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Dynamic Nuclear Magnetic Resonance. An Alternative Method for Acidity Measurements. Application to Superacids[1]

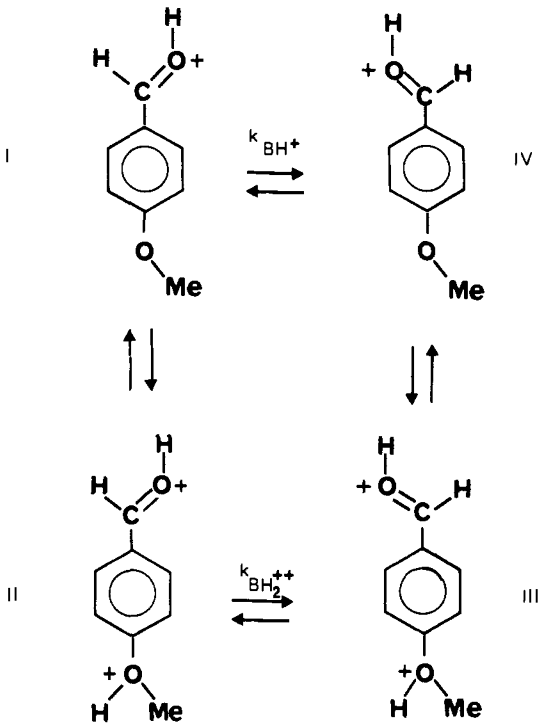
Sir:

Despite considerable work published in the field of superacid chemistry,[2] evaluation of the acidity of the superacid solvents is still in its infancy. The experimental chemistry is very much ahead of direct acidity measurements. Many kinetic and product analysis data[3,4] show that the acidity of the FSO_3H-SbF_5 system increases with increasing SbF_5 concentration at least up to the 1:1 ratio (Magic acid) and that the FH:SbF_5 system is even more acidic. However, since the pioneering work of Gillespie[5,6] on superacid acidity no progress has been reported on systems containing more than 10 mol % of SbF_5 in FSO_3H. The main reasons we suppose are the difficulties encountered in direct measurement of the BH^+/ B ratio using uv spectroscopy; besides the eventual medium dependence of the absorption maxima it is difficult to find weak enough bases with overlapping log *I* values in the strong acids.

We would like to present here an alternative method of determination of the BH^+/B ratio based on DNMR technique which seems to overcome some of the previously met obstacles. The principle is based on the well-known fact that the barrier to rotation around a single bond having some π character is very sensitive to all factors which enhance π electron delocalization.[7] For example, in the conjugate acid of the benzaldehydes[8] and acetophenones[9] the barriers to rotation around the phenyl-CO bond is about the double of the barrier in the free base. For this reason a very small amount of free base in strong acid solution can be detected monitoring the observed barrier to internal rotation.[10] In order to investigate the FSO_3H-SbF_5 system in a region overlapping earlier work, we choose the *p*-methoxybenzaldehyde indicator which is already monoprotonated on the carbonyl oxygen in pure FSO_3H with a barrier as determined by ^1H DNMR $\Delta G^{\ddagger}_{BH^+}$ = 78 kJ mol^{-1}. From 30% SbF_5 in FSO_3H up to Magic acid, the base is diprotonated and the barrier as measured by ^1H DNMR is $\Delta G^{\ddagger}_{BH^{2+}}$ = 54 kJ mol^{-1}. This is in agreement with the acidity independence of the barrier which we demonstrated in earlier work.[10]

In the intermediate acid region the observed line shape results from an overall exchange rate due to two competing processes (Scheme I): (a) the direct rotation in monoprotonated compound I → IV and (b) protonation-fast rotation in the diprotonated species-deprotonation: I → II → III → IV.

Scheme I



As the CH_3OH^+ proton cannot be observed even in Magic acid, we know that the acid-base exchange rate on this site is very fast compared to the measured intramolecular rotations. For this reason the observed rate of rotation is a function of the relative population of BH_2^{2+} and BH^+ (eq 1 and 2)

$$P_{BH_2^{2+}} + P_{BH^+} = 1 \qquad (1)$$

$$k_{obsd} = k_{BH^+}(1 - P_{BH_2^{2+}}) + k_{BH_2^{2+}} P_{BH_2^{2+}} \qquad (2)$$

at a given temperature k_{obsd} is measured from the ^1H line shape using the program DNMR3 due to Binsch;[11] $k_{BH_2^{2+}}$ and k_{BH^+} are known from the corresponding $\Delta G^{\ddagger}$ values. The relative population can then be used in an acidity function (see eq 3).

$$H_s = pK_{BH_2^{2+}} - \log \frac{P_{BH_2^{2+}}}{1 - P_{BH_2^{2+}}} \qquad (3)$$

For a number of reasons[12,13] this acidity function measured here should not be called H_0, but as our results overlap with Gillespie's values in the 5–10% SbF_5 region, this approximation will not alter the demonstration of the applicability of the DNMR method.

The value of $pK_{BH_2^{2+}}$ has been determined by measuring k_{obsd} in a region of known acidity (6-8%). We found $pK_{BH_2^{2+}} = -19.3$.

It was then possible to calculate the relation between the observed barrier to rotation and the acidity of the medium (Figure 1; curve 1). We notice that this method enables us to cover about 4-5 H_0 units below $pK_{BH_2^{2+}}$ with the same indicator as the observed barrier to rotation changes when $10^{-6} < P_{BH_2^{2+}} < 10^{-1}$.

