Kinetics and mechanism of CO substitution reactions of $M_3(CO)_{12}$ (M = Fe, Ru, Os) in the presence of (p-$CH_3OC_6H_4)_2TeO$

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Abstract

The rates and activation parameters for CO substitution of $M_3(CO)_{12}$ (M = Fe, Ru, Os) in the presence of (p-$CH_3OC_6H_4)_2TeO$ are reported. The rates are first-order in concentrations of $M_3(CO)_{12}$ and telluroxide, and zero-order in entering ligand. The $\Delta H^\ddagger$ values for these reactions vary from 11 to 14 kcal/mol, with $\Delta S^\ddagger$ values changing between −12 and −22 cal/mol K. The reactivities of $M_3(CO)_{12}$ towards R_2TeO decrease in the order Fe > Ru > Os. A mechanism was proposed in which the rate-determining step involves nucleophilic attack of the O atom of R_2TeO at a C atom of a carbonyl group. This is then followed by O atom transfer to form the good leaving group CO_2 and a reactive intermediate which readily reacts with the entering ligand to afford the formation of monosubstituted products. Compared with similar reactions of $(CH_3)_3NO$, the R_2TeO reagent has greater O atom transfer selectivity towards $M_3(CO)_{12}$ complexes. This is discussed in terms of CO bridging effects in the reaction transition states.

Introduction

The use of Me_3NO as an O atom transfer reagent in eliminating CO from metal carbonyl complexes has been especially successful in the syntheses of substituted metal carbonyl clusters [1]. In an effort to elucidate the mechanism of O atom transfer to metal carbonyl complexes, kinetic studies were made on CO substitution reactions of metal carbonyls in the presence of Me_3NO [2]. The rates of these reactions were found to be first-order in concentrations of complexes and of trimethylamine *N*-oxide, and zero-order in entering ligand concentration. A reaction mechanism was proposed which involves attack of the O atom of Me_3NO on a C atom of a CO group of metal carbonyl, converting it to CO_2 which is a good leaving group. Its departure affords a coordinatively unsaturated intermediate, which rapidly reacts with the entering ligand to give the monosubstituted product. For the iron triad complexes $M_3(CO)_{12}$ (M = Fe, Ru, Os), the relative reactivity follows the order Fe > Ru > Os, in contrast to the opposite order observed [3] for reactions of the mononuclear compounds $M(CO)_5$ of this triad. This was explained in terms of the decreasing ease of formation of bridging carbonyls [6] in the transition states for the $M_3(CO)_{12}$ complexes, which helps delocalize the negative charge developed upon nucleophilic attack of the O atom on a carbonyl carbon and facilitates reaction.

Kinetic studies have been extended to other O atom transfer reagents [4]. The reaction of $M_2(CO)_{10}$ (M = Mn and Re) with (p-$MeOC_6H_4)_2TeO$ was investigated [5], and the results were compared with that for the reaction of $M_2(CO)_{10}$ (M = Mn and Re) with Me_3NO. Both reactions yield the same monosubstituted products in the presence of the entering ligand. Although the two metal carbonyl complexes have similar reactivities towards Me_3NO, $Mn_2(CO)_{10}$ reacts 28 times faster than $Re_2(CO)_{10}$ when (p-$MeOC_6H_4)_2TeO$ is used as O transfer reagent. It was suggested [5] that this reactivity difference results from the energetics of formation of different structures of the transition states for the reactions. The less basic telluroxide would bring less electron density to the metal carbonyl, and thus require less CO bridge formation in the transition state than would the more basic Me_3NO. This then may increase the selectivity of telluroxide towards the triad metal cluster carbonyl complexes, because the reactivities would be less a factor of CO bridging for these reactions than for the reactions with Me_3NO. In order to further test the importance of CO bridging in such reactions, an investigation of the reactions of $M_3(CO)_{12}$ with (p-$MeOC_6H_4)_2TeO$ was undertaken for comparison with what is known [2] for similar reactions with Me_3NO.

