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Oxygen atom transfer reactions to metal carbonyls. Kinetics and mechanism of CO substitution reaction of Cr(CO)6 in the presence of C6H5IO

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flow. A mixture of 0.7 Torr 4 and 15 Torr C_7D_8 was employed, and the production of propene after GC separation was monitored by a quadrupole mass spectrometer. The relative intensities of the m/z 41, 42, and 43 ions were identical with those of the propene derived from SFR pyrolysis of 4 in the absence of toluene-d_8.

Copyrolysis of 3 and Toluene-d_8. Copyrolysis of 3 (0.2 Torr) and toluene-d_8 (8.3 Torr) at 550 °C was carried out in the SFR. No deuterium incorporation into 2-methyl-2-butene was detected in the mass spectrum nor did the ratio of isoprene to 2-methyl-2-butene differ from that observed in the pyrolysis of 3 in the absence of C_7D_8.

FVP of 3. Ether 3 was pyrolyzed by distillation through the FVP unit (vide supra) at 660 °C. The products were collected in a liquid N_2-cooled trap and *n*-decane was added as a GC standard. The major products, isoprene (40%), 2-methyl-2-butene (50%), and *sym*-tetramethyldisiloxane (16%), were isolated by preparative GC and characterized by GC/MS and ^1H NMR. D_3 (8%) was solely characterized by GC/MS comparison with authentic material.

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Oxygen Atom Transfer Reactions to Metal Carbonyls. Kinetics and Mechanism of CO Substitution Reaction of $Cr(CO)_6$ in the Presence of C_6H_5IO

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Reported are rates of reaction and activation parameters for the reaction of $Cr(CO)_6$ with CH_3CN in the presence of C_6H_5IO to form $Cr(CO)_5(NCCH_3)$. The rate of reaction is first order in concentrations of $Cr(CO)_6$ and of C_6H_5IO but zero order in CH_3CN concentration. Two possible mechanisms are suggested for the reaction, one is similar to that proposed earlier for corresponding reactions using $(CH_3)_3NO$ as the oxygen atom transfer reagent. A quantitative comparison between the reactivities of C_6H_5IO and $(CH_3)_3NO$ toward $Cr(CO)_6$ was not possible, but qualitatively the reaction using C_6H_5IO is orders of magnitude faster than that using $(CH_3)_3NO$. In order to dissolve polymeric $(C_6H_5IO)_n$, it was allowed to react with CH_3OH to form $C_6H_5I(OCH_3)_2$, which is soluble. However, its tetrahydrofuran solution does not react with $Cr(CO)_6$ unless H_2O is added. The rate of reaction increases with increasing H_2O concentration, and the rate varies inversely with the square of CH_3OH concentration. This behavior is explained in terms of a rapid preequilibrium that generates free reactive molecular C_6H_5IO.

Introduction

Considerable research effort has recently been devoted to the use of iodosobenzene (PhIO) as an oxygen atom transfer reagent to organic compounds, particularly in the presence of transition-metal porphyrins.[1] An example of the use of PhIO in organometallic chemistry is provided by its use[2] for the synthesis of $[\eta^5\text{-}C_5(CH_3)_5ReCONOPPh_3]BF_4$. The reaction of PhIO with metal carbenes is said[3] to be a convenient and rapid chemical method for the characterization of carbenoid metal complexes. Schardt and Hill[4] call attention to the fact that PhIO is a polymer insoluble in most solvents, but the polymer reacts with methanol to readily form $PhI(OCH_3)_2$ which is soluble in a variety of solvents. Their article also references several reports of the use of PhIO as an oxygen atom transfer reagent.

In spite of all the research activity with PhIO, we know of no kinetic study on its reactions with metal carbonyls. Our studies[5] on the kinetics and mechanisms of reactions of metal carbonyls with Me_3NO prompt us to want to investigate other oxygen atom transfer reagents. This paper presents the results of the reaction of $Cr(CO)_6$ with CH_3CN in the presence of PhIO to afford $Cr(CO)_5(NCCH_3)$.

Experimental Section

Compounds and Solvents. The carbonyl $Cr(CO)_6$ was obtained from Strem Chemicals and purified by sublimation. Iodosobenzene was synthesized by a literature method.[6] Methanol and tetrahydrofuran (THF) were dried with $Mg(OCH_3)_2$ and sodium benzophenone ketyl, respectively, and distilled prior to use.

Kinetic Measurements. Infrared spectra were recorded on a Nicolet-5DX FT-IR that uses a 0.5-mm NaCl cell. UV–visible

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[†] Lanzhou University.

