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Effect of substituents on amine *N*-oxides on the rates of O-atom transfer to metal carbonyls

Jian-Kun Shen [a], Yi-Ci Gao [b], Qi-Zhen Shi *[b] and Fred Basolo *[a]

[a] *Department of Chemistry, Northwestern University Evanston, IL 60208-3113 (USA)*
[b] *Lanzhou University, Lanzhou, Gansu (People's Republic of China)*

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Abstract

The kinetics of CO substitution in $Cr(CO)_6$ to afford $Cr(CO)_5PPh_3$ in the presence of different alkyl amine *N*-oxides, R_3NO, and aryl amine *N*-oxides, $(p\text{-X-}C_6H_4)(CH_3)_2NO$, are reported. Within each type of amine *N*-oxide, the rates of reaction increase with increasing basicity of the amine *N*-oxide. However, even at lower basicities, the aryl reagents react more rapidly than do the alkyl reagents. Competition experiments between py (pyridine) and $P(n\text{-Bu})_3$ for the coordinatively unsaturated intermediates "$M(CO)_5$" show that the discrimination abilities increase in the order Cr < Mo < W.

Introduction

The kinetics and mechanisms of oxygen atom transfer reactions of $(CH_3)_3NO$ to metal carbonyls have been investigated in some detail [1]. The rates of reaction are first-order in substrate and in $(CH_3)_3NO$ concentrations. Generally, for corresponding substrates, the rates of reaction increase with increasing CO stretching vibration frequencies. Accordingly, a mechanism was proposed in which the rate of reaction is determined by nucleophilic attack of the oxygen atom of $(CH_3)_3NO$ on the carbonyl carbon atom. There remained a need to probe factors that contribute to the O-atom transfer reagent being a good reagent, which is the subject of this report.

Previous studies [1a] show that $(CH_3)_3NO$ is a strong nucleophile compared with other nucleophiles believed to attack the carbon of metal carbonyls. It was also pointed out that $(CH_3)_3NO$ is both a good nucleophile and a good oxidizing reagent; the reactions involve oxidation of CO to CO_2 with reduction of $(CH_3)_3NO$ to $(CH_3)_3N$. This unusual property of $(CH_3)_3NO$ 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.

This paper presents kinetic results of substitution reactions of $Cr(CO)_6$ in the presence of alkyl amine *N*-oxides, R_3NO, and of aryl-amine *N*-oxides, $(p\text{-X-}C_6H_4)(CH_3)_2NO$. It also reports the results of competition experiments of different nucleophiles for the presumed "$M(CO)_5$" active intermediates.

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Experimental

Chemical compounds. $Cr(CO)_6$ was obtained from Aldrich Chemical Co. Triethylamine *N*-oxide was synthesized and purified by the literature method [2]. The compound, after recrystallization from sodium dried ethyl ether, was dried under vacuum for several hours. No water was observed in the ^1H NMR spectrum of the white crystals. $(PhCH_2)_3NO$, $PhMe_2NO$, *p*-CH_3PhMe_2NO, *p*-$C_2H_5O_2CPhMe_2NO$, and *p*-$NCPhMe_2NO$ were synthesized by the literature method [3]. PPh_3 was purified by recrystallization from anhydrous ethyl alcohol. $(CH_3)_3NO \cdot 2H_2O$ was obtained from Aldrich Chemical Co. and was dehydrated by sublimation before use. CH_2Cl_2 was dehydrated with P_2O_5 and distilled under N_2 atmosphere before use. Except for $(PhCH_2)_3NO$ and Me_3NO, all other amine *N*-oxides are highly hygroscopic. All the manipulations involving amine *N*-oxides were done in a glove-box under N_2 atmosphere.

