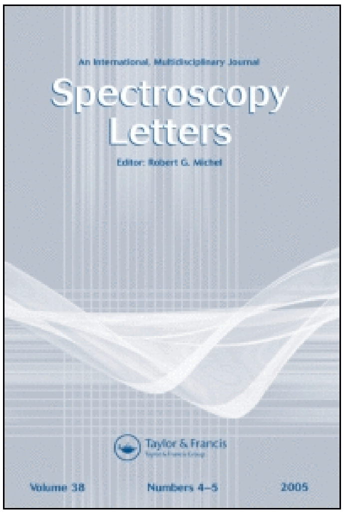

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

An Experimental Technique for Studying the Infrared Spectrum of Chemisorbed Compounds

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To cite this Article Guilbault, George G. , Scheide, E. and Das, J.(1968) 'An Experimental Technique for Studying the Infrared Spectrum of Chemisorbed Compounds', Spectroscopy Letters, 1: 4, 167 — 175

To link to this Article: DOI: 10.1080/00387016808049958

URL: http://dx.doi.org/10.1080/00387016808049958

SPECTROSCOPY LETTERS, 1(4), 167-175 (1968)

AN EXPERIMENTAL TECHNIQUE FOR STUDYING THE INFRARED SPECTRUM OF CHEMISORBED COMPOUNDS

KEY WORDS: chemisorption, infrared cell, organophosphorus compounds, gas-phase

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ABSTRACT

Two specially designed infrared cells are described for use in studying chemisorption gas-solid reactions. The gas phase spectrum of diisopropyl methyl phosphonate and dimethyl methyl phosphonate both before and after reaction with a transition metal solid, $FeCl_3$, are shown, using these new cells. Assignments are made for all bands in the spectrum of these compounds.

INTRODUCTION

In a recent paper[1] one of us (GGG) described an experimental technique for studying chemisorption reactions, in which a thin layer of finely ground crystals of the inorganic salt was placed in the bottom of a reaction finger attached to a vacuum line. A gaseous ligand was then allowed to react with the solid, the product was removed and mixed with KBr, and a spectrum was then taken of the resulting pellet using a Beckman IR 7. A more detailed study revealed this to be a poor technique in many cases; (1) in chemisorption, reaction occurs only at the surface, hence the proportion of reacted molecules to unreacted ones is very low. Thus concentration problems are introduced when the KBr pellets are made, and poor spectra are obtained in many cases; (2) elaborate precautions had to be taken to prevent atmospheric water from contaminating the sample during the process of preparing the KBr pellet. In addition, some of the complexes were unstable to atmospheric pressure and water.

An ideal method of carrying on and studying chemisorption reactions, then, would be to develop a simple, easily manipulable gas cell, which could be evacuated to very low pressures, and which would allow the continuous infrared monitoring of any reactions.

Using ideas from previous gas cells described by Smiley[2] and Eischens[3,4], cells were constructed that would meet the desired characteristics listed above. In these cells (Figures 1 and 2) a surface reaction can be induced and studied at

