d character. Already at about 11 eV, satellite lines start to appear and they soon become dense in energy. It is thus clear that the PE spectrum above 10 eV cannot be explained without the consideration of satellite lines. A detailed discussion is however not meaningful as only the qualitative aspects are amenable to a calculation for this molecule and because the calculation is only strictly applicable in the limit of high-energy exciting radiation. Above about 17 eV the density of lines becomes very large, and we observe the effect of the breakdown of the molecular orbital model of ionization. There are thus no more simple hole states.

Conclusions

The extensive CI calculations we have described have identified the importance of correlation of the metal–ligand bonding electrons in bis(π-allyl)nickel, leading to an increase in the Ni 3d population compared to that given by an RHF description. Whereas differential relaxation effects lead to a larger *decrease* in the Ni 3d ionization energies than those of the ligand π-electrons, differential correlation effects are found to lead to a significant *increase* in the metal 3d ionization energies, but to a small decrease in ligand π-ionization energies. Thus, both relaxation and correlation effects need to be considered to discuss the PE spectrum of bis(π-allyl)nickel. It is probable that the ΔSCF–CI calculations underestimate this differential correlation, by predicting the ground ionic state to be ^2A_g compared with the more likely ^2A_u contender. We have described the first calculation of the valence ionization energies of a transition-metal complex using an ab initio Green's function formalism. We find that the extended 2ph–Tamm–Dancoff approximation leads to an extremely satisfactory assignment of the PE spectrum.

Acknowledgment. We thank the SERC for support of this research. W.v.N. thanks the Fonds der Chemischen Industrie for partial support of this work.

Registry No. Bis(π-allyl)nickel, 12077-85-9.

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Infrared Matrix-Isolation Study of the 1/1 Molecular Complexes of Chlorine Monofluoride with Oxygen-Containing Bases

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Received March 12, 1985

The matrix-isolation technique has been successfully employed for the isolation and characterization of the complexes formed between chlorine monofluoride, ClF, and a variety of oxygen-containing bases. Twin-jet deposition of reactants was employed throughout, with either argon or nitrogen as the matrix material. All of the complexes isolated were characterized by the stretching vibration of the perturbed ClF subunit in the complex, shifted to lower energies by 50–100 cm^{-1}. For many of the complexes, a 3/1 doublet was observed, indicative of ^{35}Cl–^{37}Cl splitting in natural abundance. For each base, one or more perturbed vibrational modes were observed; typically, these were modes that involved motion of the oxygen atom in the base, suggesting that the interaction in the complex is through the chlorine of the ClF subunit to the oxygen atom of the base. Comparison of the spectra of the complexes observed here with those of previous studies suggests that ClF is a medium-strength Lewis acid, falling roughly between SiF_4 and GeF_4 in terms of acidity.

Introduction

The study of molecular complexes has increased in importance to chemists in all fields in the past 30 years.[1] An understanding of the nature of the interaction may be gained, trends in reactivities may be formulated, and intermediates in chemical reactions may be characterized. The discovery and interpretation of the charge-transfer spectrum of the I_2/C_6H_6 system led to a revival of interest in this area.[2] Mulliken and others who followed were able to extend Lewis acid–base theory in quantum-mechanical terms.[3-5] A number of other halogen-containing systems have been studied experimentally since this early work,[6-8] but little is known about the molecular complexes of chlorine monofluoride, ClF, in large measure due to the high reactivity of ClF at room temperature. The matrix-isolation technique was developed for the study of such highly reactive species[9,10] and their reaction products. Twin-jet deposition, in which each reagent is deposited from a separate vacuum line, allows for a very brief mixing period directly in front of the cryogenic surface, before the initial reaction products are trapped in an inert matrix. In this manner, complexes of ClF with avariety of Lewis bases might be isolated, prior to further reaction.