Kinetic study. All of the reactions were followed with a Nicolet 5PC-FT-IR spectrophotometer using a special P/N 20.500 variable-temperature IR cell with 0.6 mm AgCl windows. All of the reactions were carried out in CH_2Cl_2 and at conditions where the concentrations of amine *N*-oxides and of PPh_3 are at least ten times greater than that of $Cr(CO)_6$. In a typical experiment, a solution of Et_3NO and of PPh_3 in CH_2Cl_2 were syringed into a degassed flask which was submerged in ice-water. After the flask was vigorously shaken, an aliquot was removed and syringed into an IR cell flushed with N_2 and sealed with a rubber septum. After a few minutes of temperature equilibration, the resultant spectral changes were monitored. Rate constants k_{obsd} were obtained by following the disappearance of the CO stretching band and using eq. 1 for calculation.

$$\ln A_t = -k_{obsd}t + \text{constant} \qquad (1)$$

Base strengths. The relative base strengths of the amine oxides were measured by investigating the hydrogen-bonding interaction of these compounds with phenol in CCl_4. The O–H stretching bands in the IR broaden and shift to lower frequencies upon forming hydrogen bonds with amine oxides. Data were obtained by the literature method [4]. The results appear to be accurate to within $\pm 10\ cm^{-1}$. All the measurements were carried out at room temperature of 25 ° C, and at the same concentration of PhOH (0.127 *M*). Except for $(CH_3)_3NO$ which has a low solubility in the solvent CCl_4, the concentrations of amine oxides are equal to that of phenol.

Competition experiments. $Cr(CO)_5THF$ was synthesized in situ by photolyzing $Cr(CO)_6$ in THF solution. The known compounds [5] $Cr(CO)_5Py$ and $Cr(CO)_5P(n\text{-}Bu)_3$ were not isolated, but were prepared in situ using quantitative amounts of reagents in the presence of Me_3NO. This allowed an accurate estimate of the IR molar absorptivities of each compound in the C–O stretching region of their spectra and in CH_2Cl_2 and CH_2Cl_2/THF (4 : 1) solvents. A mixture of the ligands in CH_2Cl_2 at required concentrations were syringed into a Schlenk tube containing $Cr(CO)_5THF$ solution. The substitution reaction was complete in seconds. The absorbances at 2060 cm^{-1} and 2070 cm^{-1} which are due to $Cr(CO)_5P(n\text{-}Bu)_3$ and $Cr(CO)_5Py$ were measured, and the concentrations of the two complexes formed were calculated. Under similar conditions, competition experiments were done on oxygen atom transfer reactions of $(CH_3)_3NO$ to $M(CO)_6$ (M = Cr, Mo, W). The discrimination of the coordinatively unsaturated intermediates "$M(CO)_5$" between py and $P(n\text{-}Bu)_3$ were compared by calculating the ratio of the rate constants for the reactions of "$M(CO)_5$" with entering ligands using eq. 2.

$$\frac{[M(CO)_5P(n\text{-}Bu)_3]}{[M(CO)_5Py]} = \frac{k_{P(n\text{-}Bu)_3}}{k_{Py}} \frac{[P(n\text{-}Bu)_3]}{[Py]} \qquad (2)$$

Results

The reactions (eq. 3) were carried out in the solvent CH_2Cl_2 at 10–20 °C. All of

$$Cr(CO)_6 + R_3NO + PPh_3 \rightarrow Cr(CO)_5PPh_3 + R_3N + CO_2 \qquad (3)$$

the reactions afforded the product $Cr(CO)_5PPh_3$, as determined by its IR spectrum being in agreement with the literature [5] spectrum for the compound. The only exception to this reaction (eq. 3) was that of (p-NCC_6H_4)(Me)$_2$NO which gave the

