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Kinetic studies of CO substitution of metal carbonyls in the presence of O-atom transfer reagents*

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CONTENTS

ABSTRACT

Kinetic studies of CO substitution of metal carbonyls in the presence of O-atom transfer reagents show the reaction rates are first-order in metal carbonyl and in O-atom transfer reagent concentrations, but zero-order in entering-ligand concentration. This suggests an associative mechanism where a carbonyl C-atom is attacked by the O-atom of the reagent, affording the good leaving group CO_2 and generating an active intermediate which readily reacts with the entering ligand to produce the monosubstituted product. Metal carbonyls that have been investigated include the mononuclear compounds $M(CO)_6$ (M = Cr, Mo, W), $M(CO)_5L$, and $M(CO)_5$ (M = Fe, Ru, Os) as well as the cluster compounds ($M_3(CO)_{12}$ (M = Fe, Ru, Os), $M_2(CO)_{10}$ (M = Mn, Re), $M_3(CO)_{11}L$ (M = Fe, Ru, Os), and $M_4(CO)_{12}$ (M = Co, Ir). Most

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* Dedicated to the memory of Professor John C. Bailar, Jr.

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of the studies involve reactions with $(CH_3)_3NO$, but other O-atom transfer reagents studied include C_6H_5IO, other amine oxides, pyridine oxides, $(p\text{-}CH_3OC_6H_4)_2EO$ (E = Se, Te), $(C_6H_5)_3EO$ (E = P, As, Sb), and $(C_6H_5)_2SO$. Various factors relating to the metal carbonyls and to the O-atom transfer reagents that effect the rates of CO substitution are discussed.

1. INTRODUCTION

The generation of a vacant coordination site on the metal atom in a metal carbonyl complex is of general interest. Such "coordinatively unsaturated" species are important intermediates in catalytic processes and in the syntheses of organometallic compounds [1]. One way to generate these active intermediates is to release CO from the metal atom in a stable metal carbonyl complex. Generally speaking, this can be done in three ways: (a) thermolysis, (b) photolysis, and (c) chemical assistance. The first two methods involve providing enough energy to excite the molecules from ground states to transition states, which then is followed by cleavage of the M−C bond to generate "coordinatively unsaturated" intermediates. The third way is to use chemicals to interact with the carbonyl complexes, so as to decrease the affinity between the metal and the carbon atoms. Chemicals frequently used for this purpose are Lewis acids [2,3], Lewis bases [2,3] or redox reagents [2–5] (sometimes electrodes).

For example, it is known that the CO exchange of $Fe(CO)_5$ can be catalyzed by acid [6]. This is believed to involve protonation at the metal, taking advantage of the metal basicity [7]. However, Lewis acids often interact with metal carbonyls by accepting a pair of electrons from the oxygen atom of the carbonyl group [8]. This then results in a weakening of the M−C bond by decreasing its σ-donation to the metal atom. Lewis bases can also weaken the M−C bond by nucleophilic attack at the carbon atom of a carbonyl group [9], which decreases the π-back bonding from metal to CO. The use of redox reagents is to oxidize or reduce some very stable 18-e complexes to 17-e or 19-e complexes, which are well known [4] to be ligand-substitution labile. In this article, attention is focused on the reactions of metal carbonyls with O-atom transfer reagents. The reaction is believed to involve nucleophilic attack of an oxygen atom at the carbon atom of a carbonyl group, which annihilates CO as a ligand due to transforming it into the good leaving group CO_2 (see Scheme 1, below). This results in the formation of an active coordination site on the metal, rendering it useful in syntheses of organometallic compounds and in applications as a homogeneous catalyst.

The earliest report of the reaction of an amine oxide with a transition metal carbonyl complex was made by Hieber and Lipp [10] in 1959. It was reported that pyridine *N*-oxide reacts with $Fe(CO)_5$ to yield pyridine and iron oxides. It was later found [11] that aliphatic, aromatic and heterocyclic amine oxides were all readily deoxygenated by $Fe(CO)_5$ in boiling butyl ether to the corresponding amine. However, it was not until 1975 that Shvo and Hazum [12] first reported a facile synthesis in moderate to good yield of organic carbonyl complexes by using amine oxides to promote the formation of olefin derivatives of metal carbonyls.

Trimethylamine *N*-oxide is the amine oxide most commonly used in these reactions. It is an inexpensive, white crystalline hygroscopic material available commercially as the dihydrate. The high volatility of trimethylamine produced in the reaction leads to its facile removal from reaction mixtures. In a very detailed study [13], addition of $Fe(CO)_5$ in THF to a suspension of Me_3NO in THF was found to give a red solution with evolution of CO_2. An orange compound was isolated and identified as $Fe(CO)_4NMe_3$. Since these early reports on the reactions of Me_3NO with iron carbonyls, investigations have been extended to many other metal carbonyl complexes [14,15]. Its application has been especially successful in the syntheses of substituted metal carbonyl clusters. [16].

Despite the wide use of amine *N*-oxides in eliminating CO from metal carbonyl complexes for the syntheses of metal carbonyl derivatives, no kinetic studies had been done to elucidate the mechanisms of this type of reaction until 1987 [17]. Because of the generality of this type of reaction and its relevancy to homogeneous catalytic processes, we decided to investigate the kinetics and mechanisms of the reaction. This review is a summary of results from these studies.