While little is known experimentally about the complexes of ClF, considerable theoretical attention has been given these species.[11-13] For example, workers have calculated that the $ClF{\cdot}NH_3$ complex should be quite strongly bound, by roughly 8 kcal/mol, which is considerably more than the interaction energy in typical charge-transfer complexes. This, in turn, has led to the suggestion that a number of contributions to the binding energy are important, including an electrostatic interaction, a charge-transfer term, polarization effects, and exchange repulsion. Examination of the infrared spectra of molecular complexes of ClF may provide qualitative information about the binding in the product species, and the spectral properties of the complexes can be correlated with selected molecular parameters of the Lewis bases in question. Consequently, a study was undertaken to examine a range of molecular complexes of ClF with oxygen-containing bases in low-temperature, inert matrices.

Experimental Section

The experiments described herein were carried out on a conventional matrix-isolation apparatus, which has been described previously.[14] Acetone (Fisher), methanol (MCB), diethyl ether (Fisher), and furan (Fisher) were introduced into the vacuum system as the vapor above the liquid, after being degassed through repeated freeze–thaw cycles. ClF (Pennwalt), ethylene oxide (C_2H_4O, Matheson), dimethyl ether (Math-

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(1) Jensen, W. B. "The Lewis Acid-Base Concepts, an Overview"; Wiley-Interscience: New York, 1980.
(2) Bensei, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
(3) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 801.
(4) Mulliken, R. S.; Person, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 3409.
(5) Mulliken, R. S.; Person, W. B. *Annu. Rev. Phys. Chem.* **1962**, *13*, 107.
(6) Tamres, M. *Molec. Assoc.* **1979**, *2*, 331.
(7) Fredin, L.; Nelander, B. *J. Am. Chem. Soc.* **1974**, *96*, 1672.
(8) Hassel, O.; Stromme, K. O. *Acta Chem. Scand.* **1959**, *13*, 275.
(9) Andrews, L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 109.
(10) Barnes, A. J. "Molecular Interactions"; Ratajczak, H., Orville-Thomas, W., Eds.; Wiley: New York, 1980; Vol. 1.
(11) Lucchese, P. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1975**, *97*, 7205.
(12) Umeyama, H.; Morokuma, K.; Yamabe, S. *J. Am. Chem. Soc.* **1977**, *99*, 330.
(13) Kollman, P. *J. Am. Chem. Soc.* **1977**, *99*, 4875.
(14) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.

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eson) and perdeuteriodimethyl ether (Merck, 99% D) were obtained in lecture bottles and introduced as gases into the vacuum line. They were condensed at 77 K and purified by freeze-thaw cycles. Argon (Union Carbide) and nitrogen (Puritan) were used as the matrix materials with no additional purification. Formaldehyde was deposited directly onto the cold window by sublimation of the monomeric vapor from solid paraformaldehyde (Fisher) at 50–60 °C.

Matrices were deposited at roughly 2 mmol/h from each vacuum line, for typically 22 h, before final spectra were recorded on a Beckman IR 12 infrared spectrophotometer. Resolution was on the order of 1 cm^{-1} at 1000 cm^{-1} and slightly greater in other regions. The twin-jet mode was employed throughout due to the high reactivity of ClF; the stainless-steel manifold in which ClF was handled needed thorough conditioning with ClF between each experiment.

Results

Prior to the investigation of the products arising from the codeposition of ClF with Lewis bases, each reactant was examined alone in an argon matrix (and in a nitrogen matrix, for selected systems). The spectra obtained in these blank experiments were in good agreement with previous matrix spectra, where available, and with gas-phase studies.[15-19] In particular, the blank experiments of ClF in argon showed a sharp monomer doublet at 768 and 762 cm^{-1}, due to ^{35}Cl and ^{37}Cl in natural abundance, as well as a broad absorption with unresolved features at to lower energies, which is readily assignable to dimeric and aggregate ClF.

ClF + $(CH_3)_2CO$. Acetone was codeposited with ClF into argon matrices in several concentrations; in a typcial experiment, concentrations of Ar/ClF = 500 and Ar/$(CH_3)_2CO$ = 1000 were employed. In such an experiment, a new absorption of medium intensity was observed at 687 cm^{-1}, with a shoulder on the low-energy side at 682 cm^{-1}. In the upper spectral region, near the parent C═O stretch of acetone, a strong product absorption was noted at 1701 cm^{-1}, with a weaker, broader absorption at 1691 cm^{-1}. Finally, in the spectral region near 500 cm^{-1}, a new moderately intense absorption was noted at 556 cm^{-1}. When the concentration of acetone was increased to 500/1, these product bands were observed to increase in intensity and at the same relative rate, except for the band at 1691 cm^{-1}, which became more intense relative to the 1701-cm^{-1} product band. Similar results were obtained when nitrogen matrices were employed.

