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.

References and Notes

(1) R. J. Gillespie and T. E. Peel, *Advan. Phys. Org. Chem.*, **9**, 1 (1971).
(2) R. J. Gillespie and T. E. Peel, *J. Amer. Chem. Soc.*, **93**, 5083 (1971).
(3) R. J. Gillespie and T. E. Peel, *J. Amer. Chem. Soc.*, **95**, 5173 (1973).
(4) F. E. Condon, *Catalysis*, **6** (2), 43 (1958), an excellent review.
(5) R. L. Burwell and G. S. Gordon, III, *J. Amer. Chem. Soc.*, **70**, 3128 (1948).
(6) R. L. Burwell, Jr., R. B. Scott, L. G. Maury, and A. S. Hussey, *J. Amer. Chem. Soc.*, **76**, 5822 (1954).
(7) R. L. Burwell, Jr., L. G. Maury, and R. B. Scott, *J. Amer. Chem. Soc.*, **76**, 5828 (1954).
(8) G. S. Gordon, III, and R. L. Burwell, *J. Amer. Chem. Soc.*, **71**, 2355 (1949).
(9) C. K. Ingold, C. G. Raisin, and C. L. Wilson, *J. Amer. Chem. Soc.*, **58**, 1643 (1936).
(10) J. W. Otvos, D. P. Stevenson, C. D. Wagner, and A. Beeck, *J. Amer. Chem. Soc.*, **73**, 5741 (1951).
(11) V. N. Setkina, D. N. Kursanov, O. D. Sterligov, and A. L. Liberman, *Dokl. Akad. Nauk SSSR*, **85**, 1045 (1952).
(12) D. R. Stevenson, C. D. Wagner, O. Beeck, and J. W. Otvos, *J. Amer. Chem. Soc.*, **74**, 3269 (1952).
(13) J. E. Hofmann, *J. Org. Chem.*, **29**, 3039 (1964).
(14) D. M. Brouwer and J. M. Oelderik, *Amer. Chem. Soc. Div. Petrol. Chem., Prepr.*, **13**, 184 (1968).
(15) B. L. Evering and R. C. Waugh, *Ind. Eng. Chem.*, **43**, 1820 (1951).
(16) J. E. Hofmann and A. Schriesheim, *J. Amer. Chem. Soc.*, **84**, 953 (1962).
(17) J. E. Hofmann and A. Schriesheim, *J. Amer. Chem. Soc.*, **84**, 957 (1962).
(18) G. M. Kramer, unpublished results. The Hammett acidity of 0.5 *M* TaF_5–HF (saturated) is −13.5 ± 0.5. NbF_5–HF is similar while 0.5 *M* SbF_5–HF is about −15 ± 0.5 as reported from conductivity data.[19,20]
(19) H. H. Hyman, L. A. Quarterman, M. Kilpatrick, and J. J. Katz, *J. Phys. Chem.*, **65**, 123 (1961).
(20) H. H. Hyman and J. J. Katz in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press, New York, N.Y., 1965.
(21) H. C. Brown and M. Borkorski, *J. Amer. Chem. Soc.*, **74**, 1894 (1952).
(22) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Amer. Chem. Soc.*, **73**, 212 (1951).
(23) J. D. Roberts and V. G. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951).
(24) Unpublished results of H. Solomon and G. M. Kramer. Hydrogen chloride was liquefied at ambient conditions in a Jerguson gauge containing several grams of $AlCl_3$. No visible change in the $AlCl_3$ occurred. The gauge was equipped with a magnetically driven stirrer from an Autoclave Engineers 300-ml Autoclave and surrounded by an oil bath which could be heated. The system could be observed to undergo critical opalescence at about the critical point of pure HCl, 51°, indicating that little $AlCl_3$ is in solution.
(25) G. M. Kramer, *J. Amer. Chem. Soc.*, **92**, 4344 (1970).

Ranking Strong Acids *via* the Selectivity Parameter. II

G. M. Kramer

Exxon Research and Engineering Company, Linden, New Jersey 07036

Received May 16, 1974

Selectivity parameter measurements of 2 *M* mixtures of Lewis acids in Brϕnsted 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 Brϕnsted acid but H_0 values with different Brϕnsted 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 Brϕnsted 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.

Table I
Selectivity Parameter in 2 *M* Acid Mixtures

Acid	$C_5 + 3\text{-}MC_5^*$				$MCP + 3\text{-}MC_5^*$			
	k_{iso}, hr^{-1}	k_{ex}, hr^{-1}	I/E	$(k_{iso})_A$, hr^{-1}	k_{iso}, hr^{-1}	k_{ex}, hr^{-1}	I/E	$(k_{iso})_A$, hr^{-1}
				Solvent: HBr				
$AlBr_3$	$\gg 0.6$	0.02	>35	vf	>2.46	0.65	>3.8	vf
$GaBr_3$	>2.7	1.05	>2.6	>3	0.39	0.44	0.9	>4
TaF_5	0.028	0.16	0.17	~ 3.7	0.024^a	0.21	0.11^a	1.9
BBr_3	0	?	0	0.26	0.0015^a	0.31	0.005^a	0.12
TiF_4					0	0.32	0	0
BF_3					0	0.16	0	0
HfF_4					0	0.06	0	0
				Solvent: HF				
TaF_5	0.58	0.07	8.29	vf	0.72	0.34	2.1	vf
					0.55	0.20	2.8	vf
SbF_5	2.42	0.69	3.5	vf	>2.84	1.89	>1.50	vf
					>2.59	1.75	>1.48	vf
BF_3	>5.50	>4.24	1.30	vf	(0.004)	0.35	0.01	2.1
					0.026^a		0.07^a	
TiF_4	$>0.035^a$	0.96	0.036^a	>2.8	0.001^a	0.49	0.002^a	0.08
HfF_4	0.035^a	2.76	0.013^a	2.8	0.0006^a	0.69	0.0009^a	0.05
				Solvent: HCl				
$GaCl_3$					1.39	0.25	5.6	>5.2
$AlCl_3$			8 (est)		0.47	0.32	1.5	
BCl_3					0	0.16	0	0