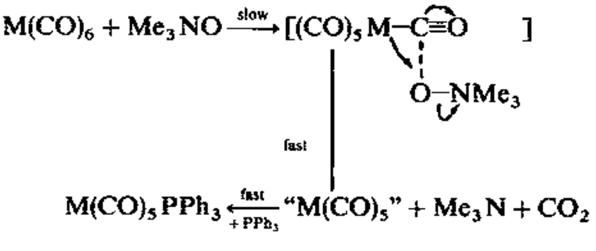
2. MONONUCLEAR METAL CARBONYLS

2.1 Reactions of $M(CO)_6$ ($M = Cr, Mo, W$) with Me_3NO

The first kinetic study [17] on O-atom transfer to metal carbonyls was on the reaction of $M(CO)_6$ ($M = Cr$, Mo, W) with PPh_3 in the presence of Me_3NO in CH_2Cl_2 (eqn. (1)).

$$M(CO)_6 + PPh_3 + Me_3NO \rightarrow M(CO)_5PPh_3 + Me_3N + CO_2 \qquad (1)$$

Rates of reaction of $M(CO)_6$ with Me_3NO in the presence of PPh_3 were found to be first-order in concentrations of $M(CO)_6$ and of Me_3NO, but zero-order in PPh_3 concentration. The second-order rate law is consistent with an associative process, where both bond-making by attack of the Me_3NO nucleophile and bond-breaking of the M–C bond contribute to the energetics of the rate-determining step. A mechanism was suggested which involves attack on a CO carbon with the formation of coordinatively unsaturated intermediates of the type "$M(CO)_5$" ($M = Cr$, Mo, W), followed then by their rapid reactions with entering ligands (Scheme 1).



Scheme 1.

This mechanism is supported by the low values of $\Delta H^\ddagger$ and negative values of $\Delta S^\ddagger$ (Table 1), which are typical of an associative reaction. An alternative four-centered mechanism was ruled out by the fact that the rate of CO replacement with PPh_3 in the presence of Me_3NO is much faster than is the rate of Me_3N replacement with PPh_3 in $M(CO)_5NMe_3$. The rate increases in the order W > Mo > Cr, although the differences are small (Table 1). Previous studies [18] suggest the ease of nucleophilic attack on the C-atom of a carbonyl correlates with its CO stretching frequency. The higher the value of ν_{CO}, the more positive is the C-atom and the more readily it is attacked by an entering nucleophile. On this basis alone, the rates are expected to vary in the order Mo > Cr > W. However, experiments show a more rapid rate of reaction for $W(CO)_6$, which is seen to be due to a more favorable $\Delta S^\ddagger$ term (Table 1). This suggests the larger size of W relative to Mo and Cr facilitates formation of a less restricted transition state for W.

Another unexpected result was that the nucleophilic strength of Me_3NO in these reactions is comparable to the strengths of CH_3^- [19(a)] and $C_6H_5CH_2^-$ [19(b), (c)] in somewhat similar reactions. This comparison is made because these reactions all involve nucleophile attack at the C-atom of a carbonyl in the rate-determining step. That Me_3NO is a strong nucleophile is due to the high negative charge on O in $Me_3N^{\delta+} \rightarrow O^{\delta-}$. It should also be noted that reactions of R^- with $M(CO)_6$ yield $M(CO)_5(COR)$ and do not result in M—CO bond cleavage, as do the reactions with Me_3NO. Since M—CO bond dissociation causes an increase in $\Delta S^\ddagger$, it follows that O-atom transfer reactions have less negative values of $\Delta S^\ddagger$ than do reactions of $M(CO)_6$ with R^- where bond dissociation does not occur. Thus, the $\Delta S^\ddagger$ of reaction enhances the reactivity of Me_3NO over R^- in these reactions.

In order to get some information on the nature of the proposed intermediate, it was decided to conduct competition experiments to determine the relative reactivities of the intermediate generated in the reaction between $Cr(CO)_6$ and Me_3NO [20], with the intermediate formed by the dissociation of $Cr(CO)_5THF$. The compound $Cr(CO)_5THF$ is known [21] to react readily in solution with good ligands to form $Cr(CO)_5L$ by a process believed to involve the intermediate "$Cr(CO)_5$". Since the same intermediate is believed to be formed in the Me_3NO reaction,

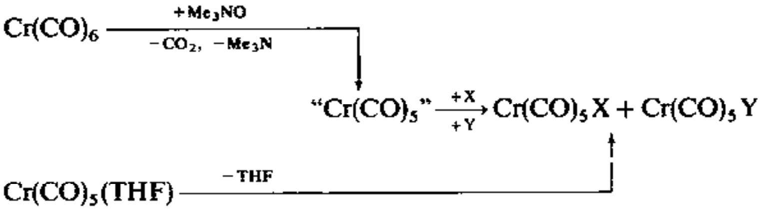
TABLE 1

Rate constants for reaction (1) at 25°C in CH_2Cl_2 and values of ν_{CO}

Compound	ν_{CO} (cm^{-1})	k_2 ($M^{-1}\,s^{-1}$)	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (cal mol^{-1} deg^{-1})
$Cr(CO)_6$	1983	0.147	12.2	−21.3
$Mo(CO)_6$	1985	0.190	13.0	−18.1
$W(CO)_6$	1980	0.366	16.7	−4.5

[a] Ref. 53.

competition experiments (Scheme 2) should show the same distribution of products from the two different reactions.



Scheme 2.

The experimental results [20] show (Table 2) that both reactions give the same ratio of products, thus supporting the formation of a common intermediate believed to be "$Cr(CO)_5$ solvent."

2.2 *Reactions of $M(CO)_5$ ($M = Fe, Ru, Os$) with Me_3NO*

The reactions of $M(CO)_5$ ($M = Fe$, Ru, Os) with Me_3NO in the presence of PPh_3 produce $M(CO)_4PPh_3$ (eqn. (2)) [22].

$$M(CO)_5 + PPh_3 + Me_3NO \rightarrow M(CO)_4PPh_3 + Me_3N + CO_2 \tag{2}$$

The reaction of $M(CO)_5$ has the same kinetic behavior as that for the reaction of $M(CO)_6$, suggesting the same type of reaction mechanism is involved in both systems (Scheme 1). The reactivities of these complexes follow the order $Os > Ru > Fe$ (Table 3), which is the same as was found [17] for the Cr-triad complexes.

