for reactions of (tmpa) $W(CO)_4$ and (DTN) $W(CO)_4$ with various

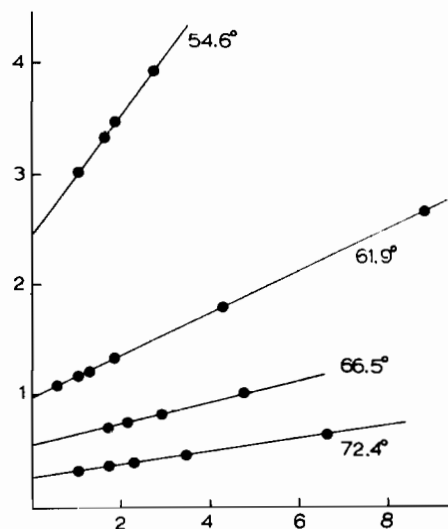


Figure 4. Plots of $1/k_{\text{obsd}}$ vs. $1/[L]$ for Reaction of (DTN)- $W(CO)_4$ with Triethyl Phosphite in Xylene at Various Temperatures. Ordinate: $10^{-3}(1/k_{\text{obsd}})$ (sec); Abscissa: $1/[L]$ (liter mole^{-1}).

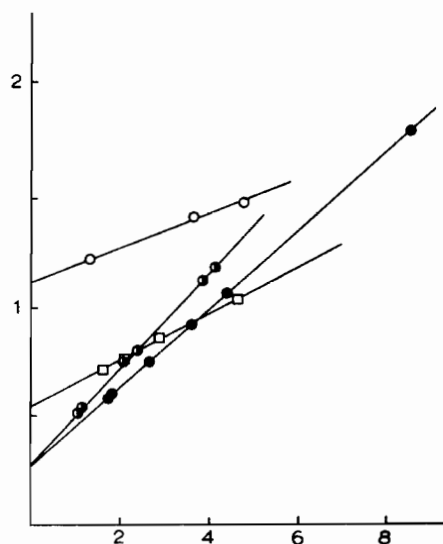


Figure 5. Plots of $1/k_{\text{obsd}}$ vs. $1/[L]$ for Reaction of (DTN)- $W(CO)_4$ with Phosphites in Xylene at 66.5° . ○: trimethyl phosphite; □: triethyl phosphite; ●: triisopropyl phosphite; ●: triphenyl phosphite. Ordinate: $10^{-3}(1/k_{\text{obsd}})$ (sec); Abscissa: $1/[L]$ (liter mole^{-1}).

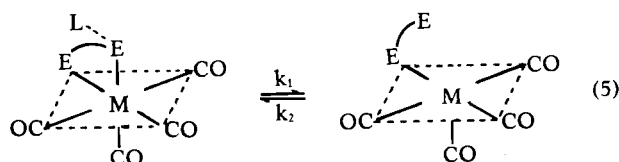
phosphites at a given temperature (Figures 3, 5) reveals, however, that contrary to expectation, common values of the y -intercepts ($1/k_1$) are not obtained. Such common values are to be anticipated since it is reasonable to expect the unimolecular dissociation of one end of the bidentate ligand to be independent of the nature of the phosphite ligand employed.

Table II. Rate Constants for Reactions of (Bidentate)M(CO)₄ Complexes with Phosphites in Xylene Solvent

Substrate Temperature	Ligand ^a	10 ⁴ k ₁ (sec ⁻¹)	k ₂ /k ₃ (mole/liter)
(tmpa)Mo(CO) ₄ 15.0°	P(OC ₂ H ₅) ₃	79.1	2.53
(tmpa)W(CO) ₄ 25.0°	P(OC ₂ H ₅) ₃	0.802	0.275
33.6°		4.14	0.471
43.0°	P[OCH(CH ₃) ₂] ₃	16.8	0.606
		24.1	1.73
(DTN)W(CO) ₄ 54.6°	P(OC ₂ H ₅) ₃	4.08	0.219
61.9°		10.4	0.201
66.5°		18.5	0.189
	P(OC ₂ H ₅) ₃	38.8	0.690
	P[OCH(CH ₃) ₂] ₃	36.0	0.756
	P(OCH ₃) ₃	8.84	0.0631
72.4°	P(OC ₂ H ₅) ₃	38.2	0.220

^a Ligand dipole moments (D), solvent: P(OCH₃)₃, 1.83, CCl₄; P(OC₂H₅)₃, 1.96, CCl₄; P[OCH(CH₃)₂]₃, 1.98, CCl₄; P(OC₂H₅)₃, 2.03, benzene.

