basic solvents which would further diminish the water–cation interaction. We can conclude, therefore, that traces of water which may be present in the basic solvents studied in this investigation, would have only a negligible effect on the measured chemical shifts.

It is also interesting to note that except for ammonia, there seems to be a good correlation between the donor number of the solvents and their basicity constants in aqueous solutions. Such correlation has been proposed by Bloor and Kidd[19] from their ^{23}Na magnetic resonance measurements on sodium iodide solutions. However, in that case, the possible correlation was somewhat obscured by the influence of the contact ion pairing on the chemical shifts.

Acknowledgment. The authors gratefully acknowledge the support of this work by a grant from the National Science Foundation. One of us (M. H.) is indebted to the Centre National de la Recherche Scientifique (Paris) and to NATO for a fellowship and to Mr. R. H. Erlich for help with the instrumentation.

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[19] E. G. Bloor and R. G. Kidd, *Can. J. Chem.*, 46, 3425 (1968).

Metal Surface Base Function. Adsorption of Boron Trifluoride and Boron Trichloride

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Abstract: In a continuing effort to characterize metal surfaces by their interaction with different classes of molecules, the base function of metal surfaces is examined *via* adsorption of BF_3 and BCl_3. Using infrared spectroscopy, the following information has been obtained about the adsorption of the pure Lewis acids BF_3 and BCl_3. BF_3 chemisorbs without dissociation on vanadium, iron, nickel, copper, and palladium films. No chemisorption on aluminum films is detected. The BF_3–metal surface complexes are quite stable with respect to air. CO replaces adsorbed BF_3 on nickel and palladium. It replaces BF_3 on iron to a much smaller extent. BF_3 chemisorbed on vanadium and copper is not replaced by CO. Chemisorbed BF_3 is electron withdrawing compared to chemisorbed CO. BCl_3 adsorbs on Fe and Ni without dissociation. Basicity of the metal surface is demonstrated to be a useful concept by showing that the displacement of BF_3 by CO correlates with the expected basicity of the surface as measured by valence-state ionization potentials.

One area of surface chemistry which is insufficiently explored with modern techniques is the chemical characterization of metal surfaces by their interaction with different classes of molecules that have evolved from studies of coordination complexes. If one takes the point of view that a metal atom in a surface can be regarded as a metal atom in a coordination complex, one becomes immediately aware of several possibilities. While metal cations are customarily regarded as acids, metal basicity has received some attention.[1] Metal basicity has recently been demonstrated through the discovery of compounds in which the metal serves as a donor toward molecular Lewis acids such as BF_3, BH_3, H^+, O_2, SO_2, and tetracyanoethylene. Since basicity of metal cations has been found to be promoted by low oxidation states, zerovalent metal atoms in a surface should be prime candidates for base functioning. Certainly a clear understanding of electron-donor properties of metal surfaces is necessary to understanding the electron-transfer processes accompanying catalytic reactions on metal surfaces.

Discussion of the nature of the chemisorption bond to metals and most discussions of coordination complexes have concentrated on adsorbates or ligands that are electron donors, *i.e.*, Lewis bases, or are σ donors and π acceptors. While a metal surface should be able to function as a pure Lewis base, there appear to have been no studies of the interaction of molecules that can serve only as Lewis acids with metal surfaces. The questions arise as to whether this type of molecule will even chemisorb and if so whether it will do so only with dissociation, and as to its relative strength of adsorption compared to such widely studied adsorbates as CO.

To be useful as surface ligands in infrared studies, molecules should adsorb without dissociation. If dissociation occurs, the surface becomes covered with fragments of varying structures, and interpretation becomes extremely difficult. There do not appear to be many chemical compounds which meet this condition. Carbon monoxide is one of the few molecules which adsorb and desorb without appreciable dissociation and, consequently, its interactions with metal surfaces have been widely studied.[2,3]

Molecular Lewis acids have vacant orbitals which can accept electrons but have no electrons available for donation. One of the most important of these is boron trifluoride, which forms adducts by accepting a share in an electron pair from a donor molecule. Corrosion experiments have shown that there is no appreciable attack by boron trifluoride on any of the metals or alloys examined at temperatures up to

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[1] D. F. Shriver, *Accounts Chem. Res.*, 3, 231 (1970).