ClF + $(CH_3)_2O$. The codeposition of ClF with dimethyl ether into argon matrices led to a number of new infrared absorptions, the most distinctive of which was an intense band at 682 cm^{-1}. This band was somewhat broad and unsymmetrical, with indication of an unresolved shoulder on the low-energy side. Distinct product absorptions were noted near several of the parent absorptions of $(CH_3)_2O$, at 904, 1078, and 1161 cm^{-1}. In the highest yield experiment, these absorptions were roughly as intense as the parent dimethyl ether bands. ClF was also codeposited with $(CD_3)_2O$ in two experiments, with Ar/$(CD_3)_2O$ = 1000 and Ar/ClF = 1000 and 300. In the more dilute ClF experiment, product absorptions were noted at 680 cm^{-1}, with a resolved counterpart at 675 cm^{-1}; these two absorptions displayed an approximately 3/1 intensity ratio. In addition, strong product absorptions were noted near two absorptions of parent $(CD_3)_2O$, at 812 and 1125 cm^{-1}, again with shoulders on the low-energy side. When the ClF concentration was increased to M/R = 300, all of the product absorptions were observed to become more intense, as is shown in Figure 1. These two reactants were also investigated in two nitrogen matrix experiments, where similar results were noted, and a high yield was obtained.

ClF + $(C_2H_5)_2O$. Diethyl ether was codeposited with ClF into argon matrices in several experiments by employing diethyl ether samples with M/R = 1000 and varying ClF concentrations. In a more dilute ClF experiment, with M/R = 700, three distinct product features were noted, the most distinctive of which appeared at 673 cm^{-1}. This band, which was quite sharp, was just on the high-energy side of the 668-cm^{-1} absorption of gas-phase CO_2, which appeared in all spectra in this study. Two additional product bands were noted, a relatively weak feature at 840 cm^{-1}, and a moderately intense, sharp feature at 1088 cm^{-1}. In subsequent experiments, as the ClF concentration was increased, all three of these product bands were observed to grow and to grow at approximately the same rate.

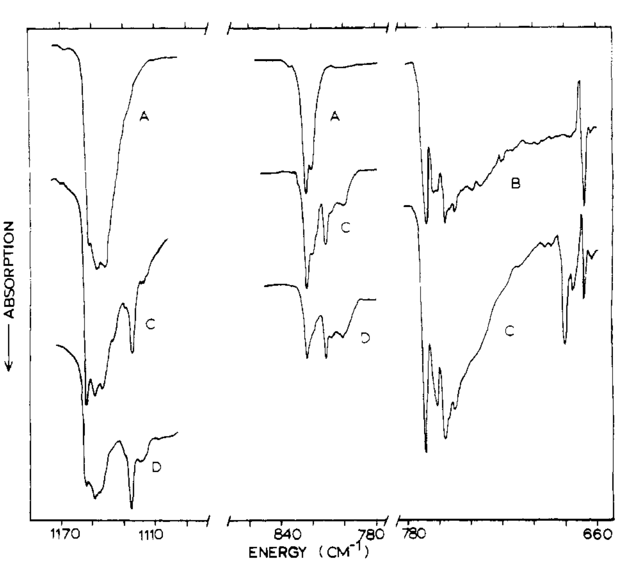

Figure 1. Infrared spectra of the products of the codeposition of ClF and $(CD_3)_2O$ into argon matrices. Traces A and B represent blank spectra of $(CD_3)_2O$ and ClF in argon, respectively. Trace C shows the spectrum arising from the codeposition in a dilute experiment, while trace D shows a more concentrated twin-jet experiment.