Although quantitative comparisons of relative activities are not known between $M(CO)_6$ ($M = Cr$, Mo, W) and $M(CO)_5$ ($M = Fe$, Ru, Os) due to the necessity of using different solvents, what is known is that the $M(CO)_6$ compounds do not react

TABLE 2

Product distribution from competition reactions for the presumed common intermediate "$Cr(CO)_5$"

$\frac{[P(n\text{-}Bu)_3]}{[Py]}$	$[Cr(CO)_5P(n\text{-}Bu)_3]/[Cr(CO)_5Py]$ from $Me_3NO + Cr(CO)_6$	$[Cr(CO)_5P(n\text{-}Bu)_3]/[Cr(CO)_5Py]$ from $Cr(CO)_5THF$
1:1	1.59	1.69
1:3	0.60	0.59
1:6	0.32	
1:9		0.25
$\frac{k_{P(n\text{-}Bu)_3}}{k_{Py}}$	1.5	1.6

TABLE 3

Rate constants for reactions of $M(CO)_5$ or $M_3(CO)_{12}$ (M = Fe, Ru, Os) with Me_3NO at 20.6°C in $EtOH/n\text{-}C_6H_{14}$ (v/v = 1/2)

Compound	ν_{CO}[a] (cm^{-1})	k_2 ($M^{-1}\,s^{-1}$)
$Fe(CO)_5$	2022.5 2000.5	2.37×10^{-2}
$Ru(CO)_5$	2036.5 2001.5	7.41×10^{-2}
$Os(CO)_5$	2035.0 1993.0	9.70×10^{-2}
$Fe_3(CO)_{12}$	2045 2015 1850	13.2
$Ru_3(CO)_{12}$	2061 2031 2012	3.05
$Os_3(CO)_{12}$	2069 2036 2015 2004	0.256

[a] Ref. 54.

with Me_3NO under experimental conditions where the $M(CO)_5$ compounds readily react. Such a large difference between the reactivities of $M(CO)_6$ and $M(CO)_5$ towards Me_3NO is in agreement with previous studies [18], which show the rates of nucleophilic attack on carbon in metal carbonyls increase with increasing CO stretching frequencies. The values of ν_{CO} for $M(CO)_6$ are near 1980 cm^{-1}, compared with values of about 2030 cm^{-1} for $M(CO)_5$.

It is further noteworthy that the mononuclear metal carbonyls $M(CO)_5$ (M = Fe, Ru, Os) and $M(CO)_6$ (M = Cr, Mo, W), respectively, have a similar order of reactivity with Me_3NO. Furthermore, for each triad the difference in rate is small (4 times for the Fe triad and 2.5 times for the Cr triad), in accord with the compensating effect of $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$. In contrast to these small differences, there are large differences [23] for rates of thermal CO substitution by a dissociative pathway in the absence of MeNO for each of the triads.

2.3 *Ligand effect on the reactions of $Mo(CO)_5L$ with Me_3NO*

It was suggested [17] that the rate-determining steps of the reactions (eqn. (1)) of $M(CO)_6$ with Me_3NO involve nucleophilic attack of the O-atom of the amine

N-oxide on a C-atom of the carbonyl group, and that the positive charge on the carbon plays an important role in determining the reactivities of metal carbonyls. This was further tested by investigating the reactions of $M(CO)_5L$ with Me_3NO in the presence of entering ligand [24]. It is known [19] that the electronic character of L controls the amount of electron density transferred to the CO groups by $M \rightarrow CO$ π-back-bonding. As the amount of back-bonding increases, the electron density on the C-atom increases, and the ν_{CO} bands decrease in energy.

The rates of the reaction

$$Mo(CO)_5L + L + Me_3NO \rightarrow Mo(CO)_4L_2 + Me_3N + CO_2 \quad (3)$$

increase with increase in ν_{CO} values (Fig. 1), which is expected, for this is the order of increase positive charge on the C-atom undergoing nucleophilic attack. Except for ligands PPh_3 and $AsPh_3$, the correlation between reaction rates and ν_{CO} values is very good. This represents a correlation with the electronic effects of ligands L in $Mo(CO)_5L$, and no correlation was found with the steric effects or cone angles [25] of L. This being the case, it is necessary to account for the effect of ligands with cone angles larger than 135°, e.g. PPh_3 (145°), $AsPh_3$ (~145°), and $P(c\text{-}Hx)_3$ (170°).

This greater bulk of the PPh_3 or $AsPh_3$ ligands may impose an enhanced cis effect [26] on adjacent COs, rendering weaker M—C bonds both in the ground and in the transition states for reaction. Such a bond-weakening effect is supported by the small value of $\Delta H^‡$ of reaction for the reaction of $Mo(CO)_5PPh_3$ (15.3 kcal mol^{-1})

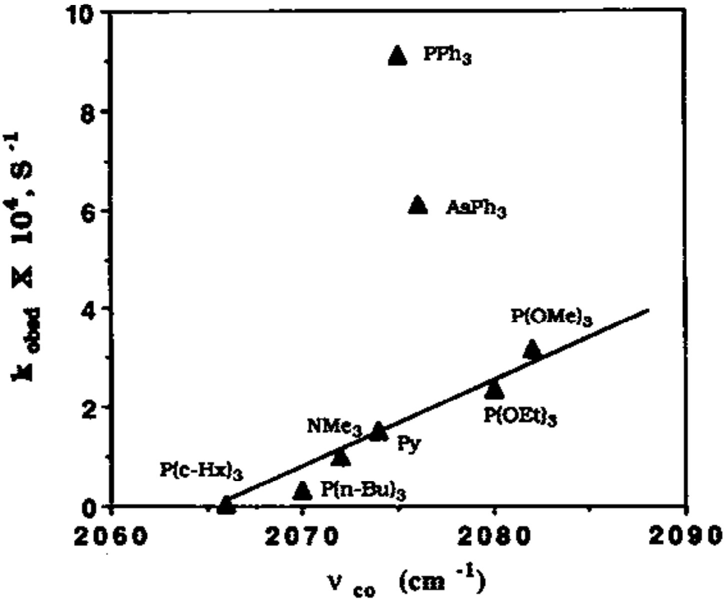


Fig. 1. Plot of k_{obsd} values for the reaction of $Mo(CO)_5L$ with Me_3NO vs. A_1 ν_{CO} bands of the complexes at 26.0°C in 1:1 (v/v) CH_2Cl_2/CH_3CN solvent.

compared with the reaction of $Mo(CO)_5P(OMe)_3$ (20.3 kcal mol^{-1}). Also, the PPh_3 (−16.4 cal deg^{-1} mol^{-1}) system has a more negative $\Delta S^{\ddagger}$ than does the $P(OMe)_3$ (−4.9 cal deg^{-1} mol^{-1}) system, indicative of more steric strain for reaction. One drawback to this discussion is that the largest ligand $P(c\text{-}Hx)_3$ system is then expected to be the fastest to react, but it is found to be the slowest to react. It may be that this ligand, notorious for its huge size, has retarded an associative pathway for reaction sufficiently to just inadvertently give it a rate that seems to correlate the ν_{CO} values.

