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Journal of Fluorine Chemistry 79 (1996) 53–57

JOURNAL OF FLUORINE CHEMISTRY

Chemisorption study of trifluoroacetyl fluoride on FeF_3 by FT-IR spectroscopy

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Received 7 December 1995; accepted 5 April 1996

Abstract

The chemisorption of trifluoroacetyl fluoride onto an iron fluoride surface calcined at 773 K has been investigated by transmission FT-IR spectroscopy. It was found that a fluoroformate surface species is formed during chemisorption at ambient temperature. The vibrational fundamentals of this species were assigned. This surface species was tentatively characterized to have a monodentate configuration. Desorption studies showed that the surface species is stable up to 773 K. Low-temperature chemisorption studies showed that $CF_3C(O)F$ chemisorbed onto the FeF_3 surface at 150 K. As the temperature was raised to 273 K, the fluoroformate surface species began to form. A mechanism to account for the $CF_3C(O)F/FeF_3$ chemisorption at ambient temperature was proposed.

Keywords: Chemisorption; Trifluoroacetylfluoride; Iron(III) trifluoride; FT-IR spectroscopy; Surface species

1. Introduction

The perfluoropolyalkylether (PFPAE) degradation observed in a tribological environment is generally understood as a Lewis acid/Lewis base interaction, where the Lewis acid is the metal fluoride and the Lewis base is the PFPAE lubricant. Kasai and Wheeler's mechanism [1] proposes that the ether oxygens of the acetal fragments of a PFPAE interact with the Lewis acid sites on AlF_3 to initiate the bond-scission process which leads to the formation of a perfluoroacyl fluoride, $R_fC(O)F$. These $R_fC(O)F$ species interact with the metal surfaces to form more metal fluorides [2]. In turn, the metal fluoride further catalyzes PFPAE degradation to form more perfluoroacyl fluorides, $R_fC(O)F$. The formation of $R_fC(O)F$ and metal fluoride forms a "snowball" cycle [3]. In the present study, the $CF_3C(O)F$ molecule has been introduced onto an FeF_3 surface to investigate the interaction between these two materials. To the best of our knowledge, this is the first chemisorption study for the $CF_3C(O)F/FeF_3$ system.

Another reason for studying this system was to examine the feasibility of using the $CF_3C(O)F/FeF_3$ system as an experimental model to evaluate the strength of a tribology thin film of PFPAE. An organic thin film resulting from the reaction of PFPAE lubricant with a M-50 flat specimen (performed on a Cameron–Plint reciprocating tribometer) was detected and analyzed by the grazing-angle-microscope/FT-IR technique. This thin film is believed to be chemisorbed onto a FeF_3 thin layer formed at the interface between the M-50 and the lubricant fluid [3]. However, the bonding strength of this organic thin film is hard to estimate. A chemisorption/desorption experiment with the $CF_3C(O)F/FeF_3$ system is an ideal model for evaluating the bond strength for the adsorbate/adsorbent system. This finding can, in turn, provide insight about the bonding strength of a tribological thin film of PFPAE.

2. Experimental details

The cell design was a modified version of the one used by Yates *et al.* [4]. The chemisorption cell was assembled from three major components: (1) the cube; (2) the nipple connector; and (3) the copper electrical feedthrough, as shown in Fig. 1. An assembled cell is shown in Fig. 2 where the nipple connector is not shown. The top portion of this assembly is a styrofoam box which was tightly connected to the two copper rods of part 3 shown in Fig. 1, so the coolant could be contained and replenished throughout the experiment.

The cube unit is a standard cube and two of its ports were capped by vacuum flanges which were mounted with KBr

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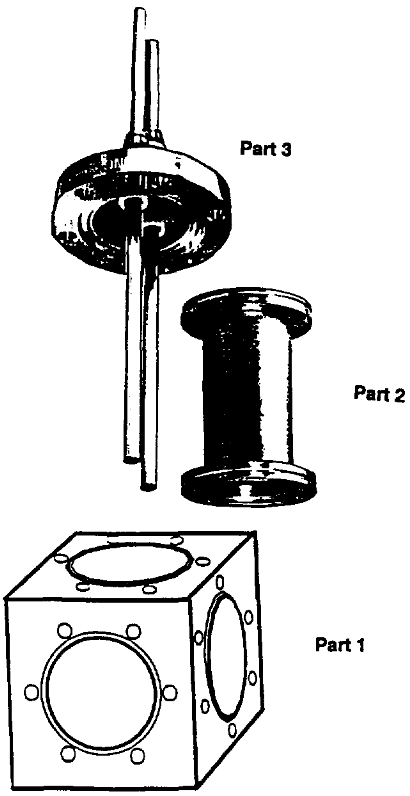

Fig. 1. The three major components used in assembling the chemisorption cell: (1) the cube; (2) the nipple connector; and (3) the copper electrical feedthrough.

