Hydride Transfer and Olefin Isomerization as Tools To Characterize Liquid and Solid Acids

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Acidic catalysts are widely used in the petroleum industry for the production of fuels and petrochemicals. Since a great variety of reactions are involved, it is important to establish procedures to correlate the properties of acids over ranges of acidity characteristic of the catalysts being employed. This account is concerned with the development of tools that are useful for classifying very strongly acidic systems and solid acids.

The procedures are primarily kinetic methods based on determinations of the stability or other properties of carbonium ions. Whereas the Hammett acidity function[1] provides a measure of acid strength and hence the extent of protonation of molecules in a given acid, the determining factor in selecting an acidic catalyst is often the relative reactivity of an ion in competitive reactions rather than its concentration.

As an example we will consider the relative extent to which a carbonium ion will undergo proton exchange reactions as opposed to isomerization as a selectivity parameter useful in characterizing strong acid systems (at least as strong as 2 M SbF_5/HSO_3F which has an H_0 value of −19). There is no reason that this scale must necessarily relate to the Hammett acidity function and no relationship has been sought. The acidity function has of course been widely applied to acid systems, but its determination has not been made for a number of strong acids. Where it has, however,[2] problems are sometimes found in relating it to catalytic activity and selectivity[3].

The Hammett function can also be estimated for solid acids[4] and generally[5,6] but not always[7,8] correlates with their catalytic properties. The failure to correlate may be due to modified activity coefficients of indicators adsorbed on surfaces, the fact that catalysts are often used at different temperatures than those used to determine Hammett functions, or the need for a different type of indicator of acidity. It is also difficult to correctly characterize the distribution of sites of varying acidity on a solid and to assess the role acidity actually plays in the reaction being catalyzed. A good survey of the relationship of H_0 to catalytic properties is available.[9]

In any case, the present work developed from concerns about relating catalyst behavior to measures of acid strength for solid acids and for liquid systems at

least as strong as concentrated sulfuric acid. The latter is the regime of the so-called super acids. At concentrations of sulfuric acid above 90% the reactivity of *tert*-alkyl cations is found to change in an important way from that in weaker acid, a major factor being their ability to take part in intermolecular hydride-transfer reactions.

It is useful to consider the intermolecular hydride-transfer reaction as a diagnostic for the presence of relatively free alkyl cationic intermediates. The species are generally believed to be the chain-carrying elements in isomerization reactions involving ion formation and sequential hydride and alkyl shifts (2-methylpentane to 3-methylpentane) in this acid. The ions will also undergo rapid proton exchange with their acidic environment[10-17] and add to olefins (the commercial alkylation reaction), but will not participate in deep-seated skeletal rearrangement in sulfuric acid. The lifetime of the ions in this acid is not known but is usually too short to permit their direct observation by spectroscopic probes such as NMR, which has assumed a preeminent role in the characterization of ions in stronger acids, due in large measure to the labors of George Olah and his collaborators in the early 1960s.[18,19]

The intermolecular-hydride-transfer, sometimes called the Bartlett, Condon, and Schneider reaction was

(1) (a) Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1932**, *54*, 2721. (b) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw Hill: New York, 1970; Vol. 9, p 263.

(2) Gillespie, R. J.; Peel, T. E. *Adv. Phys. Org. Chem.* **1971**, *9*, 1.

(3) (a) Kramer, G. M. *J. Org. Chem.* **1975**, *40*, 298. (b) Kramer, G. M. *J. Org. Chem.* **1975**, *40*, 302.

(4) Walling, C. *J. Am. Chem. Soc.* **1950**, *72*, 1164.

(5) Tanabe, K. *Solid Acids and Bases*; Academic: New York, 1970; Vol. 5, p 103.

(6) Krylov, O. *Catalysis by Nonmetals*; Academic: New York, 1970; Chapter 2, p 70.

(7) Dzisko, V. A.; Borisova, M. S.; Kotsarenko, I. S.; Kuznetsova, E. V. *Kinet. Katal.* **1962**, *3*, 728.

(8) Dzisko, V. A., *Proc. Int. Cong. Catal. 3rd*, **1964** (1965), *1*, 422.

(9) Tanabe, K. *Solid Acids and Bases*; Academic: New York, 1970.

(10) Burwell, R. L.; Gordon, G. S., III *J. Am. Chem. Soc.* **1948**, *70*, 3128.

(11) Burwell, R. L., Jr.; Maury, L. G.; Scott, R. B. *J. Am. Chem. Soc.* **1954**, *76*, 5828.

(12) Burwell, R. L., Jr.; Scott, R. B.; Maury, L. G.; Hussey, A. S. *J. Am. Chem. Soc.* **1954**, *76*, 5822.

(13) Gordon, G. S., III; Burwell, R. L. *J. Am. Chem. Soc.* **1949**, *71*, 2355.

(14) Ingold, C. K.; Raisin, C. G.; Wilson, C. L. *J. Am. Chem. Soc.* **1936**, *58*, 1943.

(15) Otvos, J. W.; Stevenson, D. P.; Wagner, C. D.; Beeck, O. *J. Am. Chem. Soc.* **1951**, *73*, 5741.

(16) Setkina, V. N.; Kursanov, D. N.; Sterligov, O. D.; Liberman, A. L. *Doklady Akad. Nauk SSSR* **1952**, *85*, 1045.

