Similarly, an ~100-fold drop in rate constant was also found for the $(bpy)_2ClRuLRuCl(bpy)_2^{3+}$ binuclear series as r increases from 6.8 to 13.8 Å.[46] With the internuclear distance difference between the pyrazine-bridged and the 4-pyridinecarboxamido-bridged binuclear complexes in our system, a rate difference of 1 order of magnitude may therefore be expected from the λ_{out} contribution. Moreover, in the pyrazine case, the π-accepting ability of the ligand will make the configurations of the Ru(II)–L and the Ru(III)–L tend to become similar[47] in the binuclear complex. This, in turn, may lead to a low inner-shell reorganization energy according to eq 15. On the other hand, in the pyridinecarboxamido case, the $(d_2^\circ - d_3^\circ)$ term in eq 15 may be significantly larger than the pyrazine species because of the σ character of the amido group. As a consequence, the inner-sphere reorganization energy also will be enhanced.

We were unable to observe any IT band for the binuclear complex IV with the 3-isomer as a bridge, probably due to the weak coupling arising from the meta position. However, for aged sample solutions, we observed a band at λ_{max} = 960 nm (ϵ_{max} = 710 M^{-1} cm^{-1}). Similar absorption at λ_{max} = 962 nm was also observed for the solution of the 4-isomer complex 30 min after its preparation. Since this 960-nm band was found only upon aging, we believe that the band is related to some decomposition compound rather than an intrinsic property of the binuclear complex itself. Similar observations were also found for a number of binuclear complexes containing the $Fe(CN)_5^{3-}$ moiety,[19,38] suggesting that the absorption may arise from some cyano-bridged binuclear cyanoferrate impurities.[19]

Acknowledgment. The support of this work by the National Science Council of the Republic of China under Grant NSC-77-0208-M033-10 is gratefully acknowledged.

---

(46) Powers, M. J.; Salmon, D. J.; Callaham, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 6731.

(47) Sutin, N. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; American Elsevier: New York, 1973; Vol. 2, p 611.

Contribution from the Departments of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, Lanzhou University, Lanzhou, Gansu, PRC, and University of Delaware, Newark, Delaware 19716

Important Factors in Oxygen Atom Transfer to Metal Carbonyls. Rate of CO Substitution of $Cr(CO)_6$ and $Fe(CO)_5$ in the Presence of $(p\text{-}CH_3OC_6H_4)_2EO$ (E = Se, Te) and of $(C_6H_5)_3EO$ (E = As, Sb). Syntheses and X-ray Structure of $Cr(CO)_5E(p\text{-}CH_3OC_6H_4)_2$

Jian-Kun Shen,[†] Yi-Ci Gao,[‡] Qi-Zhen Shi,*[‡] Arnold L. Rheingold,[§] and Fred Basolo*[†]

Received December 4, 1990

An attempt is made to obtain information on the various factors that contribute to the overall O atom transfer rates of reactions of metal carbonyls of the type M–CO + E–O → M + CO_2 + E. The metal carbonyls used were $Cr(CO)_6$ and $Fe(CO)_5$, and the O atom transfer reagents were $(p\text{-}CH_3OC_6H_4)_2EO$ (E = Se, Te), $(C_6H_5)_3EO$ (E = P, As, Sb), and $(C_6H_5)_2SO$. There was no reaction with either $(C_6H_5)_3PO$ or $(C_6H_5)_2SO$, under the experimental conditions used. The reagents that did react transfer their O atoms at the relative rates of TeO > SeO > SbO > AsO. These results, along with previously reported data, are discussed in terms of the various important factors believed to contribute to the energetics of these overall reactions. Syntheses are given of the new compounds $Cr(CO)_5E(p\text{-}CH_3OC_6H_4)_2$ (E = Se, Te), and the X-ray structure of the Te compound is reported. The Cr–Te distance in the present structure, 2.684 (1) Å, is the shortest known, and the Te atom is pyramidal.

Introduction

Although alkyl and aryl telluroxides and selenoxides are known[1] to be mild oxidizing reagents toward organic compounds, the reactions of these oxides as O atom transfer reagents toward inorganic complexes have not previously been reported. This paper is the first report of such a study, and it was prompted by our investigations[2] on the kinetics and mechanisms of O atom transfer from $(CH_3)_3NO$ to metal carbonyls.

Previous studies showed[2] that the rates for O atom transfer of $(CH_3)_3NO$ to metal carbonyls increased with increasing CO stretching frequencies of the metal carbonyls and with increasing basicities of the O atom of the amine oxides.[3] These results imply the rates of reaction are largely determined by a nucleophilic attack of the O atom of the amine oxides at a carbonyl carbon atom of the metal complexes. On this basis of viewing the rate-determining step as simply that of nucleophilic attack of the O atom on a CO carbon atom, we were surprised to find that $(CH_3)_3NO$ was as good a nucleophile as are CH_3Li[4a] and $C_6H_5CH_2MgBr$.[4b] This was initially explained in terms of "the high negative charge[5] on oxygen in $Me_3N^{\delta+} \rightarrow O^{\delta-}$".

More recently[3] the N–O bond strengths of the amine oxides were addressed in terms of their weaker bond strengths thermodynamically favoring their reaction to product. Holm[6] has tabulated thermodynamic data on available oxidation enthalpies of different O atom transfer reagents, and he has stressed the use of these data for predicting reactions in a manner analogous to the use made of values of standard redox potentials.

[†] Northwestern University.
[‡] Lanzhou University.
[§] University of Delaware.

(1) Ley, S. V.; Meerholz, C. A. *Tetrahedron* **1981**, *37*, 213.

(2) Shi, Y. L.; Gao, Y. C.; Shi, Q.-Z.; Kershner, D. L.; Basolo, R. *Organometallics* **1987**, *6*, 1528. Shen, J. K.; Gao, Y. C.; Shi, Q. Z.; Basolo, F. *Ibid.* **1989**, *8*, 2144.

(3) Shen, J. K.; Gao, Y. C.; Shi, Q. Z.; Basolo, F. *J. Organomet. Chem.* **1991**, *401*, 295.

(4) (a) Dobson, G. R.; Paxson, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5925. (b) Darensbourg, M. Y.; Conder, H. L.; Darensbourg, D. J.; Hasday, C. *Ibid.* **1973**, *95*, 5919.