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Experimental

Compounds and solvents

$M_3(CO)_{12}$($M = Fe$, Ru, Os) were obtained from Aldrich Chemical Co. and used without further purification. $P(OMe)_3$ was obtained from Merck-Schuchardt Co. $CHCl_3$ and C_2H_5OH were dried with P_2O_5 and $Mg(OC_2H_5)_2$, respectively, and distilled under a N_2 atmosphere prior to use. (p-MeOPh)$_2$TeO was synthesized and purified by the literature method [7]. Pyridine (Py) was distilled over CaH_2 prior to use.

Kinetic measurements

UV–Vis spectral measurements were obtained on a Shimadzu UV-260 spectrophotometer with 1 cm quartz cells. IR spectra were recorded on a Nicolet-5DX FT-IR spectrophotometer with a 0.5 mm CaF_2 cell. Rate data for the appearance of product metal complexes were obtained by monitoring UV–Vis spectral changes. All the reactions were performed under pseudo-first-order conditions with the concentration of O atom transfer reagent and that of ligands being at least 10 times greater than that of $M_3(CO)_{12}$. In a typical experiment with the UV spectrophotometer, solutions of (p-MeOPh)$_2$TeO and ligand in $CHCl_3$ were mixed with C_2H_5OH in a cuvette, which then was placed in a temperature-regulated jacket. Constant temperature was maintained by the internal circulating bath of a Shimadzu UV-260 thermostat. After 30 min of temperature equilibration, a solution of $M_3(CO)_{12}$ in $CHCl_3$ was syringed into the cuvette, which was then rigorously shaken, and the resultant spectral changes were monitored with time. Plots of $\ln(A_\infty - A_t)$ versus time for the appearance of products were linear over 2–3 half-lives (linear correlation coefficient > 0.995). The slopes of these lines gave values of k_{obs}.

Results

The rates of reaction (eqn. (1)) of $M_3(CO)_{12}$ with

$$M_3(CO)_{12} + (p\text{-MeOPh})_2TeO + L \longrightarrow M_3(CO)_{11}L + (p\text{-MeOPh})_2Te + CO_2 \quad (1)$$

($M = Fe$, Ru, Os; $L = P(OMe)_3$, py)

entering ligands in the presence of (p-MeOPh)$_2$TeO were monitored by following changes in the UV–Vis absorption spectra with time. Spectral changes of reaction mixtures show good isosbestic points (Figs. 1 and 2), consistent with good stoichiometric reactions affording monosubstituted products. Disubstituted products appear and fragmentation occurs for $M = Fe$ with long reaction times. In all cases, the IR spectra of the initial reaction products were in agreement with re-

