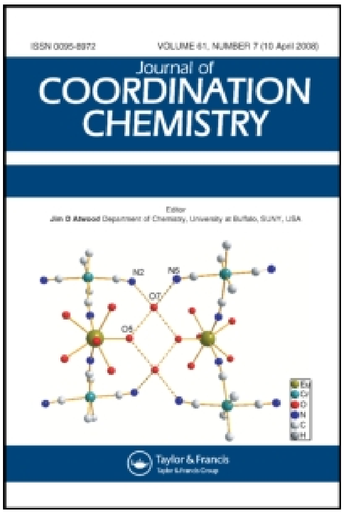

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Gerard R. Dobson[a]; Canan S. Binzet[a]; José E. Cortés[a]
[a] Department of Chemistry, North Texas State University, Denton, TX, U.S.A.

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OCTAHEDRAL METAL CARBONYLS. 56.[1] KINETICS AND MECHANISM OF LIGAND EXCHANGE IN [4-METHYL,1,2-BIS(METHYLTHIO)BENZENE]-TETRACARBONYLCHROMIUM(O)

GERARD R. DOBSON,† CANAN S. BINZET and JOSÉ E. CORTÉS
Department of Chemistry, North Texas State University, Denton, TX 76203-5068, U.S.A.

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The kinetics and mechanism of displacement of the chelating ligand bmtb (= 4-methyl-1,2-bis(methylthio)benzene) from (bmtb)$Cr(CO)_4$ by L (= tri(isopropyl) phosphite, triethyl phosphite) in chlorobenzene (CB) and 1,2-dichloroethane (DCE) have been studied. The reaction obeys a rate law,

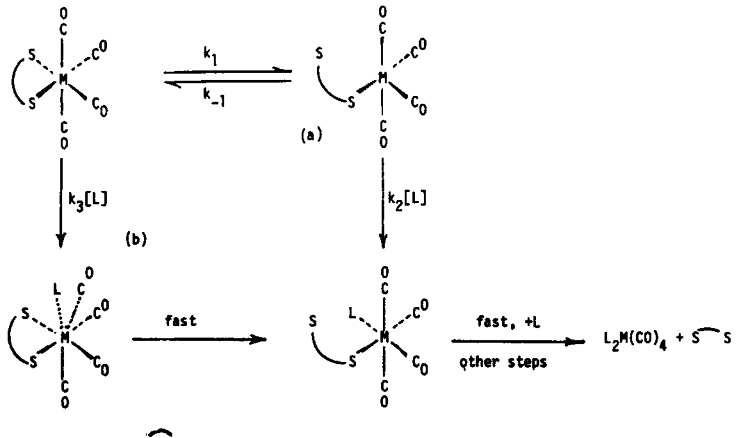
$$-d[(bmtb)Cr(CO)_4]/dt = k[(bmtb)Cr(CO)_4][L].$$

Although two limiting mechanisms, one involving rate-determining nucleophilic attack at the metal atom and the other rate-determining reversible ring-opening may be envisioned, activation data in CB taken over a 75 degree temperature range and a thousand-fold change in k demonstrate that only one reaction pathway is accessible. Despite the slightly negative entropies of activation observed, the latter mechanism is favoured based upon a comparison of the data to that obtained for other closely-related systems.

Keywords: Kinetics, chromium, carbonyl complexes, mechanism, exchange

INTRODUCTION

The displacement of chelating ligands coordinating through sulfur donor atoms from (chelate)$M(CO)_4$ complexes (=S) by alkyl and aryl phosphines and phosphites (=L) has been widely studied kinetically.[2] Two closely related reaction mechanisms which are sensitive to the steric and electronic properties of the chelating ligands have been found to be accessible, and in some instances



(1)

L = phosphine, phosphite; S⌒S = bidentate ligand coordinating through sulfur.

