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High Pressure Reactor and Cell for Electronic and Infrared Spectral Studies

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Summary

An easily constructed, simply operated, high pressure reactor and ultraviolet-visible/infrared cell is described. The apparatus is designed for spectral studies of the interaction of transition metal complexes and small gaseous molecules in the liquid phase. Elevated pressures of the reacting gases are limited to those obtained with commercial bottled gases. An example of the utility of the apparatus is provided in the detection of an unstable Ti(III) carbonyl, $TiCl_3(CO)(PEt_3)_2$, by high pressure infrared spectroscopy.

Introduction

Homogeneous reactions of transition metal complexes with small gaseous molecules are important because the metal frequently serves as a catalyst for chemical combination of these gases in binary or tertiary gas mixtures. A valuable, but vastly underutilized tool for studying this class of reactions is high pressure electronic and infrared spectroscopy. High pressure spectral techniques provide a method for detecting thermodynamically unstable species, for directly monitoring the rate of formation and disappearance of reaction intermediates, and under favorable conditions, for determining the value of equilibrium constants. The direct observation of reaction intermediates under conditions of high pressure is especially useful in establishing mechanisms of homogeneous catalysis by metal ions.

While few spectral studies of homogeneous liquid phase reactions in the pressure range of 40-450 atm have been published,$^{(1-20)}$ the value of high pressure spectral techniques is already apparent. High pressure spectral techniques take advantage of Le Chatelier's principle in raising to the detection level the concentration of thermodynamically unstable compounds, $L_{n-p}MD_q$, formed by the interaction of transition metal complexes, L_nM, and small gaseous molecules, D, (Eq. 1).

$$\begin{gathered} D_{(g)} \overset{Kd}{\rightleftharpoons} D_{(soln)} \\ L_nM_{(soln)} + q\,D_{(soln)} \overset{K_{eq}}{\rightleftharpoons} L_{n-p}MD_{q(soln)} + pL \end{gathered} \qquad (1)$$

For a given gas pressure, high pressure ultraviolet-visible spectroscopy is more sensitive than infrared spectroscopy in detecting adduct formation because the concentrations of the transition metal complex are generally one to two orders more dilute. This leads to a greater fractional conversion of reactant.

In many instances, the detection of an intermediate is possible only by use of high pressure spectral techniques because the intermediate decomposes rapidly on lowering the pressure of the reacting gas. The thermodynamically unstable compound $HIr(CO)_4$, which is formed by the interaction of $Ir_4(CO)_{12}$ in paraffin with a 1:1 mole ratio of CO and H_2 at 430 atm and 200^0,$^{(3,4)}$ was identified by high pressure infrared spectroscopy. This complex decomposes to $Ir_4(CO)_{12}$ when the pressure is released. High pressure infrared spectroscopy was used also to detect thermodynamically unstable $Rh_2(CO)_8$$^{(5,6)}$, $Rh_2(CO)_6L_2(L=PR_3)$$^{(6)}$, $HIr(CO)_3(PPh_3)$$^{(7)}$, $H_2Ru(CO)_3(PPh_3)$$^{(8)}$, trans-$Mo(CO)_2(dppe)_2$$^{(9)}$, $Pt(CO)_3PPh_3$ and $Pd(CO)_3PPh_3$$^{(10)}$, $Co_2(CO)_9$$^{(11)}$, $Ir_2(CO)_7L$ (L=phosphines)$^{(12,13)}$ and $Rh(CO)_3X(X=Cl,Br,I)$$^{(14)}$.

The existence of hydrido carbonyls and acylcobalt tetracarbonyls as intermediates in the steady state hydroformylation of olefins catalyzed by $Co_2(CO)_8$ in heptane at 150^o and 250 atm of CO/H_2 and by $Co_2(CO)_6(PBu_3)_2$ at 190^o and 80 atm of CO/H_2 was established by high pressure infrared spectroscopy(15). High pressure infrared spectroscopy was used to identify alkyl- and acyliridium intermediates in the hydroformylation of ethylene catalyzed by $HIr(CO)_3(PPr^i_3)$,(16) and to demonstrate that $RhH(CO)(PPh_3)_3$, and $RhCl(CO)(PPh_3)_2$ promoted by triethylamine are both converted to the same rhodium intermediate under hydroformylation reaction conditions.(17) The enhanced hydroformylation catalytic activity of $RhCl(CO)(PPh_3)_2$ in the presence of a small amount of cyclohexenylhydroperoxide was found by high pressure infrared spectroscopy to be due to the formation of the very active catalyst $RhCl(CO)_2(PPh_3)$[18].