(5) Nelson, S. D.; Kollman, P. A.; Trager, W. F. *J. Med. Chem.* **1973**, *84*, 4432.

(6) Holm, R. H. *Coord. Chem. Rev.* **1990**, *100*, 183. Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(7) (a) Ziegler, T.; Tschinke, V.; Ursenbach, C. *J. Am. Chem. Soc.* **1987**, *109*, 4825 and references therein. (b) Shen, J. K.; Gao, Y. C.; Shi, Q. Z.; Basolo, F. *Inorg. Chem.* **1989**, *28*, 4304. (c) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557. (d) Candlin, J. P.; Shortland, A. C. *J. Organomet. Chem.* **1969**, *16*, 289. Shojaie, A.; Atwood, J. D. *Organometallics* **1985**, *4*, 187. Poë, A. J.; Sekhar, V. C. *Inorg. Chem.* **1985**, *24*, 4377.

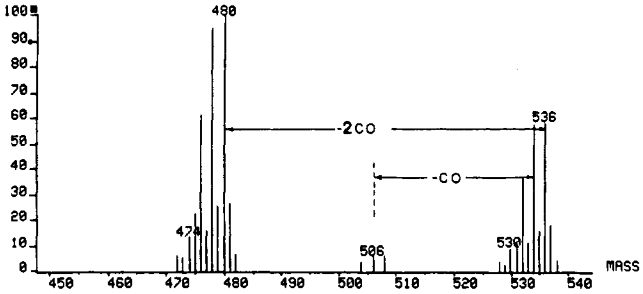


Figure 1. Mass spectrum of $Cr(CO)_5Te(C_6H_4OCH_3)_2$.

This paper attempts to assess the importance of the various factors that contribute to the rates of O atom transfer of different oxide reagents to a carbon atom of a carbonyl in $Cr(CO)_6$ or in $Fe(CO)_5$ (eq 1). The rate laws for these reactions are second-order, being first-order in the concentrations of M–CO and of E–O. The mechanism is believed to be similar to that reported earlier[2] involving a nucleophilic attack of the O atom of E–O on the C atom of M–CO, but it is necessary to keep in mind that two bond-breaking processes (M–CO and E–O) must also take place in order to yield the proposed products (eq 1). How much bond-making and how much each bond-breaking contributes to the overall energetics of the transition state of the reaction is not known. Here we report an attempt 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.

$$\text{M–CO} + \text{E–O} \rightarrow \text{“M”} + CO_2 + \text{E} \qquad (1)$$

$$\text{M} = \text{Cr, Fe; E} = \text{N, As, Sb, Se, Te}$$

(other ligands not shown on M;
alkyl or aryl groups not shown on E)

Experimental Section

Chemicals. Ph_2SO, Ph_3PO, anisole, and $TeCl_4$ were obtained from Aldrich, and $SeOCl_2$, Ph_3AsO, and Ph_3SbO were from Strem. $CHCl_3$ and THF were dehydrated with P_2O_5 and Na, respectively, and distilled under N_2 atmosphere before use. $(p\text{-}CH_3OC_6H_4)_2TeO$ was synthesized and purified by the literature method.[1] $(p\text{-}CH_3OC_6H_4)_2SeO$ was synthesized with anisole and $SeOCl_2$.[8] A 3-g sample of $SeOCl_2$ was dissolved in 20 mL of anisole, and the solution was stirred at room temperature for 3 days. Anisole was distilled off under vacuum, and the residue was recrystallized in CH_3CN. The yellow crystal was mixed with 100 mL of a 5% NaOH–water solution, and the mixture was stirred at boiling temperature for 1 h to give $(p\text{-}CH_3OC_6H_4)_2SeO$ as a white solid. The product was washed with cold distilled water three times and dehydrated under vacuum over P_2O_5 for several hours. IR (Nujol; cm^{-1}): 1583, 1574, 1491, 1466, 1440, 1378, 1308, 1297, 1245, 1178, 1167, 1058, 1026, 835, 820, 809, 786, 722.

Reduction of $(p\text{-}CH_3OC_6H_4)_2TeO$ with $Cr(CO)_6$. A 150-mg quantity of $Cr(CO)_6$ and 250 mg of $(p\text{-}CH_3OC_6H_5)_2TeO$ were dissolved in 30 mL of THF. The telluroxide was not completely dissolved. The mixture was stirred at room temperature for 10 h, THF was removed under reduced pressure, and the residue was extracted with toluene. A yellow solution was obtained after filtration. Toluene was removed, and after the yellow solid was held under a dynamic vacuum for several hours to remove $Cr(CO)_6$, it was recrystallized in pentane–toluene mixed solvent. Yield: 50% (180 mg). IR (pentane; cm^{-1}): 2062.4 (m), 1945.4 (vs). ^1H NMR (CD_2Cl_2; δ): 3.83 (s, 6 H), 6.91 (d, 4 H), 7.58 (d, 4 H). MS (m/e relative intensity): 536, 2.8 (Figure 1); 480, 4.8; 396, 10.3; 344, 66.6; 214, 100; 199, 31.6; 108, 7.9. Anal. Calcd for $C_{19}H_{14}O_7CrTe$: C, 42.74; H, 2.64. Found: C, 42.97; H, 2.69. Mass spectra were recorded by H. L. Hung on a Model VG 70SE spectrometer, and the elemental analyses were done at G. D. Searle.

Reduction of $(p\text{-}CH_3OC_6H_4)_2SeO$ with $Cr(CO)_6$. A 300-mg sample of $Cr(CO)_6$ was dissolved in 15 mL of THF. Then 15 mL of THF solution containing 200 mg of $(p\text{-}CH_3OC_6H_4)_2SeO$ was added in portions with a syringe. The mixed solution was stirred at room temperature for 6 h. THF was removed under reduced pressure, and the residue was held under a dynamic vacuum for several hours and extracted with toluene. Toluene was removed under reduced pressure, leaving the residue as a mixture of white and yellow crystals (150 mg). After several crystallizations in pentane, a white crystal was separated from the mixture. The white crystal (yield 40%), which turned out to be $(p\text{-}CH_3O_6H_4)_2Se$, was characterized by its melting point (57–58 °C)[9] and by its mass spectrum. MS (m/e, relative intensity): 290, 13; 291, 12.7; 292, 28.1; 293, 6.35; 294, 49.2; 295, 11.2; 296, 13.2; 214, 100; 199, 38.0. $Cr(CO)_5Se(C_6H_4OCH_3)_2$ was isolated as a yellow crystal. Yield: 5–10%. IR (pentane; cm^{-1}): 2067.7 (m), 1947.8 (vs), 1934.4 (s). MS (m/e, relative intensity): 486, 0.16; 430, 0.94; 346, 4.25; 294, 100; 214, 100. Anal. Calcd for $C_{19}H_{14}O_7CrSe$: C, 47.02; H, 2.91. Found: C, 47.14; H, 2.90.