[2] L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966.

[3] M. L. Hair, "Infrared Spectroscopy in Surface Chemistry," Marcel Dekker, New York, N. Y., 1967.

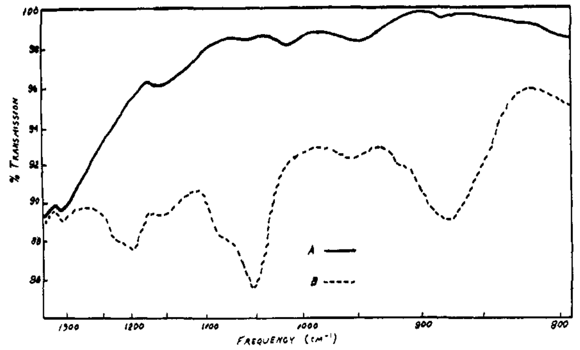


Figure 1. Boron trifluoride on vanadium: (A) background, (B) chemisorbed BF_3.

200°.[4] The technique used was not sensitive enough, however, to rule out the possibility of the formation of an adsorbed monolayer on the surface of the sample, and a later experiment indicated that such a layer is indeed formed on a reduced copper surface.[4]

Experimental Section

The wide spectral range experimental technique, which has been described in detail elsewhere,[5] consists of evaporating metals from an electrically heated tungsten filament in the presence of a small pressure of helium. The metal particles formed in the gas phase deposit in a hydrocarbon oil film on the salt windows of an infrared cell. The gas to be studied is then admitted to the cell, and the spectrum of the chemisorbed species is obtained. Spectra are recorded before and after admission of the gas to the cell. Five minutes of pumping has been found sufficient to remove all spectra due to gas-phase molecules. For three- and four-carbon-atom molecules, 30 min of pumping may be required to remove molecules dissolved in the oil film. Care was exercised to make sure that all bands which are reported to be due to chemisorbed species are indeed due to such species and not merely to gases trapped in the oil layer. All bands due to chemisorb species reported in this study were still present after the cell had been evacuated at 10^{-6} Torr for 16 hr or longer.

The spectra were obtained using Perkin-Elmer Models 21, 337, and 457 spectrometers, of which the latter two are grating instruments. The Model 21 is equipped with NaCl optics and an ordinate scale expander.

The iron, nickel, palladium, tungsten, and copper were obtained in the form of high-purity wire from A. D. McKay, Inc. The vanadium was obtained as 5-mil foil, 99.8% pure, from United Mineral and Chemical Corp. The BF_3, BCl_3, and CO were obtained as reagent grade chemicals from Matheson Scientific, Inc. The CO was purified by passage through a charcoal trap immersed in liquid air. The BF_3 and BCl_3 were used directly as supplied.

This technique has the advantage that a wide infrared spectral region is available for study. It has the disadvantage that the metal surface is covered with oil. This oil is apparently only weakly adsorbed, since many gases have been found to chemisorb readily on the metal. Essentially the oil is regarded as a solvent which has weak interactions with the systems of interest. Having a wide spectral range available aids greatly in attempts to determine structure.

Results

BF_3 chemisorbs without dissociation on vanadium, iron, nickel, copper, and palladium films. No chemisorption of BF_3 on aluminum films was detected.

Evaporated vanadium films were exposed to BF_3 at a pressure of 30 Torr for 30 min. A typical spectrum is shown in Figure 1. Table I lists the band assignments. An evaporated vanadium film containing preadsorbed BF_3 was exposed to CO at a pressure of 30 Torr for 20 min. A band due to chemisorbed CO appeared but no other changes in the spectrum were noted. Exposure of a second film containing preadsorbed BF_3 to air at a pressure of 50 Torr for 30 min had no effect on the spectrum.

