(4) Dioxane is at least 90 and probably over 98% nonpolar conformer, but is best viewed as a fluxional molecule with frequency of maximum conversion between conformers somewhat above 5 cm^{-1} (1.5×10^{11} Hz).

(5) The ternary system here may be used as a solvent system having variable amounts of π electron cloud character, but *not* for varying amounts of local electric field.

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Determination of Rotational Barriers in Four Thioamides[1]

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The hindered rotation barriers of four thioamides have been determined using the best techniques available. The proton magnetic resonance (nmr) spectra of *N,N*-dimethylthiocarbamyl cyanide reveals long-range intermethyl couplings ${}^4J_{\mathrm{HH}}$. The rotation barrier in terms of the free energy of activation is high in this molecule (23.5 ± 0.5 kcal/mol) and this suggests that the π electron density at the nitrogen contributes to the spin coupling. On reexamination of another amido-type molecule, *N,N*-dimethylnitrosamine, also with a high barrier (22.5 ± 0.5 kcal/mol) the hitherto unreported ${}^4J_{\mathrm{HH}}$ coupling is confirmed. It is suggested that this long-range coupling will correlate well with energy barriers in amides. The complete line shape fits were accomplished using both eight-site and two-site formulations. Because the coupling to chemical shift ratios are so small, the error in use of the two-site approximation is negligible. Reinvestigation of *N,N*-dimethylthiocarbamyl chloride gives kinetic parameters essentially in agreement with previous studies. Long-range coupling ${}^4J_{\mathrm{HH}}$ occurs in *N,N*-dimethylthiocarbamyl fluoride and assists in the assignment of the methyl peaks. The compound *N,N*-dimethylthiourea has a much lower barrier to rotation (13.9 ± 0.2 kcal/mol). The energy barriers are explained in terms of valance bond theory. In general the thio compounds have an energy barrier approximately 2 kcal/mol higher than corresponding amides. Using the present study of the thiourea, our previous study of *N,N*-dimethylselenourea, and valence bond structures, the hindered barrier in *N,N*-dimethylurea is estimated. This estimate agrees well with a value 2 kcal/mol lower than the measured thiourea barrier. The failure to detect the estimated barrier of 11 kcal/mol in the urea compound is ascribed to chemical shift degeneracy.

Introduction

There have been many studies of amides and amido-type molecules by nuclear magnetic resonance (nmr)[2-4] but because of the difficulties in properly measuring the rates of hindered rotation about the N–C bond, there exists only a small quantity of reliable data on these energy barriers. These data are not organized well enough to cover related structural series of amido-type systems, enabling separation of the contributing factors which determine the energy barriers experimentally or theoretically.[5-9] In our laboratory we have adopted the point of view that amide rotation rates provide a stringent test of the capabilities of the techniques of measurement of rate processes *via* the contributions to transverse nuclear spin relaxation and the effect on nmr line shapes.[10] In general the chemical shifts are small between *N*-methyl groups and long-range coupling,[11] which has largely been ignored hitherto, must be included in the theoretical analysis as well as many other precautions.[5-7,12] The measurement of ΔG^* is not, in general, sufficient, nor accessible, by simple coalescence temperature measurements in multisite exchange involving unknown chemical reaction mechanisms and it is to this end that the power of the nmr technique can be used to greatest effect.[13,14]

The almost complete absence of studies of a series of related amides is a serious drawback in any analysis of the

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factors which influence the hindered rotation (HR). Now, having the necessary techniques to make reliable measurements, we propose to study a carefully selected series and to attempt an analysis of contributing factors at several levels of sophistication.[15,16] In this present work the emphasis is on the determination of activation parameters for HR in related thioamides. Previous work on these compounds has not been extensive in varying the molecular structure in a regular manner.[17-22] One isolated measurement has been made on a selenourea compound.[23]

Experimental Section

It is convenient to refer to amido-type molecules by a short-hand notation. Let the molecule $(CH_3)_2NC(X)=Y$, be described by a function x in the following way: Yx(X). In this notation, for example, *N,N*-dimethylthiocarbamyl fluoride may be written Sx(F).

