Mechanism of Substitution of Acetone by Alkenes in Acetonepentacarbonyltungsten(0)

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Abstract: The ligand substitution reactions between $W(CO)_5(acetone)$ and alkenes yielding $W(CO)_5(alkene)$ and uncomplexed acetone have been investigated using several alkenes. The mechanism is shown to be dissociative. The structure of the alkene is an important factor in the rate of substitution and in the equilibrium ratio of $W(CO)_5$-(acetone) and $W(CO)_5(alkene)$. Generally, cis alkenes react faster and form more stable complexes than trans alkenes.

The investigation of the mechanisms of thermal substitution reactions of metal carbonyl complexes has been an area of active interest for several years.[2] After exhaustive study, it now appears that nucleophilic substitution in nickel tetracarbonyl proceeds by a dissociative-type mechanism.[3] Although a dissociative mechanism is also common for ligand substitution reactions of six-coordinate species,[2b] there is a possibility that substitution reactions of the metal(0) hexacarbonyls may proceed by an associative mechanism. The formation of $W(CO)_5(benzene)$,[4] with bonding to the benzene ring formally requiring three coordination sites, shows that tungsten carbonyl complexes may have high coordination numbers. Furthermore, Harill and Kaesz[5] have pointed out that an associative mechanism can account equally as well as a dissociative path for their observation of scrambled stereochemistry after substitution of CO for the olefin in $Mo(CO)_4(C_7H_8)$.

We report here a kinetic investigation of reaction 1, which we believe to be representative of $M(CO)_5(L)$ ligand substitution reactions, where L is replaced by L' and L and L' are weakly bound ligands.

$$W(CO)_5(acetone) + alkene \rightleftharpoons W(CO)_5(alkene) + acetone \quad (1)$$
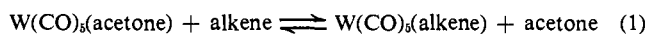
Concentration effects have been studied and several alkenes have been employed allowing conclusions to be made concerning the mechanism.

Experimental Section

(1) **Materials.** Isooctane (solvent) and acetone were Matheson Coleman and Bell Spectroquality reagents. Tungsten hexacarbonyl was obtained from Alfa Inorganics, Inc. All alkenes used were obtained commercially in purity of at least 99%.

(2) **$W(CO)_5(acetone)$.** The $W(CO)_5(acetone)$ was prepared by photolysis of $W(CO)_6$ (typically 2×10^{-3} M) in isooctane with varying concentrations of acetone.[6] The acetone complex was not isolated but was characterized by ir.[6] The reaction of $W(CO)_5$-(acetone) with 1-pentene gave a solution having an ir spectrum identical with that obtained when only $W(CO)_6$ and 1-pentene are irradiated.[7] Because of the lability of the $W(CO)_5(acetone)$, preparative irradiations were carried out in an infrared or ultraviolet-visible cell, depending on the mode of analysis. The irradiation source was an Ultraviolet Products lamp with principal output at 365 nm. Irradiation times were short to prevent secondary photoreactions,[8] with disappearance of $W(CO)_6$ being less than 25%. The concentrations of $W(CO)_5(acetone)$ produced were $\sim 10^{-4}$ M. The intensely colored $W(CO)_5(acetone)$ has an absorption maximum at 406 nm with a molar extinction coefficient of 5.14×10^3. The extinction coefficient was calculated by measuring the loss in infrared absorption due to $W(CO)_6$ at 1982 cm^{-1} and the concurrent gain in absorption at 406 nm, assuming that $W(CO)_5(acetone)$ is the only significant product of photosubstitution.

(3) **Substitution Reactions.** After $W(CO)_5(acetone)$ was produced photochemically in the uv-vis cell, the alkene was added to the solution using a syringe. The cell was then shaken vigorously and placed in a Cary 14 spectrometer, and the absorbance of $W(CO)_5(acetone)$ was measured as a function of time. The substitution reaction can also be monitored semiquantitatively by infrared spectroscopy, where both products and reactants can be observed. Most substitution reactions were carried out at room temperature (25.4°). The temperature was varied by using a cell holder with a circulating system. A Forma Scientific constant-temperature circulating bath was used, and in the temperature dependence study the photolysis to produce $W(CO)_5(acetone)$ was carried out in the presence of alkene and at the temperature of the thermal substitution reaction subsequently observed.

(4) **Spectra.** Ultraviolet–visible spectra were obtained using a Cary 14 spectrometer. Quartz 1-cm path length cells were used. Infrared data were collected using a Perkin-Elmer 225 grating spectrometer.