(17) Stevenson, D. P.; Wagner, C. D.; Beeck, O.; Otvos, J. W. *J. Am. Chem. Soc.* **1952**, *74*, 3269.

(18) Olah, G. A.; Tolgyesi, W. S.; Kuhn, S. J.; Moffat, M. E.; Bastien, I. J.; Baker, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 1378.

(19) A good summary of Olah's early contributions is provided by: Olah, G. A.; Olah, J. A. in *Carbonium Ions*; Olah, G. A., Schleyer, P. R., Eds.; Wiley-Interscience: New York 1970, Vol. II, p 17.

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Table I
Selectivity Parameter of 2 M Acid Mixtures[a]

acid	HX	I/Ei-C$_5$	I/E,MCP	acid	MX	I/E,i-C$_5$
AlBr$_3$	HBr	>35	>3.8	SbF$_5$	HF	3.5
GaBr$_3$	HBr	<2.6	0.9	SbF$_5$	HSO$_3$F	1.8
TaF$_5$	HBr	0.17	0.11	SbF$_5$	CF$_3$SO$_3$H	4.25
TaF$_5$	HF	8.29	2.4			
SbF$_5$	HF	3.5	>1.5			
BF$_3$	HF	1.3	~0.04			
TiF$_4$	HF	0.036	0.002			
HfF$_4$	HF	0.013	0.0009			
GaCl$_3$	HCl		5.6			
AlCl$_3$	HCl		1.5			

[a] I/E is the ratio of the rate constants for isomerization to that of proton exchange for a tritium-labeled mixture of 2- and 3-methylpentane rearranging to n-hexane and 2,2-dimethylbutane in the presence of either isopentane (i-C$_5$) or methylcyclopentane.[3]

reported in the 1940s to be a rapid reaction. This was rationalized by assuming formation of a labile carbonium ion intermediate during the encounter of an alkyl halide with aluminum bromide. The ion would extract a *tert*-hydride from an alkane in times estimated to be less than 0.001 s.[20] In later work it was shown that this process was the propagating step in an extremely long-chain reaction between isobutane and the *tert*-butyl ion. The reaction proceeds fast enough in solutions of aluminum bromide in 1,2,4-trichlorobenzene to provide separately averaged NMR signals for the methyl and methyne protons and has an activation energy estimated as less than 1 kcal/mol.[21] Similar activation energies were subsequently found for the reaction in the gas phase.[22]

Application of NMR to the study of stable carbonium ions was was first carried out in solutions containing antimony pentafluoride.[18] These acids permitted the formation of tertiary and secondary alkyl ions with lifetimes sufficiently long to provide characteristic spectra exhibiting strongly shifted absorption bands (when compared with those of unionized precursors). Such spectra imply that the intermediates generally are stable for a least 0.001 s. In these solutions it was common to observe a rapid rearrangement to a stable tertiary ion or group of tertiary ions, even during the reaction of primary alkyl halides, before the spectra were obtained. The possible role of protonated alkyl-cyclopropanes in these rearrangements has been probed by utilizing the intermolecular-hydride-transfer reaction to trap intermediates present in tritium-containing SbF$_5$–H(T)SO$_3$F systems.[23,24]

The observation of *tert*-cations by NMR has been extended to acid systems employing other Lewis acids such as AlBr$_3$, GaBr$_3$,[25] GaCl$_3$, and AsF$_5$.[26] Only the SbF$_5$ systems have been found to stabilize simple secondary ions such as isopropyl and cyclopentyl. It is not clear how this reflects the inherent acidity or protonating ability of the acid systems (or even how to define the acidity of the varied systems).

The observations leave unanswered questions about the relative strength and catalytic utility of the different

acid systems. Particularly vexing is the question of where the original Friedel–Crafts catalyst, AlCl$_3$, fits in. Straightforward acidity function determinations on mixed AlCl$_3$–HCl systems have not been made, probably because of the extremely low solubility of aluminum chloride in noncoordinating solvents.

One way of comparing the acid systems would be to use them to generate carbonium ions which could take part in several subsequent reactions, the relative rates of which would reflect the freedom and stability of the ions in their acidic environment. For example, one could determine the rate at which 2-methylpentane converted to 2,2-dimethylbutane as well as the rate at which it exchanged protons with another hydrocarbon and use the isomerization/exchange ratio as an indicator of carbonium ion stability. One would expect á priori the ratio to be large in an acid where cations are observable by NMR and very low in sulfuric acid where exchange predominates.

This idea has been used to provide a scale of ion-stabilizing attributes for very strong acids.[3] Just as the Hammett function can be taken as a measure of the ability of an acid system to reversibly protonate a neutral base, a table of I/E or isomerization/exchange rate ratios can be used to rank acid systems. The experiments which were conducted with a mixture of tritium-labeled 2- and 3-methylpentane and unlabeled isopentane or methylcyclopentane indicated that solutions of AlBr$_3$ and HBr or GaCl$_3$ and HCl more efficiently stabilize ions than many other Brønsted and combined Brønsted/Lewis acid systems. The latter included equivalent molar solutions of SbF$_5$ in HF, HSO$_3$F, and CF$_3$SO$_3$H. Representative data is shown in Table I.