(i) Preparation of Compounds. (A) N,N-Dimethylthiocarbamyl fluoride was prepared by adding 18 g of powdered silver fluoride (Alfa Inorganics) in small portions over 10 min to 13.9 g of bis(dimethylthiocarbamyl) disulfide (Eastman Kodak Co.) dissolved in 100 ml of acetonitrile at 30–40°. The mixture was stirred continuously, and as the reaction is instantaneous it is important to prepare the AgF in the form of fine granules since a layer of Ag_2S on the surface of the AgF rapidly hinders the reaction. The formation of Sx(F) was completed on stirring for an additional 20 min. The basis for this preparation has been described by Goshorn, *et al.*[24] After the acetonitrile was removed using a rotary evaporator the residue was washed thoroughly with ether, the ether was also removed, and then the viscous residue was vacuum distilled. The final product boiling point was 31° at 1.5 ± 1 Torr. The Sx(F) was classified by ir and nmr spectroscopy and was found to be unstable at temperatures above 30°. It should be noted that the reaction of SbF_3 with Sx(Cl), under the conditions suggested by Schrader[25] and Metzger and Wilson[26] was particularly violent and Sx(F) could not be isolated from the reaction mixture.

The sample used for nmr kinetic study consisted of an 18.2 mol % solution of Sx(F) in tetrachloroethane (TCE) with 4.6 and 1.1 mol % of dioxane and hexamethyldisiloxane (HMDS), respectively, sealed in a medium-walled sample tube under N_2 at a pressure of about 500 Torr.

(B) N,N-Dimethylthiocarbamyl chloride was obtained from the Aldrich Chemical Co., and was purified by double recrystallization from pentane. This compound may also be prepared by a method described by Goshorn[24] for the corresponding diethylthiocarbamyl chloride. The nmr sample was a 20.4 mol % solution of Sx(Cl) in CCl_4 with dioxane and HMDS as for Sx(F) above.

(C) N,N-Dimethylthiourea was prepared by a method similar to that proposed by Bennett, *et al.*,[27] for unsymmetrical ureas. A mixture of 10 g of dimethyl cyanamide (K & K Laboratories), 20.2 ml of concentrated ammonium hydroxide, and 6.8 ml of H_2O was stirred in a round-bottom three-necked flask while H_2S was bubbled slowly through the mixture for 90 min, during which time the temperature was controlled between 20 and 30°. The temperature of the bath was then reduced to 5–10° and the solution was stirred for an additional 2 hr while a white precipitate formed. The precipitate was filtered cold and washed with ice-cold aqueous ethanol. The product was further purified by recrystallization from benzene as fine white needles. The final yield was greater than 35%.

The nmr sample was prepared and sealed under vacuum in a medium-walled tube as a 3.6 mol % solution of $Sx(NH_2)$ in TCE. At this concentration $Sx(NH_2)$ formed a near-saturated solution. 1.5 and 0.9 mol % of dioxane and HMDS, respectively, were also added to the sample.

(D) N,N-Dimethylthiocarbamyl bromide, Sx(Br), could not be isolated from a solution of Sx(Cl) in acetonitrile saturated with HBr in a manner analogous to the preparation of Ox(Br).[15] Bubbling HBr into the Sx(Cl) solution appeared to cause immediate decomposition. A second preparation was attempted by allowing 15 g of bis(dimethylthiocarbamyl) disulfide dissolved in 125 ml of acetonitrile to react with 5 ml of Br_2 in the same solvent. Although a rapid reaction took place and a yellow precipitate formed, the required product again could not be isolated.

(E) A sample of N,N-dimethylthiocarbamyl cyanide was kindly provided by Professor Jan Sandström. This was used without further purification as a 3 mol % solution in TCE containing 1.2 mol % HMDS. The nmr tube was of medium thickness and sealed under N_2 at a pressure of about 500 Torr.

(F) N,N-Dimethylthiocarbamyl azide was prepared by a method previously described for the corresponding carbamyl azide.[15] A mixture of 100 ml of acetonitrile, 11.2 g of sodium azide, and 20 g of Sx(Cl) was stirred at 40° for 28 hr and a bright yellow solid formed. The acetonitrile was taken off in a rotary evaporator and the resultant slurry was taken up in benzene at 45°, filtered, and again separated. However, a vacuum distillation (135–145°, 4–6 Torr) caused some decomposition. A sample was prepared as a 20 mol % solution in CCl_4 but further decomposition prevented a reliable kinetic study.