Accordingly, attempts to obtain evidence for a ligand-substrate interaction which could affect the values of k_1 were carried out. There was found to be no observable effect of the presence of ligand on the infrared or uv-visible spectra of either substrate in xylene, nor was there observed a significant increase in the solubility of either substrate in xylene in the presence of added ligand. However, the values of k_1 obtained for both (tmpa)W(CO)₄ and (DTN)W(CO)₄ in their reactions with various phosphites at a given temperature parallel the experimentally-determined dipole moments¹⁷ of the phosphites (Table II), which may suggest a ligand-substrate interaction which would assist in the dissociation of one end of the bidentate ligand:



Further, approximately two- to threefold increases in solubility of (DTN)W(CO)₄ in hexane are noted when the solutions are made about 0.5 M in phosphite, although the relative magnitudes of the solubility increases with various phosphites do not parallel the k_1 values, or the dipole moments of the ligands.

On balance, spectroscopic evidence suggestive of

such a ligand-substrate interaction, of whatever nature, is not impressive. The variation of k_1 values with the identity of the ligand is not, however, without precedent. Angelici and Graham found the rate expressions obtained through kinetic investigations of the reactions of (2,2'-dipyridyl)M(CO)₄ (M = Cr, Mo) with various phosphites to contain a term the magnitude of which was independent of phosphite concentration, but which was dependent upon the identity of the phosphite. This term was ascribed to rate-determining dissociation of CO. Infrared, solubility and molecular weight studies failed, however, to provide corroborating evidence for a ligand-substrate interaction through which the rate data could be fully rationalized.^{4,5}

Table III. Values of k for Reactions of (Bidentate)W(CO)₄ Complexes with Triethyl Phosphite in Xylene at 72.4°.

Bidentate Ligand	k ₁ (sec ⁻¹)	k ₂ /k ₃ (mole/liter ⁻¹)
tmpa	1.0 × 10 ⁻¹	2.1
DTN	3.8 × 10 ⁻³	0.22
DTO	1.8 × 10 ⁻⁵	2.4

Table IV. Activation Parameters for Reactions of (Bidentate)W(CO)₄ Complexes with Triethyl Phosphite in Xylene

Bidentate	ΔH ₁ [*] (kcal/mole)	ΔS ₁ [*] (e.u.)	ΔH ₂ [*] - ΔH ₃ [*] (kcal/mole)	ΔS ₂ [*] - ΔS ₃ [*] (e.u.)
tmpa	31.0 ± 3.0	27.0 ± 8.4	7.6 ± 3.1	11.8 ± 8.7
DTN	27.6 ± 0.3	9.9 ± 0.8	-0.6 ± 2.8	-16.9 ± 9.7
DTO	25.7 ± 0.7	1.6 ± 2.0	-4.7 ± 1.7	-23.9 ± 4.6

Comparisons of reactions of (bidentate)W(CO)₄ (bidentate = tmpa, DTO, DTN) systems are perhaps best made through consideration of values of the rate constants (k_1 , k_2/k_3) obtained for their reactions with a given ligand (triethyl phosphite) in a common solvent (xylene). Table III gives these rate constants at 72.4°; values have been obtained through extrapolation where necessary. Comparisons of these data for bidentate = tmpa and DTN show the greater reactivity of (tmpa)W(CO)₄ to result from the much greater ease of dissociation of one end of the tmpa ligand. Activation parameters for reactions of the two complexes in question (Table IV) show this to result from a much more favorable entropy effect for the initial dissociation of tmpa than for DTN. Plausible explanations for the entropy effects observed for the (tmpa)W(CO)₄ system, which greatly differ from those observed for the other systems, are not evident.