An interesting feature of this scale is that it can be applied to acidic systems irrespective of the physical nature of the acids. Selectivity parameter determinations offer a practical advantage in classifying catalysts in that they measure the inherent properties of catalytic intermediates, rather than their concentrations.

Hydride-Transfer Equilibria: Another Characterization Tool for Strong Acids

NMR can also be used to study the position of hydride-transfer equilibria and this too provides a convenient tool for ranking strong acids. Thus the value of the equilibrium constant in solution for reaction 1

$$[R_1H]_s + [R_2^+]_s \overset{K}{\rightleftharpoons} [R_1^+]_s + [R_2H]_s \qquad (1)$$
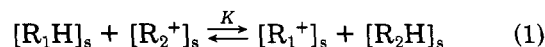
can be compared with vapor phase measurements which have been determined by mass spectrometry or can be

(20) Bartlett, P. D.; Condon, F. S.; Schneider, A. *J. Am. Chem. Soc.* **1944**, *66*, 1531.

(21) Kramer, G. M.; Hudson, B. E.; Melchior, M. T. *J. Phys. Chem.* **1967**, *71*, 1525.

(22) (a) Solomon, J. J.; Meot-Ner, M.; Field, F. H. *J. Am. Chem. Soc.* **1974**, *96*, 3727. (b) Meot-Ner, M.; Field, F. H. *J. Chem. Phys.* **1976**, *64*, 277. (c) Meot-Ner, M.; Field, F. H. *J. Am. Chem. Soc.* **1978**, *100*, 1356.

(23) Kramer, G. M. *J. Am. Soc.* **1969**, *91*, 4819.

(24) Kramer, G. M. *J. Am. Soc.* **1970**, *92*, 4344.

(25) Jensen, F. R.; Beck, B. H. *Tetrahedron Lett.* **1966**, *36*, 4287.

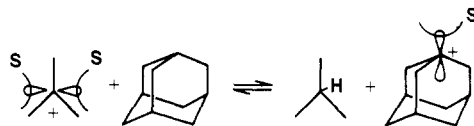(26) Brownstein, S.; Bornais, J. *Can. J. Chem.* **1971**, *49*, 7.

Figure 1. Hydride transfer equilibria between planar and bridgehead cations expected to be solvent dependent.

Table II
Hydride Transfer Equilibria Differentiate Solvent Effects in Super Acids

$$t\text{-}C_4^+ + RH \overset{\Delta G}{\rightleftharpoons} i\text{-}C_4 + R^+$$

	RH = adamantane	RH = isopentane
vapor phase	-4 ± 1^a	-2.5
AlBr$_3$,		
CH$_2$Cl$_2$	$-3.3 \pm .1$	-1.05 ± 0.2
CD$_3$Br (4 m)	-2.4	0
SO$_2$FCl	-0.6	-0.8
CH$_2$Br$_2$	-0.3 ± 0.6	-0.8
GaCl$_3$		
CH$_2$Cl$_2$	-0.1 ± 0.3	-0.4 ± 0.3
ClCH$_2$CH$_2$Cl		-0.2 ± 0.4

^{a} Houriet, R.; Schwarz, H., *Angew. Chem.* 1979, *91*, 1018.

estimated from the thermodynamic properties of the components.

Deviations of the value in solution from that in the gas phase would be expected if the products and reactants are not solvated to equal extents. Since the major effect of acidic systems on interacting with these reactants is likely to be due to solvation of the ions, an experimental determination of K or the free energy change, $\Delta G = -RT \ln K$ in solution, provides a means of estimating the relative effect of the solvent on R_1^+ and R_2^+. A choice of the reactants where one of the components yields a planar cation (*tert*-butyl) while the other affords bridgehead ions (1-adamantyl) would appear to be particularly useful to search for ionic solvation because of the possibility of interacting with the former on both sides of a vacant p orbital while only one side is available with the latter. These measurements would be probing a Doering–Zeiss model of potential solvent carbonium ion interactions,[27] Figure 1.
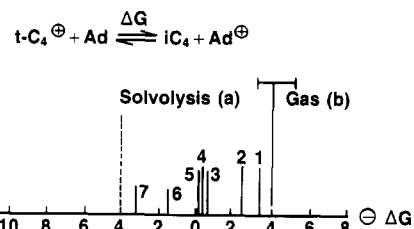
The *tert*-butyl/adamantyl pair affords the interesting prospect of being a useful probe over a considerable energy range because the vapor-phase equilibria favors the formation of the adamantyl cation by 4 ± 1 kcal/mol[28] and equilibria which might be estimated from the relative rates of solvolyses in strongly solvating media (80% ethanol in water) have for many years been expected to lie in the other direction by about the same amount. (*tert*-Butyl bromide[29] solvolyses about 1000× faster than 1-adamantylbromide[30] implying that the *tert*-butyl ion is easier to form by about 4.1 kcal/mol). Thus one anticipates an energy range of about 8 kcal from the gas phase to strongly solvating solutions which might be available for study.