(ii) Methods. All studies of exchange modified ^1H nmr spectra were made using an HA-100 spectrometer and total line shape analyses as already described.[6,12,15] The computer program GPLONK was used for iterative line shape fitting of digitized experimental data. It is now well recognized that total line shape analyses give the most reliable rate constants, and hence activation parameters, from nmr studies but some additional comments are probably in order. Standard regressional techniques[5] are used to determine the "best fit" Arrhenius plot and thus error estimates of the slope and intercept based upon the data scatter are available. However, it is of some concern to know that these statistical errors are representative of the real errors in derived activation parameters. If rate constants arbitrarily close to the true values, as determined by a minimum line shape fit deviation, are available it is not necessary to weight the ordinate Arrhenius plot points. Similarly, if temperature control is adequate, abscissa error bounds may be neglected. Now by varying the position of specific points in an Arrhenius

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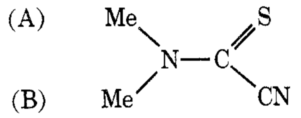
plot the sensitivity of the final activation parameters to possible errors may be considered, as outlined recently by Becker, *et al.*[28] Systematic errors in temperature tend to cause a translation of the line accompanied by a small rotation, while errors caused by incorrect chemical shifts and line widths in the absence of exchange or field inhomogeneity line shape distortions are reflected as a rotation of the plot about a point slightly above that corresponding to the coalescence temperature. It appears that fluctuations in temperature up to 1° are almost insignificant so far as the free energy of activation ΔG^* is concerned (over a large temperature range) but may be an order of magnitude more significant for the entropy of activation ΔS^*. An ideal situation with temperature-independent chemical shifts and equivalent line widths in the absence of exchange, measurable from a nonexchanging symmetrical resonance line with a natural line width of 0.3 Hz or less, permits an estimate of ΔG^* to within 0.1 kcal/mol; but ΔS^* is still an order of magnitude more sensitive to systematic errors. Therefore, in general, the regressional error quoted for ΔG^* is representative of the true error while such an error is less significant for ΔS^*. This has also been illustrated by a survey of all available data for the hindered rotation in *N,N*-dimethylcarbamyl chloride.[15]

Since the entropy of activation is very sensitive to experimental errors this parameter may be used as a check for internal reliability. That is, if the upper and lower bounds for ΔS^* can be independently obtained for a specific type of kinetic (exchange) process, and the interval so defined is sufficiently small, these bounds may be directly compared with those derived from an Arrhenius plot. In this manner, once the reliability of the overall experimental method has been established, other exchange systems which are not expected to have ΔS^* values within the prescribed interval may be studied with some confidence. The activation energy for HR in simple amides and thioamides is largely determined by changes in the bonding forces while the entropy of activation reflects changes in the freedom of atomic motion.[29] Also, as only about 12 normal vibrational modes are involved and the major structural change on entering the transition state is the lengthening of the N-C bond which is compensated for by a shortening of the C=S bond, the internal rotation to first order is a simple statistical function. Since the amides can rotate about the N-C bond in two distinct directions it may be assumed that the upper bond for ΔS^* is $R \ln 2 \simeq 1.4$ cal deg^{-1} mol^{-1} with a lower bound of zero. This relatively small interval corresponds to an error in ΔG^* of 0.1 kcal/mol. Furthermore, as there are two possible transition states for amides[2b] with very different dipolar characteristics, ΔS^* may be positive or negative depending upon the solvation structure involved for a thioamide in solution. Therefore, if the maximum allowable error in ΔG^* is 0.5 kcal/mol, the corresponding error in ΔS^* is about 4 cal deg^{-1} mol^{-1} and hence the experimentally determined value is considered to be acceptable if it is in the range from -4.0 to 4.0 cal deg^{-1} mol^{-1}. These entropy bounds may be compared with $\Delta S^* = 3.6$ cal deg^{-1} mol^{-1} as measured for the inversion of cyclohexane.[30]

Results

N,N-Dimethylthiocarbamyl Cyanide. This compound has previously been studied by Sandström,[20] who used *o*-dichlorobenzene as a solvent with a concentration of Sx(CN) of 33.3 mol %. The chemical shift between the *N*-methyl protons was reported as 0.2 ppm while the activation parameters agree satisfactorily with those reported here. In the present work we have used a less polar solvent and found unexpected but interesting spin-coupling features in the spectrum, which require at least a test of the validity of using only two sites to describe the exchange.[12] In TCE the spectrum of Sx(CN) shows two chemically shifted quartets (slow exchange limit).