2.4 Effect of substituents on amine N-oxide reactivity

The reactivity of Me_3NO in these reactions suggest it is both a good nucleophile and a good oxidizing reagent, because the reactions involve oxidation of CO to CO_2 with reduction of $(CH_3)_3NO$ to $(CH_3)_3N$. This unusual property of Me_3NO being both a good nucleophile and a good oxidizing reagent raises the question of the relation between thermodynamic oxidizing ability and kinetic reactivity of O-atom transfer for different amine *N*-oxides. In an attempt to delineate the relative importance of nucleophilic strength versus oxidation power on the rates of reaction, a study [20] was conducted on the CO substitution of $Cr(CO)_6$ in the presence of alkyl amine *N*-oxides, R_3NO, and of aryl-amine *N*-oxides, $(p\text{-}X\text{–}C_6H_4)(CH_3)_2NO$ (eqn. (4)).

$$Cr(CO)_6 + R_3NO + PPh_3 \rightarrow Cr(CO)_5PPh_3 + R_3N + CO_2 \tag{4}$$

These amine oxides with different substituents allow one to modify the negative charge on the O-atom of different amine oxides, which then changes both its nucleophilic strength and its oxidizing ability. It should be noted that an increase in the negative charge on the O-atom increases the nucleophilic strength of the amine oxide, but decreases its oxidizing power.

The experimental results show that the rate constants for alkyl amine *N*-oxides increase with decreasing aliphatic polar constants σ^* of Taft [27], which represent the inductive effects of alkyl substituents. A plot of $\ln k_2$ vs. σ^* shows a good linear correlation. Similarly the $\ln k_2$ values for para-substituted aryl amine *N*-oxides are observed to correlate the Hammett substituent constants σ_p (Fig. 2) [28]. These results show that the more negative the charge on the O-atom of the amine *N*-oxides, the faster is the reaction for analogous amine *N*-oxides. This is in accord with the most negative oxide being the best nucleophile, and with the rate-determining step for the reaction involving a nucleophilic attack by the reagent (Scheme 1).

Polarographic studies show [29] that amine *N*-oxides with electron-withdrawing substituents have higher oxidation potentials than do similar compounds with electron-donating substituents. A detailed study [30] on substituted pyridine *N*-oxides show that half-wave potentials of the first reduction waves is in linear relation with the Hammett σ_p values of the substituents. Considering that the rate-

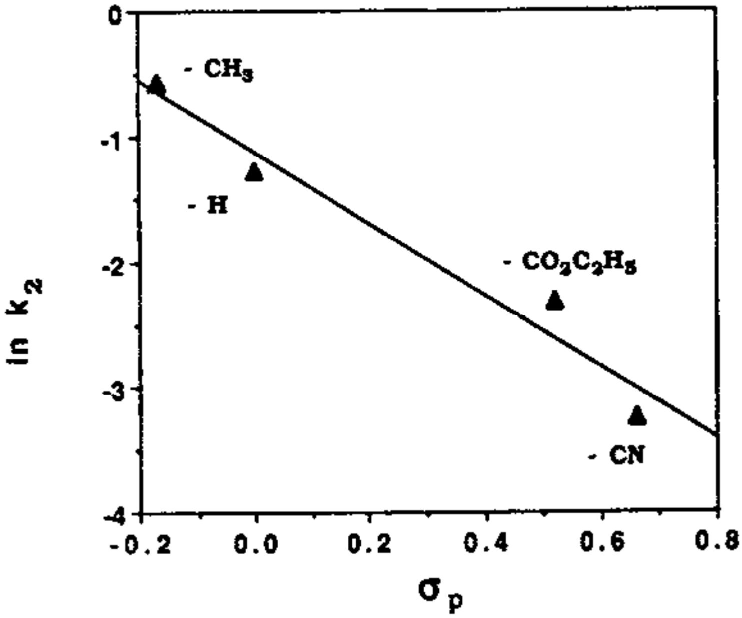


Fig. 2. Plot of ln k_2 vs. Hammett constants for reaction of $Cr(CO)_6$ with para-substituted aryl amine oxides in CH_2Cl_2 at 18.9°C.

determining-step of these O-atom transfer reactions involve a nucleophilic attack of the O-atom on a carbonyl carbon, it is not surprising that the rates decrease with increasing oxidizing ability of the amine *N*-oxides. However, the stronger the oxidizing ability of the reagent, the slower the reaction even though the oxidation of CO to CO_2 is thermodynamically favored. There is no evidence for the intermediate formation of $R_3NO^{-\cdot}$, suggesting that oxidation occurs by an oxygen atom transfer process with accompanying electron transfer.

2.5 Reactivities of other O-atom transfer reagents

In the proposed mechanism (Scheme 1) for oxygen transfer reactions to metal carbonyls, both bond-making (O—C) and bond-breaking processes (M—CO and N—O) must take place. How much each bond-making and how much each bond-breaking process contribute to the overall energetics of the transition state for reaction is not known. An attempt [31] was made to get some information on this very important point by probing the reactivities of somewhat similar E—O reagents relative to their basicities and their E—O bond strengths, while keeping the bond dissociation energies of M—CO about the same (eqn. (5)).

$$\text{M—CO} + \text{E—O} \rightarrow \text{“M”} + CO_2 + \text{E} \tag{5}$$

where M = Cr, Fe and E = N, As, Sb, Se, Te. Other ligands are not shown on M, and alkyl or aryl groups are not shown on E.