(27) Doering, W. v. E.; Zeiss, H. H. *J. Am. Chem. Soc.* 1953, *75*, 4733.
(28) (a) Houriet, R.; Schwarz, H. *Angew. Chem.* 1979, *91*, 1018. (b) Houriet, R.; Schwarz, H. *Angew. Chem. Int. Ed. Engl.* 1979, *18*, 951. (c) A recent paper suggests the equilibria favors Ad$^+$ by 8.2 kcal/mol but reasons for the discrepancy with 28a and 28b are not provided. Sharma, R. B.; Sharma, D. K., Sr.; Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* 1985, *107*, 3747.
(29) (a) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1970, *92*, 5977. (b) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* 1957, *79*, 1602.
(30) Raber, D. J.; Bingham; Harris, J. M.; Fry, L. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1970, *92*, 5977.

Acid Systems

|	
1. AlBr$_3$/CH$_2$Cl$_2$	6. SbF$_5$/SO$_2$FCl, (Cl)
2. AlBr$_3$/(4M)/CD$_3$Br	7. SbF$_5$/SO$_2$, (OH)
3. AlBr$_3$/SO$_2$FCl	8. SbF$_5$/FSO$_3$H/SO$_2$, (OH)
4. AlBr$_3$/CH$_2$BI$_2$	9. SbF$_5$/FSO$_3$H/SO$_2$FCl, (OH)
5. GaCl$_3$/CH$_2$Cl$_2$	

Figure 2. Ions nearly unsolvated in AlBr$_3$ solutions. Solvation Effects in *tert*-Butyl–Adamantyl Equilibria. (a) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1970, *92*, 5977. (b) Houriet, R.; Schawarz, H. *Angew. Chem.* 1979, *91*, 1018. (c) Points 6–9 from Arnett, E. M.; Holfelich, T. C. *J. Am. Chem. Soc.* 1982, *104*, 3522.

The hydride-transfer equilibrium involving these reactants was initially studied at low temperature (−30 to −50 °C) with solutions of aluminum bromide in several solvents. The results are included in Table II and shown in Figure 2.[31] The vertical lines depict the position of equilibrium in the noted acid, no special connotation being attached to their lengths. Before making the measurements, preliminary studies indicated that the anion was Al$_2$Br$_6$X$^-$ (when X is Cl or Br) and that 1-M solutions of the *tert*-butyl cation could readily be prepared. With gallium chloride the anions appear to be either GaX$_4^-$ or Ga$_2$X$_7^-$ and concentrated solutions of the cations are also easily made. (The aluminum bromide solution should be kept cold as, on warming, a potentially dangerous exothermic halide exchange occurs.)

The aluminum bromide/methylene chloride system affords equilibria which closely approach vapor-phase values implying that the cations are solvated to nearly equal extents and presumably weakly (the differential solvation appears to be less than 1 kcal/mol). When gallium chloride is used in the same solvent, the equilibria disfavor the adamantyl ion which suggest that the values may be affected by incomplete dissociation or ion pairing.

It would be extremely desirable to obtain comparable data with antimony pentafluoride. To date the NMR measurement has been frustrated because of an apparently rapid conversion of any alkane bearing a tertiary hydrogen to its carbonium ion when mixed homogeneously with solvents containing this acid. The solvents have included SO$_2$, HSO$_3$F, AsF$_3$, CH$_2$Cl$_2$, and SO$_2$FCl.

This problem can in principle be circumvented by determining the equilibrium for an analogous exchange reaction:

$$[R_1X]_s + [R_2^+]_s \overset{K}{\rightleftharpoons} [R_1^+]_s + [R_2X]_s \qquad (2)$$
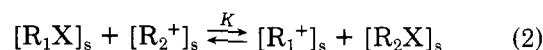
Assuming little difference in the entropy of solvation of the compounds on each side of the equilibrium, the heats of ionization of suitable compounds such as the alkyl chlorides can be used to estimate the position of

(31) Mirda, D.; Rapp, D.; Kramer, G. M. *J. Org. Chem.* 1979, *44*, 2619.

equilibrium. Such information is provided by Arnett and Hofelich[32] for solvolysis in SbF_5/SO_2FCl, a typical superacid system. The data indicate that the equilibrium between *tert*-butyl and adamantyl components does not approach the vapor phase values nearly as well as for the aluminum bromide solutions listed in Table II and therefore suggest that if ion pair dissociation is complete, the carbonium ions are more strongly solvated, less free, and probably less reactive in the SbF_5 solutions.

Arnett and Hofelich also provide data on the heats of reaction of *tert*-butyl alcohol and 1-adamantanol in several SbF_5/solvent systems. Were the alcohols to quantitatively convert to carbonium ions, the measured heats would be expected to lie in the 8-kcal range noted above, but they do not. No rationalization was proposed for the observations other than the reasonable suggestion that they appear to be related to some unknown specific solvation process.

The question of the strength of the aluminum halides has still to be determined. Some studies have been conducted by Farcasiu[33] who has attempted to use benzene as a Hammet indicator. However, both $AlBr_3/HBr$ and SbF_5/HF protonate it quantitatively, and thus benzene does not distinguish between them. On the other hand, it does show that they are stronger than TaF_5/HF.

Adamantane, an Unusual Hydride-Transfer Catalyst[34]

While conducting the hydride-transfer equilibrium measurements in $AlBr_3$–CH_2Cl_2 solutions it was noticed that the line width of the NMR signal representing the averaged methyl group of isobutane and the *tert*-butyl cation decreased sharply from about 40 to 4 Hz when adamantane was present in the system. The signal was much broader (40–60 Hz) when the *tert*-butyl cation was mixed with other hydride donors like methylcyclopentane or isopentane.