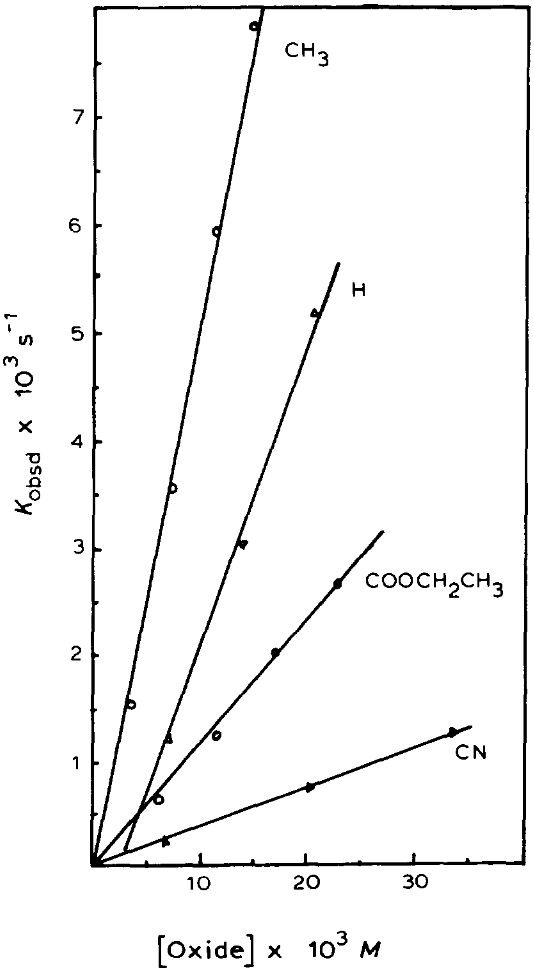


Fig. 1. Plot of k_{obsd} vs. (p-RC_6H_4)(Me_2NO) concentration for reaction 3 in CH_2Cl_2 at 18.9 °C.

Table 1

Observed rate constants for the reaction (eq. 3) with changes in PPh_3 concentration at a fixed R_3NO concentration

R_3NO	$[R_3NO]$, M	T (°C)	$[PPh_3]$, M	k_{obsd}, s^{-1}
Et_3NO	1.17×10^{-2}	9.5	9.55×10^{-3}	3.10×10^{-3}
			1.91×10^{-2}	3.32×10^{-3}
			4.20×10^{-2}	2.82×10^{-3}
$PhMe_2NO$	1.37×10^{-2}	18.9	9.55×10^{-3}	3.11×10^{-3}
			1.91×10^{-2}	2.95×10^{-3}
			3.82×10^{-2}	3.07×10^{-3}

triamine compound $Cr(CO)_5N(C_6H_4CN)Me_2$ as part of the product. Its absorption bands in the IR CO stretching region are at 2074 cm^{-1} and 1946 cm^{-1}. It should also be noted that $Cr(CO)_5PPh_3$ can react further to give $Cr(CO)_4(PPh_3)_2$.

Plots of ln A_t vs. time for all of the reactions (eq. 3) were linear over two half-lives. Plots of k_{obsd} vs. R_3NO concentrations show a first-order dependence on amine *N*-oxide concentration (Fig. 1). In all cases, the linear correlation coefficients for the kinetic plots were above 0.995. The rates of reaction do not depend on PPh_3 concentration (Table 1). The reactions obey a second-order rate law (eq. 4).

$$-\mathrm{d}[Cr(CO)_6]/\mathrm{d}t = k_2[Cr(CO)_6][R_3NO] \quad (4)$$

Second-order rate constants and activation parameters for the reactions (eq. 3) are given in Table 2.

The relative base strengths of the amine *N*-oxides are given in Table 3. The larger the values of $\Delta\nu$(O–H), the greater the base strength of the amine *N*-oxide. Thus, alkyl amine *N*-oxides are more basic than aryl amine *N*-oxides.

Table 4 contains results of the competition experiments of $P(n\text{-}Bu)_3$ vs. py for the presumed intermediates "$M(CO)_5$". Two entirely different reactions were tested for the formation of the same "$Cr(CO)_5$" intermediate. Within experimental error, the

Table 2

Second-order rate constants and activation parameters for the reactions (eq. 3)

R_3NO	T (°C)	k_3, M^{-1} s^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/mol deg
Et_3NO	9.5	0.245	10.0 ±1.0	−25.7±0.2
	19.8	0.521		
	28.0	0.772		
Me_3NO [a]	20.1	0.0996	12.2 ±0.5	−21.3±1.7
$PhMe_2NO$	18.9	0.280	9.47±0.86	−28.5±0.12
	10.6	0.182		
	27.7	0.498		
$(PhCH_2)_3NO$	10.0	0.00773	10.9 ±0.7	−29.5±0.1
	18.9	0.0154		
	28.5	0.0271		

[a] Data from Ref. 1a.