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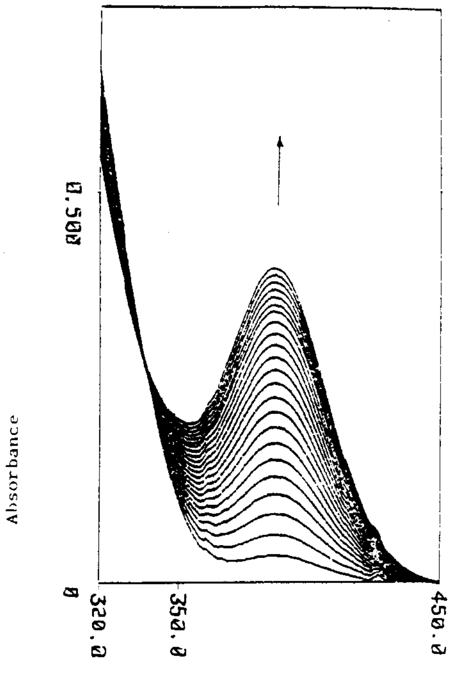

Figure 1. UV-vis absorbance changes vs time for the reaction (eq 1).

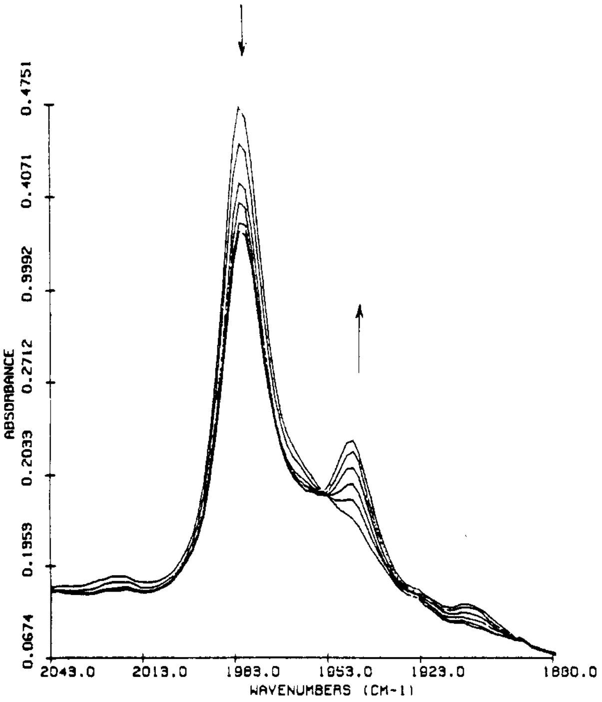

Figure 2. IR absorbance changes of ν_{CO} vs time for the reaction (eq 1).

measurements were obtained on a Shimadzu UV-240 spectrophotometer that uses 1-cm quartz cells.

The reaction of $Cr(CO)_6$ with PhIO in the presence of CH_3CN was studied at temperatures between 22 and 42 °C under an Ar atmosphere. The reaction was performed under pseudo-first-order conditions, with PhIO and CH_3CN concentrations greater than 10 times that of $Cr(CO)_6$. Rate data were obtained by monitoring UV–vis spectral changes. In a typical experiment, using a UV spectrophotometer, a solution of PhIO in CH_3OH and a solution of CH_3CN in THF were mixed in a cuvette and the cuvette was placed in a temperature-regulated jacket. Constant temperature was maintained by the internal circulating bath of the Shimadzu UV-240. After 30 min of temperature equilibration, a solution of $Cr(CO)_6$ in THF was syringed into the cuvette, the cuvette was removed and rigorously shaken, the cuvette was replaced in the light beam, and the resultant spectral changes were monitored. There was no indication of photochemically induced reactions by the UV–vis light beam, because the same results were obtained when the light beam was intermittently interrupted as when it was not during a given reaction. By also monitoring IR spectral changes, we know that the monosubstituted carbonyl $Cr(CO)_5(NCCH_3)$ was produced in the reactions.

Plots of ln $(A_\infty - A_t)$ vs time for appearance of products were linear over 2 half-lives (linear correlation coefficient >0.995). The slope of these lines gave k_{obsd}.

Table I. Observed Rate Constants for the Reaction (Equation 1) with Changes in H_2O Concentration at $[PhIO]_{total} = 2.83 \times 10^{-3}$ M, at 30 °C, and in the Mixed Solvent CH_3OH–THF 1:2 (v/v)

$[H_2O]$, M	k_{obsd},[a] s^{-1}	$[H_2O]$, M	k_{obsd},[a] s^{-1}
7.65×10^{-2}	5.03×10^{-4}	1.53×10^{-1}	1.01×10^{-3}
1.07×10^{-1}	7.18×10^{-4}	1.89×10^{-1}	1.27×10^{-3}
1.35×10^{-1}	8.59×10^{-4}		

[a] Rate constants were reproducible t o ±5%.

