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Ranking Strong Acids *via* a Selectivity Parameter. I

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The relative facility of an acid in catalyzing the isomerization of methylpentanes to 2,2-dimethylbutane and *n*-hexane and the simultaneous deprotonation of carbonium ion intermediates is used to define a selectivity parameter, $k_{\text{iso}}/k_{\text{ex}} \equiv I/E$, characteristic of the medium. I/E is used to rank Lewis acids in HBr, HCl, HF, HSO_3F, and CF_3SO_3H. Data for two I/E scales, one for exchange with isopentane and the other for exchange with methylcyclopentane, are reported.

The choice of an acid catalyst for a hydrocarbon reaction is to a large extent governed by qualitative observations rather than quantitative information about existing possibilities. This situation exists because the relative acid strength of important acids is often unknown and because firm information about the stability of ionic intermediates in most acids is virtually unavailable.

To help clarify the issues recent work, notably that of Professor R. J. Gillespie and his colleagues, has aimed at determining Hammett acidity function values, H_0, for systems employing SbF_5 as a Lewis acid.[1-3] Using nitro aromatics as indicators, he has shown that some acids have about 10^8 times the protonating ability of 100% H_2SO_4. Acids in this range are generally useful for paraffin–olefin alkylation, paraffin isomerization, and certain types of cracking reactions. Using similar techniques we are in the process of extending Gillespie's measurements to other acids, but of added importance, we have developed a new procedure to classify acids according to the manner in which they stabilize or interact with alkyl carbonium ions.

Our procedure is aimed at giving us quantitative information about the nucleophilicity of a given acid solution. Specifically it tells us if an alkyl cation can rearrange with or without deprotonating during its lifetime in the acid. It should be noted that the nucleophilicity of an acid system is not necessarily directly related to its acidity as a Brønsted acid, a property more properly evaluated by an H_0 type measurement.

This information is acquired by simultaneously reacting a hydrocarbon which contains an essentially uniform distribution of tritium around its skeleton with another molecular weight but unlabeled hydrocarbon over any acid catalyst. A "perfect" acid will allow all isomerizations to occur without hydrogen exchange while a "poor" acid, which is unable to stabilize the ion, will tend to induce faster exchange than isomerization. The ratio of isomerization to exchange rate constants, $k_{\text{iso}}/k_{\text{ex}}$ or I/E, is defined as a selectivity parameter which permits the ranking of all strong acids. This parameter should be useful until alternate exchange mechanisms become important. At very high acidities direct protonation and displacement may become significant but it is not a serious factor through 2 *M* SbF_5–HSO_3F solutions which have H_0 values > −18.

Strategical Approach to the Problem

In order to obtain the selectivity parameter, it is first necessary to prepare a suitably labeled hydrocarbon. This was done by contacting 2- or 3-methylpentane with 98% H_2SO_4 containing tracer quantities of T_2O (1 mCi/ml) for several days. In this acid, the methylpentanes isomerize without undergoing chain branching rearrangements and exchange all protons except the tertiary hydrogen.[4-13] The labeled methylpentanes were diluted with unlabeled methylpentanes and mixed with isopentane (mixture 1) or methylcyclopentane (mixture 2).

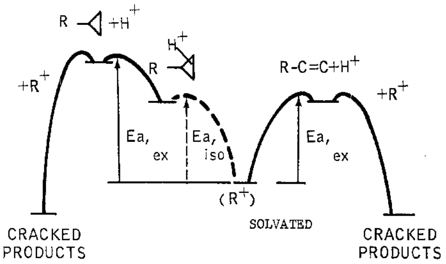
Since it is known that during the isomerization of methylpentanes to an equilibrium mixture of all isomers there is a rapid equilibration of 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane which is followed by a slower conversion of this mixture to 2,2-dimethylbutane and *n*-hexane[4,14,15] we choose the rate of the latter process, k_{iso}, as a measure of the isomerization activity of the acid.

We also measure the rate of depletion of radioactivity in the total hexane fraction. The isomerization and overall exchange processes are both assumed to follow first-order kinetics and the rate constants are obtained from log concentration or radioactivity *vs.* time plots. In the more reactive acid systems there is substantial uncertainty in the rate constants because they are based on only one or two data points at high conversion levels.