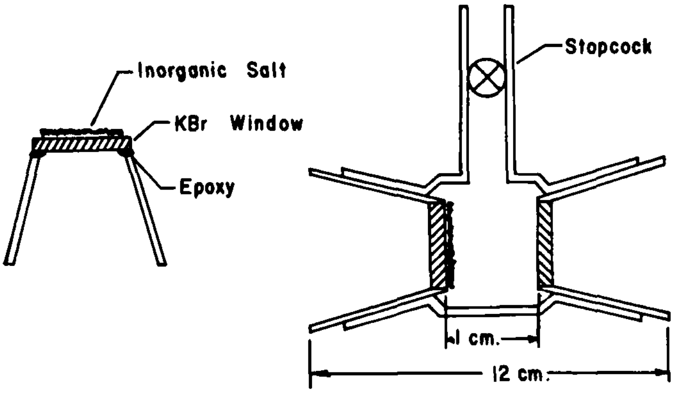

FIG. 1

Infrared Cell Type A

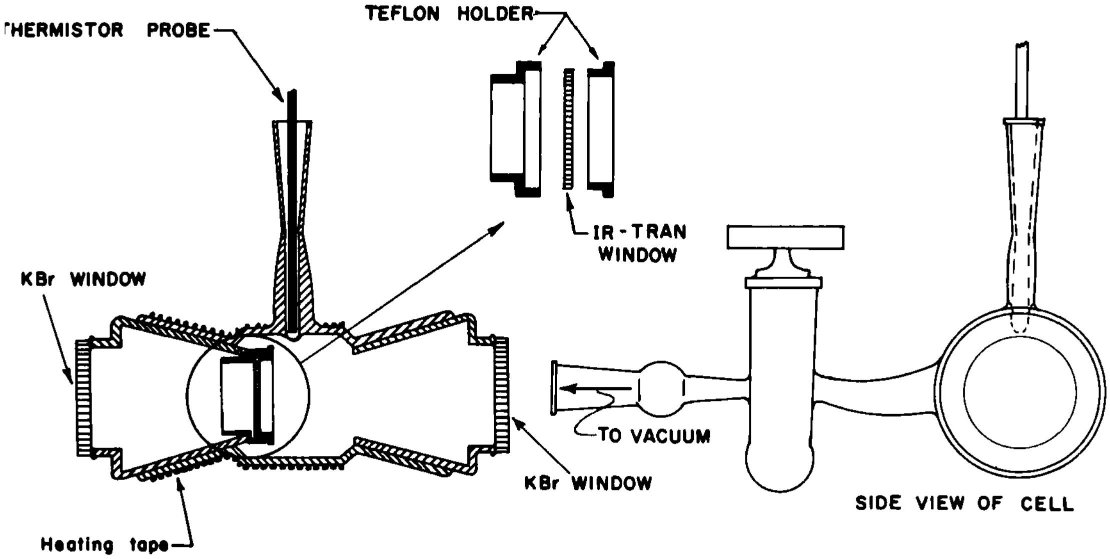

FIG. 2

Infrared Cell Type B

various pressures and temperatures. The cells can be evacuated to 10^{-7}mm, and have advantages of simplicity and convenience.

EXPERIMENTAL

Vacuum System

The high vacuum system used (Figure 3) consisted of a high capacity CENCO fore pump and a Consolidated Vacuum water cooled ultra high vacuum diffusion oil pump having a rated capacity of 10^{-8}mm of Hg. Provision for bakeout was provided, and pressures were recorded on four calibrated guages: Wallace and Tiernan (W and T) 0-20 and 0-760 mm differential guages, a Phillips cold ionization guage (0.1 mm to 10^{-6} mm) and a Consolidated hot ionization guage (10^{-4} to 10^{-9} mm).