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† Author for correspondence.

competitive: a dissociative path, in which chelate ring opening affords a five-coordinate intermediate which then can undergo competitive ring-closure or attack by L, and an "associative" path (more probably an interchange process)[3] which involves some initial interaction between L and the substrate. The two pathways are exhibited in (*1*). For the dissociative pathway, the rate law based on a steady-state concentration of intermediate (*1-a*) is shown in (*2*).

$$-d[S]/dt = k_1k_2[S][L]/(k_{-1} + k_2[L]). \qquad (2)$$

Thus, when $k_{-1} \approx k_2s[L]$, this pathway can unambiguously be identified on the basis of the observed rate law. The more usual case, however, is that $k_{-1} \gg k_2$, in which case the observed rate law is second-order, and thus is kinetically indistinguishable from the interchange pathway. In this event, attempts to distinguish the two pathways have been made on the basis of entropies of activation, which are expected to be more positive for the dissociative process.

One example of the use of this criterion is in studies of ligand-exchange of $(DTH)M(CO)_4$ complexes (DTH = 2,5-dithiahexane; M = Cr, Mo),[2a] for which, for three L, $P(OR)_3$, (R = Me, Et, Pr^i), the average activation enthalpies in 1,2-dichloroethane solvent are 104.2 and 67.8 kJ mol^{-1} for Cr and Mo and the average entropies of activation are +14.2 and −82.4 J K^{-1} mol^{-1}, respectively. On this basis it was proposed that ligand displacement for the Cr complex proceeded largely *via* the dissociative pathway, that for Mo largely *via* the interchange pathway. It has also been widely held that dissociative ring opening is inhibited by rigidity in the chelating ring,[4] since the reaction coordinate leading to ring-opening is more severely restricted than for a flexible ring backbone.

Accordingly, it was of interest to study the kinetics and mechanism of chelate ring displacement in a rigid system which is very similar to DTH (*3-a*); 4-methyl-1,2-bis(methylthio)-benzene (bmtb, *3-b*) was ideal for this purpose in view of its ease of synthesis and a report of the preparation of its tetracarbonylchromium complex by Ainscough and coworkers.[5] Herein is reported a kinetics investigation of the displacement of bmtb from $(bmtb)Cr(CO)_4$ by triethyl phosphite and tri(isopropyl) phosphite in 1,2-dichloroethane (DCE) and chlorobenzene (CB) so that the influence of chelate ring rigidity on the reaction pathway could be further investigated.

(*3*)

EXPERIMENTAL

Bmtb was synthesized from 4-methylbenzenedithiol (Aldrich) according to the procedure of Vogel[6] (m. 40–41°). The $(bmtb)Cr(CO)_4$, prepared by Ainscough and coworkers by a photochemical method,[5] was conveniently synthesized as follows: in a 500 cm^3 two-necked flask fitted with a gas dispersion tube and reflux condenser to which an oil bubbler was attached was placed 150 cm^3 of dry toluene, 3.0 g (1.5 mmol) $Cr(CO)_6$ and 2.76 g (1.5 mmol) of bmtb. The solution was refluxed under dry nitrogen with magnetic stirring for 20 hr, after which the solution was cooled, the toluene removed *in vacuo*, and the residue recrystallized from toluenehexane to afford yellow crystals of the product (m. 81–83°), uncorrected; lit. 81–82°).[5] *Analysis* (Midwest Microlab, Ltd., Indianapolis, IN). Calc. for $C_{13}H_{12}CrO_4S_2$: C, 44.82%; H, 3.47%. Found: C, 44.56%; H, 3.49%.

Tri(isopropyl) phosphite and triethyl phosphite (Aldrich) were fractionally distilled from Na under purified nitrogen at reduced pressure. The solvents DCE (Aldrich) and CB (MCB) were distilled from P_2O_5 under nitrogen. Kinetics runs were carried out as previously described.[2a] The reaction products (*cis* and possibly *trans*-$L_2Cr(CO)_4$)[7] were identified through separate infrared scans of the carbonyl stretching region (2200–1700 cm^{-1}) during the course of the reaction (higher concentrations of (bmtb)$Cr(CO)_4$ were employed in these runs) employing a Perkin Elmer 621 grating spectrophotometer.