All reactions were initiated with a small but constant amount of *tert*-butyl chloride. Some systems were unable to rapidly attain a steady-state ion concentration and for these the rate constants are crudely estimated from initial conversion data only. For most of the systems studied, however, an error of less than ±10% of the reported rate constants is estimated.

The ratio, k_{iso}/k_{ex}, is the selectivity parameter. A perfect acid would exhibit a ratio of ∞ while a "poor" acid would have a value of zero. Before proceeding further, it is appropriate to consider a general reaction coordinate diagram for the possible isomerization, exchange, and cracking reactions the ions are likely to undergo (Scheme I).

Scheme I
General Scheme Leading to Isomerization, Exchange, and Cracking *via* Olefins or Alkycyclopropanes



Hexane isomerization can take place with or without H^+ exchange, exchange being more prevalent in more nucleophilic media. Exchange occurs through alkenes or alkylcyclopropane intermediates.[25] A potentially bothersome side reaction is cracking which involves a bimolecular reaction of the same intermediates and carbonium ions.[16,17] It is possible to exchange without cracking if the concentrations of ions and intermediates are both low.

It is important to note that the relative isomerization and exchange rates are both assumed to go through a common carbonium ion intermediate. The ratio k_{iso}/k_{ex} is assumed to reflect the properties of the medium and should be independent of physical factors like stirring rates and the heterogeneity of the system.

These considerations apply to the major paths for isomerization and exchange and are consistent with many studies in H_2SO_4.[4-13] Exchange by other routes has been considered but are believed to make only a minor contribution to the data. One alternate path involves the isomerization of a tertiary tritiated ion to a secondary ion, hydride abstraction to this site, and then detritiation by hydride transfer from the tertiary position. A second involves direct proton displacement reactions on the paraffins.

The first path is believed to be of little importance because it depends on a bimolecular reaction involving an extremely low concentration of secondary ions. The second path would require an increase in exchange rate with acid strength but with the possible exception of some concentrated SbF_5 solutions there is little reason to support this mechanism in the acidity range being studied.

We arbitrarily use k_{iso}/k_{ex} as the selectivity parameter. It might be better to use $k_{iso}/(k_{ex} + k_{crack})$, but the selected ratio ought to be a fair indicator of acid character, especially where side reactions are minimized and we choose to handle our data in this way.

Experimental Conditions

Reactions have been carried out between −93 and +23°. Approximately equal volumes of the hydrocarbons and acids were used and isomerization and exchange were followed by periodically withdrawing samples for analysis on a radioassaying gas chromatograph system. In every run the reaction was initiated with a small amount of *tert*-butyl chloride which was predissolved in the hydrocarbons. The concentration of *tert*-butyl chloride in the acid was 0.12 *M*. When using liquid HBr or HCl a series of experiments of varying duration was made, each run providing one point for the kinetic analyses.

Table I
Low-Temperature Isomerization in Acid Systems $i\text{-}C_5H_{12} + 3\text{-}CH_3C_5H_{11}$*

Acid	T, °C	k_{iso}, hr^{-1} [a]
0.5 *M* SbF_5–HSO_3F	−78	0.02
2 *M* SbF_5–HSO_3F	−78	0.02
0.5 *M* TaF_5–HSO_3F	−78	0.03
2 *M* TaF_5–HSO_3F	−78	0.04
0.5 *M* NbF_5–HSO_3F	−78	0.03
2 *M* NbF_5–HSO_3F	−78	0.03
0.5 *M* $AlBr_3$–HBr	−78	0.02
2 *M* $AlBr_3$–HBr	−78	0
0.5 *M* $AlCl_3$–HBr	−93	0

[a] Isomerizations are of type A only.

