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Preliminary communication

SOLID-STATE STRUCTURE AND REACTIVITY IN SOLUTION

V*. RING-CLOSURE IN THE (η^1-2,2,8,8-TETRAMETHYL-3,7-DITHIANONANE)TETRACARBONYLTUNGSTEN(0) INTERMEDIATE

GERARD R. DOBSON*, CHARLES B. DOBSON, D. ERIC HALVERSON and
SABER E. MANSOUR

Division of Chemistry, North Texas State University, Denton, TX 76203-5068 (U.S.A.)

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Summary

Pulsed laser flash photolysis of (η^2-DTN)W(CO)$_4$ (I, DTN = 2,2,8,8-tetramethyl-3,7-dithianonane) in 1,2-dichloroethane induces ring-opening to afford the solvated [(η^1-DTN)W(CO)$_4$] intermediate II. Rates of unimolecular ring-closure for this intermediate to afford I and of bimolecular combination of I with triisopropyl phosphite (L) have been determined, as have activation parameters for the ring-closure pathway. The relatively high enthalpy of activation (12.0(6) kcal/mol) suggests distortion in I induced upon chelate ring-closure. Rates of interaction of L at an "open" coordination site (one produced via CO loss from an octahedral (chelate)M(CO)$_4$ complex) are some two orders of magnitude faster than are those for a "shielded" site produced through ring-opening, suggestive of extensive steric interaction between the bidentate ligand and L for the combination process in the latter.

A number of kinetics studies for ligand-displacement of chelating sulfur-containing ligands have been reported [1—9]. While in some systems the inferred mechanism is quite complex, an important element in each is reversible ring-opening, and competition between ring-reclosure and attack by L (L = Lewis base; phosphines, phosphites) at the five-coordinate intermediate (eq. 1).

In several instances [2—6], it has been noted that $k_{-1} \sim k_2$, a surprising result given that ring-reclosure is unimolecular, while addition of L to the intermediate is bimolecular, and thus it is to be expected that entropy considerations would favor ring-reclosure over attack by L [10].

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*Part IV see Ref. 14.

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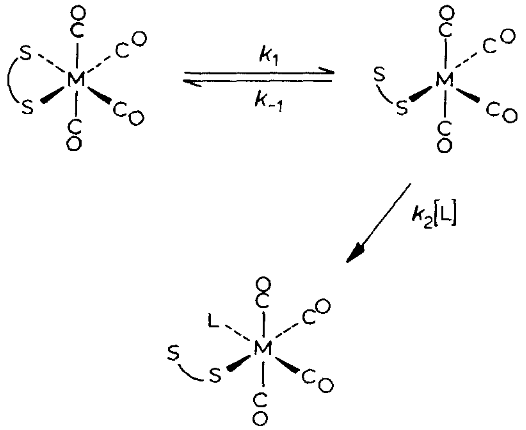
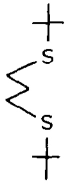


(1)

In cases for which ring-reclosure and ligand-addition have been found to be competitive, this result has been attributed to distortion of (chelate)-M(CO)$_4$ complexes from the ideal octahedral geometry which is observed, for example, in the parent hexacarbonyls [11], as a result of steric demands imposed by the chelate ring system. This distortion might thus constitute a potential energy barrier to ring-closure not present in a complex containing no chelate ring such as would be produced via the path governed by k_2 in eq. 1. In several instances, significant distortions observed in (chelate)-M(CO)$_4$ species have been correlated to unexpectedly small ratios of k_{-1}/k_2 [12–14].

The recent determination of the rate of chelate ring reclosure in (chelate)-M(CO)$_4$ complexes after ring-opening induced via pulsed laser flash photolysis has prompted a similar investigation of (DTN)W(CO)$_4$ (DTN = 2,2,8,8-tetramethyl-3,7-dithianonane (1)), of known structure [12], in an effort to determine the energy barrier to ring reclosure. The results of that study are the subject of this report.



(1)

Experimental

The synthesis of DTN and of (DTN)W(CO)$_4$ have been reported [2]. Purification of the solvents, 1,2-dichloroethane (DCE) and chlorobenzene (CB) was carried out through fractional distillation over P_4O_{10} under nitrogen. Triisopropyl phosphite (L) was purified via vacuum distillation from sodium.

Pulsed laser flash photolysis studies were carried out employing a Quantel Nd:YAG laser (355 nm, 11 ns FWHI) monitoring 430 nm. Samples of

(DTN)W(CO)$_4$ and solvent (2 mg/10 ml) in the absence and in the presence of L were degassed with purified N_2 bubbling prior to irradiation. Each experimental value for the observed rate constant* is the average of five kinetics runs. Plots of these rate constants, k_{obsd} vs. [L] in both DCE and CB are exhibited in Fig. 1.