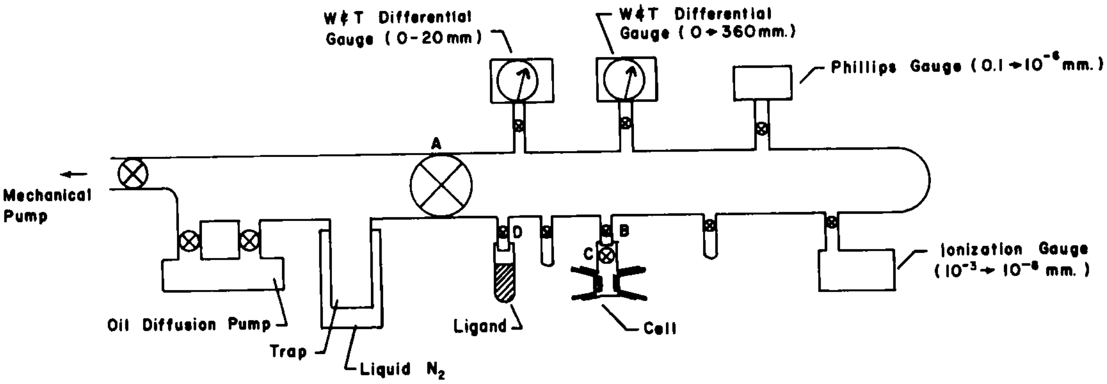

FIG. 3

Hign Vacuum System for Chemisorption Studies

IR Cell Type A

Cell A (Figure 1) is an ultimate in simplicity, consisting of a glass tube (40 mm O.D.) with a ground glass female joint (34/28 Corning 6640) fused to each end such that the overall length of the cell is 12 cm. Each of the male joints fitting in these has a potassium bromide window (1 inch diameter by 5 mm thick, Barnes Engineering) attached to the inside with an epoxy resin. The cell is attached to the vacuum line through a 4 mm stopcock, and can be easily disassembled for cleaning of the KBr windows. This cell, as well as type B described below, can be evacuated to 10^{-6} mm.

IR Cell Type B

A special IR cell was constructed for the study of gas-solid chemisorption reactions at various temperatures (20-200°C). The cell, pictured in Figure 2, consists of a glass tube (40 mm O.D.) with a ground glass female joint fused to each end (overall length 12 cm). Each of the male joints fitting in these had a KBr window, attached to the outside with epoxy resin. On the inner end of one of these male joints is fixed a teflon holder for a 25 mm IR-TRAN window. The holder consists of two pieces of teflon annular rings to keep the window in position. A 4 mm stopcock with a female ground glass joint is fitted at the center of the cell for connection to the vacuum line. Another female joint is fused at a 120° angle from this stopcock for the introduction of a thermistor probe. A thin walled glass tube closed at the inner end and fused to the joint allows the probe to come into the cell without affecting the vacuum. The stainless steel thermistor probe is connected to an Atkins multiple range resistance thermometer and the cell was heated by winding a heating type around the central part of it.

Procedure

The experimental procedure used with these cells in studying chemisorption reactions of organic ligands and inorganic transition metal salts is as follows:

The inorganic salt is deposited on the KBr window of cell A or the IRTRAN window of cell B by dropping a solution of the salt, ground to a small particle size with chloroform, onto the window. Evaporation of chloroform in a desiccator results in the deposition of very even layers. The cell is then evacuated to 10^{-6} mm, and a spectrum of the unreacted inorganic salt taken (any deviation from a straight base line indicates the presence of contamination, water of hydration, etc.).

The cell is placed back on the vacuum line and re-evacuated to 10^{-6} mm with stopcocks B and C open. The system is closed by stopcock A (Figure 3), stopcock D was opened, and the gaseous ligand is allowed to react with the inorganic salt in the cell until a definite reaction had taken place, as shown by the change in appearance of the salt (i.e. change in physical state or color). This reaction varied from a few seconds to 96^+ hours depending on the salt. The cell is then removed from the vacuum line and a spectrum is taken using a high resolution Beckman IR-7.

The cell is then evacuated to various pressures (10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6} mm) and a spectrum is recorded each time. These spectra give information as to the type of bonding in the complex (appearance, disappearance, or shift in IR bands) and to the nature of interaction (bands disappear during evacuation in physisorption or remain strong after evacuation in chemisorption).

Both cells have also been used with the vacuum line extended to the IR sample compartment. In this way the reaction can be monitored by infrared continuously.