ClF + CH_2O. ClF was codeposited with formaldehyde in a series of experiments in argon matrices; however, the method of deposition of CH_2O did not allow for the calculation of concentrations. In these experiments, a distinct, sharp absorption was noted at 716 cm^{-1}, with a weaker counterpart at 710 cm^{-1}. While these bands lie on the tail of the broad ClF aggregate absorptions, they were quite distinct and reproducible between experiments. Further, their shape and relative intensities matched closely those observed in this region when other bases were employed. In addition, a broad product absorption was noted at 1710 cm^{-1}, to the red of the C═O stretching mode of parent CH_2O, as well as a product absorption at 1488 cm^{-1}, shifted down from the parent CH_2O band at 1499 cm^{-1}.

ClF + C_2H_4O. Ethylene oxide was codeposited with ClF into argon matrices at several concentrations; a typical experiment was conducted with M/R = 1000 for each reactant. The most apparent new feature was a band of medium intensity at 692 cm^{-1}, with a low-energy counterpart at 686 cm^{-1}; as with the systems described above, these two bands showed a roughly 3/1 intensity ratio. The most intense parent absorption of C_2H_4O lies near 878 cm^{-1}, with a bandwidth of roughly 15 cm^{-1}, and (probably) several overlapping absorptions. When C_2H_4O was deposited with ClF, the overall structure of this band was somewhat altered and a new absorption was noted, at 867 cm^{-1}, which itself had a shoulder at 861 cm^{-1}. As the concentration of ClF was increased relative to C_2H_4O, this new absorption as well as the shoulder became further resolved and distinct from the parent absorption.

ClF + $(CH)_4O$. The codeposition of furan with ClF into argon matrices gave rise to several product absorptions, the most distinctive of which was noted at 657 cm^{-1}, with a weaker counterpart at 652 cm^{-1}. In the spectral regions near absorption of parent $(CH)_4O$, product bands were noted at 960 and 551 cm^{-1}, shifted from the parent absorptions at 993 and 604 cm^{-1}, respectively. These product absorptions were quite sharp and distinct, up to high concentrations.

ClF + CH_3OH. ClF was deposited with methanol in several twin-jet experiments, over a range of concentrations, into argon matrices. In an experiment with M/R = 1000 for each reagent,

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(15) Ault, B. S. *J. Mol. Struct.* **1985**, *127*, 343.

(16) Prochaska, E. S.; Andrews, L.; Smyrl, N. R.; Mamantov, G. *Inorg. Chem.* **1978**, *17*, 970.

(17) Ault, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5742 and references therein.

(18) Walther, A.; Ault, B. S. *Inorg. Chem.* **1984**, *23*, 3892 and references therein.

(19) Bach, S. B. H.; Ault, B. S. *J. Phys. Chem.* **1984**, *88*, 3600.

Table I. Product Band Positions (cm^{-1}) and Correlations for the 1/1 Complexes of Chlorine Monofluoride with Oxygen-Containing Lewis Bases[a]

base	ν_{ClF}	ν_B[b]	$\Delta\nu_{ClF}$	PA[c]	μ[d]
	762, 768				
CH_2O	710, 716	1488, 1710	52	172	2.33
CH_3OH	693, 697	1021	71	182	1.70
$(CH_2)_2O$	686, 692	867	76	188	1.89
$(CH_3)_2O$	682	904, 1078, 1161 (sh)	86	192	1.30
$(CD_3)_2O$	675, 681	812, 1125			
$(CH_3)_2CO$	682, 687	556, 1701	81	197	2.88
$(C_2H_5)_2O$	673	840, 1088	95	200	1.15
$(CH)_4O$	652, 657	551, 960	111	192	0.66

[a] Argon matrix results. [b] Vibrations of the base subunit in the 1/1 complex; see text for assignments. [c] Proton affinity of the base, in kcal/mol, from ref 30. [d] Dipole moment of the base, in D, from ref 31.

a distinct new product absorption was noted at 697 cm^{-1}, with again a feature on the low-energy side, at 693 cm^{-1}. In addition, a weak shoulder was observed at 704 cm^{-1}. The only product band observed in the methanol parent band spectral region was at 1021 cm^{-1}, near a parent methanol absorption at 1036 cm^{-1}. As the ClF concentration was increased, the product absorptions near 697 and 1021 cm^{-1} grew and became more distinct relative to the parent absorptions.

Table I summarizes product band positions for all of the above systems.