Results

We have observed that $W(CO)_5(acetone)$ undergoes reaction 1 with a number of alkenes. In Figure 1 we show the changes in the infrared absorption spectrum that occurred when a thermal exchange was carried out at room temperature. The final spectrum obtained is identical with that for the $W(CO)_5(alkene)$ synthesized photochemically.[7b] The uv–vis spectrum in the region of interest is shown in Figure 2 before and after irradiation of a solution containing $W(CO)_6$ and acetone. The intense maximum at 406 nm in the $W(CO)_5(acetone)$ spectrum and the lack of absorption at that wavelength by $W(CO)_5(alkene)$[7] allow quantitative measurement of the substitution rate. We observe rapid and almost

(1) National Institutes of Health Trainee.

(2) Reviews of metal carbonyl substitution reactions are available: (a) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968); (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967; (c) D. A. Brown, *Inorg. Chim. Acta Rev.*, **1**, 35 (1967).

(3) J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **90**, 6927 (1968).

(4) I. W. Stolz, H. Haas, and R. K. Sheline, *ibid.*, **87**, 716 (1965). These authors proposed that bonding of the benzene ring to the metal is not through a fixed double bond; rather all six π electrons are believed to contribute to the bonding.

(5) R. W. Harill and H. D. Kaesz, *ibid.*, **90**, 1449 (1968).

(6) Preparation of $W(CO)_5(acetone)$ has been reported previously: I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, **2**, 323 (1963).

(7) (a) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *ibid.*, **2**, 1264 (1963); (b) M. Wrighton, G. S. Hammond, and H. B. Gray, unpublished results.

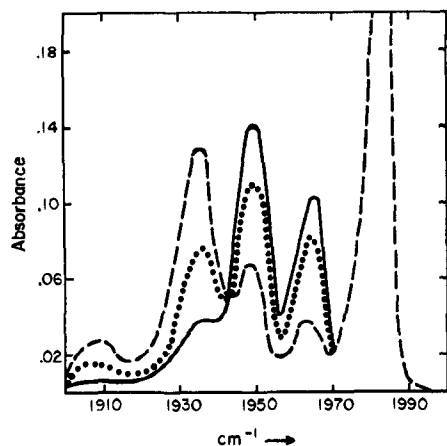(8) W. Strohmeier, *Angew. Chem.*, **76**, 873 (1964).

Figure 1. W(CO)$_5$(acetone) → W(CO)$_5$(1-pentene) followed by ir. Bands at 1950 and 1965 cm^{-1} are (WCO)$_5$(1-pentene), those at 1908 and 1935 cm^{-1} are W(CO)$_5$(acetone), and the off-scale peak at 1980 cm^{-1} is W(CO)$_6$: ---, time = 0; ···, time = 2 min; — time = 5 min. Acetone = 0.2 M, 1-pentene = 0.04 M, 0.1-mm NaCl ir cell.
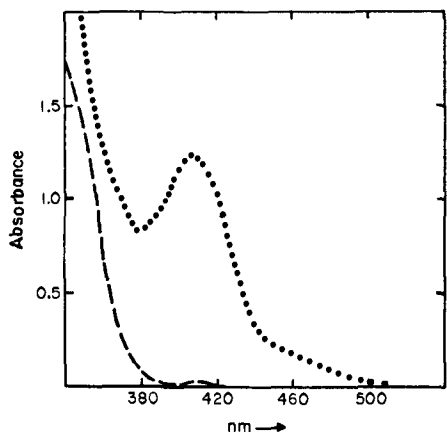

Figure 2. Absorption spectrum of W(CO)$_5$(acetone) complex (~10^{-4} M): ---, before photolysis; ···, after photolysis of W(CO)$_6$ + acetone.
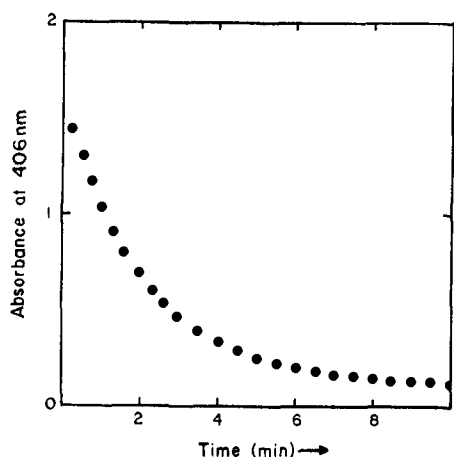