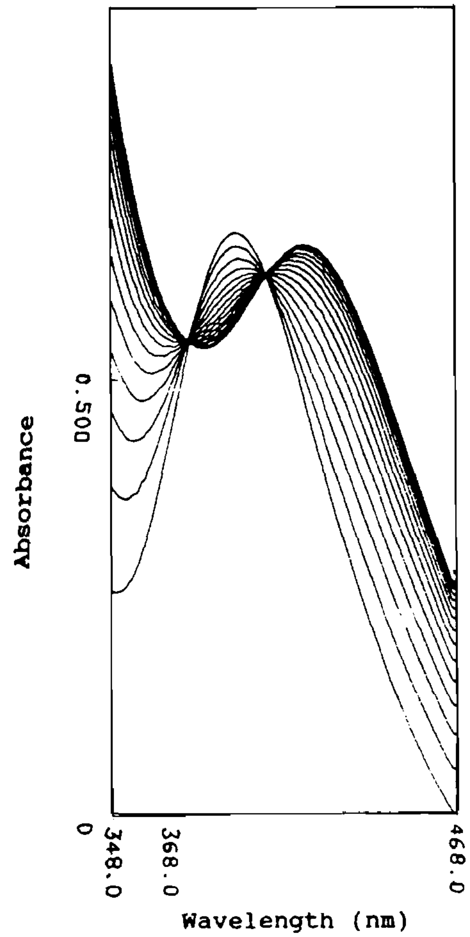


Fig. 1. UV–Vis absorbance changes vs. time for the reaction $Ru_3(CO)_{12}$ + Py + (p-MeOPh)$_2$TeO → $Ru_3(CO)_{11}$Py + CO_2 + (p-MeOPh)$_2$Te in $CHCl_3$/EtOH (vol./vol. = 99/1) mixed solvent at 11.7 °C.

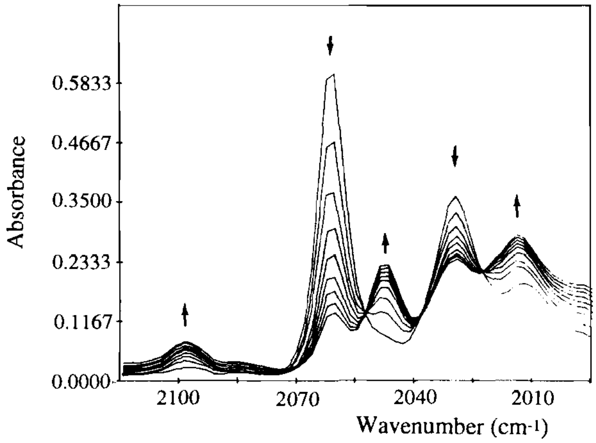


Fig. 2. IR absorbance of ν_{CO} vs. time for the reaction $Ru_3(CO)_{12}$ + $P(OMe)_3$ + (p-MeOPh)$_2$TeO → $Ru_3(CO)_{11}P(OMe)_3$ + CO_2 + (p-MeOPh)$_2$Te in $CHCl_3$/EtOH (vol./vol. = 99/1) mixed solvent at room temperature.

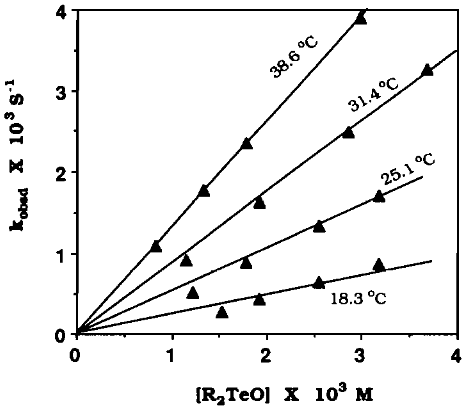


Fig. 3. Plot of k_{obs} vs. $(p\text{-MeOPh})_2TeO$ concentration for the reaction $Os_3(CO)_{12} + P(OMe)_3 + (p\text{-MeOPh})_2TeO \rightarrow Os_3(CO)_{11}\text{-}P(OMe)_3 + CO_2 + (p\text{-MeOPh})_2Te$ in $CHCl_3$ solvent.

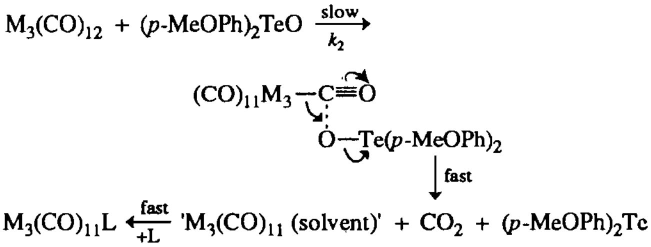
ported spectra for known compounds [8]. Plots of k_{obs} versus $[(p\text{-MeOPh})_2TeO]$ (Fig. 3) show a first-order dependence on concentration of $(p\text{-MeOPh})_2TeO$. The rates of reaction are zero-order in [L] (Table 1), and the reactions obey a second-order rate law (eqn. (2)).

$$-d[M_3(CO)_{12}]/dt = k_2[M_3(CO)_{12}][p\text{-MeOPh})_2TeO] \qquad (2)$$

Rate constants and activation parameters are given in Table 2. At fixed concentrations of $(p\text{-MeOPh})_2TeO$, the rates of reaction show an inverse dependence on the concentration of C_2H_5OH (Fig. 4).