Table II. Observed Rate Constants for the Reaction (Equation 1) with Changes in CH_3OH Concentration at 30 °C

CH_3OH–THF (v/v)	k_{obsd},[a] s^{-1}	CH_3OH–THF (v/v)	k_{obsd},[a] s^{-1}
1:2	8.59×10^{-4}	1:4	2.34×10^{-3}
1:3	1.59×10^{-3}	1:5	3.33×10^{-3}

[a] $[PhIO]_{total} = 2.83 \times 10^{-3}$ M and $[H_2O] = 1.35 \times 10^{-1}$ M. Rate constants were reproducible to ±5%.

Table III. Observed Rate Constants for the Reaction (Equation 1) with Changes in CH_3CN Concentration at 30 °C

$[CH_3CN]$, M	k_{obsd},[a] s^{-1}	$[CH_3CN]$, M	k_{obsd},[a] s^{-1}
4.42×10^{-2}	3.33	1.33×10^{-1}	3.36
8.84×10^{-2}	3.69	1.77×10^{-1}	3.50

[a] $[PhIO]_{total} = 2.83 \times 10^{-3}$ M, $[H_2O] = 0.135$ M, and CH_3OH–THF 1:5 (v/v). Rate constants were reproducible to ±5%.

Table IV. Rate Constants and Activation Parameters for the Reaction (Equation 1) Calculated Using $[PhIO]_{total}$

T, °C	k_2,[a] $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol deg)
22.0	1.56×10^{-1}	12.1 ± 0.43	−21.4 ± 1.6
27.4	2.18×10^{-1}		
32.5	3.07×10^{-1}		
42.0	6.11×10^{-1}		

[a] $[H_2O] = 0.153$ M, CH_3OH–THF 1:2 (v/v). Rate constants were reproducible to ±5%.

Results

The rates of reaction (eq 1) in CH_3OH–THF (1:2 (v/v))

$$Cr(CO)_6 + PhIO + CH_3CN = Cr(CO)_5(NCCH_3) + PhI + CO_2 \quad (1)$$

mixed solvent were monitored by following changes in the UV–visible absorption spectra with time. Spectral changes of reaction mixtures show good isosbestic points (Figures 1 and 2), which suggest stoichiometric reaction affording monosubstituted product. The IR absorbance at 1945 cm^{-1} is in good agreement with the known[7] C–O stretching vibration frequency of $Cr(CO)_5(NCCH_3)$.

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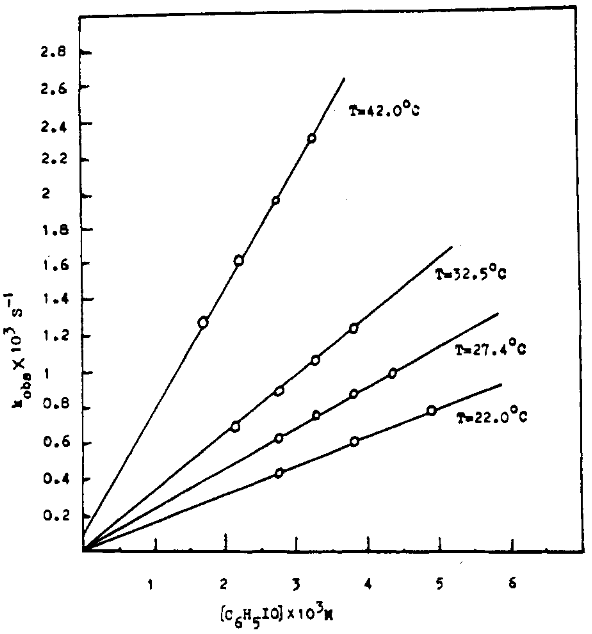


Figure 3. Plots of k_{obsd} vs $[PhIO]_{total}$ for the reaction (eq 1) in mixed solvent CH_3OH–THF 1:2 (v/v) and $[H_2O]$ = 0.153 M.