Data were analyzed employing a linear least-squares program (HP 2000 computer) at the North Texas State University Computing Center. Values of the pseudo-first-order rate constants, k_{obsd}, are given in Table I. Limits of error are given in parentheses as one standard deviation.

TABLE I

Rate constants for reaction of (dmtb)$Cr(CO)_4$ with trialkyl phosphites in CB and DCE at various temperatures.

Ligand	Solvent	Temperature (degrees)	[L] (M)	$10^4 k_{obsd}$ (sec^{-1})
$P(OEt)_3$	DCE	58.9	0.0664	1.59(1)
			0.0824	1.95(1)
			0.122	2.83(1)
			0.147	3.38(2)
			0.223	5.20(7)
			0.316	7.34(1)
			0.364	8.33(4)
			0.472	10.81(5)
$P(OPr^i)_3$	DCE	45.9	0.322	1.05(1)
			0.435	1.50(1)
			0.533	1.78(1)
			0.659	2.49(2)
			0.822	2.99(2)
			1.032	3.99(3)
			1.188	4.89(3)
			1.275	5.36(5)
		58.9	0.253	3.90(2)
			0.321	4.23(2)
			0.401	5.51(6)
			0.548	7.05(5)
			0.575	7.41(21)
			0.592	7.72(10)
			0.785	11.1(1)
			0.890	12.8(1)
			0.927	12.4(1)
			0.977	13.7(2)
			1.124	16.3(1)
		69.7	0.102	4.41(4)
			0.109	4.90(5)
			0.213	11.5(3)
			0.309	10.2(2)
			0.426	17.9(1)
			0.456	19.4(2)
			0.574	24.5(2)
			0.677	27.6(4)
			0.867	36.5(2)

Table I continued

Ligand	Solvent	Temperature (degrees)	[L] (M)	10^3k_{obsd} (sec^{-1})
$P(OEt)_3$	CB	26.5	1.1101	0.1119(6)
			1.858	01.93(2)
		38.3	0.2724	01.004(7)
			0.6444	02.53(6)
		49.1	0.2952	03.67(1)
			0.3732	04.64(2)
			0.5706	07.00(2)
			0.8106	10.2(3)
			0.9093	11.55(1)
			0.9386	11.76(6)
			1.334	16.93(12)
		59.8	0.3001	10.23(5)
			0.3007	10.59(7)
			0.3410	12.02(5)
			0.5894	18.3(4)
			0.5894	19.1(3)
		67.7	0.1231	09.29(7)
			0.3200	28.0(12)
		77.95	0.1106	22.2(2)
			0.1994	38.3(3)
		86.7	0.1034	49.8(9)
			0.1676	71.9(28)
		100.7	0.03305	39.8(27)
			0.0487	64.5(22)

RESULTS AND DISCUSSION

Plots of the pseudo-first-order rate constants (k_{obsd}) *vs* [L] for tri(isopropyl) phosphite in DCE at three temperatures are exhibited in Fig. 1. The data obey the second-order rate law (*4*).

$$-d[(bmtb)Cr(CO)_4]/dt = k[(bmtb)Cr(CO)_4][L]. \qquad (4)$$

Second-order rate constants are given in Table II. As noted above, this rate law is consistent with either of two reaction mechanisms, initial bimolecular interaction of $(bmtb)Cr(CO)_4$ with L (pathway *1-b*), for which k would equal k_3, or the reversible dissociation pathway (*1-a*). For this latter pathway, given a steady-state concentration of intermediate (*1-a*), the rate law (*2*), where $S = (bmtb)Cr(CO)_4$, is obtained. This expression reduces to the limiting rate law (*4*), for which $k = k_1k_2/k_{-1}$ when the rate of chelate ring-closure (governed by k_{-1}) is much faster than is the rate of bimolecular interaction of L with the five-coordinate "ring-opened" intermediate (governed by k_2).