Reduction of Ph_3SbO with $Fe(CO)_5$. A 150-mg sample of Ph_3SbO was added to 15 mL of a THF solution containing 100 mg of $Fe(CO)_5$. (Ph_3SbO has low solubility in THF). After the mixture was stirred at 45–50 °C for 3 days, a brown clear solution was obtained. No further reaction was observed for another 2 days according to the IR data (ν_{CO}). THF was then removed under reduced pressure, and the residue was extracted with pentane. The yellow-brown solution was concentrated and cooled in a refrigerator. The known[10] compound $Fe(CO)_4SbPh_3$ was obtained as a yellow crystal (~50 mg). Yield: 20%. The product, purified by washing with CH_3OH, was recrystallized in pentane. IR (pentane; cm^{-1}): 2048.7 (m), 1976.0 (m), 1945.7 (s). MS (m/e, relative intensity): 523, 1.6; 522, 7.2; 521, 2.2; 520, 9.5; 464, 10.4; 436, 23.2; 408, 90.5; 352, 29.2; 198, 100. Under the same experimental conditions, $Cr(CO)_6$ does not react with Ph_3SbO.

Kinetic Measurement. Reaction 1 was followed with a Nicolet 5PC-FT-IR spectrophotometer using a 0.2-mm NaCl IR cell, under conditions where the concentrations of oxides and py are at least 10 times greater than that of $Cr(CO)_6$. The highest concentration of E–O reagent used was that restricted by its limited solubility. Because $(p\text{-}CH_3OC_6H_4)_2TeO$ has a low solubility in CH_2Cl_2 or THF, the reaction was studied in $CHCl_3$. For $(p\text{-}CH_3OC_6H_4)_2SeO$, the reaction was too slow in $CHCl_3$ (no reaction was observed after 2 days at room temperature), so it was followed in THF. Constant temperatures (±0.1 °C) were maintained by an externally circulating bath (Neslab RTE-8). For comparison with Me_3NO, the reaction of $(p\text{-}CH_3OC_6H_4)_2SeO$ with $Cr(CO)_6$ was investigated in CH_2Cl_2 at one only temperature. Rate constants k_{obsd} were obtained by following the decrease of the CO stretching band at 1980 cm^{-1} and using eq 2 for calculation.

$$\ln A_t = -k_{obsd}t + \text{constant} \qquad (2)$$

Base Strengths. The relative base strengths of the oxides could be measured by investigating the hydrogen-bonding interaction of oxides with phenol.[11] The O–H stretching bands in the IR region broaden and shift to lower frequencies upon formation of hydrogen bonds with oxides. Experiments show that the O–H stretching band of C_6H_5OH broadens too much to permit accurate location of the band position when C_6H_5OH interacts with strong bases such as Me_3NO, Ph_3AsO, etc. CH_3OH, which is a weaker acid than C_6H_5OH, was chosen to determine relative base strengths of these oxides. The O–H stretching band of CH_3OH shifts less to lower frequencies than that of C_6H_5OH, but is relatively narrow and can be accurately assigned, upon formation of hydrogen bonds with these oxides. All of these data (Table III) were measured in CCl_4.

Crystallographic Structure Determination. Crystallographic data gathered on a Nicolet instrument are collected in Table IV. A yellow crystal of $Cr(CO)_5Te(p\text{-}CH_3OC_6H_4)_2$ was grown from pentane and mounted on a glass fiber. Photographic and diffraction data were used to uniquely assign the crystal to the monoclinic space group, $P2_1/n$. An empirical correction for absorption based on ψ-scan data was applied. The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included as idealized contributions. All computations used the SHELXTL (5.1) library of programs (G. Sheldrick, Nicolet XRD, Madison, WI).

Atomic coordinates are given in Table V, and selected bond distances and angles, in Table VI.

Results

The reactions (eq 3) were carried out in $CHCl_3$ for E = Te, which is not soluble in THF, and in THF for E = Se, which does not react in $CHCl_3$. All of the reactions afforded the product

$$Cr(CO)_6 + py + (p\text{-}CH_3OC_6H_4)EO \rightarrow Cr(CO)_5py + CO_2 + (p\text{-}CH_3OC_6H_4)_2E \qquad (3)$$

$$py = \text{pyridine; E} = \text{Se, Te}$$

---

[8] Adquist, F. N.; Nelson, R. E. *J. Am. Chem. Soc.* **1931**, *53*, 4033.

[9] Bergman, J. *Tetrahedron* **1972**, *28*, 3323.

[10] Cardaci, G. *Inorg. Chem.* **1974**, *13*, 368.

[11] Nelson, J. H.; Nathan, L. C.; Ragsadale, R. O. *J. Am. Chem. Soc.* **1968**, *90*, 5754.

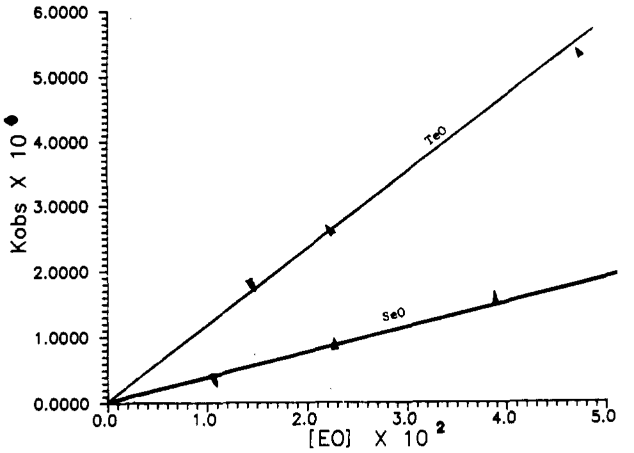


Figure 2. Plot of k_{obsd} vs $(CH_3OC_6H_4)_2EO$ concentration for the reaction (eq 3) of $Cr(CO)_6$: E = Te, 30.0 °C in $CHCl_3$; E = Se, 18.0 °C in THF.