The long-range coupling, referred to the above canonical structure, arises from inter-methyl spin-spin interactions. This is the first reported case of H-C-N-C-H $^4J_{HH}$ splitting. In view of the previously known high barrier in Sx(CN)[20] it seems reasonable that the unusually high electron density in the N-C bond might, at the nitrogen, provide a coupling mechanism for the methyl proton spins. If this premise were true, then other amido-type molecules with a high barrier should also show intermethyl proton spin coupling under appropriate conditions. This led us to reinvestigate the spectrum of *N,N*-dimethylnitrosamine (DMN). We observed intermethyl coupling in this compound at a concentration of 92 mol % in tetrabromoethane. The spin coupling constants seem to depend on solvent, temperature, and concentration in a somewhat unpredictable way. The values of $^4J_{HH}$ are both in the range 0.25 ± 0.05 Hz. We have known for some time that the resolution of the cis and trans couplings in Ox(H) depends on the solvent[31] and since the barrier in this compound is also high ($\Delta G^* \simeq 21$ kcal/mol) the apparent loss of resolution in the spectrum may be connected with the appearance of unresolved long-range inter-methyl proton-proton spin-spin coupling. Now that techniques of Fourier Transform Carr-Purcell "J" spectra are available to measure extremely small couplings (down to $\simeq$0.01 Hz),[32] these results suggest a study of these long-range couplings as a function of ΔG^* for the HR.

The *N*-methyl proton chemical shifts of Sx(CN) displayed a slight linear dependence upon temperature variation. The low-field feature was most sensitive with their separation ranging from 0.178 ppm at 130.2° to 0.108 ppm at 171.0°. We predict from this and other unpublished results[33] that $\Delta\omega < 0$ or the methyl protons cis to sulfur appear at low field. This is opposite to our findings for the compound Ox(CN) and indicates that, when compared with CN, sulfur has a more diamagnetic effect than oxygen.

N,N-Dimethylthiocarbamyl Fluoride. This compound has not previously been examined and the spectrum in the slow exchange limit reveals long-range couplings to both *N*-methyl groups from the fluorine nucleus. At room temperature $J_{\text{trans}} = 2.5 \pm 0.05$ Hz but a small variation in temperature of these couplings can be detected. At the highest temperature used (139.2°) the couplings extrapo-

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TABLE I: Summary of Kinetic Results

Compd	Mol %	Solvent	E_a, kcal/mol	ΔH^*(25°), kcal/mol	ΔS^*, cal deg^{-1} mol^{-1}	ΔG^*(25°), kcal/mol	Temp range, °C
Sx(CN)	1.9	TCE	25.2 ± 0.5	24.6 ± 0.5	3.8 ± 1.1	23.5 ± 0.5	130–171
Sx(F)	18.2	TCE	21.4 ± 0.5	20.8 ± 0.5	0.2 ± 1.2	20.7 ± 0.5	51–140
Sx(Cl)	20.0	CCl_4	18.3 ± 0.3	17.7 ± 0.3	−3.3 ± 0.9	18.7 ± 0.3	40–98
Sx(NH_2)	3.6	TCE	13.7 ± 0.2	13.1 ± 0.2	−2.8 ± 0.8	13.9 ± 0.2	−29–70

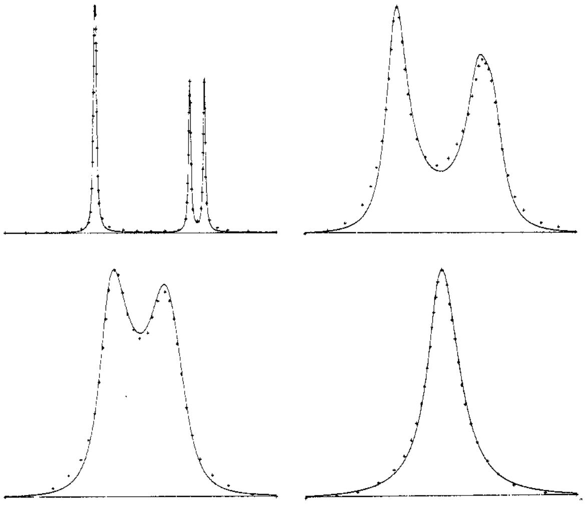


Figure 1. Fitted spectra for Sx(F) (experimental crosses over computer-simulated spectrum): top left k = 0.07 sec^{-1}, T = 50.9°, width = 39.05 Hz; top right k = 13.1 sec^{-1}, T = 109.1°, width = 47.00 Hz; bottom left k = 28.2 sec^{-1}, T = 120.4°, width = 34.01 Hz; bottom right k = 94.9 sec^{-1}, T = 139.2°, width = 25.28 Hz.

