

The Kinetics of Mo(CO)₆ Substitution Monitored by Fourier Transform Infrared Spectrophotometry

A Physical Chemistry Experiment

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Digital processing in infrared spectrophotometry has undergone tremendous advances in recent years (1, 2). Both Fourier transform (FTIR) spectrometers and microcomputer data stations for conventional dispersive instruments have become inexpensive enough² to be used in undergraduate laboratory courses. However, if these instruments serve only as replacements for older, routine instruments (e.g., for survey spectra in organic lab), most of their capabilities will be wasted. In order to expand the scope of undergraduate laboratory use of these instruments, we have developed a kinetics experiment that makes full use of the speed, accuracy, and sensitivity of FTIR spectrometers and that introduces students to the spectral storage and manipulation techniques associated with digitized data. It can be used in an undergraduate physical chemistry laboratory course to illustrate FTIR spectroscopy, simple kinetics, inorganic reaction mechanisms, and Beer's Law. This experiment has the added advantage of convenient logistics and relatively low costs; we have had as many as 120 juniors and seniors run this experiment in a semester.

Theory

The reaction studied in this experiment is the substitution (3) of a carbon monoxide ligand of Mo(CO)₆ by triphenylphosphite (P(OPh)₃),



The goal of this lab is to determine the rate law of this reaction and to propose a mechanism consistent with the data. The general rate law for this reaction is

$$\text{Rate} = -d[\text{Mo(CO)}_6]/dt = k[\text{Mo(CO)}_6]^n[\text{P(OPh)}_3]^m \quad (2)$$

where n is the order of the reaction in Mo(CO)₆ and m is the order of the reaction in P(OPh)₃ (4). To determine m and n , two kinetic runs are conducted with equal initial concentrations of Mo(CO)₆ and differing excess concentrations of P(OPh)₃. Since P(OPh)₃ is always in excess, for each kinetic run, eq 2 reduces to

$$\text{Rate} = -d[\text{Mo(CO)}_6]/dt = k_{\text{obs}}[\text{Mo(CO)}_6]^n \quad (3)$$

where k_{obs} is a different coefficient for each run and is equal to $k[L]^m$. Integration of this differential equation for $n = 0, 1$, and 2 gives the following equations:

$$n = 0 \quad [\text{Mo(CO)}_6] = -k_{\text{obs}}t + M \quad (4)$$

$$n = 1 \quad \ln [\text{Mo(CO)}_6] = -k_{\text{obs}}t + \ln M \quad (5)$$

$$n = 2 \quad [\text{Mo(CO)}_6]^{-1} = -k_{\text{obs}}t + M^{-1} \quad (6)$$

where M is the initial concentration of Mo(CO)₆. The order of the reaction in Mo(CO)₆ is determined by plotting the data using eqs 4, 5, and 6 for each kinetic run and finding which one gives the best line. Since the initial concentration of Mo(CO)₆ is equal for the two runs, the order in P(OPh)₃ can be calculated by comparing the rate coefficients for the two runs using

$$k_{\text{obs(run a)}}/k_{\text{obs(run b)}} = ([\text{P(OPh)}_3]_{\text{run a}}/[\text{P(OPh)}_3]_{\text{run b}})^m \quad (7)$$

We leave the derivation of eqs 4–7 as an exercise for the student. Once the order in P(OPh)₃ is determined, the total rate law can be written.

The reaction kinetics are followed by monitoring the CO-stretching frequencies of the metal carbonyl species. Through the use of simple group theory selection rules (5–7), it can easily be shown that Mo(CO)₆, having O_h symmetry, should have only one observed IR band. A monosubstituted Mo(CO)₅L, having C_{4v} symmetry, should have three infrared active bands (8); however, only two absorbances are experimentally observed, due to the coincidental overlap of two of the infrared active bands.

In principle, the concentrations of these two species can be determined by quantitative infrared spectrophotometry, using Beer's Law,

$$A = \epsilon l C \quad (8)$$

where A is the absorbance due to some species, ϵ is the molar extinction coefficient, l is the path length, and C is the concentration of that species. However, the absorbances of the Mo(CO)₆ and Mo(CO)₅(P(OPh)₃) overlap, so "spectral stripping" (i.e., subtraction) is needed to separate and to quantify the two spectral components. Given the spectrum of a solution that contains both species, subtraction of a weighted amount of the spectrum due to Mo(CO)₆ will produce a difference spectrum with contributions due only to the product, whose concentration can then be easily calculated from Beer's law. The concentration of Mo(CO)₆ at any given time, t , is then derived using

$$[\text{Mo(CO)}_6]_{(t=0)} = [\text{Mo(CO)}_6]_t + [\text{Mo(CO)}_5\text{(P(OPh)}_3)]_t \quad (9)$$

Once the Mo(CO)₆ concentrations have been measured as a function of time, eqs 4, 5, and 6 can be used to determine the order of the reaction in Mo(CO)₆, and eq 7 can be used to calculate the order in P(OPh)₃.