Table I. Observed Rate Constants for Reaction 3 (E = Te)[a] with Different py Concentrations at 39.5 °C

[py], M	$10^4 k_{obsd}$, s^{-1}
0[b]	5.57
0.124	7.30
0.620	6.94

[a] $[(p\text{-}CH_3OC_6H_4)_2TeO] = 2.24 \times 10^{-2}$ M. [b] Reaction of eq 5.

Table II. Second-Order Rate Constants and Activation Parameters for Reaction 3

E	T, °C	k_2, $M^{-1}\,s^{-1}$	ΔH^*, kcal/mol	ΔS^*, cal/(mol K)
Te	18.5	3.62×10^{-3}		
	30.0	1.17×10^{-2}		
	39.5	3.26×10^{-2}	18.3 ± 0.7	−6.9 ± 0.5
Se	18.0	3.81×10^{-3}		
	30.0	1.02×10^{-2}		
	40.0	2.10×10^{-2}	13.6 ± 1.4	−22.9 ± 0.7

$Cr(CO)_5py$, as determined by the agreement of its IR spectrum with the literature.[12] Plots of ln A_t vs time for the reactions (eq 1) were linear over 2 half-lives. Plots of k_{obsd} vs R_2EO concentrations show a first-order dependence on $[R_2EO]$ (Figure 2). The low solubilities of the R_2EO reagents limited the range of concentrations that could be used. In all cases, the linear correlation coefficients are above 0.995. The rates of the reactions do not depend on py concentration (Table I). The reactions obey a second-order rate law (eq 4). The second-order rate constants

$$-d[Cr(CO)_6]/dt = k_2[Cr(CO)_6][R_2EO] \qquad (4)$$

and activation parameters for the reactions (eq 1) are given in Table II.

Under the same experimental conditions, neither Ph_2SO nor Ph_3PO reacts with $Cr(CO)_6$ or $Fe(CO)_5$. Ph_3AsO can accelerate CO substitution of $Fe(CO)_5$ with $P(n\text{-}Bu)_3$, to give the monosubstituted product $Fe(CO)_4P(n\text{-}Bu)_3$. The second-order rate constant for this reaction is given in Table III. A similar reaction mixture of PPh_3 and Ph_3AsO gives a mixture of mono- and bis(triphenylphosphine) products. Ph_3SbO does not dissolve in these solvents, so the synthesis of $Fe(CO)_4SbPh_3$ was achieved in a heterogeneous reaction mixture, but kinetic data were not obtained.

The relative base strengths of the oxides are given in Table III. The larger value of $\Delta\nu_{O-H}$, the greater the base strength of the oxide. These measurements show that base strengths of the oxides decrease in the order $R_3NO > R_2TeO \sim R_3AsO \sim R_3SbO > R_2SeO > pyO > R_3PO > R_2SO$.

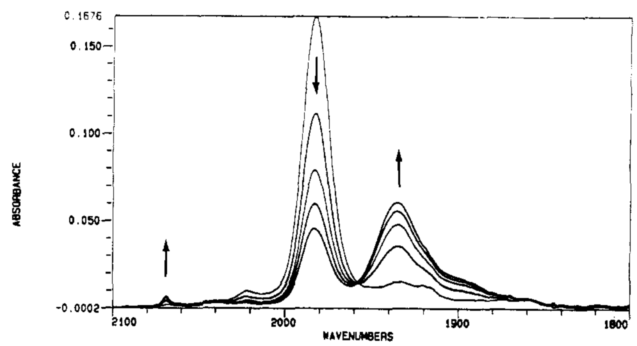


Figure 3. Infrared ν_{CO} absorbance changes vs time for the reaction (eq 3) of $Cr(CO)_6$ with $(CH_3OC_6H_4)_2TeO$ in $CHCl_3$ at 18.5 °C.

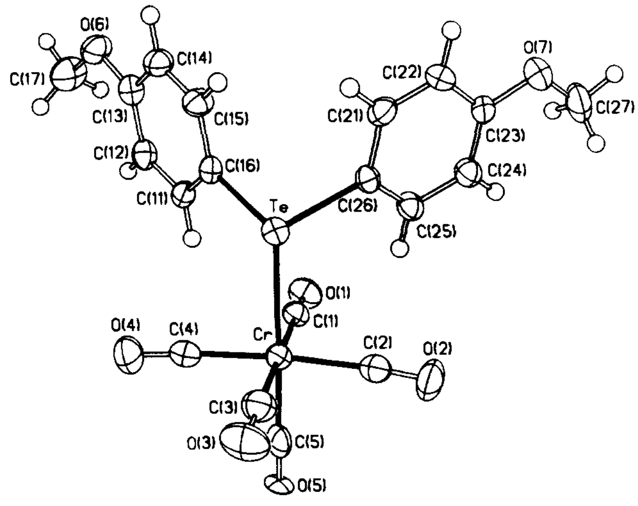


Figure 4. Molecular structure of $Cr(CO)_5Te(p\text{-}CH_3OC_6H_4)_2$ drawn with 35% probability ellipsoids.

In the absence of pyridine, the reactions of $Cr(CO)_6$ with $(p\text{-}CH_3OC_6H_4)_2EO$ afford $Cr(CO)_5E(p\text{-}CH_3OC_6H_4)_2$ (eq 5).

$$Cr(CO)_6 + (p\text{-}CH_3OC_6H_4)EO \rightarrow Cr(CO)_5E(p\text{-}CH_3OC_6H_4)_2 + CO_2 \qquad (5)$$

$$E = Se, Te$$

These two new compounds were characterized by elemental analyses and mass spectroscopy, and an X-ray structural determination was done on the telluride. Their mass spectra show that the relative peak intensities of the fragmented $Cr(CO)_nE(p\text{-}CH_3OC_6H_4)_2$ species are higher for E = Te than for E = Se, which is consistent with the greater stability of the Te compound. For both compounds, the relative intensities of these species are accurately consistent with values obtained from isotope cluster abundance calculations (Figure 1).