RESULTS AND DISCUSSION

The spectra of gaseous diisopropyl methyl phosphonate obtained with these cells, before and after interaction with $FeCl_3$, are shown in Figure 4. The spectra of gaseous DIMP was similar to that of liquid DIMP[5] except for the P-O stretching frequency which was shifted from 1247 cm^{-1} to 1266 cm^{-1} and the P-O-C vibration frequency which was shifted (Table 1) from 990 cm^{-1} (vs) and 1014 cm^{-1} (vs) to 995 (vs) and 1018 cm^{-1} (s). The P-O-C bond might be expected to give rise to two characteristic frequencies, one arising

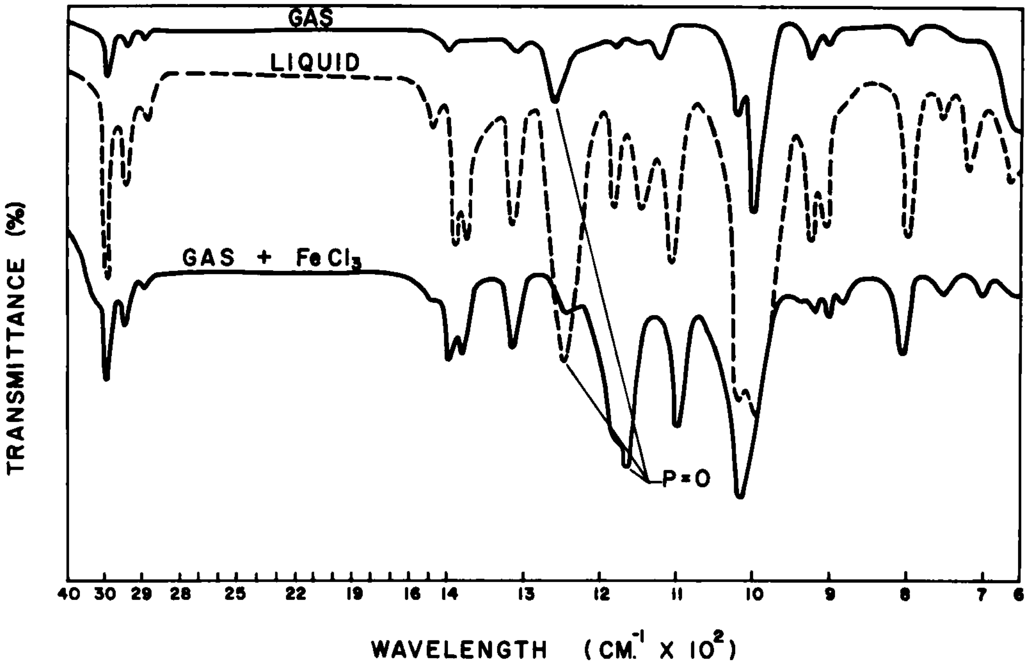

FIG. 4

Infrared Spectra of Diisopropyl Methyl Phosphonate in Gaseous and Liquid States Before and After Interaction with $FeCl_3$

from the P-O vibration, modified by the O-C link (1018 cm^{-1}) and the other from the O-C linkage modified by the phosphorus atom (995 cm^{-1}).

The salt, $FeCl_3$, exhibited a strong interaction with DIMP, as evidenced by a frequency shift to lower wave numbers of the phosphoryl stretching frequency (1266 to 1167 cm^{-1}, $\Delta\gamma = 99$ cm^{-1}), and an effect on the P-O and O-C vibrations of the P-O-C bond (Table 1).

Similar spectra were obtained for gaseous dimethyl methyl phosphonate (DMMP) and DMMP-$FeCl_3$ complex, and these results are reported in Table 2. Again a strong chemisorption reaction was observed, the phosphoryl

TABLE 1

Infrared Bands and Assignments for Liquid DIMP and for Gaseous DIMP Before and After Interaction with $FeCl_3$