The rate constants obtained may be compared to those for $(DTH)Cr(CO)_4$ in its chelate ring displacement reaction in the same solvent and with the same L (Table II), for which it is interesting to note that rates of reaction are very similar at a reaction temperature of about 55°.[2a] However, activation parameters for the two systems (Table III), in particular, entropies of activation

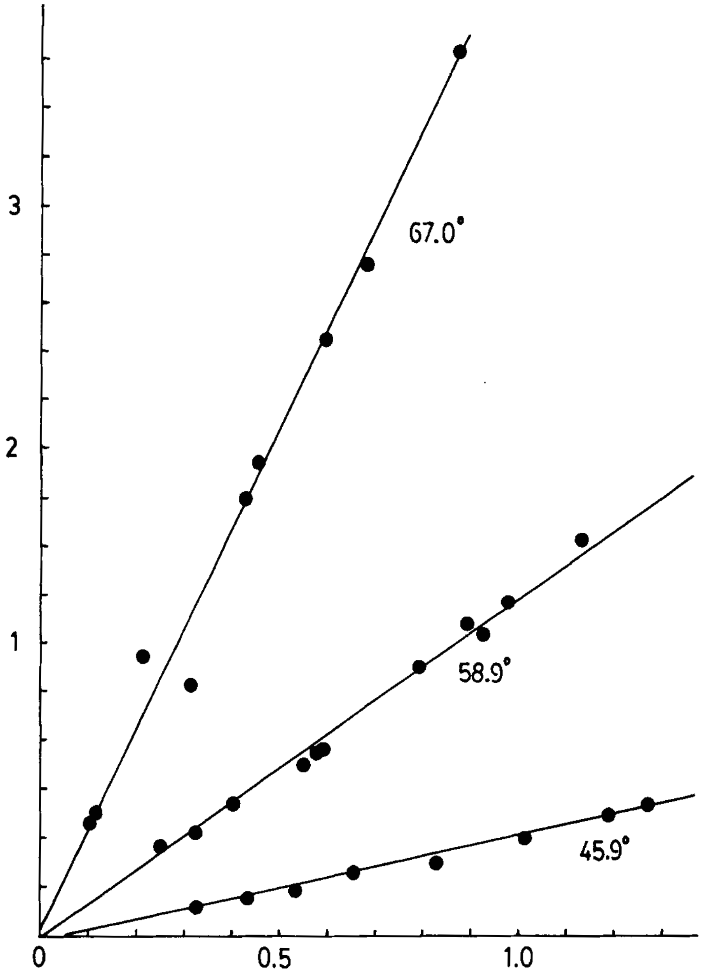

FIGURE 1 Plots of k_{obsd} *vs* $[P(OPr^i)_3]$ for the reaction of $(bmtb)Cr(CO)_4$ with that ligand in 1,2-dichloroethane at various temperatures. *Ordinate:* $10^3 k_{obsd}$, sec^{-1}. *Abscissa:* $[P(OPr^i)_3]$, M.

TABLE II
Second-order rate constants for displacement of chelating ligands coordinating through sulfur by trialkyl phosphites in DCE.

Complex	Temp. (degrees)	L	$10^5 k$ (M^{-1} sec^{-1})	Reference
$(bmtb)Cr(CO)_4$	57.9	$P(OEt)_3$	2.28(1)	this work
	45.9	$P(OPr^i)_3$	0.452(13)	
	58.9		1.44(5)	
	67.9		4.1(18)	
$(DTH)Cr(CO)_4$	44.3	$P(OPr^i)_3$	0.252	2a
	55.5		1.04	
	63.9		2.39	

TABLE III

[a]Activation parameters for displacement of chelating ligands coordinating through sulfur by trialkyl phosphites in DCE.