The structure of $Cr(CO)_5Te(p\text{-}CH_3OC_6H_4)_2$ is shown in Figure 4. The coordination geometry at Cr is only slightly distorted from a regular octahedral structure. The largest distortion, being in the C(2)–Cr–C(4) angle, 174.3 (3)°, likely results from a steric interaction with the overlying phenyl rings. Only three compounds containing Cr–Te bonds are available for comparison: $[Ph_4P]_2[Cr(CO)_4(\eta^2\text{-}Te_4)]$ (2.753 (2) and 2.699 (2) Å),[13] $[\overline{CpCr(CO)_3}]_2Te$ (2.799 (1) and 2.814 (1) Å),[14] and $(Et)\overline{NC_2H_4N(Et)}C{=}TeCr(CO)_5$ (2.765 (4) Å).[15] Within this limited pre-

---

(12) Kraihanzel, C. S.; Cotton, F. A. *Inorg. Chem.* **1963**, *2*, 533.

(13) Flomer, W. A.; O'Neal, S. C.; Kolis, J. W.; Jeter, D.; Cordes, A. W. *Inorg. Chem.* **1988**, *27*, 969.

(14) Hermann, W. A.; Rohrmann, J.; Ziegler, M.; Zahr, T. *J. Organomet. Chem.* **1984**, *273*, 221.

(15) Lappert, M. F.; Martin, T. R.; McLaughlin, G. M. *J. Chem. Soc., Chem. Commun.* **1980**, 635.

Table III. Rate Constants for O Atom Transfers of Different Oxides to Metal Carbonyls

R_nEO	$\Delta\nu_{O-H}$, cm^{-1}	E–O bond strengths, kcal/mol	T, °C	k_2, M^{-1} s^{-1}	solvent
		Reactions with $Cr(CO)_6$			
Me_3NO	400 ± 5	61[a]	19	9×10^{-2}	CH_2Cl_2[b]
				2.85×10^{-3}	$CHCl_3$
C_6H_5IO		53[a]	22	1.56×10^{-1}	THF–CH_3OH[c]
$(p\text{-}CH_3OC_6H_4)_2TeO$	300 ± 5	52[d]	19	3.4×10^{-3}	$CHCl_3$
$(p\text{-}CH_3OC_6H_4)_2SeO$	280 ± 5	73[d]	20	no reacn	$CHCl_3$
				1.4×10^{-4}	CH_2Cl
				5.5×10^{-3}	THF
		Reactions with $Fe(CO)_5$			
pyO	268 ± 5	73[e]	45	1.15×10^{-6}	$(CH_3)_2CO$[f]
Ph_3AsO	302 ± 5	107[g]	57	4×10^{-6}	THF
Ph_3SbO	296 ± 5	107[g]	57	$\geq 4 \times 10^{-6}$	THF
Ph_3PO	242 ± 5	127[e]	40–50	no reacn	THF
Ph_2SO	225 ± 5	87[e]	40–50	no reacn	THF

[a] Reference 27. [b] Reference 2. [c] Reference 23. [d] Values estimated by using E–O diatomic molecular bond strengths. [e] Reference 6. [f] Reference 3. [g] Reference 26.

Table IV. Crystallographic Data for $Cr(CO)_5Te(p\text{-}CH_3OC_6H_4)_2$

(a) Crystal Parameters	
formula	$C_{19}H_{14}CrO_7Te$
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	10.468 (2)[a]
b, Å	9.442 (3)
c, Å	20.672 (7)
β, deg	100.35 (2)
v, Å^3	2009.9 (11)
Z	4
cryst dimens, mm	0.24 × 0.32 × 0.36
cryst color	yellow
D(calc), g/cm^3	1.764
μ(Mo Kα), cm^{-1}	20.63
temp, °C	23
T(max),/T(min)	1.20
(b) Data Collection	
diffractometer	Nicolet R3m
monochromator	graphite
radiation	Mo Kα
2θ scan range, deg	4–52
data collected: h,k,l	±13,12,26
no. of rflns collected	4542
no. of indpt reflns	4158
R(merg), %	2.1
indpt rflns obsd ($F_o \geq 3\sigma(F_o)$)	2842
std rflns	3 std/197 rflns
var in stds	<1%
(c) Refinement	
$R(F)$, %	4.29
$R_w(F)$, %	4.60
Δ/σ (max)	0.02
$\Delta(\rho)$, e Å^{-3}	0.82
N_o/N_v	11.2

[a] Unit-cell parameters were obtained from the angular settings of 25 reflections, 22° ≤ 2θ ≤ 30°.

Table V. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $Cr(CO)_5Te(p\text{-}CH_3OC_6H_4)_2$

	x	y	z	U[a]
Cr	2 (1)	7973 (1)	1050 (1)	42 (1)
Te	1873 (1)	7621 (1)	2110 (1)	40 (1)
O(1)	164 (5)	11157 (5)	1197 (3)	65 (2)
O(2)	1877 (6)	7959 (7)	87 (3)	84 (3)
O(3)	−335 (6)	4806 (6)	834 (3)	92 (3)
O(4)	−2111 (5)	7684 (6)	1870 (3)	78 (2)
O(5)	−2141 (5)	8484 (7)	−103 (3)	45 (2)
O(6)	670 (5)	11079 (6)	4519 (2)	66 (2)
O(7)	6847 (4)	11053 (6)	1818 (3)	69 (2)
C(1)	132 (6)	9967 (8)	1157 (3)	45 (2)
C(2)	1238 (7)	7981 (8)	458 (3)	53 (2)
C(3)	−161 (7)	5991 (8)	928 (4)	62 (3)
C(4)	−1294 (6)	7820 (7)	1577 (3)	50 (2)
C(5)	−1375 (7)	8277 (7)	305 (4)	59 (3)
C(11)	300 (6)	9738 (7)	2818 (3)	45 (2)
C(12)	14 (6)	10499 (7)	3355 (3)	48 (2)
C(13)	831 (6)	10396 (7)	3963 (3)	50 (2)
C(14)	1922 (6)	9525 (8)	4025 (3)	53 (2)
C(15)	2179 (6)	8755 (7)	3494 (3)	49 (2)
C(16)	1370 (5)	8857 (6)	2889 (3)	40 (2)
C(17)	−451 (8)	11926 (10)	4498 (4)	82 (4)
C(21)	4647 (6)	8745 (8)	2449 (3)	51 (2)
C(22)	5720 (6)	9517 (8)	2378 (3)	56 (3)
C(23)	5715 (6)	10396 (8)	1854 (3)	51 (2)
C(24)	4587 (6)	10576 (7)	1401 (3)	51 (2)
C(25)	3464 (6)	9812 (7)	1476 (3)	47 (2)
C(26)	3493 (5)	8891 (6)	1982 (3)	39 (2)
C(27)	6888 (8)	12006 (10)	1297 (4)	81 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Selected Bond Distances and Angles for $Cr(CO)_5Te(p\text{-}CH_3OC_6H_4)_2$