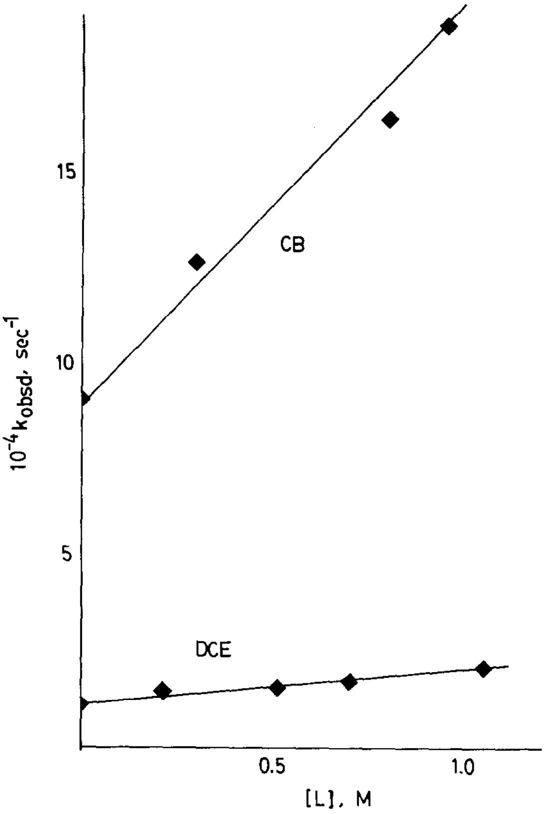


Fig. 1. Plots of k_{obsd} vs. [L] for reaction of [(η^1-DTN)W(CO)$_4$] with triisopropyl phosphite in DCE and CB at 22°C.

Results and discussion

Scheme 1 illustrates possible reaction pathways which have been inferred from pulsed laser flash photolysis studies for a number of (chelate)M(CO)$_4$ systems (M = Cr, Mo, W) [15—17]. Plots of k_{obsd} vs. [L] (Fig. 1) for the disappearance of the intermediate generated from (DTN)W(CO)$_4$ obey the rate law of eq. 2, where the observed rate constants, $k_{obsd} = k_{-1} + k_2[L]$, and

$$-d[\text{Int}]/dt = k_1[\text{Int}] + k_2[\text{Int}][L], \qquad (2)$$

plots of $\ln(A_t - A_\infty)$ vs. time (A_t and A_∞ are the absorbances of the reaction solutions at time t and infinite time, respectively) were linear over several

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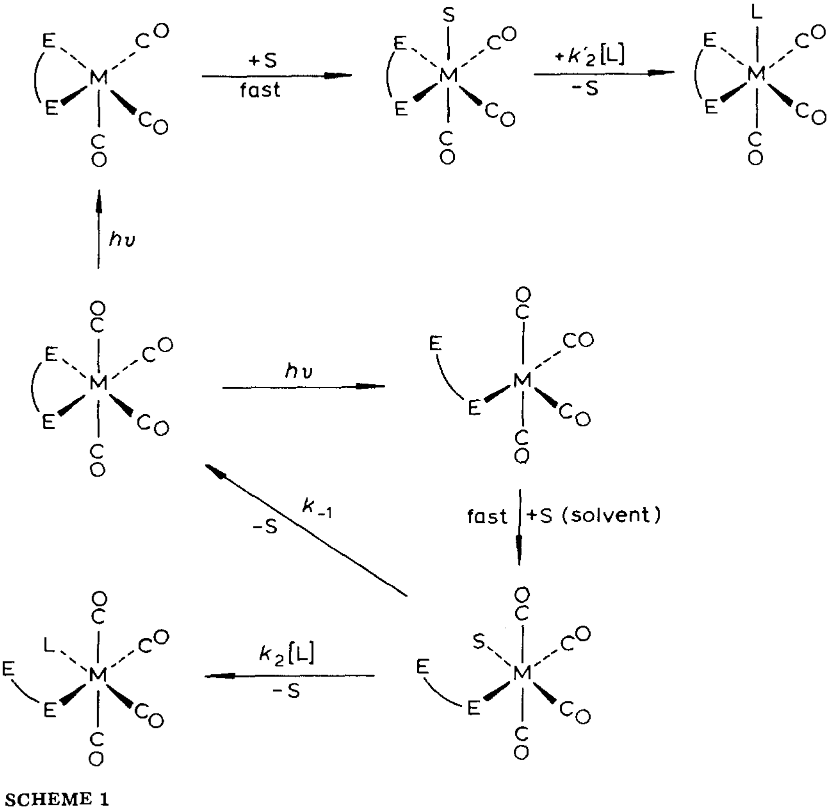
*Values of individual values of k_{obsd} are available from the authors on request.