Discussion

The reactions of $M_3(CO)_{12}$ (M = Fe, Ru, Os) with entering ligands (L = $P(OMe)_3$, Py) in the presence of $(p\text{-MeOPh})_2TeO$ affords the monosubstituted products $M_3(CO)_{11}L$ (eqn. (1)). This was confirmed by the fact that the IR spectra of all reaction products in the CO stretching region were in good agreement with reported spectra for the known compounds [8]. The rates of disappearance of $M_3(CO)_{12}$ follow a second-order rate law (eqn. (2)), first-order in the concentrations of $M_3(CO)_{12}$ and of $(p\text{-MeOPh})_2TeO$, but zero-order in L concentrations (Table 1). This rate law and kinetic behavior is the same as that reported earlier for the corresponding reactions of mononuclear metal carbonyls and metal clusters, suggesting the same mechanism is involved for these reactions. The rate-determining step of the O atom transfer reactions is believed to involve a nucleophilic attack of the O atom of $(p\text{-MeOPh})_2TeO$ on a C atom of a CO (Scheme 1), accompanied by an inner sphere electron-transfer process.



Scheme 1.

This results in the oxidation of CO to CO_2, which is a good leaving group. Its departure from the cluster generates the 'coordinatively unsaturated' active intermediate '$M_3(CO)_{11}$ (solvent)', which then readily reacts with the entering ligand to form the monosubstituted product $M_3(CO)_{11}L$.

The associative rate-determining pathway is further supported by the activation parameters for the reactions,

TABLE 1. Observed rate constants for the reaction (eqn. (1)) at different ligand concentrations

$M_3(CO)_{12}$	L	T (°C)	$[R_2TeO] \times 10^3$ (M)	$[L] \times 10^3$ (M)	$k_{obs} \times 10^3$ (s)
$Fe_3(CO)_{12}$[a]	$P(OMe)_3$	12.0	2.06	2.00	10.9
				6.65	10.6
				13.3	10.7
$Ru_3(CO)_{12}$[a]	Py	18.2	0.940	0.436	0.598
				0.872	0.616
				1.91	0.625
	$P(OMe)_3$	18.2	1.03	0.575	0.838
				1.15	0.815
				2.30	0.862
$Os_3(CO)_{12}$[b]	Py	38.4	3.18	0.555	5.81
				1.11	5.78
				3.33	5.85

[a] In $CHCl_3$–C_2H_5OH (vol./vol. = 99/1). [b] In $CHCl_3$.

TABLE 2. Second-order rate constants and activation parameters of the reactions (eqn. (1))

$M_3(CO)_{12}$	L	T (°C)	k_2 ($M^{-1}S^{-1}$)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol K)
$Fe_3(CO)_{12}$[a]	Py	5.4	2.72	11.6 ± 0.7	−14.5 ± 2.4
		11.1	4.00		
		18.2	5.82		
		25.2	12.5		
	$P(OMe)_3$	5.1	2.70	11.8 ± 0.4	−14.1 ± 1.1
		12.0	4.98		
		18.6	7.70		
		25.0	12.1		
$Ru_3(CO)_{12}$[a]	Py	11.8	0.308	13.8 ± 0.8	−12.3 ± 2.5
		18.2	0.598		
		24.8	1.08		
		32.2	1.63		
	$P(OMe)_3$	11.8	0.317	13.3 ± 0.9	−13.9 ± 3.2
		18.2	0.723		
		24.8	1.15		
		32.2	1.72		
$Os_3(CO)_{12}$[a]	Py	25.1	0.0345		
$Os_3(CO)_{12}$[b]	Py	18.3	0.348	11.4 ± 0.4	−21.5 ± 1.2
		25.1	0.602		
		31.4	0.927		
		38.6	1.30		
	$P(OMe)_3$	18.3	0.352	12.0 ± 0.3	−19.4 ± 0.7
		25.1	0.551		
		31.6	0.921		
		38.4	1.39		

[a] In $CHCl_3$–C_2H_5OH (vol/vol. = 99/1). [b] In $CHCl_3$.