(a) Bond Distances (Å)			
Cr–Te	2.684 (1)	C(2)–O(2)	1.106 (10)
Cr–C(1)	1.898 (7)	C(3)–O(3)	1.145 (10)
Cr–C(2)	1.934 (8)	C(4)–O(4)	1.140 (9)
Cr–C(3)	1.892 (8)	C(5)–O(5)	1.072 (9)
Cr–C(4)	1.891 (7)	Te–C(16)	2.130 (6)
Cr–C(5)	1.932 (7)	Te–C(26)	2.133 (6)
C(1)–O(1)	1.126 (9)		
(b) Bond Angles (deg)			
C(16)–Te–C(26)	95.5 (2)	Te–Cr–C(2)	92.5 (2)
Cr–Te–C(16)	107.8 (1)	Te–Cr–C(3)	91.3 (2)
Cr–Te–C(26)	108.0 (2)	Te–Cr–C(4)	90.8 (2)
Te–Cr–C(1)	90.1 (2)	Te–Cr–C(5)	177.9 (2)

cedent, the Te–Cr distance in the present structure, 2.684 (1) Å, is the shortest known. The Te atom is pyramidal; the sum of the angles at Te is 311.3°.

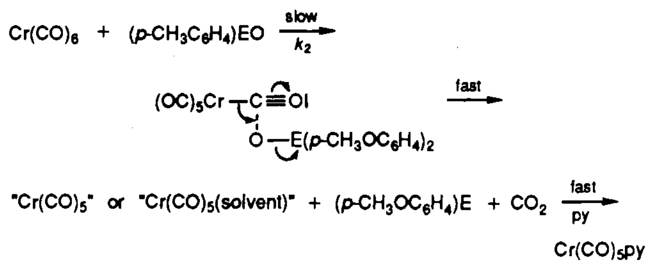
Discussion

The new compounds $Cr(CO)_5E(p\text{-}CH_3OC_6H_4)_2$ (E = Se, Te) were synthesized by the reactions between $Cr(CO)_6$ and $(p\text{-}CH_3OC_6H_4)_2EO$ (eq 5). Both complexes are stable solids at room temperature, even when exposed to air. The much higher reaction product yield of the tellurium, relative to the selenium, complex may suggest it is more stable than is the corresponding selenium complex. If this stability relation is correct, then it is contrary to the information[16] suggesting that complexes of metals in their normal or higher oxidation states with ligand atoms of the sulfur family decrease in stability in the order S > Se > Te. However, recent studies[17] support the present observation that, for metals

---

[16] Murray, S. G.; Hartley, F. W. *Chem. Rev.* **1981**, *81*, 365.

Scheme I



in low oxidation states, complexes with ligand atoms of the oxygen family decrease in stability in the order Te > Se > S > O. This order of stability was attributed to the greater importance of metal-to-ligand π-bonding for metals in low oxidation states relative to the same metals in higher oxidation states. Furthermore, for a given family of ligand atoms, an increase in π-bonding with increase in atomic number of the ligand atom is believed to occur due to the greater polarizability of the heavier ligand atom.

The reactions investigated (eq 3) obey a second-order rate law (eq 4), being first-order in oxide concentrations and in metal complex concentration but zero-order in the entering ligand concentration. This is the same rate behavior reported ealier[2] for similar reactions said to proceed by an associative pathway. The relatively small ΔH^* and the negative value of ΔS^* (Table II) are characteristic of an associate mechanism. In the presence of pyridine, $Cr(CO)_5py$ was produced stoichiometrically (eq 3) (Figure 3). The mechanism proposed earlier[2] for such reactions is consistent with all of the kinetic data (Scheme I).

Our early[2] description of this mechanism suggested merely that the rate-determining step is a nucleophilic attack on the C of M–CO, and, further, that the stronger the nucleophile and the more positive the carbon, the faster the reaction. This gross concept of the proposed mechanism is still believed valid. However, the gross reaction process does not address some of the more intimate details of the overall reaction. What follows is an attempt to describe the reaction mechanism in as much detail as possible, within the constraints of the experimental evidence available at present.

The first gross simplification is that of representing the intermediate as the "coordinatively unsaturated" species "$Cr(CO)_5$" in solution. Surely, as a ligand leaves its coordination site and goes into solution, it does not create a vacuum at the spot vacated: solvent moves in to occupy the "open" spot. Basolo and Pearson[18] essentially made this point in the first edition of their book in 1958.

It now appears clear that, for the solution chemistry of $Cr(CO)_6$, the active intermediate originally represented in quotation marks as "$Cr(CO)_5$", in order to stress the fact that the exact species is not known, should now more correctly be designated "$Cr(CO)_5$(solvent)". This is due to the elegant research being done in several laboratories attempting to understand the solvation/desolvation reactions that take place after flash photolysis of metal carbonyls in solution. What is found[19] is that very rapid (picosecond) solvation of "$Cr(CO)_5$" takes place to give "$Cr(CO)_5$(solvent)", even for "noncoordinating" solvents such as alkanes. Others[20] have also studied the strengths (ca. 10 kcal/mol) of Cr–alkane bonds by time-resolved photoacoustic calorimetry, and still others[21] have focused attention on the replacement of solvent molecules such as alkanes from "$Cr(CO)_5$(solvent)".