Acyl intermediates were identified by high pressure infrared spectroscopy when n-tetradecane solutions of $CH_3Mn(CO)_5$, $CH_3Mn(CO)_4L$ (L=tertiary phosphine or phosphite), and $CH_3Fe(CO)_2(C_5H_5)$ were subjected to 300 atm carbon monoxide(19). Tetrahedral acetatoiodocobalt(II) complexes, $[Co(OAc)_{4-n}I_n]^{2-}$ and CoI_4^{2-} were identified in the electronic spectra of aqueous solutions of methanol, coblat(II) acetate and iodide ion under 290 atm carbon monoxide and dihydrogen(1,2). This reaction leads to cobalt(II)-catalyzed formation of acetic acid.

High pressure infrared spectroscopy has been used to measure the rate and determine the mechanism of the water shift reaction homogeneously catalyzed by $Fe(CO)_5$ in the presence of sodium or potassium hydroxide(20).

Each of the high pressure spectrophotometric cells which have been described in the literature(1,19,21-25) has its advantages and disadvantages. The advantages of our apparatus are that it is economical to construct, adaptable for use in most commercial spectrophotometers with only minor alterations to the cell compartment, simple to operate, and usuable both for ultraviolet-visible and infrared spectral measurements. Furthermore, the cell compartment adaptations are such that they can be easily and rapidly removed. This eliminates restraints on the use of the pressure apparatus on spectrophotometers scheduled for routine studies by several research or instructional units.

Design and Construction

Schematic drawings of the jacketed reactor and spectral cell are provided in Fig. 1 and Fig. 2, respectively. Machinist's drawings and a detailed description of the apparatus, including the commercial source of components, will be provided on request.

The reaction vessel shown in Fig. 1 has a solution capacity of approximately 50 ml. It may be used over a temperature range of -30° to 100°. Temperatures are monitored by a thermocouple (not shown) mounted in the head. The reactor is constructed entirely of 316 stainless steel.

The reactor head plate (2) is fitted with three right-angle, forged-body Whitey Microvalves (4) welded to the head, a 5/16" safety valve and rupture disk (3), a graduated 0/3000 psi pressure gauge (1) and a stainless steel

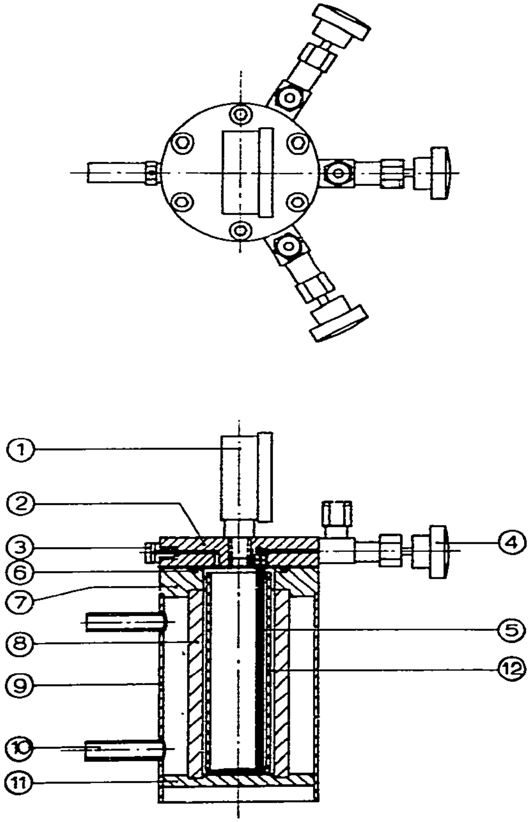

Fig. 1 High pressure jacketed reactor.