Rate and activation data for the reactions of (DTO)W(CO)₄ and (DTN)W(CO)₄ with triethyl phosphite in xylene allow a comparison of two systems which differ only in the size of the chelating ring of the bidentate ligand. The respective values of k_1 and k_2/k_3 (Table III) indicate the greater reactivity of (DTN)W(CO)₄ to result from a greater ease of dissociation of one end of the DTN ligand, and a

(17) J. G. Verkade, private communication.

greater difficulty of its return. Activation data (Table IV) show the enhanced ease of dissociation of DTN relative to DTO to result from an entropy effect, perhaps resulting from strain in the six-membered ring. Other comparisons can perhaps best be made through the assumptions that H_c and H_a (Figure 6) are very similar for reactions of $(\text{DTO})\text{W}(\text{CO})_4$ and $(\text{DTN})\text{W}(\text{CO})_4$ with a given phosphite. These assumptions would appear reasonable in that the relative energies of the intermediates 2-A should be little affected by a trimethylene, rather than an ethylene substituent on the bonded sulfur. A similar electrophilic nature for the two intermediates should also result in similar activation energies for attack

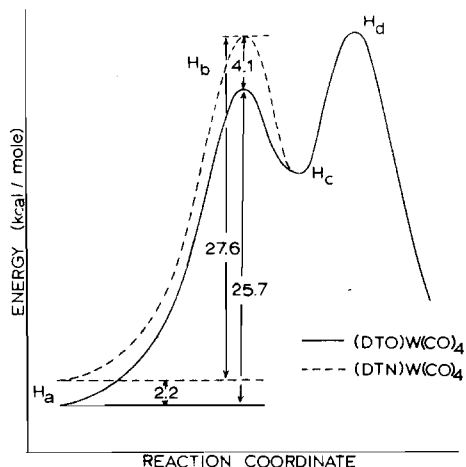


Figure 6. Potential Energy Diagram for Reaction of (Bidentate) $\text{W}(\text{CO})_4$ Complexes with Triethyl Phosphite in Xylene.

of $\text{P}(\text{OC}_2\text{H}_5)_3$ on 2-A. It would not appear unreasonable to anticipate steric effects resulting from differences in DTO and DTN to be unimportant in 2-A. Granting these assumptions, it can be seen (Figure 6) that the return of the free end of the bidentate ligand is 4.1 kcal./mole less energetically favorable for the six-membered ring, and that the ground state energy for $(\text{DTN})\text{W}(\text{CO})_4$ is 2.2 kcal/mole greater than for $(\text{DTO})\text{W}(\text{CO})_4$. This latter value compares very favorably with results obtained for ethylenediamine and 1,3-propanediamine complexes of Cu^{II} and Ni^{II} . Heat of formation data show the six-membered ring to be destabilized relative to the five-membered ring by 1.3 and 2.2 kcal/mole per chelate ring for the Cu and Ni complexes, respectively.¹⁸ Destabilization of $(\text{DTN})\text{W}(\text{CO})_4$ relative to $(\text{DTO})\text{W}(\text{CO})_4$ is also strongly supported by infrared data. Weakened σ - and π -bonding in $(\text{DTN})\text{W}(\text{CO})_4$ should lower its carbonyl stretching frequencies relative to those for $(\text{DTO})\text{W}(\text{CO})_4$, if it is accepted that changes in π -bonding exert the dominant influence on carbonyl stretching spectra. The observed carbonyl stretching frequencies for $(\text{DTO})\text{W}(\text{CO})_4$ ($\nu_{\text{CO}} = 2019, 1906, 1889, 1868 \text{ cm}^{-1}$)¹² and $(\text{DTN})\text{W}(\text{CO})_4$ ($\nu_{\text{CO}} = 2019, 1902, 1883, 1848 \text{ cm}^{-1}$) are in accord with this expectation.

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(18) I. Paulsen and J. Bjerrum, *Acta Chem. Scand.*, 9, 1407 (1955).