half lives. This rate law is identical to that observed for similar studies involving (NP)M$(CO)_4$ (NP = 1-diethylamino-2-diphenylphosphinoethane; M = Cr, Mo) in the absence and presence of L in DCE or CB, for which photolytically-induced ring-opening followed by competitive ring reclosure and attack at the [(η^1-NP)M$(CO)_4$] intermediate by L (paths governed by k_{-1} and k_2, respectively, Scheme 1) were inferred [15]. This scheme dictates that the product of the interaction of the intermediate with L affords (η^1-DTN)(L)W$(CO)_4$; in several instances, *cis*-(η^1-DTN)(L)W$(CO)_4$ products have been characterized [6].



SCHEME 1

In the present study, as was observed for the (NP)M$(CO)_4$ systems, significant differences in rate for each reaction pathway as a function of the identity of the solvent (Fig. 1), indicative of interaction of the solvent and the [η^1-DTN)W$(CO)_4$] intermediate, were observed. The rates via each path are about an order of magnitude greater in the less polar CB than in more polar DCE, indicative of a greater ease of solvent displacement via either path for CB.

Activation parameters from data at five temperatures over a range of 23.9 to 61.7°C for the ring-reclosure path in DCE were determined to be, $\Delta H^{\neq}$ 12.0(6) kcal/mole and $\Delta S^{\neq}$ 0.7(17) eu. The entropy of activation is not unreasonable in view of the inferred displacement of solvent proposed on the basis of the solvent-dependence for this pathway. The enthalpy of activation, the first to be reported for ring-closure in a metal carbonyl system, might be considered to be surprisingly high for a process which involves a five-coordinate, if solvated intermediate. It suggests a barrier to ring-reclosure, one which may result from distortions induced upon ring-closure; such distortions are observed to be present in $(DTN)W(CO)_4$ in the solid state [12].

TABLE 1

RATES OF REACTION OF FIVE-COORDINATE INTERMEDIATES IN DCE VIA VARIOUS PATHWAYS [a]

Intermediate	L	$10^6 k_{-1}$ (sec^{-1})	$10^6 k_2$ ($M^{-1} sec^{-1}$)	$10^6 k'_2$ ($M^{-1} sec^{-1}$)
$[(\eta^2\text{-phen})Cr(CO)_3]$ [b]	$P(OPr^i)_3$	—	—	3.1(2)
	$P(OEt)_3$	—	—	3.2(1)
$[(\eta^1\text{-NP})Cr(CO)_4]$ [c]	$P(OPr^i)_3$	0.109(2)	0.027(3)	—
$[(\eta^1\text{-NP})Mo(CO)_4]$	$P(OPr^i)_3$	0.042(1)	0.011(2)	—
$[(\eta^2\text{-BTE})Cr(CO)_3]$ [d]	$P(OPr^i)_3$	—	—	2.8
$[(\eta^1\text{-DTN})W(CO)_4]$	$P(OPr^i)_3$	0.0117(4)	0.0081(6)	—

[a] The pathways are those shown in Fig. 1. [b] phen = *o*-phenanthroline; ref. 16. [c] NP = 1-diethylamino-2-diphenylphosphinoethane; ref. 15. [d] BTE = 2,2,7,7-tetramethyl-3,6-dithiaoct-4-ene; ref. 17.

The ratios of k_2/k_{-1} are 0.70 (DCE) and 0.78 (CB). The competitive ability via association between L and the intermediate compared to ring-reclosure (similar values of $\Delta G^{\neq}$) is surprising given that a significantly less favorable entropy of activation is expected for the associative path. This observation suggests a lower $\Delta H^{\neq}$ for attack by L, which in turn might indicate less distortion from ideal octahedral geometry in $(\eta^1\text{-DTN})(L)W(CO)_4$ than in $(DTN)W(CO)_4$. Unfortunately, structural data for this comparison are not available.

This point is further emphasized through comparison of available data for reaction in DCE of such five coordinate intermediates via the three reaction paths illustrated in Scheme 1 (Table 1). It can be seen that interaction of L at an "open" coordination site (one not involving ring-opening, governed by k_2') is some two orders of magnitude faster than is ring-closure. While it is possible that this effect might arise in part from differing degrees of solvation of the respective intermediates, it is more reasonably attributed to distortion induced through ring-closure, but not through association of a monodentate ligand with an intermediate.

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