Figure 3. Decay of absorbance at 406 nm during the substitution reaction W(CO)$_5$(acetone) → W(CO)$_5$(1-pentene).

complete substitution when 1-pentene is about 0.1 M, acetone is about 0.1 M, and W(CO)$_5$(acetone) is about 10^{-4} M. Equilibrium may be established in 10 min. The absorbance at 406 nm as a function of time under
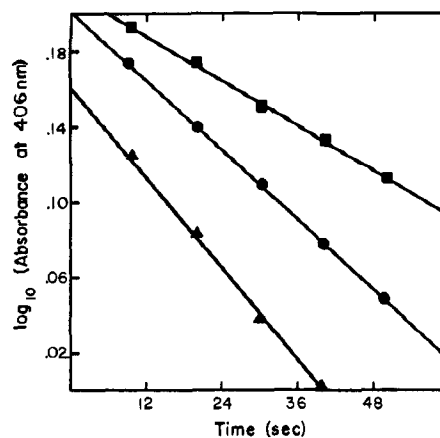

Figure 4. Plots of log (A_{406}) vs. time during substitution with 1-pentene (●), cis-2-pentene (▲), and trans-2-pentene (■). Acetone = 0.136 M, alkene = 0.09 M.
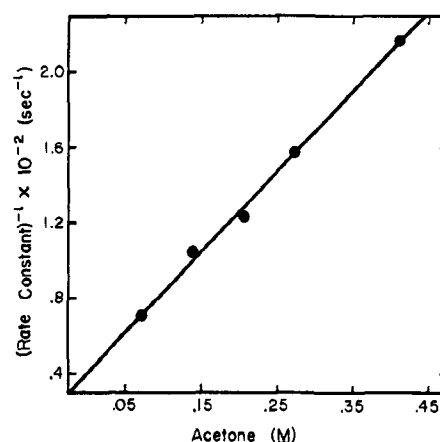

Figure 5. Acetone concentration effect on substitution reaction using 1-pentene (0.09 M).

these conditions is shown in Figure 3. Analysis of the data is described below.

Concentration Dependencies. Plots of log (absorbance at 406 nm) against time were linear to greater than 25% conversion, although the slopes were different in the presence of various alkenes. Illustrative plots are shown in Figure 4. In Figure 5 we show the repression of the initial rate by increasing acetone concentration, where 1-pentene is the alkene. Figure 6 shows the effect of varying the concentration of 1-pentene.

Temperature Effects. The temperature effect on the substitution rate using 1-pentene is shown in Figure 7. The energy of activation determined from the slope of the line is 7.0 kcal/mol. There appeared to be no marked temperature dependence of the equilibrium constant over the range studied.

Structural Effects. In Table I we have summarized rate constants k_{obsd} for the substitution reactions involving several alkenes. Rate constants were determined from the slopes of the plots of log (absorbance at 406 nm) against time. There is clearly a structural dependence. The C-6 alkenes generally have larger rate constants than the C-5 alkenes.[9] The more sub-

(9) The C-6 alkenes have very fast reproducible exchange rates, but cloudy precipitates sometimes formed after disappearance of W(CO)$_5$-(acetone).
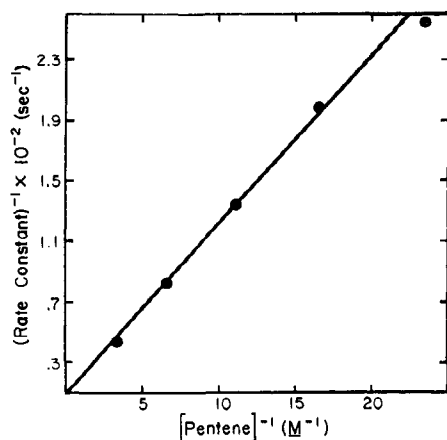
Figure 6. 1-Pentene concentration effect on substitution reaction; acetone = 0.136 M.

Figure 7. Temperature effect on the substitution reaction using 1-pentene (0.09 M) and acetone (0.14 M).

stituted alkenes react more slowly than the less hindered alkenes. There is also a clear difference between cis and trans alkenes. The equilibrium constant, eq 2, is also dependent upon the alkene used. In Table II

Table I. Pseudo-First-Order Rates of Substitution[a]

Alkene	$k_{obsd} \times 10^3$, sec^{-1}	Rel rate constant
1-Pentene	7.55	1.00
cis-2-Pentene	9.89	1.31
trans-2-Pentene	4.60	0.61
2-Methyl-2-butene	1.28	0.17
1-Hexene	36.8	4.90
cis-3-Hexene	34.3	4.57
trans-2-Hexene	21.3	2.84
cis-3-Methyl-2-pentene	9.98	1.33
trans-3-Methyl-2-pentene	11.7	1.56
1-Heptene	16.2	2.16
2,4-Dimethyl-2-pentene	0.98	0.13

[a] Acetone = 0.136 M; alkene = 0.09 M.