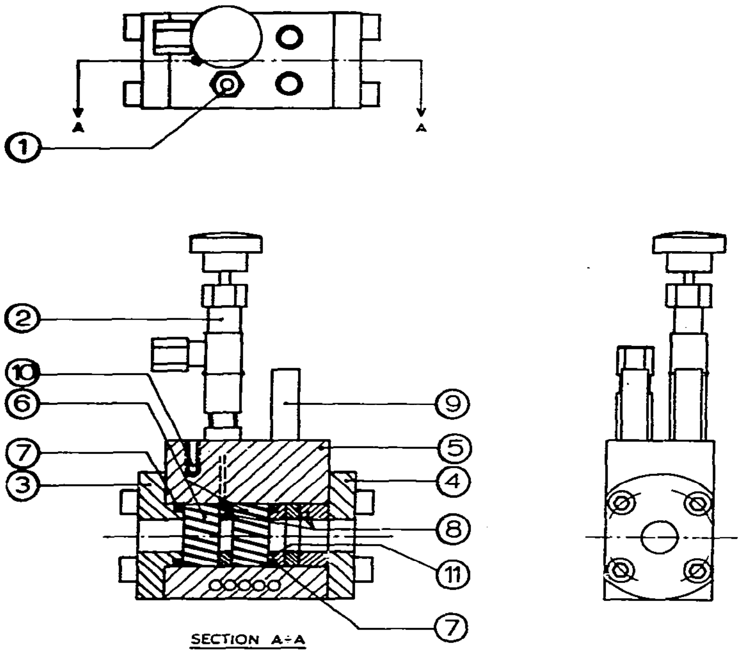

Fig. 2 High pressure jacketed ultraviolet-visible/infrared cell.

siphon (5). The head plate is secured to the body by six Allen head bolts and sealed with a recessed Viton O-ring (6).

The jacketed reactor body consists of a top plate (7), barrel (8), jacket (9), base plate (11), and inlet and outlet connectors (10) assembled in a welded construction. A glass liner (12) protects the solution from interaction with stainless steel. A Teflon siphon should be substituted for stainless steel if solution contact with metal in the reactor is to be strictly avoided. The size of the reactor is sufficiently large to permit several runs per charge. This feature is particularly useful when testing reversibility and reproducibility.

The jacketed cell shown in Fig. 2 is constructed entirely of 316 stainless steel and may be used both for electronic spectra and infrared spectra. The body (5) is made of a single piece of machined bar stock. Five cross channels in the base of the body permit circulation of the temperature regulating fluid around the cell body. The cavity is covered by welded plates. Circulating liquids are introduced and removed through connectors (9). Stainless steel Swagelok-to-pipe thread adapter (1) and a right-angle, forged-body Whitey Microvalve (2) are the inlet and outlet connections for the spectral samples, respectively. They are located at what is referred to as the front of the cell. A thermocouple well (10) is located in front and between the inlet and outlet connections. The inlet and outlet channels for the spectral solutions are arranged so as to give optimum displacement.

The face plates (3 and 4) are held in place by four Allen head bolts. The use of bolted face plates is desirable because it eliminates scoring of windows. The circular apertures in the face plates are 12.7 mm in diameter.

Stainless steel spacers (8) may be arranged to give path lengths of 5, 10, 15 and 20 mm. A 5 mm path length is shown in the drawing. Transparent optical grade fused quartz disc windows (6), 25.4 mm in diameter and 12.7 mm thick, are used for electronic spectra.

The cell is sealed by two Viton O-rings. One O-ring is mounted on a recessed spacer (11) and the second (7) on the front face plate (3).

The spectroscopic cell is connected to the reactor by 1/8 in. o.d. stainless steel tubing. The separation of the reactor and cell, and the relatively small volume of the liquid in the spectrophotometric cell improves operational safety and minimizes solution spray should a window fail.

Cylindrical optical flats of KRS-5 material(26) (25.4 mm diameter and 12.7 mm thick) are used for infrared spectra. These windows have a transmittance range of 250-16,700 cm^{-1}. KRS-5 is a water-insoluble, thallium(I) bromide thallium(I) iodide material with a modulus of rupture of 3.8×10^3 psi (11.1×10^3 kg cm^{-2})(26). A maximum safe operating temperature of 200^0 is reported for this material. Because of the toxicity of thallium compounds, these windows should be handled with protective gloves.

The substitution of other optical crystals(26) and window material of the Irtran series(27) for KRS-5 is a matter of preference. The necessary thickness to unsupported diameter ratio, t/D, to withstand a load pressure P(psi) for a cylindrical window of a material having a modulus of rupture Fa(psi) is given by Eq. 2(26).

$$\frac{t}{D} = 1.06\left(\frac{P}{Fa}\right)^{\frac{1}{2}} \qquad (2)$$

A modest safety factor of 4 is included in this equation. Our cell, with the KRS-5 windows, is designed to withstand load pressures up to 370 atm. It has been used routinely at pressures ranging from 50-170 atm.