The E—O bond strengths of R_2EO decrease in the order S > Se > Te, and for R_3EO the order is P > As ~ Sb (Table 4). The E—O bond strengths were attributed [32] to σ-donation from E to O and π-back-bonding from occupied p-orbitals of oxygen to empty d-orbitals of the E-atom. Since the π-back-bonding interactions decrease in the order 3d > 4d > 5d, the basicities of the oxides increase in the order 3d < 4d < 5d and the E—O bond strengths change in the opposite order.

The relative base strengths of the oxides were measured by investigating hydrogen-bonding interactions of the oxides with MeOH (Table 4) [33]. The O—H stretching bands in the IR broaden and shift to lower frequencies upon forming hydrogen bonds with the oxides. The larger the shift, the stronger the basicity of the oxides. Apart from those of amine oxides, the basicities of the oxides increase with increasing atomic number within each family of elements. This relative basicity order is consistent with what is expected based on E—O π-bonding interactions which decrease in the order 3d > 4d > 5d [32].

TABLE 4

Rate constants for O-atom transfer reactions of different oxides to metal carbonyls[a,b]

R_nEO	$\Delta\nu_{O-H}$ (cm^{-1})	E—O Bond strengths (kcal mol^{-1})	t (°C)	k_2 ($M^{-1} S^{-1}$)	Solvents
Me_3NO[a]	400 ± 5	61[c]	19	9×10^{-2}	CH_2Cl_2[d]
				2.85×10^{-3}	$CHCl_3$
C_6H_5IO[a,e]		53[c]	22	1.56×10^{-1}	THF–CH_3OH
(p-$CH_3OC_6H_4)_2TeO$[a]	300 ± 5	52[f]	19	3.4×10^{-3}	$CHCl_3$
(p-$CH_3OC_6H_4)_2SeO$[a]	280 ± 5	73[f]	20	No reaction	$CHCl_3$
				1.4×10^{-4}	CH_2Cl_2
				5.5×10^{-3}	THF
pyO[b]	268 ± 5	73[g]	45	1.15×10^{-6}	$(CH_3)_2CO$[h]
Ph_3AsO[b]	302 ± 5	107[i]	57	4×10^{-6}	THF
Ph_3SbO[b]	296 ± 5	107[i]	57	$\geqslant 4 \times 10^{-6}$	THF
Ph_3PO[b]	242 ± 5	127[g]	40–50	No reaction	THF
Ph_2SO[b]	225 ± 5	87[g]	40–50	No reaction	THF

[a] k_2 for reactions of $Cr(CO)_6$ with oxides.

[b] k_2 for reactions of $Fe(CO)_5$ with oxides.

[c] Ref. 55.

[d] Ref. 17.

[e] Ref. 36.

[f] Estimated values using E—O diatomic molecular bond strengths.

[g] Ref. 56.

[h] Ref. 20.

[i] Ref. 57.

Neither Ph_2SO nor Ph_3PO react with $Cr(CO)_6$ or with the more reactive $Fe(CO)_5$, and this is attributed to their having the strongest E—O bond and weakest basicity within each family of elements. The reactions investigated, i.e.

$$Cr(CO)_6 + R_2EO \rightarrow Cr(CO)_5ER_2 + CO_2 \quad (6)$$

$$Cr(CO)_6 + R_2EO + Py \rightarrow Cr(CO)_5Py + R_2E + CO_2 \quad (7)$$

$E = Se, Te$; $R = p\text{-}CH_3OC_6H_4$

$$Fe(CO)_5 + Ph_3EO \rightarrow Fe(CO)_4EPh_3 + CO_2 \quad (8)$$

$E = As, Sb$

obey a second-order rate law, and are believed to proceed by the same type of mechanism as proposed [17] (Scheme 1) for reactions of Me_3NO. The interesting result of this study is that R_2TeO and R_2SeO react much faster than R_3EO ($E =$ As, Sb). Although Ph_3AsO and Ph_3SbO have about the same basicities as does $(p\text{-}CH_3OC_6H_4)_2TeO$, their E—O bonds are twice as strong as is that of Te—O (Table 4). This greater bond strength may account for the fact that As—O and Sb—O are poorer O-atom transfer reagents than is Te—O, and it implies that E—O bond-breaking makes a considerable contribution to the overall energetics of the transition state.

2.6 *Effect of substituents on iodosobenzene reactivity*

The use of iodosobenzene (PhIO) as an O-atom transfer reagent to organic compounds has attracted considerable attention, particularly in the presence of transition metal porphyrins [34]. The use of PhIO to eliminate CO in a metal carbonyl complex was reported in the synthesis of $[\eta^5\text{-}C_5(CH_3)_5Re(CO)(NO)PPh_3]BF_4$ [35]. It therefore also appeared of interest to investigate the O-atom transfer reaction of PhIO towards metal carbonyls [36]. Iodosobenzene is an insoluble polymer, $(PhIO)_n$, but it reacts with and dissolves in methanol as the ester $PhI(OCH_3)_2$ [37].

Addition of $Cr(CO)_6$ and CH_3CN to such a solution of $PhI(OCH_3)_2$ results in no reaction, but addition of water accelerates the formation of $Cr(CO)_5(NCCH_3)$. A kinetic study of the reaction in CH_3OH–THF solvent shows the rate is first-order in concentrations of $Cr(CO)_6$, PhIO and H_2O, but inversely proportional to the square of CH_3OH and zero-order in CH_3CN concentrations. These observations are consistent with the following step-wise reactions:

$$PhI(OCH_3)_2 + H_2O \overset{K}{\rightleftharpoons} PhIO + 2CH_3OH \quad (9)$$

$$Cr(CO)_6 + PhIO \xrightarrow{k_2} [Cr(CO)_6\text{–}PhIO] \quad (10)$$

$$[Cr(CO)_6\text{–}PhIO] \rightarrow \text{“}Cr(CO)_5(\text{solvent})\text{”} + PhI + CO_2 \qquad (11)$$

$$\text{“}Cr(CO)_5(\text{solvent})\text{”} + CH_3CN \rightarrow Cr(CO)_5NCCH_3 \qquad (12)$$

The mechanism of the rate-determining step (eqn. (10)) for the reaction is believed to be similar to that for Me_3NO (Scheme 1) with attack on C by the O-atom of PhIO. Not knowing the actual concentration of molecular PhIO in the solutions, it was not possible to compare quantitatively the reactivity of PhIO with that of Me_3NO towards $Cr(CO)_6$. However, qualitatively it is certain that PhIO is orders of magnitude more effective as an O-atom transfer reagent in this reaction than is Me_3NO.