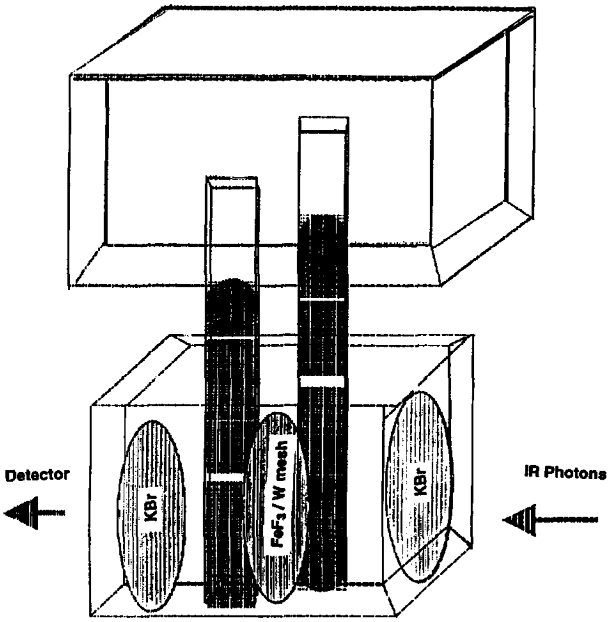

Fig. 2. A simplified representation of the chemisorption cell with an operating temperature range between 125 K and 1000 K.

windows. The ends of the two copper feedthroughs rods, shown in part 3 of Fig. 1, were flattened. A small tungsten mesh sheet (with 0.0013 wire, 140 × 140 count) was fastened onto the flat portions of the two copper rods of part 3. The thermocouple leads (K-type) and a stainless steel dosing tube (1/8 in diameter, pointing toward the center of the two copper rods of part 3 from an oblique angle) were welded with the flange of part 3. A digital thermometer was used to monitor temperatures. Current provided from a power supply was provided to the tungsten mesh to attain high temperatures. The operational temperature range was 125 K to 1000 K. The cell was evacuated by means of a metal vacuum line equipped with a turbomolecular pump to a background pressure of 10^{-7} Torr.

Iron fluoride powder (ca. 0.8 g) was pressed with a rectangle-shaped tungsten mesh under 20 000 psi to form a thin wafer with the mesh. This sample was tightly fastened at the flat portion of the copper feedthrough rods with the thermocouple tip spot-welded on the mesh. The FeF_3/W surface temperature was kept at 500 °C overnight and the surface was gradually cooled to ambient temperature. Almost all the absorbed water was pumped away and 97% of the iron was still in the Fe^{III} state after calcination based on the Mossbauer data [1]. Iron(III) fluoride was purchased from Aldrich Chemical Company, Milwaukee, WI. Trifluoroacetyl fluoride was purchased from PCR, Inc., Gainesville, FL, and was used with no further purification.

Infrared spectra were recorded with a Nicolet 740 series FT-IR spectrometer in the 4000–400 cm^{-1} range at 4 cm^{-1} resolution. A KBr beam splitter and a DTGS detector were used. The subtraction technique was used throughout this study. All the spectra reported here were difference spectra which were obtained by subtracting the IR spectra with and without a given amount of trifluoroacetyl fluoride. The chemisorption cell was positioned and remained stationary during the entire course of data acquisition, thus minimizing any possible artifacts. The pressure was monitored with MKS Baratron capacitance manometers covering a range from 10^{-3} to 10^{3} Torr.