The line narrowing was curious since it suggested that adamantane, a compound whose derivatives were known to solvolyze much more slowly than isobutane's for reasons often attributed to the difficulty of forming a nonplanar bridgehead carbonium ion, was actually catalyzing the intermolecular-hydride-transfer between isobutane and the *tert*-butyl ion. The phenomenon being observed was reproducible and could be obtained by either adding adamantane to a solution of the *tert*-butyl ion or isobutane to a solution of the adamantyl cation and integration of the spectra accounted quantitatively for all the components.

If, as is believed, the hydride-transfer reaction is being catalyzed, the event provides an interesting example of the acceleration of a reaction having an exceedingly low activation energy. The fact that the activation energy is low implies that the rate increase is associated with favorable entropic changes in bringing the reactants to the hydride-transfer transition state when adamantane
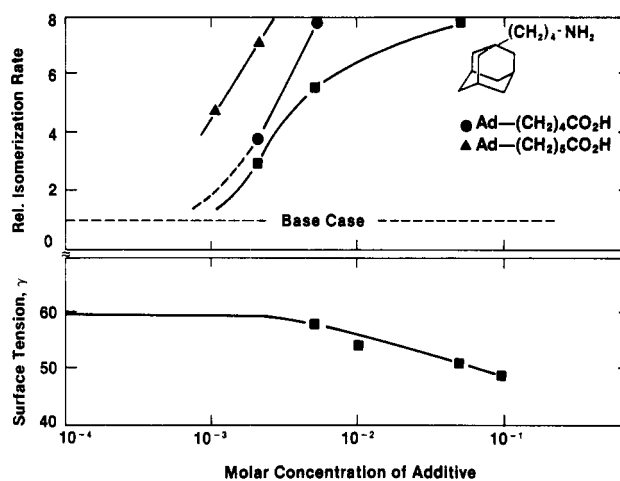
(32) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 3522.
(33) (a) Farcasiu, D.; Fisk, S. L.; Melchior, M. T.; Rose, K. D. *J. Org. Chem.* **1981**, *47*, 453. (b) Farcasiu, D. *Acc. Chem. Res.* **1982**, *15*, 46.
(34) (a) Kramer, G. M. Presented orally at the 185th American Chemical Society Meeting, Seattle, 1983. Adamantane's use as a catalyst is discussed in 6 patents: U.S. Patent 4 357 481, U.S. Patent 4 357 482, U.S. Patent 4 357 483, U.S. Patent 4 357 484, U.S. Patent 4 424 387, and U.S. Patent 4 560 825. (b) Kramer, G. M. *Tetrahedron* **1986**, *42*, 1071.

Figure 3. Surface-active adamantyl derivatives prove to be highly effective catalysts. Relative rate of $3MC_5$ isomerization (96% H_2SO_4).

is present. (Eliminating an activation energy of 1 kcal/mol entirely would lead at most to an 8-fold increase in the Arrhenius rate constant at -40 °C.)

An examination with molecular models of the nature of the nonbonded interactions present when a *tert*-alkane reacts with a planar alkyl cation makes it clear that the alkyl groups of both components approach one another closely. The normal transition state most likely is linear with the hydride being symmetrically located between the donating and receiving carbon atoms. The nonbonded interactions between the remote alkyl units probably serve to "freeze" the configuration so that free rotation about the C–H–C axis of one group relative to the other is prevented.

In the corresponding transition state involving adamantane and an alkyl cation, the nonbonded interactions are much less because of the rigid nature of the adamantyl system. Essentially free rotation is then expected, a factor which a zero-order calculation suggests may raise the preexponential term in the Arrhenius equation by 10- to 100-fold.

If this argument is correct, adamantane should be a general catalyst for reactions limited by the intermolecular hydride-transfer rate. This property has been examined by adding adamantane to solutions of 3-methylpentane being isomerized by sulfuric acid under heterogeneous conditions. The reaction is accelerated in proportion to the amount of adamantane present. It may also be catalyzed by adding a surface active adamantyl derivative to sulfuric acid. Studies with 4-(1-adamantyl)butylamine have shown that at just about the concentration required to begin to suppress the surface tension of sulfuric acid, the reagent becomes an effective catalyst, Figure 3.

Hydride Transfer: A Missing Ingredient with Many Solid Acids

The preceding illustrates how the hydride-transfer reaction may be used in several ways to determine useful properties of strongly acidic systems. It is a characteristic reaction of relatively free carbonium ions and its possible use in providing a new means of scaling solid acids of the strength typically used in catalytic cracking applications was naturally considered.