Reaction was conducted in a series of small Hastelloy C vessels which were compatible with the acids studied. The acids characterized in this program are $AlBr_3$–HBr, $AlCl_3$–HCl, HF, SbF_5–HF, TaF_5–HF, NbF_5–HF, HSO_3F, SbF_5–HSO_3F, TaF_5–HSO_3F, NbF_5–HSO_3F, CF_3SO_3H, SbF_5–CF_3SO_3H, TaF_5–CF_3SO_3H, and NbF_5–CF_3SO_3H.

Measurements were made at several molar concentrations of the Lewis acid. The range was normally 0.5–2.0 although 5 *M* SbF_5–HF solutions were also studied. The Lewis acids, $AlBr_3$ and SbF_5, were distilled in glass equipment before use. Aluminum chloride was sublimed in an N_2 atmosphere and TaF_5 and NbF_5 were utilized as received from the Ozark-Mahoning Co. Anhydrous HBr and HCl (Matheson) were used as received. Hydrogen fluoride was distilled in an all steel apparatus and HSO_3F was distilled in glassware. Trifluoromethanesulfonic acid was distilled in glassware and conductivity measurements indicated it had 2 mol % water. As indicated in the text there is some uncertainty about the stability of CF_3SO_3H and the solutions containing Lewis acids.

Results and Discussion

It has been indicated that when 3-methylpentane isomerizes there are some rearrangements which occur relatively easily and others which occur more slowly. For this work we distinguish between the reactions which lead to the relatively rapid equilibration of 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane, which will be called type A isomerizations, and the isomerization of this mixture of isomers to *n*-hexane and 2,2-dimethylbutane, type B. Type B isomerization rates are used in the selectivity parameter, k_{iso}/k_{ex}.

type of isomerization: definitions

$$2\text{-MC}_5 \rightleftharpoons 3\text{-MC}_5 \rightleftharpoons 2,3\text{-DMC}_4 \qquad \text{A}$$

$$2\text{-MC}_5 + 3\text{-MC}_5 + 2,3\text{-DMC}_4 \xrightarrow{s} n\text{-C}_6 + 2,2\text{-DMC}_4 \qquad \text{B}$$

Type A isomerizations at low rates were found in all HCl, HBr, and HSO_3F systems at −78 or −93° (see Table I). Type B isomerizations, however, were negligible and the exchange rates were also relatively slow. These experiments provide base case or background information for higher temperature studies but are not used in further assessing the acid solutions.

The same systems and additional ones based on HF and CF_3SO_3H have been studied at ambient conditions. Both the isomerization and exchange rates are listed in Table II, and an example of the approach to isomerization and exchange equilibrium in 2 *M* SbF_5–HSO_3F is shown in Figure 1. Both reactions reached equilibrium in less than 2 hr. At

Table II
Isomerization and Exchange in Acid Systems, 23°
$i\text{-}C_5H_{12}$ + $(3\text{-}CH_3C_5H_{11})$*

Acid	"B" k_{iso}, hr^{-1}	k_{ex}, hr^{-1}	I/E
0.7 M $AlBr_3$–HBr	>1.1	0.25	>4.3
2 M $AlBr_3$–HBr	$>>0.6$	0.02	$>35/1$
1.9 M $AlCl_3$–HCl	>0.8	0.25	>3.3
1.6 M $AlCl_3$–HCl	>1.6	0.24	>6.6
0.45 M $AlCl_3$–HCl	1.1	0.74	1.5
0.37 M $AlCl_3$–HCl	0	0.26	0
HF	0	0.03	0
0.5 M SbF_5–HF	1.76	0.68	2.6
2 M SbF_5–HF	2.42	0.69	3.5
5 M SbF_5–HF	2.98	1.84	1.6
0.5 M TaF_5–HF	0.76	0.56	1.35
2.0 M TaF_5–HF	0.58	0.07	8.29
0.5 M NbF_5–HF	1.37	2.52	0.54
HSO_3F	1.42	>3.34	0.42
2 M SbF_5–HSO_3F	1.42	0.79	1.80
2 M TaF_5–HSO_3F	0.72	0.62	1.16
CF_3SO_3H	0	>5.92	0
2 M SbF_5–CF_3SO_3H	2.68	0.62	4.25
2 M TaF_5–CF_3SO_3H[a]	4.89	4.76	1.03
2 M NbF_5–CF_3SO_3H[a]	2.59	>4.49	<0.58

[a] Unidentified products formed in this acid.