late to J_{trans} = 2.1 ± 0.05 Hz and J_{cis} = 0.23 ± 0.05 Hz. Because of the small magnitude of the cis coupling a relative sign determination using the methods of multisite exchange was not possible.[5] The couplings were assumed to be of the same sign, consistent with previous determinations of relative signs in amides.[5-7,34] A set of representative line shape fits are included in Figure 1 while the activation and rate data appear in Table I.

There is a strong linear dependence of the internal chemical shift $\Delta\omega$ upon temperature variation. At 51° $|\Delta\omega|$ = 0.190 ppm. This variation is manifest mainly by the high-field methyl feature, which also displays the largest scalar coupling. These data indicate that $\Delta\omega > 0$, oposite to Sx(CN). The parent compound, Ox(F), was reported to have a chemical shift $|\Delta\omega| \simeq +0.01$ ppm while the larger scalar coupling, also appearing at high field, was given as J_{trans} = 0.8 Hz, and J_{cis} = 0.3 Hz. Since the cis and trans π couplings are expected to be similar,[35] the large differences between trans couplings in Ox(F) and Sx(F) are thought to be effects brought on by increased asymmetry in the ground-state wave function due to the presence of sulfur. Thus the changes caused by substitution indicate that $\Delta\omega$ may be allied to J_{trans} (in mechanism) while J_{cis} derives from a somewhat substituent independent effect, or effects which largely cancel one another.

N,N-Dimethylthiocarbamyl Chloride. Sx(Cl) has previously been studied. Newman, *et al.*,[36] found ΔG^* = 19.0 kcal/mol at 266°K while Sandström[20] reports 19.1 kcal/mol at 250.2°K. The solvent for the former study was 94 mol % CCl_4 while the latter used 73 mol % *o*-dichlorobenzene. Both of these numbers appear slightly high. The kinetic data for this simple two-site case appears in Table I.

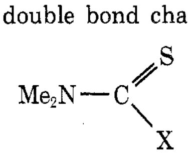
There is a small nonlinear dependence of $\Delta\omega$ upon temperature, varying from 2.1 Hz at 30° to 1.8 Hz at 95°. We have estimated $\Delta\omega > 0$, curiously similar in sign and magnitude to $\Delta\omega$ for Ox(F)[5] suggesting that the d orbital contributions to the magnetic anisotropy at the *N*-methyls by sulfur and chlorine are similar in magnitude but differ in sign. The free energies of activation for these compounds are also the same within experimental error. A possible trend is now apparent, namely, that ΔG^* and $\Delta\omega$ will be similar in the series Ox(F), Sx(Br), Sex(Br); Ox(Cl), Sx(Br), Sex(I); etc. A consequence is that $\Delta\omega$ for Ox(Br) and Sx(Br) is almost degenerate,[33] a prediction which should be experimentally tested once Sx(Br) is isolated.

N,N-Dimethylthiourea. This compound displays a large internal chemical shift, $|\Delta\omega|$, varying linearly from 0.313 ppm at −29° to 0.234 ppm at +70°. The low-field methyl feature is most sensitive implying $\Delta\omega < 0$. The kinetic results are summarized in Table I.

Discussion

The present study extends considerably the reliable energy barrier determinations for thioamides. The free energies of activation (in kcal/mol at 25°) for the present work are Sx(CN), 23.5 ± 0.5; Sx(F), 20.7 ± 0.5; Sx(Cl), 18.7 ± 0.3; and Sx(NH_2), 13.9 ± 0.2. The corresponding ΔG^* values for the simple amides are Ox(CN), 21.4 ± 0.6;[16] Ox(F), 18.1 ± 0.6;[5] Ox(Cl), 16.5 ± 0.5;[16] and an estimated barrier of approximately 5.0 for Ox(NH_2).[2b] The estimate for Ox(NH_2) was not made from nmr data quantitatively but was suggested as upper limits, set because the variation with temperature of the spectrum showed no effects attributable to decrease in exchange rate.[2b] As was pointed out in a recent note[23] the barriers in thioamides are generally about 2 kcal/mol higher than in corresponding oxyamides while selenoamides possess barriers about 1 kcal/mol higher again. The regularity of trends thus makes the hitherto estimated barrier for Ox(NH_2) quite incongruous.