3. Results and discussion

3.1. Room-temperature chemisorption

Fig. 3 shows the chemisorption of $CF_3C(O)F$ onto a calcined FeF_3 surface at ambient temperature. Fig. 4 shows the spectrum of $CF_3C(O)F$ in the gaseous phase at ambient temperature, the IR bands assigned by Berney [5]. It is obvious that the carbonyl stretching band (1897 cm^{-1}) and the C–F (1097 cm^{-1}) stretching band shown in Fig. 4 disappeared as the compound chemisorbed onto the FeF_3 surface. On detailed examination, the symmetric and asymmetric CF_3 stretching bands (1333 cm^{-1}, 1212 cm^{-1}) and the C(O)F deformation band (760 cm^{-1}) disappeared as well. A new doublet at 1615 cm^{-1} and 1473 cm^{-1} was formed as shown in Fig. 3. It is interesting to note that the lower limit of the

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[1] Mossbauer spectra were obtained with a constant acceleration electromechanical transducer operated in fly-back mode. Spectra were obtained at room temperature with a ^{57}Co source in a rhodium matrix.

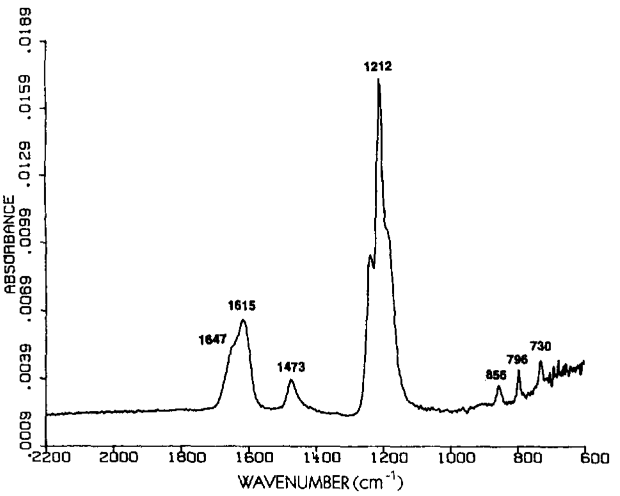

Fig. 3. FT-IR spectrum of gaseous $CF_3C(O)F$.

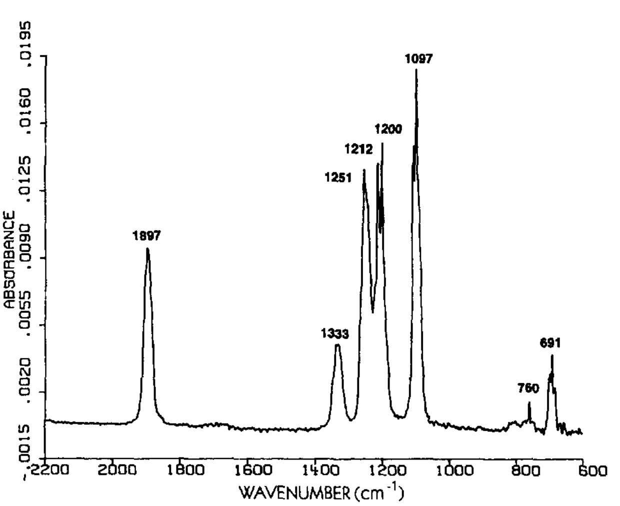

Fig. 4. FT-IR spectrum of $CF_3C(O)F$ chemisorbed onto a calcined FeF_3 surface at ambient temperature.

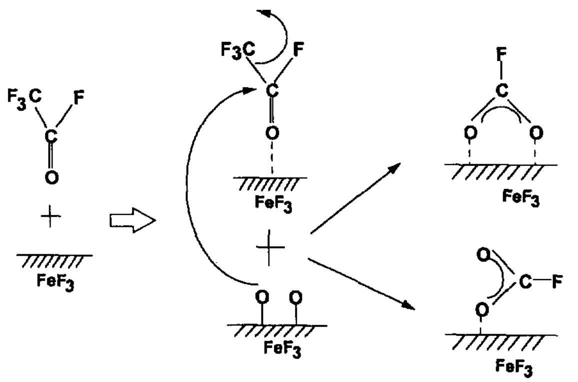

Fig. 5. A schematic representation of the formation of a fluoroformate surface species.

chemisorption spectrum is about 600 cm^{-1} (in the case of alumina, the lower limit is about 1000 cm^{-1}). Hence, the small bands present in the region between 1000 cm^{-1} and 600 cm^{-1} can be analyzed.