Introduction of electron-donating or electron-withdrawing groups on the phenyl ring is expected to affect the reactivity of the monomeric reactive species, but also to affect the rapid pre-equilibria (eqns. (13) and (14)).

$$X\text{–}C_6H_4I(OCH_3)_2 + H_2O \rightleftharpoons X\text{–}C_6H_4IO + 2CH_3OH \qquad (13)$$

$$n\text{-}X\text{–}C_6H_4IO \rightleftharpoons (X\text{–}C_6H_4IO)_n \qquad (14)$$

where $X = CH_3$, H, CO_2Na, NO_2. Assuming the monomer $X\text{–}C_6H_4IO$ is the reactive species, then it follows that any enhancement of its concentration by substituents on the iodosobenzenes will increase the rates of reaction. It is of interest that all the substituted iodosobenzenes used show [38] higher reactivities compared with C_6H_5IO, suggesting that steric effects play an important role. Furthermore, for a given substituent, the rates of reaction decrease in the order ortho- > meta- > para-. Steric effects of substituents are believed to retard the association of iodosobenzenes (eqn. (14)) and formation of $X\text{–}C_6H_4I(OCH_3)_2$ (eqn. (13)) in solution and to increase the concentrations of the reactive monomeric species. Ortho-substituents would have the strongest steric effect compared with meta- and para-substituents, and they are found to be the most reactive.

An attempt was made [38] to elucidate the Hammett σ effect of substituents of para-substituted iodosobenzenes on the rapid pre-equilibrium, K, and on the rate-determining step, k_2, for the proposed mechanism. Since it is known [20] that the rates of reaction of $Cr(CO)_6$ with amine N-oxides correlate Hammett σ, it can be assumed that there would be a similar linear relationship for a plot of $\ln k_2$ vs. Hammett σ between reactions of $Cr(CO)_6$ and $X\text{–}C_6H_4IO$ compounds. This requires that $\ln k_2 = c\sigma_p + b$ (where c and b are constants). Neither k_2 nor K are experimentally determined; what is determined is Kk_2. However, it is possible to estimate $c\sigma_p$ from $\ln Kk_2$ and the resulting $\ln K_e = \ln Kk_2 - c\sigma_p$ should indicate the electronic effects of X on the formation of $p\text{-}X\text{–}C_6H_4I(OCH_3)_2$. The data show that, when $c = -20$, a plot of $\ln K_e = \ln Kk_2 + 20\sigma_p$ vs. Hammett σ_p gives a straight line for all five of the $p\text{-}X\text{–}C_6H_4IO$ compounds studied (Fig. 3). The slope of this line is positive, indicating that the formation of $X\text{–}C_6H_4I(OCH_3)_2$ is favored by electron-donating groups. This means there is a lower concentration of the reactive monomeric species

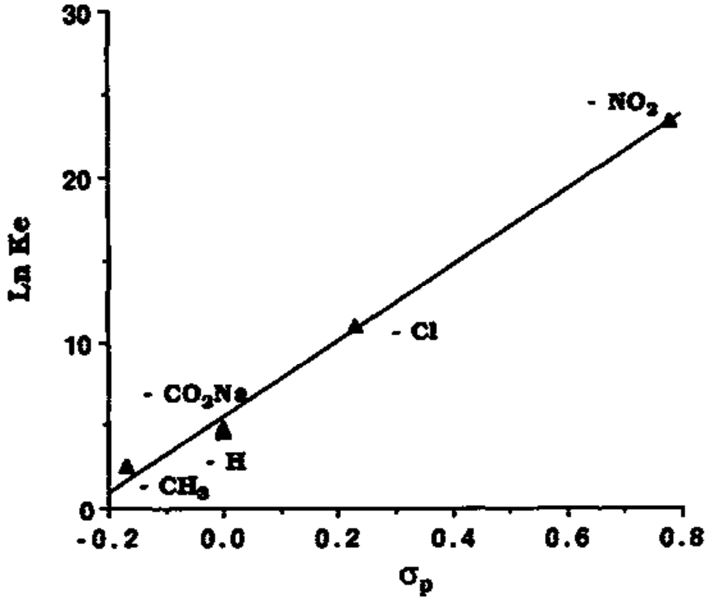


Fig. 3. Plot of ln $K_e = \ln Kk_2 + 20\sigma_p$ vs. Hammett constants for reactions of $Cr(CO)_6$ with p-XC_6H_4IO at 25°C in CH_3OH–THF 1:2 (v/v) solvent.

X–C_6H_4IO present, so the reaction rate may decrease even though the basicity and nucleophilic strength X–C_6H_4IO increases with increasing electron-donating substituents R. The observed reactivity order is the net result of electronic effect on both the pre-equilibrium and the nucleophilic rate-determining step.

3. METAL CARBONYL CLUSTERS

3.1 Reactions of $M_3(CO)_{12}$ (M = Fe, Ru, Os) with Me_3NO

It is known [39] that mechanisms of thermal and photochemical CO substitutions of metal carbonyl clusters may differ from corresponding mononuclear metal carbonyls. Having studied the kinetics and mechanisms of CO substitution of mononuclear metal carbonyls in the presence of O-atom transfer reagents, it was decided to investigate similar reactions of metal carbonyl clusters. These investigations were initiated [40] with the reactions between $M_3(CO)_{12}$ and Me_3NO (eqn. (15)).