Table 3

Second-order rate constants for the reactions (eq. 3) at 18.9°C

Amine oxides	R	$\sigma^{\star}$ [a]	σ_p [b]	$\Delta\nu$(O–H) (cm^{-1})	$E_{1/2}$ (V)	k_2 (M^{-1} s^{-1})
Et_3NO	C_2H_5	−0.100		980±10		0.463
Me_3NO	CH_3	0		920±10	−1.40 [c]	0.0901
$(PhCH_2)_3NO$	CH_2Ph	0.215		850±10	−0.72 [c]	0.0154
PyO [e]				370	−1.2 (H_2O)	
					−2.297 (DMF)	1.15×10^{-6}
(p-RC_6H_4)Me_2NO	CH_3		−0.17	800±10	−0.23 [c]	0.573
	H		0	790±10	−0.304 [d]	0.280
	$CO_2C_2H_5$		0.52	740±10		0.119
	CN		0.66	720±10		0.0390

[a] Ref. 6a. [b] Ref. 12. [c] Ref. 6, at pH = 4.2 in water solution. [d] Ref. 6, at pH = 4.0 in water solution. [e] The second order rate constant is for the reaction:

$$Fe(CO)_5 + PyO + PPh_3 \rightarrow Fe(CO)_4PPh_3 + Fe(CO)_3(PPh_3)_2 + Py + CO_2$$

in acetone at 45.2°C. PyO cannot transfer its O-atom to $Cr(CO)_6$ at these experimental conditions.

Table 4

Product distribution from competition reactions

$\frac{[P(n\text{-}Bu)_3]}{[Py]}$	$[M(CO)_5P(n\text{-}Bu)_3]/[M(CO)_5Py]$ for reaction 3			$[Cr(CO)_5P(n\text{-}Bu)_3]/$ $[Cr(CO)_5Py]$ from $Cr(CO)_5THF$
	Cr	Mo	W [a]	
1:1	1.59	2.6	4.5	1.69
1:3	0.60	0.87		0.59
1:6	0.32			
1:9		0.31		0.25
$\frac{k_{P(n\text{-}Bu)_3}}{k_{Py}}$	1.5	2.6	4.5	1.6

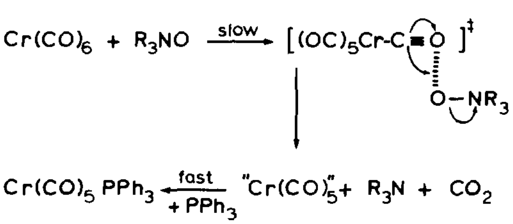
[a] ν(CO) of the two complexes are close to each other, the distribution was estimated at $[P(n\text{-}Bu)_3]/[Py]$ = 1:1.

same product distribution of $Cr(CO)_5P(n\text{-}Bu)_3$ and $Cr(CO)_5py$ was obtained from the two reactions.

Discussion

The rates of the reactions (eq. 3) are first-order in amine N-oxide and in $Cr(CO)_6$ concentrations, but zero-order in $[PPh_3]$. These results, as well as the low values of $\Delta H^{\ddagger}$ and negative values of $\Delta S^{\ddagger}$, suggest an associative mechanism. The mechanism proposed [1] earlier for CO substitution reactions of metal carbonyls in the presence of $(CH_3)_3NO$ is in accord with Scheme 1.