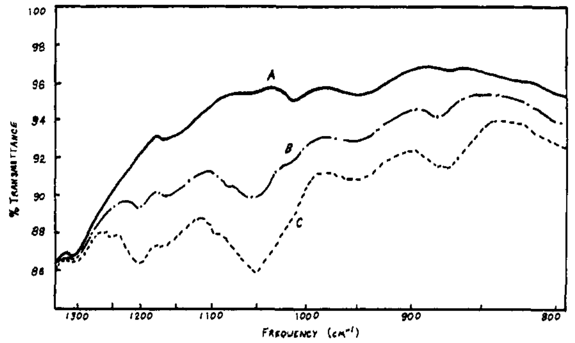


Figure 2. Boron trifluoride and CO on iron: (A) background, (B) CO added after BF_3, (C) chemisorbed BF_3.

Table I. Frequencies (cm^{-1}), Intensities, and Band Assignments for Boron Trifluoride on Vanadium, Iron, Nickel, and Palladium at 25°

BF_3 on vanadium	BF_3 on iron	BF_3 on nickel	BF_3 on palladium	Assignment
1220 (sh)	1250 (sh)	1235 (sh)	1190 (sh)	^{10}B–F stretch (asym)
1200 (s)	1205 (m)	1200 (m)	1120 (s)	^{11}B–F stretch (asym)
1091 (sh)	1095 (sh)	1070 (sh)		^{10}B–F stretch (sym)
1055 (s)	1060 (s)	1040 (s)	1050 (w)	^{11}B–F stretch (sym)
915 (w)	895 (w)	910 (w)	840 (sh)	^{10}B–F bend
895	880 (m)	890 (m)	825 (s)	^{11}B–F bend
2010 (m)	1980 (s)	2070 (s) 1930 (s)	2070 (s) 1940 (s)	Added CO

Evaporated iron films were exposed to BF_3 at a pressure of 30 Torr for 1 hr and spectra were taken. One of these films was then exposed to CO at a pressure of 30 Torr for 15 min, with the result that part of the BF_3 was displaced. Results are shown in Figure 2 and Table I. Exposure of an iron film containing preadsorbed BF_3 to air at a pressure of 100 Torr for 30 min had no effect on the spectra.

Evaporated nickel films were exposed to BF_3 at a pressure of 30 Torr for 1 hr. The spectra were similar to those of BF_3 on vanadium and iron. Bands are listed in Table I. Exposure of a nickel film containing preadsorbed BF_3 to CO at a pressure of 30 Torr for 20 min resulted in the replacement of most of the BF_3 by CO. Exposure of such a film to air at a pressure of 50 Torr for 20 min had almost no effect on the spectrum.

Evaporated palladium films were exposed to BF_3 at a pressure of 30 Torr for 30 min. Subsequently, one film was exposed to air at a pressure of 80 Torr for 30 min. Spectra taken before and after exposure to air showing the frequency shifts caused by air are shown in Figure 3. Table I shows the band assignments. When a palladium film containing preadsorbed BF_3 was exposed to CO at a pressure of 30 Torr for 15 min, most of the BF_3 was replaced.

Figure 4 shows a spectrum taken after exposure of a copper film to BF_3 at a pressure of 20 Torr for 20 min.

(4) F. Hudswell, J. Nairn, and K. Wilkinson, *J. Appl. Chem.*, **1**, 333 (1951).

(5) G. Blyholder, *J. Chem. Phys.*, **36**, 2036 (1962).

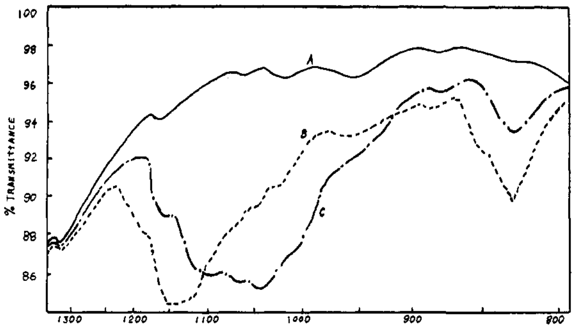


Figure 3. Boron trifluoride and air on palladium: (A) background, (B) chemisorbed BF_3, (C) air added.