Table II. Equilibrium Constant for Reaction 1

Alkene	K_{eq}[a]
1-Pentene	20.7
cis-2-Pentene	8.2
trans-2-Pentene	2.7
1-Heptene	21.5
2-Methyl-2-butene	~0.9
1-Hexene	>20

[a] See eq 2.

we see that the equilibrium lies in favor of W(CO)₅(al-

$$K_{eq} = \frac{[W(CO)_5(alkene)][acetone]}{[W(CO)_5(acetone)][alkene]} \qquad (2)$$

kene) under our conditions for most of the alkenes. Equilibrium constants and relative rates for the alkenes do not seem to be simply related except that at equilibrium the very slow rates correspond to large amounts of W(CO)₅(acetone) and very fast rates result in little or none.

Discussion

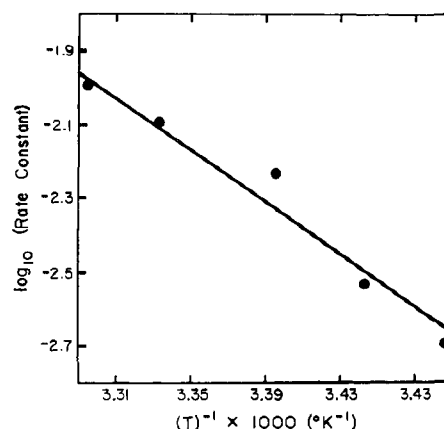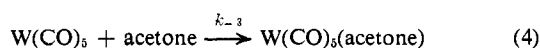**Mechanism.** The results support the mechanism outlined in steps 3–6 below. The mechanism proposed is of the dissociative type.

$$W(CO)_5(acetone) \xrightarrow{k_3} W(CO)_5 + acetone \qquad (3)$$

$$W(CO)_5 + acetone \xrightarrow{k_{-3}} W(CO)_5(acetone) \qquad (4)$$

$$W(CO)_5 + alkene \xrightarrow{k_4} W(CO)_5(alkene) \qquad (5)$$

$$W(CO)_5(alkene) \xrightarrow{k_{-4}} W(CO)_5 + alkene \qquad (6)$$

By going to low conversion, we can ignore the reverse reaction 6. The rate of disappearance, R, of W(CO)₅-(acetone) is related to the reagent concentrations by (7). Equation 8 is the observed rate expression.

$$\frac{1}{R} = \frac{1}{k_3[W(CO)_5(acetone)]}\left(1 + \frac{k_{-3}[acetone]}{k_4[alkene]}\right) \qquad (7)$$

$$R = k_{obsd}[W(CO)_5(acetone)] \qquad (8)$$

The dissociative mechanism then predicts the linear plots for observed initial rate constants shown in Figures 5 and 6. The ratio of the rates of capture of W(CO)₅ by acetone and 1-pentene is just k_{-3}/k_4, which can be obtained from the slope to intercept ratio in either Figure 5 or 6. The ratio k_{-3}/k_4 for the 1-pentene reaction is found to be ~0.6. This value for the capture ratio is in good qualitative agreement with the observation that large amounts of both W(CO)₅(acetone) and W(CO)₅(1-pentene) are formed when W(CO)₆ is irradiated to produce W(CO)₅ in the presence of equimolar amounts of 1-pentene and acetone.

The proposed dissociative mechanism for ligand exchange can easily account for scrambling of the carbonyl groups during formation of Mo(CO)₆ from Mo-(CO)₄(C₇H₈).[5] The stereoisomerization may take place via equilibration of C_{4v} and D_{3h} pentacarbonyl intermediates. Evidence for both of these structures of Mo(CO)₅ has been obtained,[10] and the barrier to interconversion is expected to be small.[11]

(10) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, **85**, 1013 (1963).