The increase in the energy barrier for this compound is connected, in valence bond terms, with a greater contribution from canonical structure II because the C=S bond has less double bond character than the C=O bond. The



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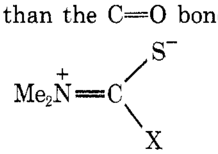

II

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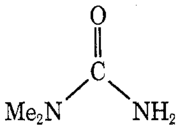
barrier appears to be a similar function of the substituent X in both amides and thioamides. The sharing of delocalized π energy in related urea structures leads to a much lower energy barrier. Major contributing canonical valence bond structures for $Ox(NH_2)$ can be written in three forms (III-V).



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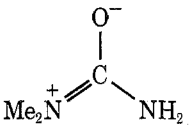

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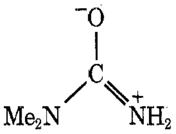

V

Ignoring the small effect of methyl substitution (in place of hydrogen) on nitrogen, the N-C bond π electron density in $Ox(NH_2)$ will be approximately one-half of that in the simple amide Ox(H). Thus, taking $\Delta G^* = 21 \pm 0.5$ kcal/mol for Ox(H),[2b] the estimated ΔG^* in $Ox(NH_2)$ becomes 10.5 kcal/mol. This value agrees quite well with an estimated 11.9 kcal/mol that can be obtained by using a figure of 2 kcal/mol less than the thiourea $Sx(NH_2)$. The reason that research workers have failed to detect a barrier to rotation in $Ox(NH_2)$ is most rationally explained by a small internal chemical shift which approaches zero (and then changes sign) at temperatures which are low enough to slow down the rotation significantly.

Surface Acidity of Transition Metal Modified Aluminas. Infrared and Nuclear Magnetic Resonance Investigation of Adsorbed Pyridine

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The surface acidity of transition metal modified aluminas was investigated by means of pyridine adsorption. Both infrared and wide-line nmr spectroscopy of adsorbed pyridine were studied. It was observed that alumina and both Co and Ni impregnated alumina contained only Lewis acid surface sites, whereas alumina impregnated with Mo, either in the presence or absence of Co or Ni, contained both Lewis and Brønsted surface acid sites. Relationships between the ratio of the various types of Lewis to Brønsted surface acid sites and integrated infrared absorption bands were derived. The Lewis to Brønsted acid site ratios were approximately the same with calcined and reduced modified aluminas. Wide-line nmr spectra indicate that the physically adsorbed pyridine on both calcined and reduced modified aluminas has considerable mobility, while chemisorbed pyridine shows much broader spectra.

Introduction

Spectroscopic investigations of surfaces have received considerable attention in recent years because they can provide information about the interaction between adsorbed species and the surface. Surface acidity is one property that has received particular attention for it can play a significant role in determining the behavior of solid surfaces.[1] A variety of probe molecules has been utilized to both qualitatively ascertain the acidity as well as provide a measure of the distribution and strength of the acid sites.

Pyridine, which is both a Lewis and Brønsted base, has been used successfully as a probe to characterize the acidity of oxide surfaces.[1-10] The ability to distinguish Lewis and Brønsted surface acidity using a pyridine probe has resulted in studies of the following surfaces, *inter alia:* η-Al_2O_3,[2] γ-Al_2O_3,[3] δ-Al_2O_3,[4] silica-alumina,[5,6] zeolites,[7-9] and chromia.[10] Recent compilations of surfaces studies are given by Tanabe[1a] and Basila.[1b]

The surface properties of the above oxides are significantly altered by incorporation of a second metal oxide. The manner in which the surface acidity is modified upon such an addition is the subject of this investigation.

Parry[2] showed that pyridine adsorbed on either Lewis or Brønsted acid sites of an oxide surface will produce sharp bands in the infrared spectral region 1400-1650 cm^{-1}.

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