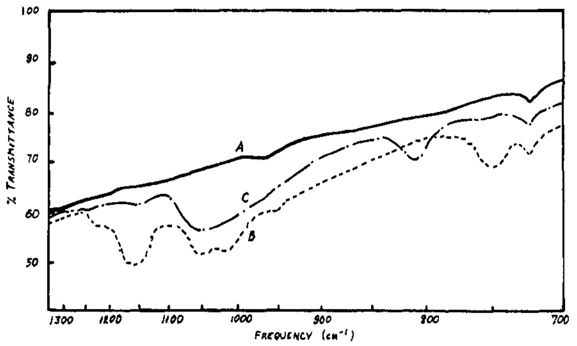


Figure 4. BF_3 and trimethylamine on copper: (A) background, (B) chemisorbed BF_3, (C) chemisorbed trimethylamine and BF_3.

Subsequent exposure to CO at a pressure of 30 Torr for 25 min did not change the spectrum. Band assignments are in Table II. Exposure of a BF_3-containing copper film to trimethylamine at a pressure of 30 Torr for 4 hr produced the bands shown in Figure 4 and Table II, indicating that the trimethylamine largely displaced the chemisorbed BF_3.

Table II. Frequencies (cm^{-1}), Intensities, and Band Assignments for Boron Trifluoride and Trimethylamine on Copper at 25°

BF_3 on copper	BF_3 and TMA on copper	Assignment
1215 (m)	1150 (w)	^{10}B–F stretch (asym)
1170 (s)		^{11}B–F stretch (asym)
1060 (s)		^{10}B–F stretch (sym)
1020 (s)		^{11}B–F stretch (sym)
	1050 (s, b)	B–F stretch or C–N stretch
760 (sh)		^{10}B–F bend
740 (s)		^{11}B–F bend
	1240 (w)	CH_3 rock
	815 (s)	C–N stretch

The chemisorption of boron trichloride was investigated only on iron and nickel. Evaporated iron films were exposed to BCl_3 at a pressure of 50 Torr for 1 hr and the cells were evacuated for 1 hr. Figure 5 shows a representative spectrum taken using a 5× scale expansion. The band assignments shown in Table III indicate that the BCl_3 observed is not dissociated.

Spectra taken after exposure of nickel films to BCl_3 at a pressure of 50 Torr for 3 hr and evacuation for 2 hr were similar to those of BCl_3 on iron. A typical spectrum is shown in Figure 5. Table III lists the band assignments. A nickel film containing preadsorbed BCl_3 was exposed to CO at a pressure of 30 Torr for 30 min. The spectrum was changed very little.

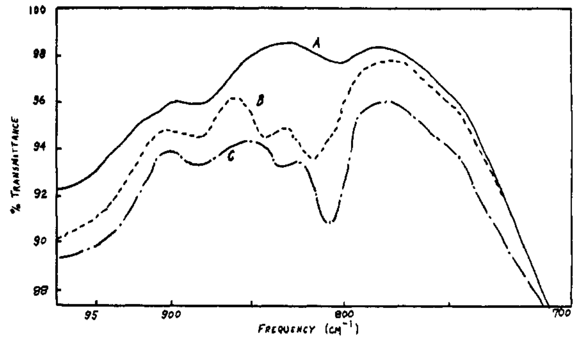


Figure 5. BCl_3 on iron and nickel: (A) background, (B) BCl_3 on iron, (C) BCl_3 on nickel.

Table III. Frequencies (cm^{-1}), Intensities, and Band Assignments for Boron Trichloride Chemisorbed on Iron and Nickel at 25°

BCl_3 on iron	BCl_3 on nickel	BCl_3 gas[a]	Assignment
840 (w)	830 (w)	995 (vs)	^{10}B–Cl stretch (asym)
815 (m)	810 (m)	955 (vs)	^{11}B–Cl stretch (sym)

[a] R. Scruby, J. Lacher, and J. Park, *J. Chem. Phys.*, **19**, 386 (1951).