$$M_3(CO)_{12} + L + Me_3NO \rightarrow M_3(CO)_{11}L + Me_3N + CO_2 \qquad (15)$$

where M = Fe, Ru, Os; L = PPh_3, $AsPh_3$, $P(OPh)_3$. The reactions are too fast to follow by conventional methods in CH_2Cl_2, but the reaction is retarded by using protonic solvent. A quantitative study of effect of EtOH on the rate of reaction of $Os_3(CO)_{12}$ with Me_3NO shows that the rate is inversely proportional to the concentration of EtOH in $CHCl_3$ (Fig. 4). This suggests that protonic solvents can strongly retard the nucleophilicity of Me_3NO by hydrogen bonding with the O-atom of the amine oxide (eqn. (16)).

$$Me_3NO + C_2H_5OH \rightleftharpoons Me_3N{-}O\cdots H{-}OC_2H_5 \quad (16)$$

The reactions follow a second-order rate law, identical with that observed for corresponding reactions of mononuclear metal carbonyls. In spite of the general correlation between increasing rates of nucleophilic attack on carbon for mononuclear metal carbonyls with increasing values of ν_{CO}, just the opposite is observed for this cluster triad with relative rates of $Fe_3(CO)_{12} > Ru_3(CO)_{12} > Os_3(CO)_{12}$ (Table 3). Since this indicates ground states do not control these relative rates, it is necessary to consider factors affecting stabilities of the reaction transition states. Gross and Ford [41] report the same rate order for the reaction of $M_3(CO)_{12}$ with CH_3O^- to form $[M_3(CO)_{11}C(O)OCH_3]^-$. This reaction also involves attack of the O-atom on a C-atom, and it was suggested that rates decrease in the order Fe > Ru > Os because the stability of the transition states for the reactions decrease in this same order. The reason given for such an order of transition state stability is that bridging COs are more electron-withdrawing [42] and can better accommodate the developing negative charge on the metal cluster as CH_3O^- attacks a carbonyl carbon in the transition state. Because of the longer M—M bond distance going down the iron triad, it becomes increasingly difficult to form bridging COs to

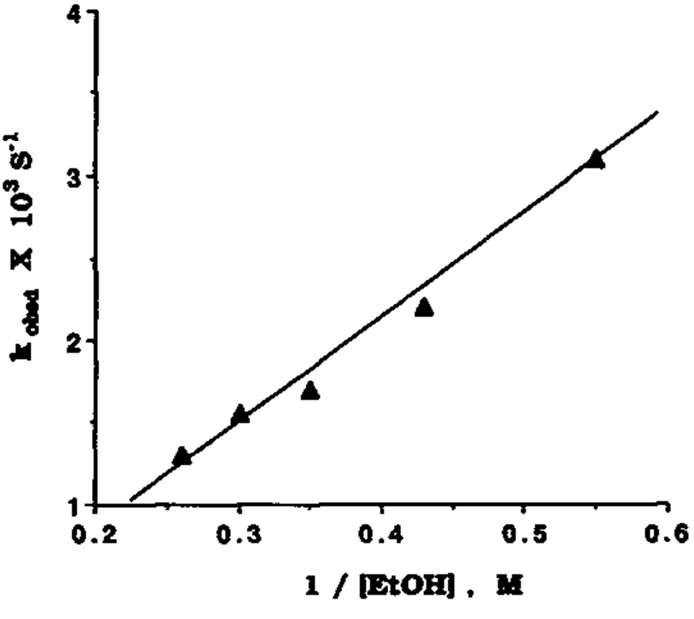


Fig. 4. Plot of k_{obsd} vs. $1/[C_2H_5OH]$ for the reaction of $Os_3(CO)_{12}$ with Me_3NO in $CHCl_3/C_2H_5OH$ solvent at 24.7°C and $[Me_3NO] = 4.60 \times 10^{-3}$ M.

delocalize negative charge accumulating in the transition state. Although the addition of Me_3NO to $M_3(CO)_{12}$ in the transition state does not develop a negative charge on the cluster, as does the addition of CH_3O^-, attack by the negative O-atom of $Me_3N^{\delta+}-O^{\delta-}$ does increase the electron density in the cluster. This may be sufficient to require carbonyl bridge formation in the transition state for the reaction, and to account for the relative rates observed.

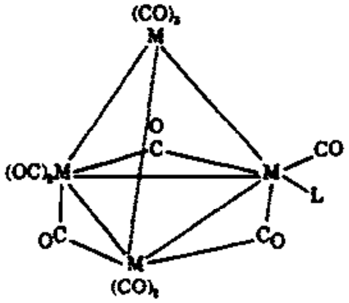
The explanation for the observed reactive order for iron triad metal clusters is further supported by the results of a kinetic study [22] of CO substitution by PPh_3 for the $M(CO)_5$ (M = Fe, Ru, Os) compounds in the presence of Me_3NO. The rates of reaction for $M_3(CO)_{12}$ clusters are much faster than for $M(CO)_5$ (Table 3). For Fe, the rate difference is about two orders of magnitude, whereas it is approximately one order of magnitude for Ru, and $Os_3(CO)_{12}$ reacts at about the same rate as does $Os(CO)_5$. That the largest rate difference between $M_3(CO)_{12}$ and $M(CO)_5$ is for Fe and the smallest is for Os was rationalized in terms of formation of bridging carbonyls in the transition state for reaction of the metal carbonyl clusters. This is believed to be the case because it is known that the degree of difficulty in forming bridging COs in $M_3(CO)_{12}$ clusters increases in the order Fe > Ru > Os [43]. Thus, Os would experience the greatest rate retardation. This might explain why the Os cluster reacts at about the same rate as does $Os(CO)_5$, whereas the largest difference in rate is for Fe which has bridging COs in the cluster ground state, and the difference for Ru is an intermediate of Fe and of Os.