A reaction mechanism can be proposed from the observed rate law. There are three limiting reaction mechanisms for substitution reactions: associative, dissociative, and interchange (9). The associative mechanism involves the addition of an entering ligand to a substrate,



This reaction would be second order overall, first order in each reactant. A dissociative reaction, shown in eq 11, occurs

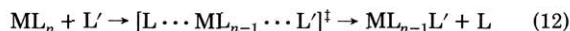
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² A number of low-cost FTIR spectrometers are commercially available from, among others, Nicolet Analytical Instruments, 5225-1 Verona Rd., Madison, WI 53711; and Mattson Instruments, 633 Odana Rd., Madison, WI 53719. In addition, most dispersive instruments now have reasonably priced microcomputer data stations available.

by a rate-determining initial loss of a ligand from the substrate followed by addition of the entering ligand, similar to an S_N1 reaction.



This reaction is first order in ML_n and zero order in L' . The interchange mechanism is similar to an S_N2 reaction in that there is no observable intermediate of coordination number different from the starting material. This reaction, shown in eq 12, is first order in each reactant.



The student can determine which of these mechanisms are consistent with the observed data and what further experiments are necessary to distinguish between them.

Experimental Procedure

The equipment required for this experiment includes a Fourier Transform Infrared Spectrophotometer (or a conventional IR spectrophotometer with microcomputer work station), a constant-temperature apparatus, shown in Figure 1 (requires flask, condenser, heating mantle, magnetic stirrer, and Variac), a 0.05-cm IR solution

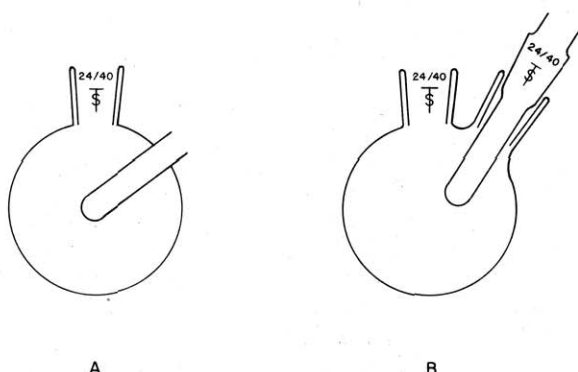


Figure 1. Two designs for an inexpensive constant-temperature apparatus. Design A requires some glass-blowing expertise; design B can be prepared from commercially available glassware (e.g., Ace Glass #7630 inner member joint and #6927 250-mL two-neck round-bottom flask).

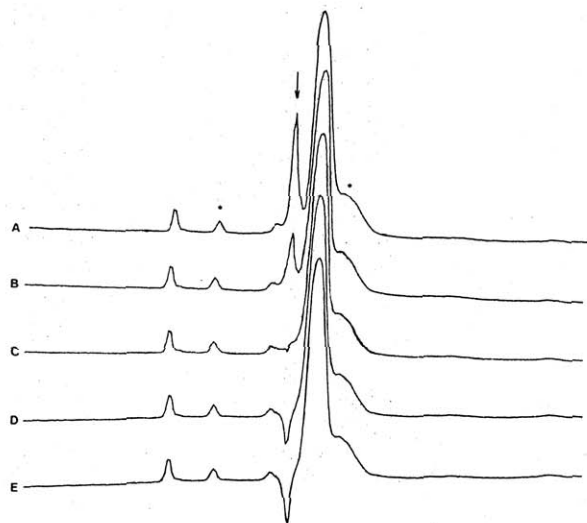


Figure 2. Spectral stripping of a FTIR spectrum of a solution containing both $Mo(CO)_6$ and $Mo(CO)_5(P(O)Ph)_3$. The band marked with the arrow is due to $Mo(CO)_6$. From spectrum A to E, increasing amounts of the spectrum of $Mo(CO)_6$ are being subtracted. Spectrum C represents the optimal difference spectrum. The peaks marked with asterisks are due to a negligible amount of $Mo(CO)_4(P(O)Ph)_3$. The spectral range is from 2200 to 1750 cm^{-1} .

cell, and assorted volumetric glassware. Reagent-grade molybdenum hexacarbonyl, triphenylphosphite, and decalin were used without further purification; $Mo(CO)_6$ and $P(O)Ph_3$ are both potentially toxic so solutions should be prepared in a vented hood. Similarly, it is best if the constant-temperature apparatus is also kept in a fume hood.