Discussion

Boron trifluoride chemisorbed strongly on vanadium, iron, nickel, palladium, and copper films. Evacuation at 10^{-6} Torr for 18 hr did not remove the BF_3 bands from these surfaces. No chemisorption was detected on aluminum films. Apparently the electrons in metallic aluminum are too tightly held for it to exhibit base character.

From the appearance of the chemisorbed spectra (Figures 1 and 2) and the band intensities and frequencies (Tables I and II), it was concluded that BF_3 chemisorbed without appreciable dissociation. Naturally occurring BF_3 is a 4:1 mixture of the $^{11}BF_3$ and the $^{10}BF_3$ isotopes. A spectrum of gaseous BF_3 shows doubling of each frequency because of this.[6] In the chemisorbed spectra, this doubling was exhibited, usually in the form of a moderately intense band due to the ^{11}B isotope, with a shoulder at a higher frequency, due to the ^{10}B isotope.

It was expected from simple valence theory that when the planar BF_3 molecule chemisorbed on a metal surface it would be distorted, reducing the size of the F–B–F angles. It was also expected that the B–F symmetric stretching vibration, which is ir inactive in the gas spectrum, would become ir active in the chemisorbed spectra as a consequence of this distortion. Such behavior has been observed in a number of BF_3 charge-transfer complexes.[7–13]

(6) J. Vanderryn, *J. Chem. Phys.*, **30**, 331 (1959).
(7) A. Katritzky, *J. Chem. Soc.*, 2049 (1959).
(8) R. Amster and R. Taylor, *Spectrochim. Acta*, **20**, 1487 (1964).
(9) J. Gobeau and H. Mitschelen, *Z. Phys. Chem. (Frankfurt am Main)*, **14**, 61 (1958).
(10) W. Paterson and M. Onyszchuk, *Can. J. Chem.*, **39**, 986 (1961).
(11) M. Beg and H. Clark, *ibid.*, **38**, 119 (1960).

These anticipated features were observed in the spectra of BF_3 chemisorbed on metal films. A second doubled frequency appeared in the B–F stretching region, and the asymmetric and symmetric stretching frequencies were much closer together than in the gas spectrum, indicating that the F–B–F angle decreased[14] upon adsorption. Table IV compares the frequencies for chemisorbed BF_3 and the corresponding frequencies reported for several BF_3 charge-transfer complexes.

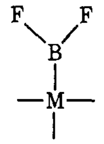
Table IV. Comparison of Infrared Frequencies (cm^{-1}) for Boron Trifluoride Chemisorbed on Metal Films and for Boron Trifluoride Complexes

Complex	B–F stretch (asym)	B–F stretch (sym)	B–F bend
BF_3 gas[a]	1454–1505	(888)[i]	691–718
TMA–BF_3[b]	1135–1150	911–933	
Pyridine·BF_3[b]	1125–1165	893–952	
TMA·BF_3[c]	1142–1165	932–952	547–550
$NH_3 \cdot BF_3$[d]	1144–1210	982–1028	735
$N_2H_2 \cdot BF_3$[e]	1035–1200		725–775
TMP·BF_3[f]	1175–1200		
$[IrClCO(P(C_6H_5)_3)_2] \cdot BF_3$[g]	1138	931–960	
$(C_6H_5)_3P \cdot BF_3$[g]	1000–1150	888–915	
MA·BF_3[h]	1165–1190	956	
$C_5H_5N \cdot BF_3$	1107–1171	902–932	
BF_3 chemisorbed on metal films (Tables I and II)	1120–1250	1020–1095	740–915

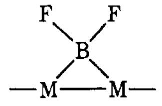
[a] Reference 6. [b] Reference 7. [c] Reference 8. [d] Reference 9. [e] Reference 10. [f] Reference 11. [g] Reference 12. [h] Reference 13. [i] Inactive in infrared, active in Raman.