Crescent-shaped teflon spacers of nominal 0.1 mm thickness were used for infrared studies. These spacers were positioned so as not to obstruct the addition and removal of sample solution. Equally good results were obtained by using no spacers at all and adjusting face plate bolts to give the path length for best spectra.

Viton A O-rings were used both in the reactor and the cell. This material swells slightly when exposed to benzene or toluene over extended periods, but it is resistant to halogenated aromatic and aliphatic hydrocarbons. Viton A O-rings can be used over the temperature range -29° to 204°. If neoprene ring seals are used in place of Viton A, the temperature should not be raised above 90° because the seals take a permanent set around this temperature.

Application

High pressure infrared spectroscopy was used to detect the presence of a relatively unstable complex, $TiCl_3(CO)(PEt_3)_2$. When a benzene solution of $TiCl_3(PEt_3)_2$ is subjected to 800 psi of CO for a period of 16 hr at room temperature, a new absorption band due to the carbonyl complex, appears at 1875 cm^{-1} between two intense solvent peaks (Fig. 3). This spectrum is reproducible. Yields of the carbonyl product never exceeded 14%, for pressures as high as 1600 psi and reaction times as long as 48 hr. The disadvantage to isolation of product by unfavorable thermodynamics is compounded by the near impossibility of separating unreacted starting material by solvent extraction or fractional crystallization. Analysis of the electronic spectra of solutions of the reaction mixture gave the quantity of unreacted starting material and by difference the quantity of $TiCl_3(PEt_3)_2$ associated with the adduct. Thermal decomposition of the

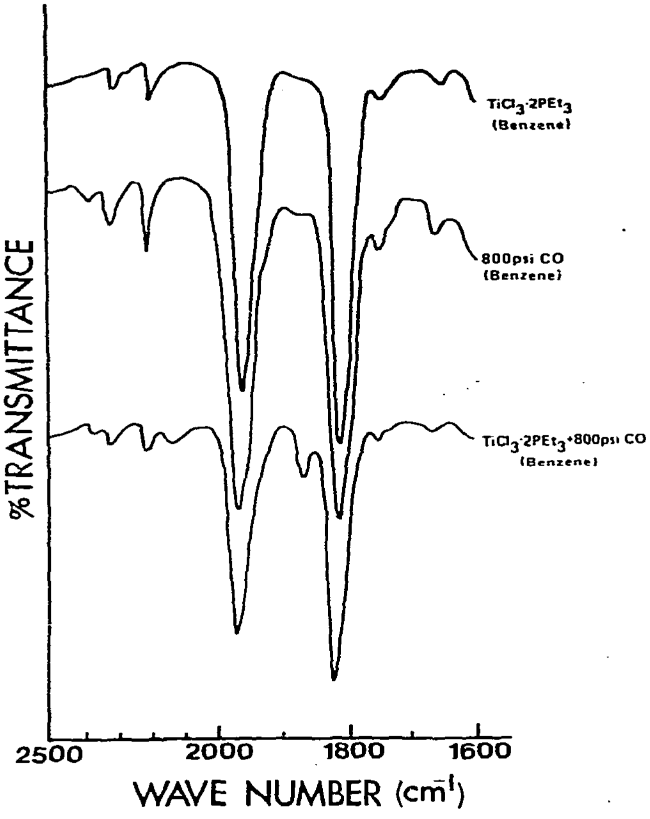

Fig. 3. Infrared spectrum of $TiCl_3(PEt_3)_2$ in benzene as a function of CO pressure.

crystalline product mixture and quantitative measurement of the released carbon monoxide by standard vacuum line techniques established the stoichiometry.

The crystalline carbonyl complex decomposes at 40-42° with the release of carbon monoxide and formation of $TiCl_3(PEt_3)_2$. To our knowledge, this relatively unstable titanium carbonyl complex is the only example of a Ti(III) carbonyl. These results provide yet another example of the usefulness of high pressure spectroscopy.

The apparatus described above also has been used in measuring the effect of high pressures of carbon monoxide and dinitrogen on electronic spectra of transition metal complexes. Research in this area is continuing and will be the subject of a separate publication.

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