Dicussion

Product Identification. The codeposition of ClF with a number of oxygen-containing bases into argon matrices gave rise to new infrared spectral features, which could not be assigned to either parent species. Rather, these new absorptions can be assigned to a reaction product, for which a variety of possibilities can be envisioned. Since ClF is a highly reactive molecule, the possibility of rearrangement or elimination reactions must be considered. However, the spectra obtained with this wide range of bases were consistent, in that product absorptions invariably occurred near absorptions of one of the parent species. Moreover, for all of the bases, a new absorption near 700 cm^{-1} was noted, to the red of the parent ClF absorption. These results collectively suggest that the acid (ClF) and base reactants have maintained their structural integrity during the deposition process and product formation, but are perturbed in the resultant product. This result is indicative of complex formation rather than rearrangement and is in keeping with results of a range of previous matrix-isolation studies.[17-20]

Molecular complexes of different stoichiometries might be formed during the deposition process, the most likely of which is a 1/1 complex, in view of the low concentrations employed throughout (up to M/R = 1000 in may cases). However, it should be noted that in a few experiments, notably those employing acetone and ClF, a second product was noted in the carbonyl stretching region whose intensity decreased more rapidly with decreasing ClF concentration than did the first product absorption. This concentration dependence suggests a higher order dependence on ClF and probably a 2/1 complex involving two ClF molecules and one acetone. Nonetheless, the primary absorptions observed in each experiment are assigned to the 1/1 molecular complex of ClF and the base in question.

Band Assignments. The spectra of the molecular complexes of ClF with the Lewis bases under consideration were all characterized by a sharp doublet absorption near 700 cm^{-1}. While the exact position of this double varied somewhat with base, as will be discussed below, it is some 50–100 cm^{-1} to low energy of the ClF monomer stretching mode. The doublet structure, with a 3/1 intensity ratio, is identical with that anticipated for the isotopic ^{35}Cl–^{37}Cl splitting of a single chlorine atom species and is nearly identical with the structure observed for monomeric ClF. The magnitude of the splitting, roughly 6 cm^{-1}, is also that anticipated for a nearly harmonic ClF oscillator. Moreover, this product band in the $(CH_3)_2O{\cdot}ClF$ complex did not shift appreciably when $(CD_3)_2O$ was employed, which demonstrates that this absorption arises from the acid subunit in the complex. Consequently, the product absorption in each system near 700 cm^{-1} is assigned to the stretching mode of the ClF subunit in the 1/1 molecular complex. In a few of the systems, the ^{37}Cl isotopic peak at lower energies was not clearly resolved, but a shoulder was sufficiently apparent as to suggest a single chlorine atom species.

For each of the bases under consideration, at least one product band was observed in the region near a vibrational mode of the parent, as listed in Table I. For example, when $(CH_3)_2O$ was employed, product absorptions were observed at 904, 1078 and 1161 cm^{-1}, shifted from parent modes at 926, 1098, and 1167 cm^{-1}. These three parent modes have been assigned to the symmetric C–O–C stretch, the antisymmetric C–O–C stretch, and the CH_3 rocking vibration.[17] Assignment to the same modes of the perturbed base subunit in the complex is straightforward. When diethyl ether was codeposited with ClF, two base modes were observed, at 840 and 1088 cm^{-1}. The former lies near the symmetric C–O–C stretching mode of the parent at 850 cm^{-1}, while the latter occurs near several parent bands around 1100 cm^{-1}. On the basis of intensities, the nature of the different vibrations, and the direction of shift, this mode is most likely assigned to the antisymmetric C–O–C stretching mode, which occurs[17] for the parent at 1131 cm^{-1}. The greater shift for this mode in the diethyl ether complex relative to that in the dimethyl ether complex relfects the greater basicity of diethyl ether. For the remaining bases, comparison to the literature spectrum of the parent base makes band assignment straightforward. For the acetone complex, the product absorption near 1700 cm^{-1} is readily assigned to the carbonyl stretching mode, while the 556-cm^{-1} product band is assigned to the C—C=O bending mode.[18] For the methanol complex, a single product band was observed at 1021 cm^{-1} and is assigned to the carbon–oxygen stretch, some 17 cm^{-1} to the red of the parent vibrational mode.[17] For the two ring systems studied, ethylene oxide and furan, perturbed ring deformation modes[15] were observed, at 867 cm^{-1} and at 551 and 960 cm^{-1}, respectively. Finally, for the $ClF{\cdot}OCH_2$ complex, product absorptions were noted at 1710 and 1488 cm^{-1}, in each case slightly to lower energy of the parent modes that have been assigned[19] to the carbonyl stretch and to the in-plane CH_2 bending mode. The magnitude and direction of these shifts are in accord with previous studies of complexes of these bases. Assignment of the product absorptions to these modes in the complex is consequently made.