The results show that the rate constants for alkyl amine N-oxides increase with decreasing aliphatic polar constants $\sigma^{\star}$ [6a] introduced by Taft as the inductive effects of alkyl substituents (Table 3). A plot of ln k_2 vs. $\sigma^{\star}$ shows a good linear correlation (Fig. 2). Similarly the ln k_2 values for aryl amine N-oxides are observed to correlate the Hammett substituent constants σ_p (Table 3 and Fig. 3) [6b]. A similar correlation is observed with the values of $\Delta\nu$(O–H) (Table 3) which reflect



Scheme 1

the relative base strengths of the amine *N*-oxides. These results show that the more the negative charge on the oxygen 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.

Polarographic studies show [7] that amine *N*-oxides with electron-withdrawing substituents have higher oxidation potentials than do such compounds with electron-donating substituents. A very detailed study [8] 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 determining step of these O-atom transfer reactions involves a nucleophilic attack of the oxygen

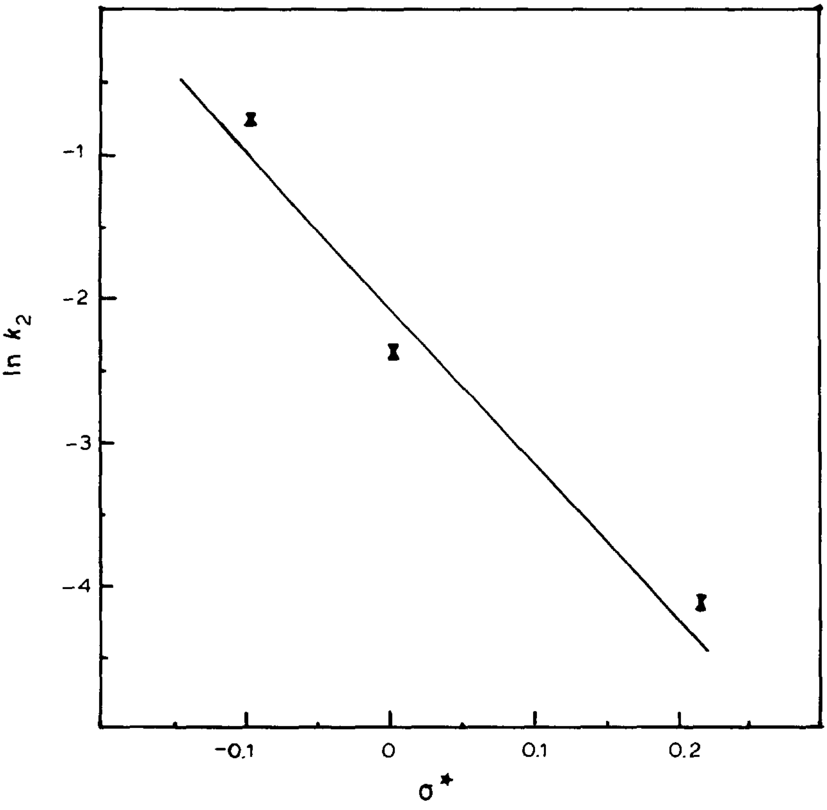


Fig. 2. Plot of ln *k* vs. aliphatic polar constants σ^* for reaction 3.