Diisoprophyl methyl phosphonate		$+FeCl_3$		
Liquid	Gas	(10^{-6} mm)	Assignment	
719 (m)	723 (vw)	700 (w)	C-P stretching	
750 (w)		747 (w)	P-O stretching (symmetrical)	
792 (s)	790 (m)	807 (s)		
901 (s) 917 (s) } d	900 (w) 919 (m) } d	900 (w) 917 (w) } d	CH_3 wagging	
990 (vs) 1014 (vs,sh) } d	995 (vs) 1018 (s) } d	1012 (vs)	O-C of P-O-C P-O of P-O-C	
1110 (s)	1115 (m)	1093 (s)	O-C stretching	isopropoxy
1142 (m)	1142 (vw)	1143 (m,sh)	C-C-C (asym.) stretching	
1180 (m)	1182 (m)	1182 (s,sh)	CH_3 wagging, O-C	
1247 (vs)	1266 (s)	1167 (vs)	P=O stretching	
1313 (s)	1315 (m)	1313 (s)	CH_3 wagging	
1376 (s) 1386 (s) } d	1389 (m)	1376 (s) 1387 (s) } d	CH_3 symmetrical deformation	
1466 (w)		1452 (w) 1465 (w) } d	CH_3 bending, CH_3 (asym.) deformation	
2890 (w)	2880 (vw)	2875 (vw)	CH stretching	
2945 (m)	2940 (w)	2937 (m)	CH_3 stretching	
2985 (s)	2985 (s)	2985 (s)	(sym. and asym.)	

(s) = strong; (m) medium; (w)= weak; (vs)= very strong; (vw)= very weak; (sh)= shoulder; (d)= doublet.

stretching frequency shifting from 1276 to 1173 cm^{-1}, $\Delta\nu$ = 103 cm^{-1}, and the P-O and O-C bands of the P-O-C bond shifting from 1051 and 1076 cm^{-1} to 1021 and 1052 cm^{-1}, respectively. All peaks observed for the gas-solid complexes were as strong after evacuation to 10^{-6} mm as in the original spectra, indicating strong chemisorption reactions in each case.

Further work is now is progress to develop vacuum cells in which chemisorption gas-solid reactions can be

TABLE 2

Infrared Bands and Assignments for Liquid DMMP and for Gaseous DMMP Before and After Interaction with $FeCl_3$

Dimethyl methyl phosphonate		$+FeCl_3$	
Liquid	Gas	(10^{-5} mm)	Assignment
714 (s)	716 (vw)		C-P stretching
788 (s) } d	792 (w) } d	795 (w)	P-O stretching (sym.)
820 (vs)	820 (m)	828 (m)	CH rocking
915 (vs)	920 (m)	915 (m)	CH_3 wagging
1035 (vs) } d	1051 (vs) } d	1021 (m) } d	P-O of P-O-C
1060 (vs)	1076 (s,sh)	1052 (s)	O-C of P-O-C
1186 (m)	1185 (w)		P-O-CH_3
1246 (vs)	1276 (s)	1173 (s)	P=O stretching
1315 (s)	1315 (m)	1314 (m)	CH_3 wagging
1422 (w)			CH_3 bending
1465 (m)			CH_3 (asym.) deformation
1512 (vw)			
2865 (m)	2850 (w)	2856 (vw)	CH_3 stretching (sym. and asym.)
2935 (w,sh)			
2960 (s)	2960 (m)	2961 (vw)	CH stretching
3000 (m,sh)			

(s) = strong; (m) medium; (w) weak; (vs) = very strong; (vw)= very weak; (sh) shoulder; d = doublet.

studied in the far-IR, UV and visible regions of the electromagnetic spectrum.

ACKNOWLEDGMENT

The financial support of the Army Research Office (Grant No. Da-ARO-D-31-124-G906) is gratefully acknowledged.

REFERENCES

1. G. G. Guilbault, Anal. Chem. Acta 39, 260 (1967).
2. V. N. Smiley, Rev. Sci. Instr. 34, 820 (1963).
3. R. P. Eischens, S.A. Francis and W. A. Pliskin, J. Phys. Chem. 60, 194 (1956).
4. R. P. Eischens, Science 146, 486 (1964).
5. J. Maarsen, Recueil 76, 713 (1957).