One might anticipate a considerably larger number of product absorptions than the two to four that were observed for these complexes. However, previous studies[17-21] have shown that many of the vibrational modes of the base subunit are quite insensitive to complexation and do not shift appreciably from the position of the free base. These modes are obscured by the intense parent absorptions, and only those vibrations that are particularly sensitive to coordination (see below) are detected. One might also anticipate the formation of new vibrational modes, involving motion of the acid subunit relative to the base subunit and arising from the loss of rotational and translational degrees of freedom. However, the relatively weak interaction coupled with the relatively high masses put these new modes at very low frequency; very likely, they lie below 200 cm^{-1}.

Structure and Bonding Trends. While no definite conclusions can be reached about the detailed structure of the molecular complex, intuitively the ClF should interat with the oxygen atom of the base, by analogy to the theoretical calculations on ClF–amine complexes. The vibrational modes of the base subunit that were perturbed in the product complex were almost always those modes involving oxygen atom motion (i.e. the C–O–C symmetric and antisymmetric stretching modes of dimethyl ether and the C=O stretching modes of acetone and formaldehyde). This suggests that coordination is at the oxygen atom, which is con-

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(20) Ault, B. S. *Inorg. Chem.* **1981**, *20*, 2817.

(21) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; 3rd ed.; Wiley-Interscience: New York, 1978; and references therein.

sistent with the structure of the complexes of these bases with Bronsted acids. For example, the HCl–furan complex has been shown to involve hydrogen bond formation from HCl to the oxygen atom in the furan ring.[22] For the $ClF{\cdot}CH_3OH$ complex, a hydrogen-bonded complex might well be envisioned also. However, the key spectroscopic feature of such a complex would be a substantial red shift and intensification of the O–H stretching mode, as is characteristic of hydrogen-bonded species.[23] Such a spectral feature was not observed; rather, the only perturbed methanol vibration detected was the C–O stretch, supporting coordination at the oxygen atom. For the acetone complex, interaction of the fluoride portion of ClF with the carbonyl carbon must be considered, by analogy to the well-known catalytic attack of F^- at this site in solution. This type of interaction should lead to observable perturbation of the C–O stretch (as was observed) *and* the two C–C stretching modes. This was not observed, which lends support to interaction at the oxygen atom. This is probably due to the less polar nature of F in ClF relative to F^-. Further, the complex of HF with acetone has been shown[24] to involve hydrogenbond formation to the oxygen, rather than fluoride attack at the carbon (and HF is substantially more polar than ClF). The orientation of the ClF molecule cannot be directly determined, but the best dipole moment determinations all suggest a partial positive charge on the chlorine,[25,26] which would argue that the chlorine is oriented toward the oxygen atom. This result is in agreement with recent theoretical calculations on ClF complexes.[11-13]

The shift of the ClF stretching mode to lower energies is typical of halogen complexes; the halogens are σ^* acceptors, and acceptance of electron density from the Lewis base into the empty σ^* orbitals weakens the bond in the halogen diatomic.[1] This, in turn, leads to a lowering of the force constant and vibrational frequency of the complexed molecular halogen. The position of the ClF stretching mode in each of the complexes represents the degree of electron transfer to ClF from the particular base. Earlier studies of hydrogen-bonded complexes have correlated shifts with proton affinity and dipole moment of the bases. Table I presents a series of such comparisons, from which it can be seen that proton affinity qualitatively predicts the observed trends in $\Delta\nu_{\mathrm{ClF}}$. The dipole moment of the base fares rather poorly in such a comparison, probably because the dipole moment reflects the electronic distribution over the entire molecule, while the proton affinity reflects more directly the electronic distribution in the region of the oxygen atom, where interaction occurs. The proton affinity correlation is not perfectly monotonic, but does provide a relatively good measure of the strength of interaction of a reference acid, ClF in this case, with a series of Lewis bases.