Prepare two 10-mL decalin solutions, the first with 1.0 mM $Mo(CO)_6$ and 10 mM $P(O)Ph_3$ and the second with 1.0 mM $Mo(CO)_6$ and 50 mM $P(O)Ph_3$. The use of toluene in the constant temperature flask gives a running temperature of 110 °C at reflux, which makes the rate of the reaction fast enough so the two kinetic runs can be completed in a 4-h lab period. Since the rate of the reaction is negligible at room temperature the timing can be started when the solution is added to the sidearm of the flask.

Set the parameters on the FTIR to plot spectra from 2200 to 1750 cm^{-1} . Record and store a spectrum of neat decalin to be used for the background in all subsequent spectra. Take an initial spectrum (time = 0 min) of the first solution, and then pipet the remainder of the solution into the sidearm of the constant temperature apparatus. Remove aliquots after 5, 15, 25, 35, 45, and 55 min of heating, and take spectra. Record the absorbance values of all the peaks, and from each spectrum subtract the initial spectrum with a weighting factor just large enough to bring the ν_{CO} band of $Mo(CO)_6$ at 1984 cm^{-1} to 0.00 absorbance. An example of such spectral stripping is shown in Figure 2. Record the absorbance due to $Mo(CO)_5(P(O)Ph)_3$ from this difference spectrum. Repeat the above procedure for the solution with the 50-fold excess $P(O)Ph_3$.

Data is most easily analyzed in a four-step procedure. 1. Tabulate the wavenumber of the peak maxima, the absorbance, and the concentration of $Mo(CO)_6$ and $Mo(CO)_5(P(O)Ph)_3$ for each set of spectra. The molar absorptivity of $Mo(CO)_5(P(O)Ph)_3$ at 1965 cm^{-1} is 11,000 $M^{-1} cm^{-1}$, as determined from a pure sample that had been synthesized in the usual way (8). Equations 8 and 9 can be used to calculate the concentration of $Mo(CO)_6$. 2. Determine the order of the reaction in $Mo(CO)_6$ by the appropriate plots (eqs 4–6). Calculate the rate coefficient for each run. 3. Determine the order of the reaction in $P(O)Ph_3$ by comparing the rate coefficients of the two kinetic runs (eq 7). 4. Based on the results of steps 2 and 3 above, propose a mechanism or mechanisms. If two mechanisms fit the rate law, describe other experiments that can distinguish between the choices.

The spectra shown in Figure 3 are from a kinetic run with a 10-fold excess of $P(O)Ph_3$ after 55 min at 110 °C. The subtraction of the initial spectrum yields the spectrum of $Mo(CO)_5(P(O)Ph)_3$, as shown.

Discussion

Often the most time-consuming part of this lab is learning to operate the instrument. Most FTIR instruments can store several spectra, so all the data manipulation does not have to be completed in the 10 min between samples. The experi-



Figure 3. IR spectra from a kinetic run. Spectrum A is the initial spectrum of $Mo(CO)_6$ in the presence of a 10-fold excess of $P(O)Ph_3$; spectrum B is the spectrum after 55 min at 110 °C; spectrum C is the optimal difference spectrum showing only the contributions of $Mo(CO)_5(P(O)Ph)_3$. The spectral range is from 2200 to 1750 cm^{-1} .

ment as described above works well in a lab where the students rotate through a number of experiments in the course of the semester, with everyone doing the experiments in a different order. Other applications can also be used in such a laboratory course. Angelici (4) reports that, with a very large excess of P(OPh)_3 present (~ 500 -fold), the rate law for this reaction has two terms, one that is zero-order in P(OPh)_3 from a dissociative mechanism and another that is first-order in P(OPh)_3 from an associative mechanism. This could be verified by an entire class of students, each set of lab partners being responsible for a few data points.³ Another alternative would be to determine the rate coefficients as a function of temperature, with each set of lab partners responsible for one temperature. This class effort would allow the measurement of the activation parameters ($k = A \exp$

(E_a/RT)) for CO substitution, and further discussion of mechanisms could be made from the size of A and E_a .

Acknowledgment

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³ This approach to undergraduate kinetics experiments has been used successfully by Gordon L. Johnson, Kenyon College (personal communication).