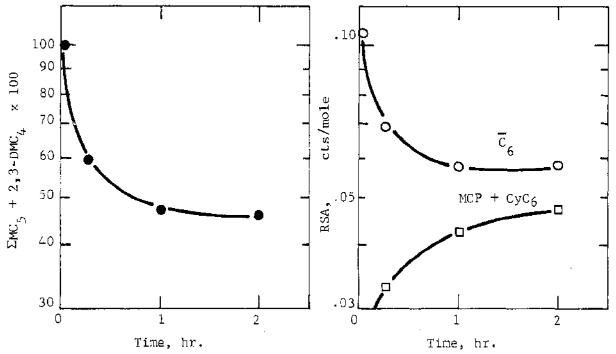


Figure 1. Isomerization and exchange equilibrium reached rapidly in 2 M SbF_5–HSO_3F. RSA or relative specific activity is a measure of the radioactivity of the sample.

Table III
Selectivity Parameter, I/E

	HF[a]	HF[b]	HSO_3F[b]	CF_3SO_3H[b]
SbF_5	2.6	3.5	1.8	4.3
TaF_5	1.4	8.3	1.2	1.0
NbF_5	0.5			<0.5
None	0	0	0.4	0

[a] 0.5 M MX_n. [b] 2.0 M MX_n.

Table IV
Isomerization and Exchange in HSO_3F, 23°
MCP + (3-Methylpentane)*

Lewis acid, M	k_{iso}	k_{ex}	I/E
SbF_5, 2	2.0	1.6	1.2
TaF_5, 2	0.8	0.9	0.9
NbF_5, 2	0.7	1.0	0.7

this time the average C_6 molecule had a relative specific activity (RSA) of 0.057 counts/molecule while an average naphthene, methylcyclopentane or cyclohexane, had an RSA of 0.047. If we assume that there are 13 exchangeable protons in C_6H_{14} and 11 exchangeable protons in the alicyclic compounds, we find the average counts per proton to be nearly identical in both sets of molecules, (0.00438 count/H)C_6H_{14} and (0.00427 count/H)C_6H_{12}. Thus, all exchangeable protons have been equilibrated.

The data indicate a wide range in behavior of the acid systems varying from 2 M $AlBr_3$ in HBr in which ions isomerize more readily than they exchange to HF and CF_3SO_3H in which exchange is faster. It might be noted that our estimate of k_{iso} for 2M $AlBr_3$–HBr is very low because the system was at equilibrium at the time of sampling. Nevertheless, little detritiation of the hexanes had occurred in this time or in more prolonged experiments.

The data in Table II can be regrouped to compare the selectivity parameter, I/E, when SbF_5, TaF_5, and NbF_5 are added to HF, HSO_3F, and CF_3SO_3H (see Table III). When this is done, we find that SbF_5, TaF_5, and NbF_5 lead to the same ordering of 0.5 M solutions in HF and 2 M solutions in HSO_3F and CF_3SO_3H. In all of these, isomerization with solutions containing SbF_5 proceed with less exchange than occurs with TaF_5 and NbF_5. The ordering of the acids is apparently proportional to the acidity of the systems as measured on the H_0 scale,[18-20] which indicates that SbF_5–HF is about 2 units more acidic than TaF_5–HF which in turn is slightly more acidic than NbF_5–HF.

The 0.5 M solutions of TaF_5–HF are nearly saturated and ought to reflect a maximum acidity at ambient conditions. Hence it is extremely interesting to find that the selectivity parameter increases when an excess of TaF_5 is added. It is known that TaF_5 dissolves in HF far beyond its solubility limit when the acids are mixed in the presence of hydrocarbons. This indicates that some complex of TaF_5 and organic matter, probably a soluble carbonium ion–TaF_6 salt, is formed. The presence of this material evidently serves the useful purpose of mainly deaccelerating the exchange reaction and the system behaves as though it were more acidic and less nucleophilic.