(11) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

C_{4v} ⇌ D_{3h}
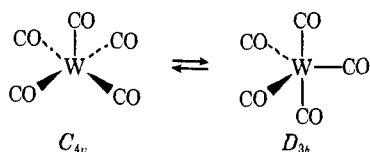
The overall activation energy for substitution of 1-pentene for acetone is only 7 kcal/mol, indicating that the ketone is very weakly bound in the complex. The measured equilibrium constants indicate a maximum standard free energy change of less than 2 kcal/mol, and the constants do not depend strongly on temperature. Consequently, we infer that the heats of formation of the alkene complexes are only slightly greater than that of the acetone derivative. Appearance of the dissociative mechanism for ligand substitution can obviously be related to the fact that the labile ligands are very weakly bound. Substitution by an associative mechanism, perhaps involving metastable seven-coordinate intermediates, may occur when more strongly bound ligands are involved. For example, the mean binding energy of the carbonyl groups in $Mo(CO)_6$ is 35.9 kcal/mol,[12] which is consistent with an associative contribution to the rate in substitution reactions of $Mo(CO)_6$.[13]

Structure–Reactivity Relationships. Substitution rate and equilibrium constants are summarized in Tables I and II. The results indicate that steric hindrance is an important factor in determining the binding affinity of the alkenes, since equilibrium constants fall off as the number of alkyl substituents attached to the double bond is increased. While the donor ability of the π electrons must contribute significantly to binding, as evidenced by the fact that most alkenes are bound more strongly than acetone, among the alkenes variations in this donor ability are apparently overshadowed by steric factors.

The relative equilibrium constants within the C-5 alkenes appear to be largely dependent on steric effects. In 1-pentene the steric crowding of carbonyl groups and double bond substituents is minimal since three of the four positions on the double bond are taken up by hydrogens. The 2-pentenes are less stable, with steric hindrance being enhanced by an additional alkyl substituent, and the 2-methyl-2-butene yields the least stable complex with three alkyl groups. The difference between cis- and trans-2-pentene may also be due to steric effects. In trans-2-pentene the alkyl substituents are symmetrically arranged and will not allow as favorable a positioning of the $W(CO)_5$ as in cis-2-pentene, where the alkyl substituents are on the same side of the double bond. In the cis-2-pentene complex,

the $W(CO)_5$ can move somewhat away from the two alkyl substituents by being on the opposite side of the double bond, where the two hydrogen substituents offer relatively little steric hindrance. In trans-2-pentene there is large steric crowding on both sides of the double bond and this prevents substantial binding with the π electrons of the double bond. The preference for cis alkenes and for ethylene is also exhibited by the silver ion.[2b]

The kinetic effects are not easily rationalized since they do not closely parallel binding constants. Even though cis-2-pentene is bound less firmly than 1-pentene, the former reacts more rapidly in capturing $W(CO)_5$. This indicates that the interactions which dominate binding are not fully developed in the transition state for the capture reaction. Very simply, we can guess that the transition state occurs before the ligand has settled into its final configuration enough to allow full development of steric strains. The extra alkyl group on cis-2-pentene makes it a more nucleophilic agent and may enhance the rate of $W(CO)_5$ capture. Inductive effects have been noted in substitution reactions of π-allyl- and acylcobalt carbonyls.[14] In addition, electron-releasing groups on the benzene ring in arenemetal carbonyls retard the rate of benzene group exchange.[15] The latter fact is in accord with our observation that the rate of capture of $W(CO)_5$ by cis-2-pentene is greater than by 1-pentene. It is apparent that both steric and electronic effects are important considerations in the rate and the equilibrium position of reaction 1. However, the general increase in the rate of reaction with the hexenes is not easily understood and warrants further investigation.

We are currently investigating relative complex stabilities and reactivities with other ligands. Also, we are evaluating the importance of the thermal substitution step in the $W(CO)_6$ photoassisted isomerization of olefins.[16] It is possible that $W(CO)_5$(olefin)–olefin substitution is the rate-determining step in the reaction. The photoisomerization reactions are temperature dependent,[17] and experiments are now in progress to determine the effect quantitatively for a number of olefins.

(12) F. Calderazzo, R. Ercoli, and G. Natta, "Organic Synthesis via Metal Carbonyls," Vol. I, I. Wender and P. Pino, Ed., Wiley, New York, N. Y., 1968, p 43.
(13) R. J. Angelici and J. K. Graham, *J. Amer. Chem. Soc.*, **88**, 3658 (1966).
(14) R. F. Heck, *ibid.*, **85**, 655, 6518 (1963).
(15) W. Strohmeier and H. Mittnaeht, *Z. Phys. Chem. (Frankfurt am Main)*, **29**, 339 (1961); **34**, 82 (1962); W. Strohmeier and R. Muller, *ibid.*, **40**, 85 (1964).
(16) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **92**, 6068 (1970).
(17) M. Wrighton, G. S. Hammond, and H. B. Gray, unpublished observations.