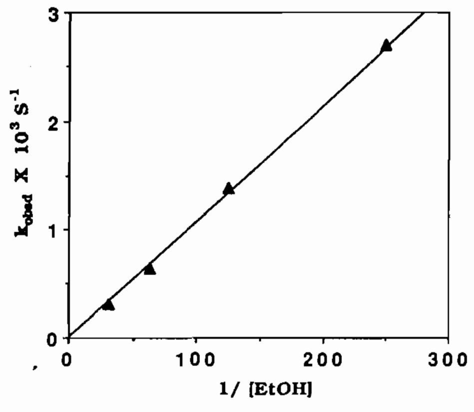


Fig. 4. Plot of k_{obs} vs. 1/[EtOH] for the reaction $Ru_3(CO)_{12} + P(OMe)_3 + (p\text{-}MeOPh)_2TeO \rightarrow Ru_3(CO)_{11}P(OMe)_3 + CO_2 + (p\text{-}MeOPh)_2Te$ at 24.8 °C with $[(p\text{-}MeOPh)_2TeO] = 5.15 \times 10^{-4}$ M.

which exhibit low values of $\Delta H^{\ddagger}$ and negative values of $\Delta S^{\ddagger}$ (Table 2). The rates of reaction (eqn. (1)) in pure $CHCl_3$ solvent are too fast to follow by ordinary spectral techniques. Deactivation of the telluroxide was achieved by adding C_2H_5OH to the reaction solution. A quantitative study of the effect of added C_2H_5OH shows that the rates of reactions are inversely proportional to the concentration of C_2H_5OH in the solvent (Fig. 4). This appears to be due to the rapid hydrogen-bonding equilibrium (eqn. (3)) which decreases the

$$(p\text{-}MeOPh)_2TeO + C_2H_5OH \rightleftharpoons (p\text{-}MeOPh)_2TeO\text{---}H\text{–}OC_2H_5 \quad (3)$$

concentration of the active free telluroxide in the reaction mixture. Similar results were observed for the reaction of $M_3(CO)_{12}$ with Me_3NO [2].

Previous studies [9] showed that the rates for O atom transfer reaction increased with increasing CO stretching frequencies of the metal carbonyls and with increasing basicities of the O atom of the transfer reagent. These results imply the rate-determining step involves nucleophilic attack of the O atom on a C atom of CO. The results (Table 2) show that the rates of reactions decrease in the order $Fe_3(CO)_{12} > Ru_3(CO)_{12} > Os_3(CO)_{12}$, which is contrary to what is expected on the basis of the IR values of ν_{CO}. These ν_{CO} values suggest that the positive charge on carbon of the carbonyl groups increases in the order Fe < Ru < Os [10], and this would enhance nucleophilic attack in the same order [6]. Therefore the reason given for the contrary order observed is that the transition state has the ability to form bridging carbonyls in the decreasing order Fe > Ru > Os [4]. Bridging carbonyls are more electron withdrawing [11] and can better accommodate the developing negative charge on the metal cluster in the transition state, which in turn facilitates nucleophilic attack and enhances reactivity.