For the purposes of the present study, designed only to give the gross aspects of the mechanisms of reactions of the type given by eq 3, the question then arises as to what changes should be made in the mechanism depicted in Scheme I. The answer seems to be that "$Cr(CO)_5$" should be represented as "$Cr(CO)_5$(solvent)". However, since the solvent is such a good leaving group and since some good nucleophiles at higher concentrations may even compete with the solvent to form product directly, the actual unknown active intermediate involved does not markedly alter the rates of reaction (eq 1).

Of fundamental importance in considering the intimate details of the mechanism depicted in Scheme I are the energetic contributions of the different factors involved to the stability of the transition state of the reaction. The contributions of each of these to the rates of reaction may be impossible to quantify, but the individual processes involved and the relevant experimental data available are discussed here. First, it is important to note that the transition state formed by nucleophilic attack of the O atom of an O atom transfer reagent must undergo several intramolecular transformations before going to "immediate" products. These transformations are (1) the bond-making between the O atom of the oxide and the C atom of the carbonyl, (2) the bond-breaking of the Cr–CO bond, (3) the bond-breaking of the E–O bond, and (4) the redox process involving inner-sphere electron transfer resulting in the oxidation of CO to CO_2 and the reduction of E–O to E.

Direct, or indirect, quantitative data are available on each of these four transformations, and use was made[2] of this information in assessing the effect of the nature of the substrate and of the nucleophile O atom transfer reagent on the relative rates of reaction. For example, the rates of reaction generally increase with increasing values of ν_{CO} of the metal carbonyls, which are believed to contain more positively charged C atoms that are more susceptibile to nucleophilic attack.[22] Prior to this paper, except for a study on C_6H_5IO),[23] all of the reports on the kinetics of this type of reaction (eq 1) involved amine *N*-oxides as nucleophiles/O atom transfer reagents.[24] It was found that, for a given metal carbonyl, the rates of reaction increase with increasing basicity/electron density for the O atom of the amine *N*-oxide.[3] This is as expected, for it means the O atom transfer reagent would then be a stronger nucleophile, and it would have a greater tendency to attack the positive C atom of a carbonyl ion the metal carbonyl.

One other feature of these reactions (eq 1) that was considered[3] is that they are redox reactions, with CO being oxidized to CO_2 while EO is reduced to E. However, it was found that the rates of reaction decrease with increasing oxidizing ability of the amine oxides. This finding emphasizes the point that the basicity or nucleophilic strength of the amine oxide in the rate-determining step of the reaction is more important energetically than is its redox potential. That amine oxides can act both as good nucleophiles and as adequate oxidizing reagents was attributed[3] to their highly negatively charged O atoms in $R_3N^{\delta+}$–$O^{\delta-}$ and their weak N–O bond strengths.

This paper reports new experimental data (Table III) on this type of reaction (eq 1) for O atom transfer reagents other than amine *N*-oxides. An attempt is made to qualitatively understand how the relative rates of reaction are affected by the basicities of the O atom transfer reagents and by their E–O bond strengths. In general, the results obtained for these systems are much the

---

(17) (a) Hoch, M.; Rehder, O. *J. Organomet. Chem.* **1985**, *288*, C25. (b) Belforte, A.; Calderazzo, F.; Vitali, D.; Zanazzi, P. F. *Gazz. Chim. Ital.* **1985**, *115*, 125. (c) Freeman, J.; Basolo, F. *Organometallics* **1991**, *10*, 256.

(18) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 1st and 2nd eds.; John Wiley and Sons: New York, 1958, 1967; p 99 (1st ed.); pp 133, 134 (2nd ed.).

(19) (a) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *68*, 1941. (b) Simon, J. D.; Peters, K. S. *Chem. Phys. Lett.* **1983**, *68*, 53. (c) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6751. (d) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1987**, *91*, 5538. (e) Wang, L., Zhu, X.; Spears, K. G. *J. Am. Chem. Soc.* **1988**, *110*, 8695. (f) Wang, L., Zhu, X.; Spears, K. G. *J. Phys. Chem.* **1989**, *93*, 2. (g) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1989**, *93*, 291. (h) Joly, A. G.; Nelson, K. A. *J. Phys. Chem.* **1989**, *93*, 2876.

(20) (a) Yang, G. K.; Vaida, V.; Peters, K. S. *Polyhedron* **1988**, *7*, 1619. (b) Morse, J.; Parker, G.; Burkey, T. J. *Organometallics* **1989**, *7*, 2471.

(21) (a) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. A. *J. Organomet. Chem.* **1974**, *69*, 259. (b) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220. (c) Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344. (d) Zhang, S.; Dobson, G. R. *Inorg. Chim. Acta* **1989**, *165*, L11.

(22) Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1961. Koelle, V. J. *J. Organomet. Chem.* **1978**, *133*, 53.

(23) Shen, J. K.; Gao, Y. C.; Shi, Q. Z.; Basolo, F. *Organometallics* **1988**, *7*, 531.

(24) Basolo, F. *Polyhedron* **1990**, *9*, 1503.

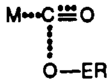
same as the observations made earlier[3] with the amine *N*-oxide reagents. For example, it also appears that the rates of reaction of these O atom transfer reagents increase with increasing values of ν_{CO} (or formal (+) charge on the C atom being attacked). Thus, the reaction of (p-$CH_3OC_6H_4$)TeO with $Cr(CO)_6$ (ν_{CO} = 1980 cm^{-1}) requires hours in $CHCl_3$ solution, but the same reaction with $Fe(CO)_5$ (ν_{CO} = 2022 cm^{-1}) is complete in minutes. Although neither Ph_3AsO nor Ph_3SbO reacts with $Cr(CO)_6$, both reagents react with $Fe(CO)_5$ (Table III). Also similar to the amine *N*-oxides, solvents have a strong effect on the rates of reaction (eq 1). As shown in Table III, the rates of reaction increase in the order THF > CH_2Cl_2 > $CHCl_3$, and this was attributed[2] to hydrogen bonding decreasing the nucleophilic strength of the reagent, e.g. E–O > E–O- -$HCCl_3$.