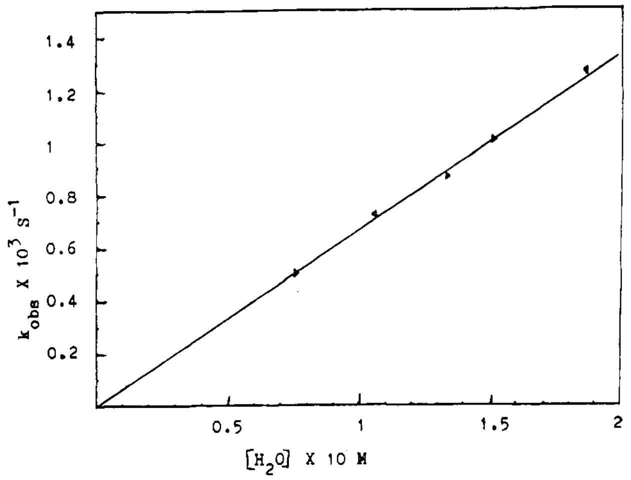


Figure 4. Plot of k_{obsd} vs $[H_2O]$ for the reaction (eq 1) at 30 °C, in mixed solvent CH_3OH–THF = 1:2 (v/v), and $[PhIO]_{total} = 2.83 \times 10^{-3}$ M.

Plots of k_{obsd} vs $[PhIO]_{obsd}$ show a first-order dependence of iodosobenzene (Figure 3). Rates of the reaction (eq 1) are first order in $[H_2O]$ (Figure 4), inversely proportional to the square of CH_3OH concentration (Figure 5), and zero order in $[CH_3CN]$; as is shown by the data in Tables I, II, and III, respectively.

At fixed concentrations of water and methanol, plots of k_{obsd} vs $[PhIO]_{obsd}$ provide reaction rates at various temperatures, which permit estimates of activation parameters (Table IV).

Discussion

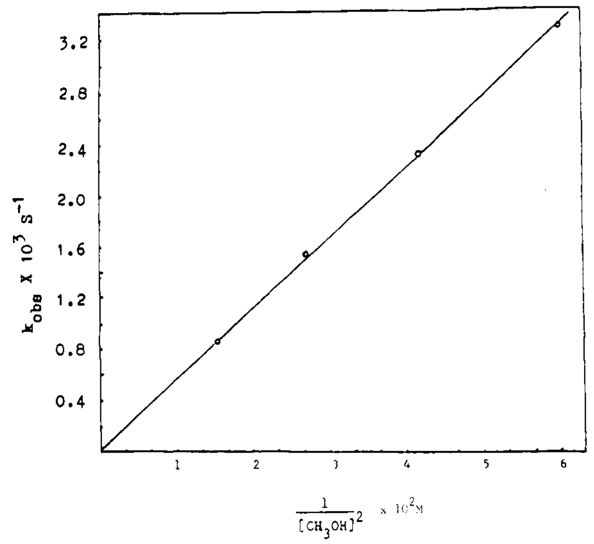
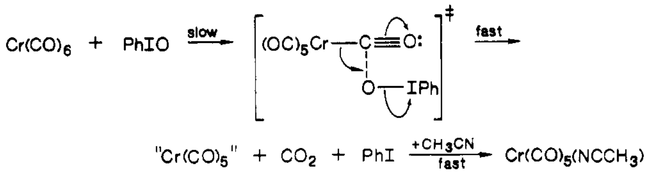


Figure 5. Plot of k_{obsd} vs $1/[CH_3OH]^2$ for the reaction (eq 1) at 30 °C, with added $[PhIO]_{total} = 2.83 \times 10^{-3}$ M, and $[H_2O]$ = 0.135 M.

Scheme I



Polymeric $(PhIO)_n$ was allowed to react with methanol to give $PhI(OCH_3)_2$ dissolved in methanol. To this solution was added sufficient tetrahydrofuran (THF) to give a mixed solvent of CH_3OH–THF (1:2 (v/v)). Addition of $Cr(CO)_6$ and CH_3CN to this solution results in no reaction at room temperature, but addition of water catalyzes the formation of $Cr(CO)_5(NCCH_3)$. A kinetic study of the reaction shows the rate is first order in concentrations of $Cr(CO)_6$, total $[PhIO]_{total}$ (Figure 3), and H_2O (Figure 4); inversely proportional to the square of CH_3OH (Figure 5); and zero order in CH_3CN (Table I). These observations are consistent with the following reactions (eq 2–5).

$$PhI(OCH_3)_2 + H_2O \xrightleftharpoons{\text{fast}} PhIO + 2CH_3OH \qquad (2)$$

$$Cr(CO)_6 + PhIO \xrightarrow[k_2]{\text{slow}} [Cr(CO)_6\cdots PhIO]^{\ddagger} \qquad (3)$$

$$[Cr(CO)_6\cdots PhIO]^{\ddagger} \xrightarrow{\text{fast}} \text{“}Cr(CO)_5\text{”} + PhI + CO_2 \qquad (4)$$

$$\text{“}Cr(CO)_5\text{”} + CH_3CN \xrightarrow{\text{fast}} Cr(CO)_5(NCCH_3) \qquad (5)$$