Such catalysts are among the most widely used in the world and there is much ongoing research aimed at

Table III
Isobutane Cracking Selectivity is Highly Catalyst Dependent

product, mol %	Mullite, 700	SiO₂–Al₂O₃, 650	ultrastable Y 450	ultrastable Y 500	HZSM-5 450	HZSM-5 500
methane	9.2	5.3	0.5	2.5	6.3	18.7
ethylene	0.6	0.4	0.2	1.3	3.7	10.9
ethane			0.1	0.5	0.5	1.6
propylene	7.9	5.3	0.2	0.9	5.0	8.1
propane		0.3	2.7	11.6	5.9	9.6
butenes	9.2	11.6	0.6	1.5	1.2	2.7
n-butane		0.6	4.0	7.9	1.0	1.3
isobutane	72.9	76.2	89.8	69.5	75.1	43.7
pentenes			0.1	0.2	0.2	0.6
pentanes			1.8	3.7	0.7	1.0
C₆–C₁₀	0.2	0.3	tr	0.4	0.4	1.8

(Note: the column header row spans "catalyst at temp, °C" with "ultrastable Y" covering the 450/500 columns and "HZSM-5" covering the next 450/500 columns.)

improving their lot. What are not available are widely reliable tools for evaluating the catalysts.

To develop a useful procedure it was first assumed that the acidity of conventional catalysts would be sufficient to generate carbonium ion intermediates. If so, it should be possible to use an analogous procedure to that employed in setting up the I/E scale. Accordingly, preliminary experiments were carried out in which the conversion of isobutane to *n*-butane and mixtures of butylenes was studied, the relative rates of which were intended to provide a useful characterization of the acidic solids.

The reaction was conducted by flowing isobutane at atmospheric pressure and high temperatures over a series of representative solid acids including amorphous silica alumina of the type used commercially for many years, as well as crystalline, ultrastable Y and HZSM-5 zeolites (molecular sieve catalysts) in their protonic forms. Products were determined with an on-line gas chromatograph.[35]

The results were unexpected. With all of the amorphous systems the products were found to contain methane, propylene, butenes, and hydrogen, but essentially no *n*-butane, Table III.

These products are the same as those obtained in control experiments using mullite beads in place of the catalysts. The extent of reaction varied from one catalyst to another but the product distributions (decomposition to methane and propylene vs. butylenes and hydrogen) remained nearly constant. One important difference was that the more active catalysts tended to isomerize the butenes nearly to equilibrium whereas only isobutylene was obtained with the nonacidic mullite beads.

The product distribution changed completely when the ultrastable Y catalyst was used. *n*-Butane as well as a number of products which could be attributed to a carbonium ion chain cracking sequence were now formed in addition to relatively small amounts of methane and butenes. These results have led t⸱ a model for isobutane's conversion as involving initial oxidation to form a radical cation whose fate is a function of the catalyst. Over the amorphous acids it undergoes the cleavage reactions to products normally expected from free radicals. The same initiation is proposed over the amorphous zeolite but here the olefins function as intermediaries in the formation of chain-carrying carbonium ions. This implies that the

(35) McVicker, G. B.; Kramer, G. M.; Ziemiak, J. *J. Catal.* 1983, *83*, 286.
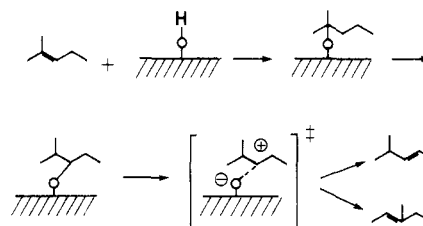
• Methyl Group Migration Requires More Carbonium Ion
  Character in [   ]‡ Than Double Bond Migration

• Carbonium Ions are Not Intermediates on Most Solid Acids

Figure 4. Skeletal isomerization aided by stronger solid acids.

ultrastable Y is a much stronger acid than amorphous SiO₂–Al₂O₃.

The HZSM-5 catalyst provides a product resembling that obtained with the amorphous acids more closely than it does the ultrastable Y. At 400–500 °C it is more active than the acidic faujasite and affords much more ethylene than the other catalysts. It is relatively ineffective at isomerizing isobutane to *n*-butane and yields much methane and propylene.

Product selectivities obtained with this material are often attributed to the fact that reactions are occurring in narrow pore channels which tend to inhibit bimolecular processes involving bulky reactants. Such inhibition might be responsible for the small yield of *n*-butane if HZSM-5 is capable of generating alkyl carbonium ion intermediates. On the other hand, the behavior of this system is also consistent with the presence of strongly oxidizing but mildly acidic sites.

One of the most important results of the isobutane study was the finding that the amorphous solid acids had the ability to extensively isomerize isobutylene to linear butenes without forming an intermediate capable of abstracting a hydride ion from isobutane. Clearly the intended use of the selectivity of isobutane's conversions as a diagnostic of the utility of these acids is inappropriate. On the other hand, the ability of the solids to skeletally rearange isobutylene suggests that olefinic rearrangements might be suitable.