It is of interest to note that $Fe_3(CO)_{12}$ reacts 360 times faster than $Os_3(CO)_{12}$ (Table 3). This larger difference in the reactivities of the complexes towards telluroxide compared with that toward Me_3NO (40 times) is consistent with what was observed for reactions of the carbonyl $M_2(CO)_{10}$ complexes. Although the absolute reactivities of $(p\text{-MeOPh})_2TeO$ and Me_3NO cannot be compared because of the unknown concentration of free oxide, the telluroxide has greater selectivity in the reactions with the triad metal cluster complexes. Since it is known [4] that telluroxide is less basic than $(CH_3)_3NO$, it follows that less negative charge is developed on the metal cluster in the transition state for the reaction with telluroxide than with Me_3NO. It is believed that negative charge on the metal cluster is one of the driving forces for the formation of bridging COs [12]. The more basic Me_3NO puts more negative charge on the cluster, making it easier for CO bridge formation in the transition state for the reaction with Me_3NO than with $(p\text{-MeOPh})_2TeO$. This may account for the greater selectivity of the telluroxide reagent.

This rationalization for the greater selectivity of $(p\text{-}CH_3OC_6H_4)_2TeO$ over $(CH_3)_3NO$ is supported by the rates of reactions of $M(CO)_6$ (M = Cr, Mo, W) with $(CH_3)_3NO$ [2] and with $(p\text{-}CH_3C_6H_4)_2TeO$. The rates of reactions of $M(CO)_6$ (M = Mo, W) with the telluroxide were measured, in order to compare them with that for $Cr(CO)_6$ [4]. The results show that the rates decrease in the order Mo > W > Cr (Table 3), and that the differences in rates are small as was observed [2] for reactions of $M(CO)_6$ with $(CH_3)_3NO$. However, the relative reactivity order of $M(CO)_6$ towards $(p\text{-}CH_3OC_6H_4)_2TeO$ is different from that with $(CH_3)_3NO$ (W > Mo > Cr) [2]. This difference may result from the weaker Mo–CO bond compared with W–CO and Cr–CO [13]. Therefore the M–CO bond-breaking process contributes more in the reaction transition state for reactions of $(p\text{-}CH_3OC_6H_4)_2TeO$ than for reactions of $(CH_3)_3NO$. Such an explanation is consistent with R_2TeO being less basic than is $(CH_3)_3NO$, and that bond-making in the transition state is less important for the reaction with R_2TeO than with $(CH_3)_3NO$.

TABLE 3. Second-order rate constants for reactions of metal carbonyl complexes with oxides

Complex	k_2 with R_2TeO (s^{-1} M^{-1})	k_2 with Me_3NO (s^{-1} M^{-1})
$Fe_3(CO)_{12}$	12.5[a]	4.18[c]
$Ru_3(CO)_{12}$	0.959[a]	0.822[c]
$Os_3(CO)_{12}$	0.0345[a]	0.104[c]
$Mn_2(CO)_{10}$	1.07×10^{-2}[b]	0.272[d]
$Re_2(CO)_{10}$	3.84×10^{-4}[b]	0.172[d]
$Cr(CO)_6$	3.62×10^{-3}[e]	0.147[g]
$Mo(CO)_6$	1.06×10^{-2}[f]	0.190[g]
$W(CO)_6$	5.96×10^{-3}[f]	0.366[g]

[a] At 25 °C. [b] Ref. 5 at 24 °C. [c] Ref. 2b at 25.6 °C. [d] Ref. 5 at 23.4 °C. [e] Ref. 4 at 18.5 °C in $CHCl_3$. [f] At 18.5 °C in $CHCl_3$. [g] Ref. 2 at 25 °C in CH_2Cl_2.

It was suggested [14] that the $(p\text{-MeOPh})_2TeO$ compound might be associated in the solid state or in solution, based on the fact that some of these heavier element oxides, such as Ph_3SbO [15], do form dimers. Unfortunately the results of this study cannot answer the question of association of $(p\text{-MeOPh})_2TeO$ in solution, but the first-order dependence of the rate of reaction on the concentration of $(p\text{-MeOPh})_2TeO$ suggests the associated species could not predominate in solutions of the concentrations used in this study.

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