Unfortunately the equilibrium constant K for the rapid preequilibrium (eq 2) is not known, but it is represented by eq 6. The unknown reactive, or effective, concentration

$$K = \frac{[PhIO]_{effective}[CH_3OH]^2}{[PhI(OCH)_3)_2][H_2O]} \qquad (6)$$

of PhIO is then given by eq 7. At the experimental con-

$$[PhIO]_{effective} = K\frac{[PhI(OCH_3)_2][H_2O]}{[CH_3OH]^2} \qquad (7)$$

ditions of $[CH_3OH] >>> [H_2O]$, the iodosylbenzene is essentially totally present in solution as the dimethoxide. This means that $[PhI(OCH_3)_2] = [PhIO]_{total}$, and that eq 7 becomes eq 8. Since the rate-determining step (eq 3)

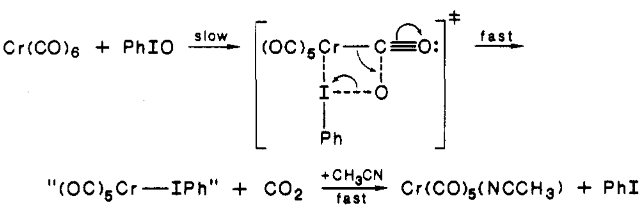
$$[PhIO]_{effective} = K\frac{[PhIO]_{total}[H_2O]}{[CH_3OH]^2} \qquad (8)$$

has the rate law (eq 9) it follows that the rate is also first order in the experimental concentration of $[PhIO]_{total}$.

$$\text{rate} = k_2[Cr(CO)_6][PhIO] \qquad (9)$$

The mechanism of the rate-determining step (eq 3) for reaction, like that reported[5] for reactions of metal carbonyls with Me_3NO, is believed to involve attack on carbon by the oxygen atom of PhIO. This then permits the ox-

Scheme II



idation of CO to the good leaving group CO_2, resulting in formation of the coordinatively unsaturated reactive intermediate "$Cr(CO)_5$" (eq 4). The intermediate is in turn rapidly captured by the entering ligand to give the product $Cr(CO)_5(NCCH_3)$ (eq 5) (Scheme I). An alternative four-centered mechanism had been suggested[3] earlier for such a reaction (Scheme II). Although the four-centered mechanism for reactions of Me_3NO is not involved[5] because the replacement with entering ligand of Me_3N coordinated to the metal is too slow, the replacement of coordinated PhI would be fast enough to permit such a mechanism. Therefore, it is not known if the detailed mechanism is that represented by Scheme I or by Scheme II.

Extrapolation of the plot in Figure 4 to zero for $1/[CH_3OH]^2$ (which represents infinite concentration of CH_3OH, and zero concentration of $[PhIO]_{effective}$) shows that within experimental error k_{obsd} is zero. This suggests that $PhI(OCH_3)_2$ does not react, but that free molecular PhIO is an extremely reactive oxygen atom transfer reagent toward $Cr(CO)_6$. Since we do not know the equilibrium constant for (eq 2), we cannot calculate the concentration of PhIO in our reaction mixtures. Suffice to say the concentration of molecular PhIO in solution must be very low because the species present at the conditions of high CH_3OH concentrations is mostly $PhI(OCH_3)_2$. It is believed the reactive PhIO in solution is molecular because the solutions are clear, and they become cloudy due to formation of the insoluble polymer $(PhIO)_n$ when too much water is added. The kinetic studies were all made with clear solutions.

Not knowing the concentration of molecular PhIO in the reaction solutions, it is not possible to quantitatively compare the reactivity of PhIO with that of Me_3NO toward $Cr(CO)_6$. Qualitatively it is certain that PhIO is orders of magnitude more effective as an oxygen atom transfer reagent in this reaction than is Me_3NO. The only entering ligand used was CH_3CN, because it gave good spectral changes in the UV for monitoring the reaction. Only very small changes in spectra were observed when the entering ligand was PR_3, and $P(OR)_3$ ligands rapidly react directly with methanol solutions of $PhI(OCH_3)_2$ in the absence of $Cr(CO)_6$.

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Registry No. $Cr(CO)_6$, 13007-92-6; CH_3CN, 75-05-8; PhIO, 536-80-1; H_2O, 7732-18-5.

Supplementary Material Available: Table of additional values of k_{obsd} at different conditions (1 page). Ordering information is given on any current masthead page.