Isomerization of 2-Methylpent-2-ene: Useful for Scaling Solid Acids

The isomerization of 2-methylpent-2-ene is a particularly useful reaction to probe the relative acidity of solids of moderate strength because the olefin can convert to a large number of products whose relative rates of formation are expected to reflect the relative freedom of cationic intermediates. For example, its

Table IV
2-Methylpent-2-ene Isomerization on Halided γ-Alumina[a]

halide, wt %		relative rate[b]	selectivity[c]
Cl	F		
		1.0	0.10
0.6		3.4	0.20
0.9		5.2	0.22
1.2		13	0.30
1 5		32	0.45
	0.6	42	0.68
	0.9	95	1.24
	1.2	240	2.24
	1.5	270	2.48

[a] Conditions: 1.0 atm, 250 °C, 10.5 cm³ olefin/min, 138 cm³ He/min, 1.0 g of catalyst, 1.0 h on feed. [b] Relative rates of isomerization of 2-methylpent-2-ene to *trans*-3-methylpent-2-ene. [c] Selectivity measured by the *tert*-3-methylpent-2-ene/(*cis* + *trans*)-4-methylpent-2-ene ratio. Equilibrium value = 2.70.

conversion to 4-methylpent-2-ene and 3-methylpentenes can formally be thought of as proceeding through protonation to form a *tert*-cation or alkoxy-compound which rearranges by a 1,2 hydride shift to a secondary ion which experiences a proton loss or methyl migration (Figure 4).[36]

The proton loss and methyl shift are then competing reactions of a common intermediate over varied energy surfaces. The deprotonation involves the transfer of a proton from a carbon atom adjacent to the one bearing the formal charge to a basic site on the surface while an olefin is formed.

The transition state for the methyl shift must look quite different. If it is a concerted reaction it would involve the movement of the alkyl group to a symmetrical bonding situation between two carbon atoms whose bonding to the surface is in a state of flux. It would not be unreasonable to expect the alkyl shift to require a more fully developed carbonium-ion-like species than that needed for deprotonation and this would be expected to follow the inherent acidity of the solid. Thus the stronger the acid, the more readily would group migration occur and the ratio of rates for the alkyl migration to double-bond formation would be expected to rise.

To examine these relationships the isomerization of 2-methylpent-2-ene was studied by passing vapors of the olefin over 1-g portions of catalysts contained in a cylindrical stainless steel reactor. The reaction was normally conducted at 250–350 °C while flowing 150 cm³/min of a mixture of 7% olefin in helium at atmospheric pressure over the catalyst. The products passed through an on-line Varian gas chromatograph containing a capillary column which was able to resolve all hexene isomers. The data was treated to determine the ratio of the rates of forming *trans*-3-methylpentene and *cis*- and *trans*-4-methylpent-2-ene. This selectivity ratio was obtained for γ-alumina and a series of chlorided and fluorided aluminas.

This parameter is listed along with the relative rates of isomerizing 2-methylpent-2-ene to *trans*-3-methylpentene in Table IV. The results indicate that fluorination is more effective than chlorination in increasing the cationic character of the rearranging intermediate and probably the acidity of the catalyst. This is reflected in both the rates of conversion and in the se-

(36) Kramer, G. M., McVicker, G. B.; Ziemiak, J. *J. of Catal.* **1985**, *92*, 355.

Table V
2-Methylpent-2-ene Isomerization Ranks Solid Acids[a]

catalyst	mole ratio[b]	MAT activity[37]
γ-Al₂O₃	0.10	8
2% SiO₂–Al₂O₃	0.13	16
2% SiO₂–Al₂O₃	0.11	18
2% SiO₂–Al₂O₃	0.12	20
3.4% SiO₂–Al₂O₃	1.07	34
5% SiO₂–Al₂O₃	0.22	17
5% SiO₂–Al₂O₃	0.62	23
15% SiO₂–Al₂O₃	0.62	23
15% SiO₂–Al₂O₃	0.76	27
commercial-DA-1 13% SiO₂–Al₂O₃	2.47	60

[a] Conditions: 1.0 atm, 250 °C, 10.5 cm³ olefin/min, 139.5 cm³ He/min, 1.0 g cat. 1.0 h on feed. [b] *trans*-3-methyl-2-ene/(*cis* + *trans*)-4-methylpent-2-ene.
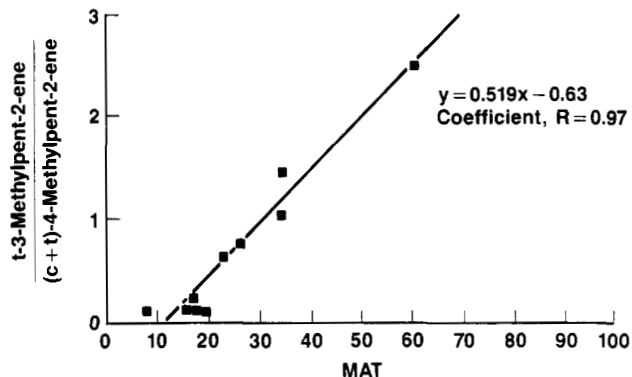

Figure 5. Product selectivity while isomerizing 2-methylpent-2-ene correlates with MAT activity of amorphous silica–alumina catalysts. The MAT number is a measure of the extent of conversion of an East Texas gas oil under a specific set of conditions.[37]

lectivity ratio. These attributes could not be deduced from acidity estimates made by the chemisorption of NH₃ or 3,5-dimethylpyridine which respectively found about 195 and 285 umol/g of acid sites on the aluminas, independent of the extent of halogenation.

The selectivity ratio was also determined for a series of silica–alumina catalysts and compared with a standard measure of cracking activity, the MAT number. The MAT number is a measure of the extent of conversion of an East Texas gas oil under a specific set of conditions.[37] The comparison shows the selectivity ratio to be linearly related to the MAT number for a number of amorphous solid acids having widely different activities

Table V contains a summary of results obtained for a series of catalysts used in establishing the selectivity–MAT correlation which is shown in Figure 5.