Complex	L	ΔH* (kJ mol^{-1})	ΔS* J K^{-1} mol^{-1}
[b]$(DTH)Cr(CO)_4$	$P(OEt)_3$	109.6(29)	37.7(84)
	$P(OPr^{i})_3$	100.0(38)	3.3(75)
[c]$(DTO)Cr(CO)_4$	$P(OEt)_3$	102.5(17)	20.5(59)
[d]$(dto)Cr(CO)_4$	$P(OEt)_3$	117.6(29)	56.1(96)
	$P(OPr^{i})_3$	104.2(13)	12.1(33)
[e]$(BTE)Cr(CO)_4$	$P(OEt)_3$	91.6(13)	−7.1(42)
	$P(OPr^{i})_3$	88.7(17)	−20.1(46)
[f]$(bmtb)Cr(CO)_4$	$P(OPr^{i})_3$	87.0(59)	−34.3(180)
[g]$(bmtb)Cr(CO)_4$	$P(OPr^{i})_3$	87.4(8)	−16.7(21)

[a]For consistency, all activation parameters have been recalculated from the original data. [b]DTH = 2,5-dithiahexane; ref. 2a. [c]DTO = 2,2,7,7-tetramethyl-3,6-dithiaoctane; ref. 2b. [d]dto = 3,6-dithiaoctane; ref. 2i. The values of k_{obsd} for L = $P(OEt)_3$ in DCE given in that paper are too large by a factor of exactly 10. [e]BTE = *cis*-bis(*t*-butylthio)ethylene; ref. 2j. [f]This work. [g]This work; CB solvent.

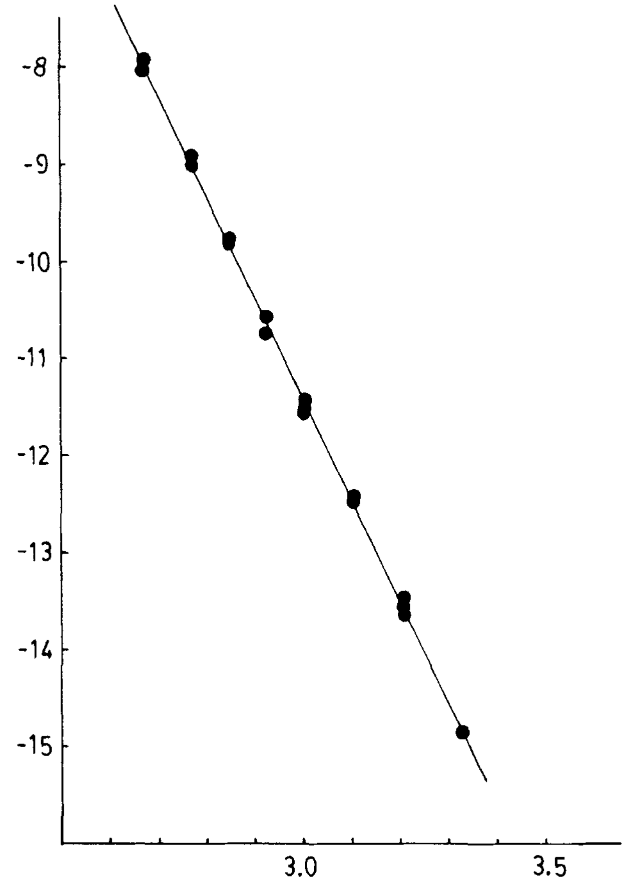

FIGURE 2 Eyring plot for the reaction of $(bmtb)Cr(CO)_4$ with triethyl phosphite in chlorobenzene at various temperatures. *Ordinate*: $10^3(1/T)$, °K^{-1}. *Abscissa*: ln(k/T), M^{-1} sec^{-1} °K^{-1}.