The 1/1 complexes of oxygen-containing bases with both Lewis and Brønsted acids have been studied over the years; comparison of the spectral features of these complexes with the ClF complexes observed here help to provide information about the Lewis acidity of ClF (as opposed to its reactivity). The symmetric C–O–C stretching mode of dimethyl ether has emerged as a particular useful vibrational mode in this regard; this mode was observed at 917 cm^{-1} in the 1/1 complex with SiF_4,[17] at 892 cm^{-1} with GeF_4[18] and at 884 cm^{-1} with BBr_3.[27] The observation of this mode at 904 cm^{-1} in the present ClF study indicates that the Lewis acidity of ClF roughly falls between that of GeF_4 and that of SiF_4, a conclusion which is substantiated by comparison of the spectra of acetone complexes of these acids.[18,28] While this cannot provide a quantitative measure, such as fluoride ion affinity does, it does provide some indication of strength of ClF as a Lewis acid, information which has not previously been available. Larson and McMahon have recently discussed gas-phase Lewis acidities thoroughly, and the results obtained here should be put in the context of that work also.[29]

Acknowledgment. The authors gratefully acknowledge support of this research by the National Science Foundation through Grant CHE 84-00450. B.S.A. also thanks the Dreyfus Foundation for a Teacher-Scholar grant.

(22) Legon, A. C. *J. Chem. Phys.* **1983**, *78*, 3545.
(23) Pimentel, G. C.; McClellan, A. L. "The Hydrogen Bond"; W. H. Freeman: San Francisco, CA, 1960.
(24) Johnson, G. L.; Andrews, L. *J. Phys. Chem.* **1984**, *88*, 5887.
(25) Gilbert, D. A.; Roberts, A.; Griswold, P. A. *Phys. Rev.* **1949**, *76*, 1723.
(26) Janda, K. C.; Klemperer, W. *J. Chem. Phys.* **1983**, *78*, 3509.
(27) Hunt, R. L.; Ault, B. S. *Spectrosc.: Int. J.* **1982**, *1*, 45.
(28) Ault, B. S.; Lorenz, T., unpublished data.
(29) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766.
(30) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.
(31) R. Weast, Ed. "Handbook of Chemistry and Physics", 62nd ed.; Chemical Rubber Co.: Boca Raton, FL, 1982; pp E-60, E-72.

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Molten Lithium Sulfate–Sodium Sulfate–Potassium Sulfate Eutectic: Lux–Flood Acid–Base Reactions of Transition-Metal Sulfates and Oxides

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Received August 14, 1984

The solubility and reactivity of seven first-row transition-metal sulfates in the ternary eutectic (78 mol % Li_2SO_4, 8.5 mol % Na_2SO_4, 13.5 mol % K_2SO_4) and in the ternary eutectic containing sodium carbonate have been studied and the transition-metal oxide products identified. The reactions of six, more acidic, transition-metal oxides with pure melt and with added sodium carbonate were studied and stoichiometries established. Additions of potassium pyrosulfate dissolved all the oxides, in some cases with reduction (to Mn(II) and Co(II)), and the thermal stabilities of the resulting solutions were determined.

Introduction

Molten sulfates are of considerable economic importance because they form the reactive films causing the corrosion of high-temperature boilers and heat exchangers. Thus a systematic chemistry of transition metals in such solutions has a considerable practical relevance, as it also has to the catalysts promoting the oxidation of sulfur dioxide by air in the manufacture of sulfuric acid, which primarily consist of vanadium solutions but also contain transition metals as "promotors". However until now little work has been published on acidic–basic reactions of transition metals, and a more systematic study seemed overdue.

The earlier references to acid–base reactions in molten alkali-metal sulfates (using the Lux–Flood definition of acids as oxide acceptors) began with the work of Lux himself, who reported the reactions of titanium(IV) oxide as an acid in sodium sulfate at 950 °C when a series of titanates was formed.[1] More recently

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0020-1669/85/1324-4254$01.50/0