The stability of the BF_3–metal surface complexes is striking. Most of them are stable in the presence of air and CO. Air at pressures up to 100 Torr had no effect on BF_3 adsorbed on iron, nickel, and vanadium and did not completely remove BF_3 from palladium surfaces (Figure 3). The oxide bands usually produced when air is added to nickel films[15] did not appear. CO had no effect on spectra of BF_3 chemisorbed on copper. Similarly, there was no change in bands due to BF_3 chemisorbed on vanadium, although chemisorption of CO took place, as evidenced by a new band appearing at 2010 cm^{-1}. On nickel and palladium most of the BF_3 was displaced by CO. When a nickel film was exposed to a 1 : 1 mixture of BF_3 and CO at a total pressure of 60 Torr, chemisorbed bands due to both BF_3 and CO appeared in the spectrum.

The possibility of some other structure, particularly BF_2-containing structures, being on the surface was considered. Our general experience with this technique suggests that surface coverages of less than about 5% for a particular species may lead to its infrared band intensities being too low to be observed. Therefore, our discussion is of the major surface species and the presence of small amounts of other species cannot be excluded. A structure of the type



would be expected to have approximately planar-trigonal symmetry about the boron atom. Comparison of spectra might be made here to BF_3 itself or to CH_3BF_2 which has bands[16] at 1400, 1780, 620, and 470 cm^{-1} which are attributed to B–F bonds. This is not too different from the BF_3 spectrum. Our surface species do not show a band around 1400, and while the oil bands in this region might interfere some, they are only of medium intensity, and the presence of gaseous BF_3 clearly distorts the oil band shapes so that the presence of another band in this region is not readily missed. In the case of V, a spectrum was run out to 450 cm^{-1} without any low-frequency bending vibration being detected. Therefore, a three-coordinate boron structure containing two fluorine atoms seems unlikely to us. A four-coordinate boron structure of the type



has also been considered. Here comparison may be made to CHF_3, which has bands[17] at 1209, 1152, 699, and 509, and CH_2F_2, which has bands[18] at 1116, 1090 and 528 cm^{-1}, which are attributed to the presence of fluorine. The bands for CHF_3 are quite similar to those for tetrahedrally structured BF_3 in coordination complexes, so the comparison of boron and carbon compounds is reasonable. The two fluorine atom containing compound CH_2F_2 is noted to lack any bands in the 700-cm^{-1} region where the three fluorine atom compounds all contain bands. While far from conclusive, this at least suggests that our surface species is more likely to contain BF_3 than BF_2. Another nonconclusive but supportive fact is that CO coadsorbs with the surface species from BF_3. A BF_2 structure requires dissociation of a fluorine atom to form most probably a metal–fluorine bond. Adsorption of oxygen on our metal surfaces prevents CO adsorption. A similar effect may be expected for fluorine adsorption. All of the above taken together with the agreement of the spectra of the surface species with that for BF_3 complexes lead us to conclude that the major surface species is an undissociated BF_3 group.

The CO bands themselves were shifted to somewhat higher frequencies (about 10 wave numbers) in the presence of chemisorbed BF_3, indicating an electron-withdrawing species. A shift in this direction also occurs in the BF_3-substituted carbonyl, $[IrClCO(P(C_6H_5)_3)_2] \cdot BF_3$.[12]

In one experiment a copper film with preadsorbed BF_3 was exposed to trimethylamine, which replaced much of the BF_3 (Figure 4). Since trimethylamine is not too strongly adsorbed on copper films, dissociation occurring upon long exposure, the BF_3 is apparently not strongly adsorbed on copper.

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(12) R. Scott, D. Shriver, and L. Vaska, *J. Amer. Chem. Soc.*, **90**, 1079 (1968).

(13) M. Taillandier and E. Taillandier, *Spectrochim. Acta, Part A*, **25**, 1807 (1969).

(14) N. Colthup, L. Daly, and S. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 182.

(15) G. Blyholder, *Proc. Int. Congr. Catal.*, 3, 657 (1964).

(16) Von W. Schabacher and J. Goubeau, *Z. Anorg. Allg. Chem.*, **294**, 187 (1958).

(17) H. D. Rix, *J. Chem. Phys.*, **21**, 1077 (1953).