Why this is so is a matter of speculation. A plausible reason for the small effect on isomerization is that the soluble salt exerts a common ion effect on the alkyl cation concentration, *i.e.*, reduces it. This would be consistent with the apparent drop in k_{iso} from 0.76 to 0.58 hr^{-1} in proceeding from 0.5 to 2.0 M TaF_5–HF. Not easily understandable, however, is the larger drop in the rate of exchange. One might have expected that an increased concentration of TaF_6^- would augment the exchange and further studies of this phenomenon are planned.

The Selectivity Parameter Is Compressed by Methylcyclopentane. The preceding data were obtained with mixture I. In Table IV are shown comparable data obtained with mixture II where methylcyclopentane, MCP, is used in place of isopentane. It was expected that MCP would function as a cracking inhibitor and prevent cracking reactions which make it difficult to interpret some of the kinetic information in the prior experiments. MCP did suppress cracking but surprisingly led to generally faster isomerization and exchange rates than were found when isopentane was used. The I/E ratios lie in the same order as before but the ratio is reduced markedly. The reduction stems from the relatively more rapid increase in the rate of exchange.

The selectivity parameters obtained with both hydrocarbons are compared in Table V. It might be expected that using MCP will lead to an increase in the total concentration of ions dissolved in the acid because the methylcyclopentyl ion normally appears to be more stable than any of the alkyl ions.[21-23] If this is so, there might be a concomitant increase in isomerization rates, in counterion and ole-

Table V
Selectivity Parameter Is Affected by the Hydrocarbon

Hydrocarbon	2 *M* SbF_5–HSO_3F	2 *M* TaF_5–HSO_3F
Isopentane	1.8	1.2
Methylcyclopentane	1.2	0.9

Table VI
Selectivity Parameter of 2 *M* Acid Solutions[a]

Acid	*I/E*
$AlBr_3$–HBr	>35
TaF_5–HF	8.3
$AlCl_3$–HCl	8 est.
SbF_5–CF_3SO_3H	4.3
SbF_5–HF	(3.5)
SbF_5–HSO_3F	1.8
TaF_5–HSO_3F	1.1
TaF_5–CF_3SO_3H	1.0
NbF_5–CF_3SO_3H	0.6

[a] Obtained with the *i*-C_5H_{12}-3-MC_5* mixture.

Table VII
Selectivities of 0.5 *M* Acid Solutions[a]

Acid	*I/E*
(0.7) $AlBr_3$–HBr	4.3
SbF_5–HF	2.6
$AlCl_3$–HCl	1.5
TaF_5–HF	1.4
NbF_5–HF	0.5

[a] Obtained with the *i*-C_5H_{12}-3-MC_5* mixture.

fin concentrations, and a reduction in acidity of the solution. The latter effects would tend to accelerate exchange. Thus, both isomerization and exchange rates should increase upon raising the ionic strength and this is seen in the data. For example, the isomerization rate constant in 2 *M* SbF_5–HSO_3F increased from 1.41 to 2.00 hr^{-1} when isopentane was replaced with MCP. Offsetting increases in the exchange rate led to the compression in Table V.

Ranking the Acids. In Table VI, the selectivity parameter for 2 *M* solutions of the acids listed in Table II is tabulated. The ordering indicates that $AlBr_3$–HBr provides the best ion stabilizing medium. As there is no simple relationship between this composite property and proton activity one cannot say that $AlBr_3$–HBr is also the strongest Brønsted acid. In Table VII a shorter comparison of 0.5 *M* solutions is shown.

Although both of the comparisons indicate that $AlBr_3$–HBr provides the most stabilizing acid, the data in these tables should be used with care. Reasons for caution are that some of the systems are heterogeneous and there are large differences in solution properties of the Brønsted acids. In some cases the data may be biased by cracking or the fact that some of the acids may be inherently unstable.

These problems clearly exist for $AlCl_3$–HCl where sight glass studies indicate there is virtually no solubility of $AlCl_3$ in HCl[24] and its concentration in hydrocarbons is likewise known to be low. This system is certainly heterogeneous and if reaction occurs in different phases it might affect the selectivity parameter. Similarly CF_3SO_3H–MX_n systems may rate highly but the prolonged stability of CF_3SO_3H is uncertain. In particular, during isomerization with TaF_5–CF_3SO_3H a number of low molecular weight and unidentified products were produced and conclusions on these systems are tentative.