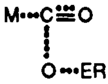
The relative basicity of these oxides was determined (Table III). Apart from those of the amine *N*-oxides, the basicities of the oxides increase with increasing atomic number within each family of elements E ($R_3PO < R_3AsO < R_3SbO$; $R_2SO < R_2SeO < R_2TeO$). The nitrogen atom is anomalous because it does not have d orbitals, so it forms the most polar bond possible with the O atom by donating its lone pair of electrons to the oxygen. In contrast to this, the P and the S family of elements do have empty valence d orbitals, which have the proper symmetry to overlap with the filled p orbitals on the O atom. These d orbitals can then decrease the electron density on oxygen by a dπ–pπ bonding interaction. Such an interaction is reported[25] to decrease in the order 3d > 4d > 5d, resulting in an increase in electron density on the oxygen of E–O in the order 3d < 4d < 5d. The larger electron density on the O atom of the 5d system agrees with the increase in basicity order 3d < 4d < 5d and with the rates of O atom transfer reactions, which increase in the order 3d < 4d < 5d, for each of the P and S family of elements (Table III). Such a correlation is expected, since the O atom with the higher electron density would have a greater tendency to attack the carbonyl C atom.

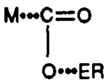
Another consequence of the dπ–pπ bonding interaction between E and O in these oxides is that the bond strengths decrease in the order 3d > 4d > 5d. Since such π-bonding is not available to nitrogen, this may account for its having the weakest N–O bond strength of the nitrogen family of elements. Because heterocyclic E–O bond cleavage is involved (Scheme I), the E–O bond strength must contribute to these rates of reaction. A comparison of the E–O bond strengths of the two triads shows (Table III) that the sulfur group elements have weaker E–O bonds than do the corresponding elements of the phosphorus group.

Although Ph_3AsO and Ph_3SbO have about the same basicities as does (p-$CH_3OC_6H_4$)$_2$TeO, their E–O bonds are twice as strong as Te–O (Table III). 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. This observation implies that E–O bond-breaking is very important in the transition state.

That E–O bond strengths alone do not control the rates of reaction is clearly demonstrated by the activation parameters and rates of reaction of the Se–O and Te–O systems. Both react at about the same rate, but the rate for Se–O is entropy controlled (ΔS^{*} = −22.9 cal/(mol K)) and that for Te–O is enthalpy controlled (ΔH^{*} = 18.3 kcal/mol) (Table II). This does not necessarily mean E–O bond-breaking is insignificant in the transition states. The reaction state state could be described by the following structures:


I


II


III

In structure I, O···C bond-making is shown prior to E–O bond-breaking. In structure III, E···O bond-breaking is shown to follow O–C bond-making. Structure II represents the synchronous processes of O···C and O···E bond-making and bond-breaking, respectively. Additional structures need to be drawn if the M···C bond-breaking is to be included. This is not done because it is known[7] that stable binary mononuclear metal carbonyls have similar M–C bond strengths (ca. 35–40 kcal/mol), and all would make about the same contribution to the transition state of the reaction. With that ssumption, the three structures shown may represent the limits of what could be important in the reactions of the transition states.

Increasing basicity of the oxide facilitates C–O bond-making, and decreasing E–O bond strength facilitates E–O bond-breaking. The C–O bond-making is enthalpy (ΔH^{*}) favored and entropy ($-\Delta S^{*}$) disfavored. The E–O bond-breaking is entropy ($+\Delta S^{*}$) favored. The ΔH^{*} values depend not only on M–C and E–O bond-breaking but also on C–O bond-making. The more stable O atom transfer reagents could avoid breaking their stronger E–O bonds in the transition state to provide an energy-favorable pathway, but this would result in a more negative ΔS^{*} and thus retard the reaction. Since (p-$CH_3OC_6H_4$)$_2$SeO is less basic than is (p-$CH_3OC_6H_4$)$_2$TeO (Table III) and since the Se–O bond is stronger than the Te–O bond, it suggests that the Se system would more closely resemble structure I than would the Te system. This is consistent with the activation parameters (Table II) showing a more negative ΔS^{*} value and a lower ΔH^{*} value for the formation of the transition state of the Se system compared to the Te system.

Considering only the enthalpy change for the rate-determining step of the reaction, it can be estimated that in the gas phase the reaction requires an E–O bond strength of less than 90 kcal/mol (eqs 6–8). Since Ph_3AsO and Ph_3SbO both have their E–O bond

$$M(CO)_n \rightarrow M(CO)_{n-1} + CO \quad \Delta H^{7} \sim 35\ \text{kcal/mol} \quad (6)$$

$$CO(g) + O(g) \rightarrow CO_2(g) \quad \Delta H = -127\ \text{kcal/mol} \quad (7)$$

$$\text{net:}\ M(CO)_n + O(g) \rightarrow M(CO)_{n-1} + CO_2(g) \quad \Delta H = -90\ \text{kcal/mol} \quad (8)$$

energies over 100 kcal/mol (Table III), neither should react on the basis of ΔH alone. However, in solution each does transfer its O atom to $Fe(CO)_5$. This is but another example of the importance of solvation energies, and/or of ΔS, in controlling the thermodynamics of chemical reactions. Unfortunately, it must now be concluded that no quantitative assessment is as yet possible of each of the factors believed to contribute to the rates of O atom transfer in these reactions (eq 1).

Acknowledgment. We thank the USA-PRC Cooperative Science Program for the support of this collaborative research. The program is funded by the U.S. National Science Foundation and by the PRC National Natural Science Foundation. J.-K.S. thanks Northwestern University for a University Fellowship. We are grateful to Professor Anthony Barrett for suggesting the use of (p-$CH_3OC_6H_4$)$_2$TeO.

Supplementary Material Available: Tables of observed rate constants, k_{obsd}, for the reaction (eq 3) of $Cr(CO)_6$ with changes in (p-$CH_3OC_6H_4$)$_2$EO (E = Se, Te) concentration, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (3 pages); a listing of structure factors (17 pages). Ordering information is given on any current masthead page.

---

(25) Malhorta, K. C. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1929.

(26) Tsvetkov, V. G.; Aleksandrov, Y. A.; Glushakova, V. N.; Skorodumova, N. A.; Kolyakova, G. M. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1980**, *50*, 198.

(27) Tabushi, I. *Coord. Chem. Rev.* **1988**, *86*, 1.