Because of the disappearance of the fundamental vibrations related to the CF_3 group and the umbrella deformation mode assigned at 691 cm^{-1} [5], it is proposed that the C–C bond is broken as this compound chemisorbs onto the calcined surface and a fluoroformate surface species is formed. The 1615 cm^{-1} and 1473 cm^{-1} bands are attributed to the $\nu_{as,\ OCO}$ and $\nu_{s,\ OCO}$ vibrations, respectively, for the fluoroformate surface species. Ng *et al.* [6] observed and assigned this same species in their desorption study of the $(C_2F_5)_2O$/alumina system. The mechanism of the formation of this species is shown in Fig. 5. The oxygen atoms were present in the FeF_3 surface mainly from the decomposition of $CF_3C(O)F$ in the very early chemisorption stage. In turn, they attacked the carbon atoms of the carbonyl groups and the C–C bond groups were broken. Hence, the CF_3 groups left the molecules and fluoroformate surface species were formed.

This formate surface species can be anchored to the FeF_3 surface in a bidentate or monodentate configuration. The C(O)F deformation mode at 760 cm^{-1} of the gaseous $CF_3C(O)F$ disappears and two new bands are formed at 730 cm^{-1} and 795 cm^{-1}. The former band can be assigned tentatively as the deformation mode of the C(O)F group with the oxygen attached to the FeF_3 surface, while the latter can be attributed to the C(O)F with a free oxygen atom. Consequently, a monodentate surface species is proposed to be present. A comparison of the vibrational fundamentals between gaseous $CF_3C(O)F$ and the fluoroformate surface species and tentative assignments of the fluoroformate species are listed in Table 1.

The conclusion that a fluoroformate surface species is present is different from the results obtained for the chemisorption study of $CF_3OCF(CF_3)C(O)F$ onto alumina at room temperature [7]. Because of the presence of the ν_{C-F} band of the C(O)F functional group in that study, it is believed that a hydrogen bond is formed between the $CF_3OCF(CF_3)C(O)F$ and the isolated hydroxy sites available on alumina surfaces. In contrast, for the $CF_3C(O)F/FeF_3$ system, the fluoroformate surface species is proposed to be present. Harrison and Guest [8] have reported the existence of a fluoroformate surface species for the CF_3COOH/SnO_2 system.

Table 1
Vibrational assignments for $CF_3C(O)F$ and fluoroformate surface species

Assignment	$CF_3C(O)F$ (gaseous) (cm^{-1})	Fluoroformate (chemisorbed) (cm^{-1})	Assignment
$\nu_{C=O}$	1897		–
		1615 (1647)	$\nu_{as,OCO}$
		1473	$\nu_{s,OCO}$
ν_{CF_3}	1333		–
$\nu_{FCF_2(a')}$	1251		–
$\nu_{FCF_2(a'')}$	1212		–
ν_{CF}	1097	1212	ν_{CF}
		796	$\delta_{C(O)F(free)}$
$\delta_{C(O)F}$	760		–
		730	$\delta_{C(O)F(chemisorbed)}$
δ_{CF_3}	691		–

[a] Berney [5].

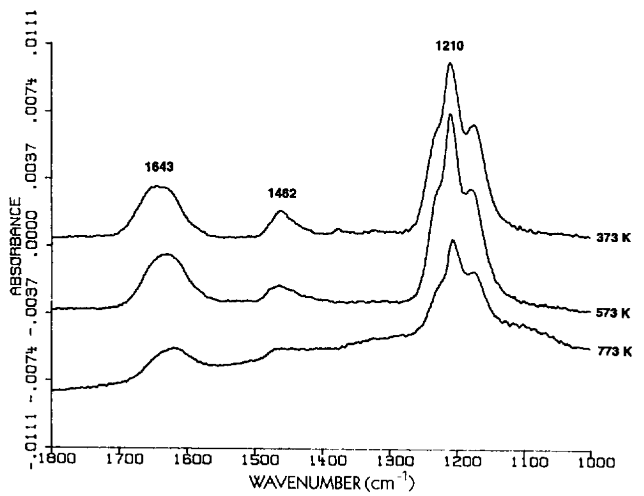

Fig. 6. Desorption spectra of fluoroformate surface species at different temperatures: (A) 373 K; (B) 573 K; (C) 773 K.

3.2. Desorption study

Desorption studies were performed and the resultant spectra obtained at different temperatures are shown in Fig. 6. All the bands corresponding to the chemisorbed fluoroformate species are still observable even at 773 K but with diminished band intensities. This clearly indicates that the fluoroformate surface species is stable and that the $CF_3C(O)F/FeF_3$ system can be a useful model system for estimating the strength of the surface films produced in our tribology experiments.