3.2 Reactions of $M_2(CO)_{10}$ (M = Mn, Re) with Me_3NO and with $(p\text{-}CH_3OC_6H_4)_2TeO$

Reactions of $M_2(CO)_{10}$ (M = Mn, Re) with Me_3NO and with $(p\text{-}CH_3OC_6H_4)TeO$ in the presence of Py or PPh_3 in $CHCl_3$ yield monosubstituted complexes [44]. The rates for the reaction of $Mn_2(CO)_{10}$ with Me_3NO is about the same as that of $Re_2(CO)_{10}$. This is consistent with what is expected based on the ground states of the reactants. The two metal carbonyls have identical structures, with a single M—M bond and no bridging COs, and about the same ν_{CO} values [45]. In the transition states, steric acceleration due to the larger Re and electronic acceleration due to M_2CO bridging each may contribute about equally to the reaction rates. Interestingly, the reaction of $Mn_2(CO)_{10}$ with $(p\text{-}CH_3OC_6H_4)_2TeO$ is 28 times faster than that of $Re_2(CO)_{10}$. Since the telluroxide is less basic than is the amine oxide, the driving force to form bridging COs in transition state may be enough for $Mn_2(CO)_{10}$ but not for $Re_2(CO)_{10}$. Thus telluroxide has greater selectivity towards metal carbonyl clusters than does the amine oxide. This suggestion is supported by the activation parameters for the reactions with telluroxide. The results show that the slower rate of reaction of $Re_2(CO)_{10}$ with $(p\text{-}CH_3OC_6H_4)_2TeO$ is due to its higher $\Delta H^\ddagger$ value (20.4 kcal mol^{-1}). The lower $\Delta H^\ddagger$ value (16.2 kcal mol^{-1}) and more negative $\Delta S^\ddagger$ value (−13 cal mol^{-1} K^{-1}) for $Mn_2(CO)_{10}$ compared with that for $Re_2(CO)_{10}$ ($\Delta S^\ddagger = -6$ cal mol^{-1} K^{-1}) may reflect more significant bridging CO formation in transition state for the $Mn_2(CO)_{10}$ reaction [46]. The formation of bridging COs will stabilize the transition state (lower $\Delta H^\ddagger$), but it will require reorganization (more negative $\Delta S^\ddagger$).

3.3 Reactions of $M_4(CO)_{11}L$ (M = Co, Ir) with Me_3NO

The significance of bridging COs on the reactivities of metal clusters was further tested by studying CO substitution of $M_4(CO)_{11}L$ [47] (M = Co, Ir; L = PPh_3, $P(n\text{-}Bu)_3$, $P(OMe)_3$, $P(OEt)_3$) in the presence of Me_3NO. The results show that $Ir_4(CO)_{11}L$ reacts faster than does $Co_4(CO)_{11}L$ for all the analogous compounds studied. It is known [48] that the phosphorus ligand substituted clusters $M_4(CO)_{11}L$ have the same bridging CO structures (I).



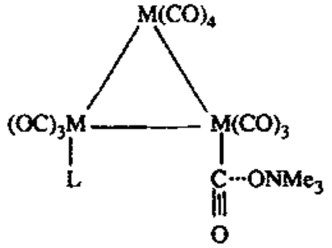
I

(M = Co, Rh, Ir)

Therefore, it is expected that effects of bridging COs in the cluster on the transition state may not differ significantly. Consequently, the relative stabilities of the transition state due to bridging COs would have about the same effect on the rates of the reactions of $Co_4(CO)_{11}L$ and of $Ir_4(CO)_{11}L$. This may account for the observation that the Ir clusters react 2–7 times faster than do the corresponding Co compounds, in accord with the higher values of ν_{CO} for the Ir compounds.

3.4 Ligand effect on the reactions of $M_3(CO)_{11}L$ (M = Fe, Ru, Os) with Me_3NO

The CO substitution reactions of $M_3(CO)_{11}L$ [49] (M = Fe, L = $P(OMe)_3$, $P(OEt)_3$; M = Ru, Os, L = $P(OMe)_3$, $P(OEt)_3$, $P(n\text{-}Bu)_3$, PPh_3, $AsPh_3$, $SbPh_3$) were studied in order to test ligand effect on the reactivities of the complexes. For phosphite derivatives, the relative rates are $M_3(CO)_{11}P(OMe)_3 > M_3(CO)_{11}P(OEt)_3$. For other ligand-substituted complexes, the rate increases with increasing stretching frequency of the CO bands in the IR spectra. This is consistent with what is expected based on the proposed mechanism, in which the rate-determining step involves nucleophilic attack at the C-atom of a carbonyl. For a given ligand, its inductive effect decreases in the order Fe > Ru > Os (Table 5). Since the electronic effect of the ligand on the carbonyl group is mainly transferred through chemical bonds between them, it is expected that the COs of unsubstituted metal atoms are more reactive than COs of the same metal atom with L (**II**).



II

This is supported by ^{13}C NMR chemical shifts of $Os_3(CO)_{11}(PEt_3)$ [50], which shows that ^{13}C δ values of COs on the substituted metal atom are shifted to lower field due to paramagnetic effect caused by the electron density brought about by M—C back π-bonding [51]. Furthermore, a shorter M—M bond may enhance the electronic effect of L on the rate of the reaction. The observed order for the electronic effect of the ligand in this triad agrees with the M—M bond length order Fe < Ru < Os [52].

4. CONCLUSIONS

Systematic kinetic studies on CO substitution reactions of metal carbonyl complexes reveals that the reaction is first-order in concentrations of metal carbonyl and of O-atom transfer reagents, zero-order in entering-ligand concentrations. The rates of reaction increase with increasing positive charge on the C-atom of a carbonyl group, or with increasing negative charge on the O-atom of the oxides, and the rates decrease with increasing E—O bond strength in the oxides. The reactivities of these O-atom transfer reagents can be modified by using different solvents. The bridging CO groups in metal carbonyl clusters play an important role in determining the

TABLE 5

Rate constants (k_2, M^{-1} S^{-1}) for reactions of $M_3(CO)_{11}L$ (M = Fe, Ru, Os) with Me_3NO in $CHCl_3$ at 4.5°C

L	M = Fe	M = Ru	M = Os
CO	47.1	8.50	0.784
PPh_3		0.140	0.0180
$P(OEt)_3$	0.0676	0.0640	

reactivities of these complexes towards O-atom transfer reagents. All of these results are consistent with the proposed mechanism, which involves nucleophilic attack of the O-atom of the oxides on a C-atom of a carbonyl group accompanied by O-atom transfer to form CO_2 and a "coordinatively unsaturated" intermediate, which then rapidly reacts with the entering ligand.

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