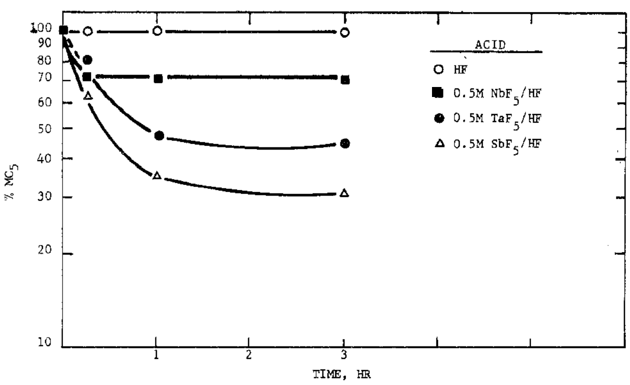


Figure 2. *I/E* and long-lived ions go together.

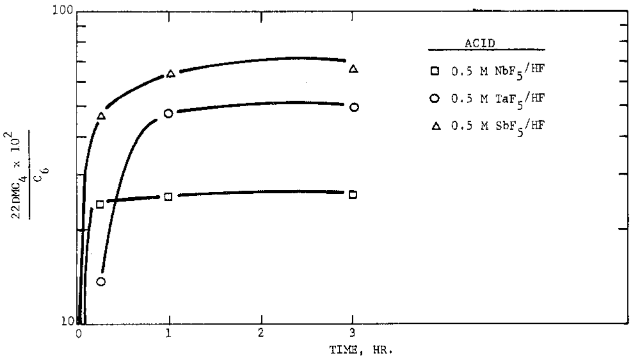


Figure 3. Equilibrium 2,2-DMC_4 not obtained with NbF_5–HF.

Another concern is that cracking reactions occurred to varying degrees with $AlBr_3$–HBr, $AlCl_3$–HCl, SbF_5–HF, TaF_5–HF, and NbF_5–HF during the reactions of isopentane and 3-methylpentane. Cracking was severely reduced in later work with methylcyclopentane, and the trends established with isopentane have been generally repeated but full comparisons are not yet available.

In spite of these problems an indication that the selectivity parameter provides more than a qualitative comparison of the acids may be obtained by examining the apparent catalyst life of the 0.5 *M* solutions of SbF_5, TaF_5, and NbF_5 in HF (see Figure 2). These acids had selectivity parameters of 2.6, 1.4, and 0.5 and both the SbF_5 and TaF_5 solutions had sufficient catalyst life to allow isomerization to approach equilibrium. (With SbF_5 the product distribution is slightly distorted because of cracking which tends to selectively remove the reactive components leaving an excess of 2,2-dimethylbutane and *n*-hexane.)

Of more significance, however, is the observation that in the NbF_5 solution, rapid initial isomerization was followed by nearly immediate cessation, the reaction stopping with 25% 2,2-dimethylbutane in the product whereas about 50% should be present at equilibrium. In HF alone, there is essentially no formation of 2,2-dimethylbutane under comparable conditions; see Figure 3.

These results may be taken to mean that following solvolysis of the initiator, *t*-C_4H_9Cl, one generates an alkyl ion with increasing stability in the acids: HF < NbF_5–HF < (TaF_5–HF, SbF_5–HF). In HF, perhaps because its acidity is lower than the other acids, the initial butyl ion concentration appears to be immediately lowered and whatever C_6 ions form do not have sufficient "freedom" or reactivity to undergo the skeletal rearrangement to a 2,2-dimethylbutyl ion. In NbF_5–HF, the C_6 ions first formed do undergo this rearrangement, but a side reaction which evidently destroys the active isomerizing intermediate must occur simultaneously because of the severe change. In TaF_5–HF and SbF_5–HF the stability of the intermediates is evidently prolonged because of the relatively smoother and continual isomerization to equilibrium which is found.