3.3. Low-temperature chemisorption

Fig. 7 shows the chemisorption spectrum of $CF_3C(O)F$ onto the FeF_3 surface at 150 K. As compared with the gaseous spectrum shown in Fig. 3, most of the bands are the same except with a band shift of the $\nu_{C=O}$ band of 17 cm^{-1}, 43 cm^{-1} and 57 cm^{-1}. As the temperature was gradually raised to 273 K, the only noticeable band is located at 1210 cm^{-1} as shown in Fig. 8. A weak band at 1642 cm^{-1} was also discernible. This spectrum is similar to that obtained for ambient temperature chemisorption shown in Fig. 3. Apparently, at 273 K, the C–C bond is broken and a fluoroformate surface species is formed.

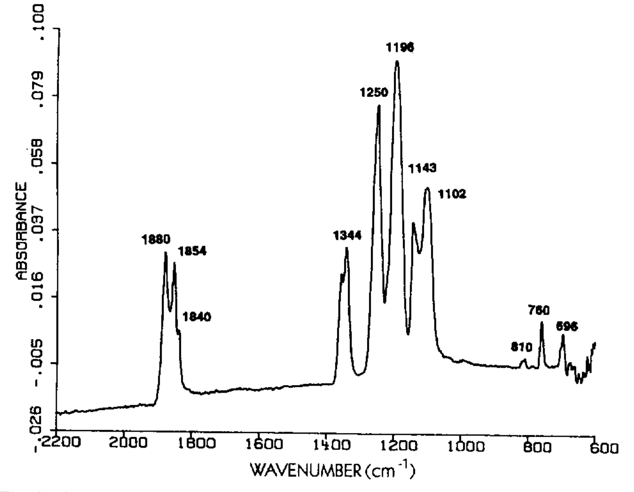

Fig. 7. Chemisorption of $CF_3C(O)F$ onto a calcined FeF_3 surface at 150 K.

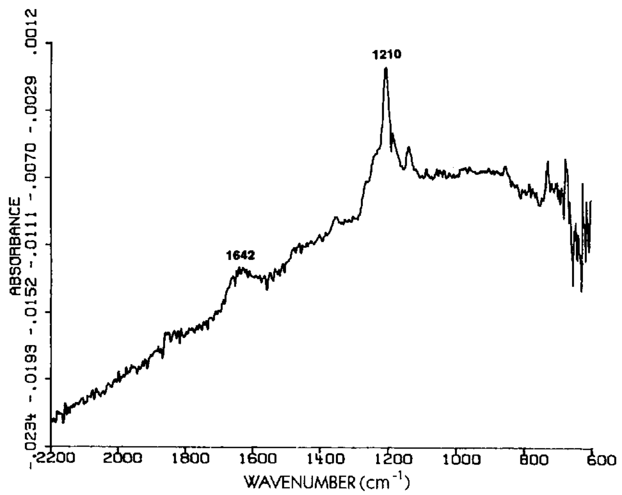

Fig. 8. Desorption spectrum of the fluoroformate surface species at 273 K.

4. Conclusion

1. A fluoroformate surface species was formed when the $CF_3C(O)F$ chemisorbed onto the calcined FeF_3 surface at ambient temperature.
2. The fluoroformate surface species is tentatively proposed to have a monodentate configuration and its vibrational fundamentals were assigned.
3. The chemisorption process commenced at 150 K in the present system. As the surface temperature was raised to 273 K, the C–C bond was broken and a fluoroformate species formed.
4. Desorption studies showed that the fluoroformate surface species is stable up to 773 K.

Acknowledgments

This work was supported by the Materials Directorate of Wright Laboratory, Wright–Patterson Air Force Base, OH, USA. The authors are indebted to Dr. H.L. Paige of the Wright Laboratory, Wright–Patterson Air Force Base, OH and for valuable discussions during the preparation of this manuscript. The authors are also indebted to Professor Ng of the Chemistry Department of Cleveland State University for her insights in the preparation of the discussion section of this manuscript. The authors would like to express their thanks to Dr. J. Zabinski of Wright Laboratory and Dr. G. John of the Air Force Institute of Technology, Wright–Patterson Air Force Base, OH for the analysis of a calcined FeF_3/W specimen by Mossbauer spectroscopy.

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