On the other hand, with the protonated *p*-methoxybenzaldehyde, the C═OH$^+$ proton is shifted 2 ppm downfield on second protonation, and we may use the classical NMR shift method[14] as complementary information on the BH_2^{2+}/BH^+ ratio. (δ_{BH^+} = 14.8; $\delta_{BH_2^{2+}}$ = 12.4 ppm.) The $pK_{BH_2^{2+}}$ can also be calculated from data obtained in the 8% SbF_5 region for known acidity and we find $pK_{BH_2^{2+}} = -19.5$. The calculated curve of δ C═OH$^+$ vs. H_0 is plotted on Figure 1 (curve 2). It

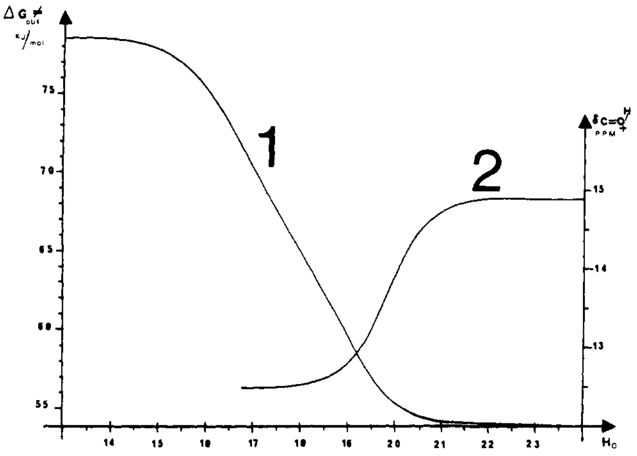


Figure 1.

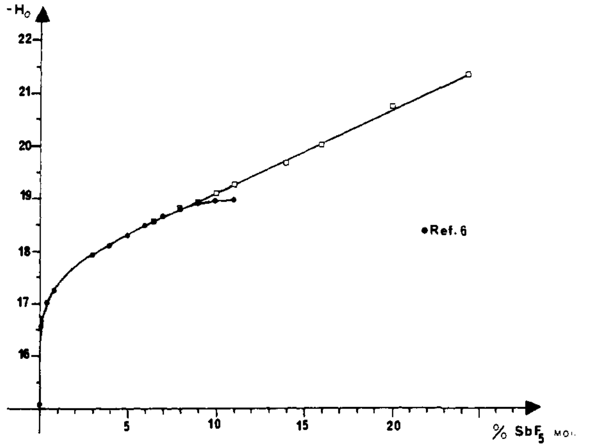


Figure 2.

is easy to see how the two methods are complementary and allow measurement of the acidity over 5 units of the scale.

By application of the experimental $\Delta G^{\ddagger}{}_{obsd}$ and δ C=OH$^+$ values on the calculated curves 1 and 2, it is possible to evaluate the acidity of the FSO_3H-SbF_5 mixture from 8 to 25 mol % of SbF_5 (Figure 2). Our values first overlap with Gillespie's values and show a continuous increase in acidity on SbF_5 addition. The discrepancy in the 9-10% region can probably be ascribed to some lack of accuracy due to the use of diprotonated indicators in uv determination. The extrapolation to higher SbF_5 concentrations suggests for magic acid a H_0 value of nearly −25, which is much stronger than previously stated. As almost all the exchange rates could be measured in the −20 to +20 °C temperature range, we neglected as a first approximation the temperature dependence of the acidity.

Despite the fact that aromatic carbonyl compounds do not behave like true Hammett bases, we feel, considering the wide range of pK available,[15] that these indicators using the DNMR method may be useful not only to determine relative acidities of much stronger superacids but eventually also for reinvestigation of less acidic systems.

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Origin of the Anomalous Soret Spectra of Carboxycytochrome P-450

Sir:

The cytochrome P-450 class of heme proteins are important hydroxylating enzymes involved in detoxification, drug metabolism, carcinogenesis, and steroid biosynthesis.[1] The compounds are named for the red shifted Soret band of the CO-ferrous derivatives, occurring at wavelengths 30 nm longer than the usual CO-heme complex. This prominent optical feature plays an important role in biochemical assays of the protein and in characterizing synthetic porphyrin analogues.[2-4] In this note we present an electronic interpretation of the anomalous absorption based on: (1) polarized single crystal absorption spectra of bacterial cytochrome P-450_{cam} which show an intense optical transition at 363 nm with the same polarization as the Soret band at 446 nm; (2) similar spectra shown by tin(II), lead(II), arsenic(III), antimony(III), bismuth(III) metalloporphyrins, which have one intense band in the 350-380-nm region and another in the 440-480-nm region; (3) model synthetic compounds for CO-P-450 reported elsewhere,[2-4] which show that the strong near-uv band and red shifted Soret band can be attributed to mercaptide as a fifth ligand; and (4) iterative extended Huckel (IEH) calculations, which provide a common interpretation of these similar spectra.

The major experimental finding is the characterization of an optical transition in the near-ultraviolet (uv) region of the CO-P-450_{cam}[5] spectrum at 363 nm, which has the same integrated intensity as the Soret [B(π-π^*)] band at 446 nm (Figure 1). The intense near-uv band has been observed previously in CO-P-450_{cam} solution spectra, but its significance was not explored.[6] The single-crystal spectrum (Figure 1) shows that this uv band has the same polarization as the Soret band, indicating that both bands have the same symmetry. Moreover, the total integrated intensity of the CO-P-450_{cam} bands at 446 and 363 nm is within 10% of the total integrated intensity observed in the same region in carboxyhemoglobin (COHb).[7] In COHb two bands are observed at 421 and 345 nm;[8] however, in COHb the near-uv band has only 40% of the integrated absorption strength of the Soret band and is identified as an N(π-π^*) band.[8,9] There are two possible interpretations for the dramatic change in spectrum between COHb and CO-P-450_{cam}: (1) The N(π-π^*) and B(π-π^*) states of CO-P-450 strongly interact for some unknown reason causing a redistribution of intensity and a shift of both bands to the red