3.3(7.5) J K^{-1} mol^{-1} for $(DTH)Cr(CO)_4$[2a] *vs* −34.3(18.0) J K^{-1} mol^{-1} for $(bmtb)Cr(CO)_4$ differ significantly. These values suggested that different mechanisms which, given the similar reaction conditions employed might well be competitive, could be operative for $(dmtb)Cr(CO)_4$, and prompted a study of the activation parameters for the system over a wider temperature range. If two competing mechanisms were indeed operative over the temperature range accessible, a curved Eyring plot would be anticipated. Accordingly, the reaction of $(dmtb)Cr(CO)_4$ with $P(OEt)_3$ was investigated over a temperature range of 26° to 101° in CB. The data (Table I) obey rate law (*2*), and the Eyring plot, shown in Fig. 2, is linear. It thus may be concluded that only one mechanistic pathway is accessible, although two competing pathways as discussed above have been observed in a number of related systems, including the hexacarbonyls themselves.[8]

In order to determine which of the two limiting mechanisms is more applicable to the displacement of dmtb from $(dmtb)Cr(CO)_4$, it is instructive to compare activation parameters for displacement of chelating ligands by alkyl phosphites for a variety of $(chelate)Cr(CO)_4$ complexes in DCE. These data are given in Table III. Their similarities strongly suggest that all reactions proceed *via* similar mechanisms. It is observed, not unexpectedly, that the two "rigid" ring systems have lower enthalpies of activation and more negative entropies of activation than do the ring systems which have ethylene backbones. For the dissociative mechanism (*1-a*), the observed entropies of activation are equal to $\Delta S^*_1 + \Delta S^*_2 - \Delta S^*_{-1}$. For a rigid ring compared to a flexible one, it is reasonable to expect ΔS^*_1 to be less positive and ΔS^*_{-1} to be less negative as a consequence of an increase of degrees of freedom upon ring-opening, and a decrease of degrees of freedom upon ring-closure.

Further evidence for the dissociative pathway in these systems has come from determination of the volumes of activation for $(dto)Cr(CO)_4$ (dto = 3,6-dithiaoctane) and $(BTE)Cr(CO)_4$ (BTE = *cis*-bis(*t*-butylthio)ethylene) in their reactions with triethyl phosphite in DCE.[9] In both systems the volumes of activation are positive, supportive of a dissociative process, despite the observation that for the latter complex the entropy of activation for chelate ligand displacement by L is slightly negative.[2j]

It is interesting to note that the free energies of activation for these systems are quite similar, and thus in these systems there is little kinetic effect of ring-rigidity. A lower enthalpy of activation in the rigid ring complexes may be attributable to lowered basicities of the coordinating sulfurs as a consequence of the electron-withdrawing capabilities of the centers of unsaturation in the rigid ring backbones.

The results for $(chelate)Cr(CO)_4$ complexes in which the chelate ring coordinates through S may be contrasted to their analogues coordinating through N, for which significant sensitivity of mechanism to chelate ring-rigidity is observed.[4] In these systems, however, a third reaction pathway, involving rate-determining M-CO bond fission, is also competitive as a consequence of the "labilization" of the M-CO bond by the "hard base", *N*.[4c] Thus, for ligands of comparable basicities, a relatively small influence of ring rigidity could significantly alter the partitioning of rate among the available competitive pathways. In contrast, no pathway involving dissociative loss of CO has been noted for any $(chelate)M(CO)_4$ complex containing coordinating sulfur atoms.[2]

A most significant determinant of reaction mechanism in octahedral metal carbonyls and derivatives is the size of the metal atom. Thus, for the hexacarbonyls themselves, for example, decreased reactivity *via* associative paths relative to that observed for the corresponding complexes of Mo and W has been attributable to the small size of Cr. Many examples of this influence could be cited.[4a–4d,8a,8b] On this basis, and in the light of the evidence presented above, there is no reason to attribute the slightly negative entropies of activation observed for chelate ring closure in (bmtb)$Cr(CO)_4$ to an associative pathway.

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