Thus, there is a clear distinction between Lewis acids in HF which have a high selectivity parameter and allow isomerization to 2,2-dimethylbutane and those with low values where the catalyst becomes deactivated. If the comparison can legitimately be made between different acids, HF, HSO_3F, CF_3SO_3H, HCl, and HBr, the selectivity parameter may provide the first consistent scale for a quantitative comparison between the strong acids. As such, it should complement acidity function studies (H_0) currently being carried out in these and other laboratories on the strong acid systems. At this time the ordering in Tables VI and VII is unique in providing the first comparison of $AlBr_3$–HBr, $AlCl_3$–HCl, the older strong acid systems, and a variety of other acids which are of current interest as "superacids," "magic" acids, and generally strong acid media.

Registry No.—$AlBr_3$, 7727-15-3; HBr, 10035-10-6; $AlCl_3$, 7446-70-0; HCl, 7647-01-0; HF, 7664-39-3; SbF_5, 7783-70-2; TaF_5, 7783-71-3; NbF_5, 7783-68-8; HSO_3F, 7789-21-1; CF_3SO_3H, 1493-13-6; isopentane, 78-78-4; methylcyclopentane, 96-37-7.

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Ranking Strong Acids *via* the Selectivity Parameter. II

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Selectivity parameter measurements of 2 *M* mixtures of Lewis acids in Brønsted acids are reported. Overlapping comparisons of inorganic bromides and fluorides in HBr rank the acids as $AlBr_3 > GaBr_3 > TaF_5 > BBr_3 > BF_3$, TiF_4, HfF_4. Lewis acids are found to exhibit their acidity more easily in HF than in HBr. Two scales, $(I/E)_{i\text{-}C_5}$ and $(I/E)_{MCP}$, are found to correlate with one another. They also relate to H_0 measurements within a given Brønsted acid but H_0 values with different Brønsted acids do not permit an estimate of the ion stabilizing properties of the system.

It has recently been proposed that strong acids can be characterized by their ability to stabilize carbonium ions.[1] The ratio of two reactions of methylpentanes, namely the rate of isomerization to 2,2-dimethylbutane and *n*-hexane divided by the rate of exchange of protons with isopentane or methylcyclopentane, is defined as the selectivity parameter, $(I/E)_{i\text{-}C_5}$ or $(I/E)_{MCP}$, which measures the ion stabilizing capacity of the acid.

The I/E ratio is an empirical kinetic parameter offering insight into the overall or inherent ability of an acid to permit the rearrangement of ions with a minimum of proton transfer from the ion or a protonated alkylcyclopropane intermediate to the acid. It does not measure the position of an ion $\rightleftharpoons$ olefin + H^+ or H^+–R-cyclopropane $\rightleftharpoons$ H^+ + R-cyclopropane equilibrium, but one would expect that these shift increasingly to the left as I/E increases.

The initial work provided I/E values for $AlBr_3$–HBr, $AlCl_3$–HCl, and SbF_5, TaF_5, and NbF_5 in HF, CF_3SO_3H, and HSO_3F. Although this permits an immediate ranking of the acid systems with respect to ion stability it is not clear if it provides a real comparison of the acid strength of the Lewis acids since different Brønsted acids were used as solvents. Thus, while $AlBr_3$–HBr has a larger I/E than SbF_5–HF or SbF_5–HSO_3F, one may ask if this reflects the fact that $AlBr_3$ is a stronger acid than SbF_5 or if HBr is a less nucleophilic solvent which provides a better medium than HF or HSO_3F. One means of answering this is to determine I/E with the same Lewis acids in both HBr and HF or other solvents. Thus, one of the objectives of the current work was to obtain overlapping comparisons of the selectivity parameter and hence the relative strength of Lewis acids in HBr and HF. Another objective was to evaluate a wider range of systems than previously studied and a third objective was to compare the $(I/E)_{i\text{-}C_5}$ and $(I/E)_{MCP}$ scales more closely. Finally, it was hoped that the I/E scales could be related to H_0 (Hammett acidity function) measurements which should provide a measure of proton activity where such data are available.