The selectivity ratio serves as a useful indicator of the relative freedom of cationic intermediates and possibly the acidity of amorphous silica–alumina systems. The probe provides the best laboratory procedure we know of to correlate with the behavior of a wide range of cracking catalysts (in the MAT test). This implies that the conversion of the East Texas gas oil is essentially an acid-catalyzed reaction which may be stimulated by relatively mild acids.

It should be noted that the correlation with the MAT number has not yet been established for the halided systems nor for an extensive range of highly acidic zeolites. The latter are molecular-sieve catalysts and related catalysts have been reported to provide products

(37) ASTM Test D 3907-80.

which in large measure are dictated by the size and shape of the sieves and their supporting network, i.e., HZSM5.[38]

Summary

Several tools have been developed which are useful in diagnosing the relative utility of very strong acids (often called superacids) as catalysts, as well as the relative ability of solid acids to support carbonium ion processes.

The ability of strong acids to stabilize carbonium ions which isomerize rather than deprotonate is one measure

of their usefulness. Another lies in their capacity to stabilize relatively unsolvated carbonium ions. The latter can be assessed when hydride-transfer equilibria can be measured or estimated. This has been done for equilibria involving adamantyl and *tert*-butyl ions.

The freedom of intermediates participating in acid catalyzed reactions on solids can also be probed by determining the way by which they partition themselves into different reaction channels. Paths requiring the development of an increasing amount of carbonium-ion-like character appear to be preferentially aided as catalyst activity and probably acidity increase. These considerations have been used to establish the relative rates of converting an olefin into a methyl shifted and a double bond shifted product as an important characterizing selectivity parameter for solid acids.

(38) Argauer, R. J.; Landolt, R. G. U.S. Patent 3 702 886. Chang, C. D.; Lang, W. H.; Silvestri, A. J. U.S. Patent 3 894 106. Butter, S. A., Kaeding, W. W.; Jurewicz, A. T. U.S. Patent 3 894 107. Chang, C. D., Silvestri, A. J.; Smith R. U.S. Patent 3 928 483.

Naturally Occurring Cyclohexene Oxides

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Cyclohexene oxides are a small group of natural products which have aroused widespread interest amongst natural product and synthetic chemists in the last 10 years owing to their unusual structures, biogenesis, and biological activity.
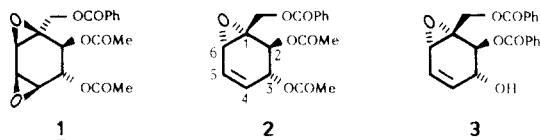
Crotepoxide 1, senepoxide 2, and pipoxide 3 were discovered during the period between 1968–1970 from *Croton macrostachys*,[1,2] *Uvaria catocarpa*,[3] and *Piper hookeri*,[4] respectively. Due to the report by the late Professor Kupchan that crotepoxide (1) has a significant inhibitory activity against Lewis lung carcinoma in mice, the compound has become very well-known and is thus responsible for generating interest in this field. Consequently, in the following years the chemical community saw several syntheses of crotepoxide[5–7] and senepoxide,[8–11] including, also, the proposal of a biogenetic pathway to this family of compounds.[12] However, it was to be another decade before new members

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Scheme I

Scheme II
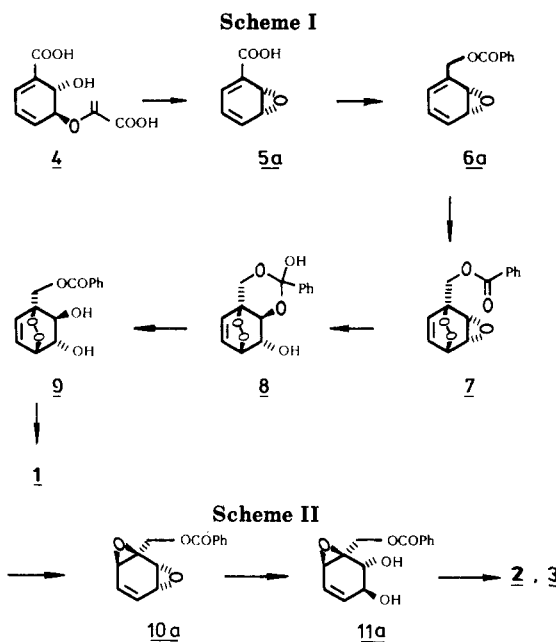
of the family were discovered which clarified their biogenesis.

In the meantime the absolute stereostructures of crotepoxide (1), and subsequently of senepoxide (2), were conclusively established by X-ray crystallography.[13,14] The stereostructure of pipoxide (3) was also proposed,[4] albeit based on that of senepoxide (2), which was later proved to be incorrect.

(1) S. M. Kupchan, R. J. Hemingway, P. Coggon, A. T. McPhail, G. A. Sim, *J. Am. Chem. Soc.* 1968, 90, 2982.
(2) S. M. Kupchan, R. J. Hemingway, R. M. Smith, *J. Org. Chem.* 1969, 34, 3898.
(3) R. Hollands, D. Becher, A. Gaudemer, J. Polonsky, *Tetrahedron* 1968, 24, 1633.