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The spectra of BCl_3 chemisorbed on iron and nickel show two B–Cl stretching bands in the 810–840-cm^{-1} region, the weaker band due to the ^{10}B isotope, the stronger to the ^{11}B isotope (Figure 5 and Table III). The frequencies are in accord with those reported by Katritzky[7] for a number of substituted pyridine–BCl_3 complexes. In the seven complexes he studied, the B–Cl stretching frequencies appeared between 818 and 843 cm^{-1}.

Johnson and Shriver[19] have reported infrared data for one of the few metal–BCl_3 adducts yet prepared, $(C_5H_5)_2WH_2 \cdot BCl_3$. They assigned the B–Cl asymmetric stretch to a band at 755 cm^{-1}, although several bands were found in the 800–850-cm^{-1} region.

Unlike BF_3 chemisorbed on nickel, BCl_3 chemisorbed on nickel was not replaced by carbon monoxide. In fact, exposure of a nickel film containing preadsorbed BCl_3 to CO resulted in an increase in the intensity of the B–Cl stretching bands. This change in intensity is probably related to a change in the dipole moment of adsorbed BCl_3 molecules caused by the chemisorption of CO. The CO bands were very weak, indicating that not much CO was adsorbed.

These results with BF_3 and BCl_3 indicate that transition metal surfaces do indeed exhibit basic properties in appropriate circumstances. The molecules BF_3 and BCl_3 have been shown to adsorb without dissociation on V, Fe, Ni, Pd, and Cu. However, these results do not require that all adsorbed BF_3 and BCl_3 be undissociated but do indicate that those species whose infrared spectra are sufficiently intense to be observed in the spectral region covered are undissociated.

The variation in displacement of BF_3 by CO on the metal surfaces may be correlated with the expected basicities of the different metals. Basic character is expected to increase with an increase in the ease of donating electrons, which will increase as valence-state ionization potentials decrease. From the data in Table V it is seen that the valence-state ionization potentials decrease as one goes from Cu to V across the first-row transition metals. Since BF_3 adsorbs with the metal acting purely as a base, the strength of BF_3 adsorption is expected to directly vary with metal base strength. Thus on V, the strongest base, BF_3 is not displaced by CO, while on Ni, a weaker base, BF_3 is replaced by CO and Fe occupies an intermediate position both with respect to basicity and BF_3 replacement by CO. Not only then has the basicity of transition metal surfaces been shown, but also it is demonstrated that basicity is a useful concept in understanding the properties of adsorbed species.

Table V. Valence-State Ionization Potentials (cm^{-1}) for Removing a d Electron from a $3d^n4s^1$ State

V	51,400	Co	75,000
Cr	57,900	Ni	80,900
Mn	64,100	Cu	86,000
Fe	70,000		

Acknowledgment. This investigation was supported in part by Research Grant No. 00818 from the Air Pollution Control Office, Environmental Protection Agency.

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Photochemistry of Borazine. Evidence for a Borazyne Intermediate[1]

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Received July 21, 1971

Abstract: Photolysis of borazine with 1849-Å radiation produces H_2, borazanaphthalene, diborazinyl, and a nonvolatile polymer. The quantum yield for hydrogen formation and the rate of polymer deposition in the presence and absence of inert gases have been studied as functions of pressure. A mechanism is proposed involving internal conversion from an excited singlet state of borazine to a vibrationally excited ground state. Experimental observations indicate that a molecule $B_3N_3H_4$ (a borazyne) is a probable photochemical intermediate. The quantum yield for H_2 production at 1 mm is 0.21 ± 0.02. This value decreases with increasing borazine pressure and with the addition of inert gas (Ar, H_2, and cyclohexane). In equimolar mixtures of borazine and borazine-d_6 rapid photochemical hydrogen–deuterium exchange is observed, and at low pressure the exchange quantum yield varies linearly with pressure.

Qualitative photochemical studies of borazine have shown that borazine reacts in the gas phase with H_2O,[2] NH_3,[2] alcohols,[3,4] and methyl halides[5] to yield B-monosubstituted derivatives. The mechanism of the borazine–D_2 reaction[6] was the first quantitative

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