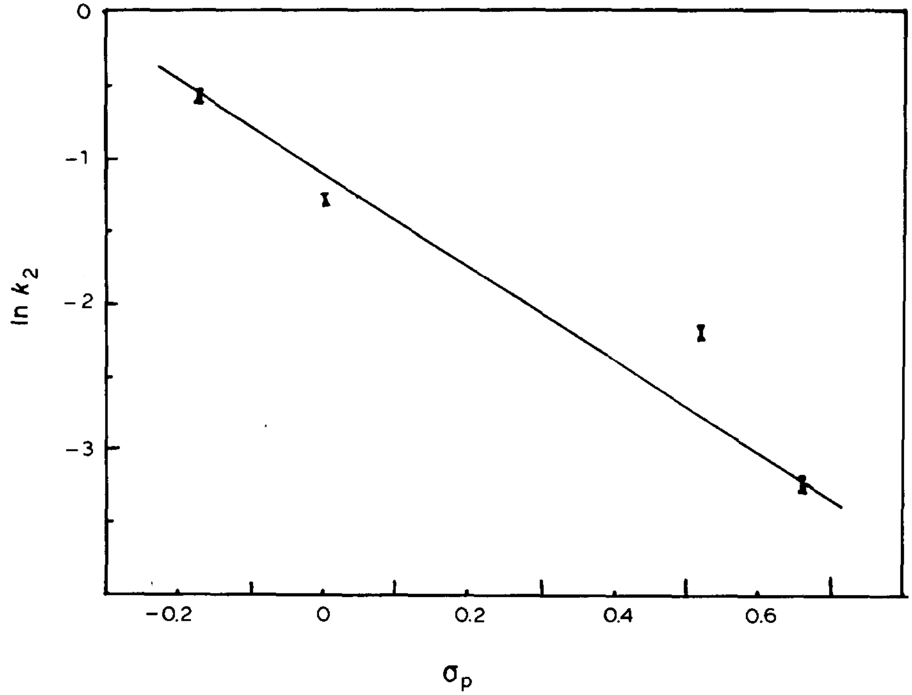


Fig. 3. Plot of ln k_2 vs. Hammett substituent constants σ_p for reaction 3.

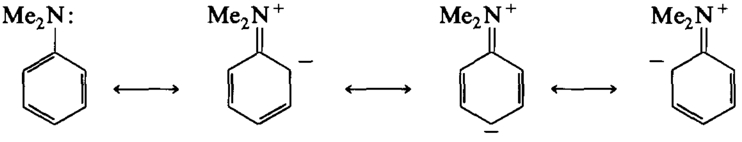
atom on a carbonyl carbon, it is not surprising that the rates decrease with increasing oxidizing ability of the amine *N*-oxides. A good oxidizing amine *N*-oxide has less electron density on its oxygen atom which renders it less reactive towards a carbonyl carbon.

Compared with other nucleophiles amine *N*-oxides act both as good nucleophiles and good oxidizing reagents to metal carbonyls. As nucleophiles, they have high negative charges on their O-atoms [9]. As oxidizing reagents, their N–O bond is very weak. The oxidation of CO to CO_2 is thermodynamically favored. Considering the reactions 5 and 6 and neglecting the bond energy difference between Cr–C and Cr–P, the net enthalpy of reaction is ΔH ca. -67 kcal/mol. This makes the process thermodynamically irreversible, and may partially be the reason that the O-atom transfer reaction is so fast. Because of delocalization of electron density in pyridine *N*-oxide, the O-atom has a lower negative charge and the N–O bond order is 1.5 (ν(N–O) are 1243 cm^{-1} for PyO and -950 cm^{-1} for R_3NO) [11]. Its O-atom transfer reaction to a metal carbonyl is much slower (Table 3) than that of tertiary-amine *N*-oxides.

$$CO_{(g)} + O_{(g)} \rightarrow CO_{2(g)} \quad \Delta H = -127.7 \text{ kcal/mol} \tag{5}$$

$$R_3NO_{(g)} \rightarrow R_3N_{(g)} + O_{(g)} \quad \Delta H = 61 \text{ kcal/mol [10]} \tag{6}$$

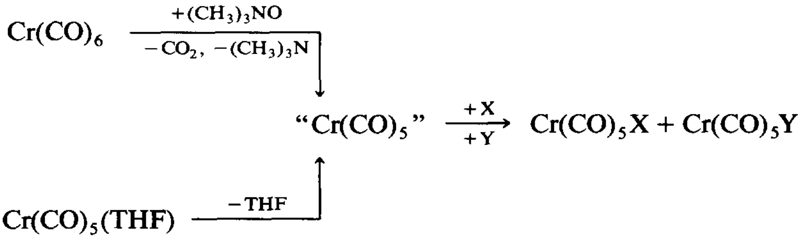
The data in Table 3 show that for each separate types of amine *N*-oxides, alkyl or aryl, the rates of reaction increase with increasing base strengths of the amine *N*-oxide. This is in accord with the rate determining step (Scheme 1) involving a nucleophilic attack of the basic oxide oxygen on a carbonyl carbon. Compared with alkyl amine *N*-oxides, aryl amine oxides are less basic (Table 3), but the aryl systems react with carbonyls faster than do the alkyl systems. Although complete coplanarity of the amine group and the aromatic ring in aryl amine is not achieved, a substantial degree of resonance stabilization does occur [12].



This may result in a weaker N–O bond in aryl amine oxides relative to alkyl amine oxides, and it may account in part for the greater reactivity of the aryl compounds. The activation parameters show that a lower $\Delta H^{\ddagger}$ value for $PhMe_2NO$ is the reason for its faster reaction with the metal carbonyl complex. This suggests that along with importance of the basic strength of the amine *N*-oxides is the ease with which the N–O bond breaks in the transition state for reaction.

That the nucleophilic strength of $(CH_3)_3NO$ towards carbonyls of metal carbonyls is similar to that of CH_3Li [13] and $C_6H_5CH_2MgBr$ [13] was not expected [1a]. A possible explanation is that there is a rapid electron transfer to afford the radicals $Cr(CO)_6^+$ and $(CH_3)_3NO^-$, followed by the rate determining nucleophilic attack of the radical anion which is expected to be a good nucleophile. ESR experiments, done in CH_2Cl_2 at room temperature, show a very weak resonance at $g = 1.980$ which appears to be due to $Cr(CO)_6^+$ [14] but there was no resonance in the region expected for $(CH_3)_3NO^-$. Furthermore, addition of the radical trap CCl_3Br to a reaction mixture of $Cr(CO)_6 + (CH_3)_3NO + PPh_3$ results in the loss of the ESR signal, but the reaction (eq. 3) affording $Cr(CO)_5PPh_3$ proceeds at the same rate as that without added radical trap. These results suggest the formation of $Cr(CO)_6^+$ has nothing to do with the reaction to form $Cr(CO)_5PPh_3$. It may be possible that small amounts of oxygen get into our system, resulting in the formation of enough $Cr(CO)_6^+$ to be seen by ESR. Also the oxidation of $Cr(CO)_6$ to $Cr(CO)_6^+$ has a $E_{1/2} = 1.53$ V [14], which means it cannot be oxidized by these amine *N*-oxides with reduction potentials of $E_{1/2} \sim 2$ V [7].

Another way to test the mechanism of the reaction (Scheme 1) is to compare the discriminating reactions of the intermediate "$Cr(CO)_5$" presumed in this mechanism with the presumed same intermediate produced by an entirely different reaction. If the two different reactions give the same ratio of $Cr(CO)_5X$ and $Cr(CO)_5Y$ products, then this supports a mechanism which forms the same intermediate in both reactions (Scheme 2). Our results show (Table 4) the two reactions to give the same ratio of products, thus supporting the formation of a common



Scheme 2

intermediate. That "$Cr(CO)_5$" is not very discriminating between entering nucleophiles is understandable on the basis of its very high reactivity [15]. Also investigated were the discriminating properties of "$Mo(CO)_5$" and of "$W(CO)_5$", generated by the reactions of $M(CO)_6$ with $(CH_3)_3NO$. The results (Table 4) show that the discriminating abilities of "$M(CO)_5$" increase in the order Cr < Mo < W. At present, we have no explanation for this discrimination order, but it may have something to do with the fact that what we, and others, refer to as coordinatively unsaturated species "$M(CO)_5$" in solution are in fact $M(CO)_5$(solvent) [16]. The "noncoordinating" solvent can then be a good leaving group which is readily replaced by presumably an I_d mechanism. Thus the competition reported is more correctly represented for $M(CO)_5$(solvent), where the M–solvent bond strength is known [16] to increase in the order Cr < Mo < W, which is consistent with the observed order of increasing discriminating power of the active intermediates.

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