[a] Estimated by assuming $k_{iso} = \frac{1}{80}(k_{iso})_A$, as reported in $AlCl_3$–HCl at 100° (B. L. Evering and R. C. Waugh, *Ind. Eng. Chem.*, 43, 1820 (1951)). vf, very fast.

Experimental Section

The experimental conditions were slightly different from those previously reported.[1] The current reactions were carried out in 10- or 45-ml Hastelloy C reactors with about 1:3 hydrocarbon to acid volume ratios. Two molar mixtures or solutions of Lewis acids in hydrogen halides were prepared on the assumption of ideal behavior of the components. Sufficient hydrogen halide was used to ensure the presence of a liquid HX phase in all experiments. As before, a 0.12 *M* solution of *tert*-butyl chloride in the hydrocarbon was used to initiate the reactions.

Commercially available BCl_3, BBr_3, BF_3, TiF_4, HfF_4, $GaCl_3$, and $GaBr_3$ without further purification as well as the TaF_5 and SbF_5 previously employed were used in this work. Selectivity parameters were obtained in HBr, HF, and HCl. Most of the reactions were run with both isopentane and methylcyclopentane.

Results

A composite of the selectivity parameters obtained in 2 *M* solutions or mixtures of Lewis acids in HBr, HF, and HCl in this and prior work is reported in Table I. The table lists k_{iso}, the rate constant for the conversion of an equilibrium mixture of 2-MC_5, 3-MC_5 and 2,3-DMC_4 to 2,2-DMC_4 and *n*-C_6; k_{ex}, the constant for proton exchange between the tritium labeled C_6 reactants and unlabeled *i*-C_5 or MCP; I/E which is k_{iso}/k_{ex}; and $(k_{iso})_A$, the rate constant for the conversion of 3-MC_5 to 2-MC_5.

Because of the range of activity of the systems studied, all of these parameters have been utilized in ranking and characterizing the acids.

Discussion

(A) Relative Strength of Lewis Acids. In HBr. The relative strengths of many strong Lewis acids are unknown although various orders have been proposed. A good review of the extent and limitations of acidity estimtes is provided by Satchell and Satchell[2] and a summary of information on the metal fluorides has been made by Haartz and McDaniel.[3] The I/E scale may permit a more extensive comparison but until now has not allowed a direct comparison of fluorides with other halides because of differences in the solvent.

To avoid this problem, HBr was chosen as the common solvent for investigating a series of metal bromides and fluorides. HBr was picked because thermodynamic considerations suggested that metal fluorides would be stable and not undergo fluoride–bromide exchange. This is primarily because metal–fluoride bonds are stronger than metal–bromide bonds. Metal chlorides were not studied in HBr because in many instances they are known to rapidly exchange. It should be noted that HF could not be used as a common solvent for the bromides because of the immediate formation of metal fluorides.

The Lewis acids studied include $GaBr_3$, BBr_3, TaF_5, HfF_4, BF_3, and TiF_4 in addition to $AlBr_3$ which was investigated earlier. Experiments were also attempted with SbF_5 but mixing was extremely poor owing to its apparent insolubility in HBr and its high viscosity, so that no meaningful results were obtained. The solubility of the Lewis acids in HBr was not determined so that the I/E characterization of the formal 2 *M* "solutions" is very possibly that of saturated solutions in the majority of cases. Solubility determinations would be extremely valuable but would require considerably different equipment than was available for this work. In any case, the systems reported were all well mixed.

The relative acidity of the Lewis acids in HBr lies in the order $AlBr_3 > GaBr_3 > TaF_5 > BBr_3 > (TiF_4, BF_3, HfF_4)$. This order is deduced by sequentially using the data in Table I as criteria. First, we use the $(I/E)_{MCP}$ and $(I/E)_{i\text{-}C_5}$ ratios. Next we utilize k_{iso} which is the rate constant of the slowest rearrangement, and then we turn to $(k_{iso})_A$, the rate constant for the facile isomerization of 3-MC_5 to 2-MC_5.

This clearly orders the acids from $AlBr_3$ to TiF_4. The error in determining any of the rate constants increases with the rapidity of reaction and is estimated at less than ±10% where k is between 2 and 0.05 hr^{-1}. It becomes very

Table II
Ion Stability Is Proportional to Acid Strength in HBr

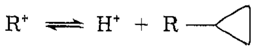
	$(k_{iso})_{MCP}$	Rel $[R^+]$	k_{ex}	$[Ex/R^+]_{norm}$
$AlBr_3$	>2.46	1	0.65	1
$GaBr_3$	0.39	0.16	0.44	4.2
TaF_5	0.024	0.010	0.21	32.0
BBr_3	0.0015	0.0006	0.31	794.0

large with faster reactions and little quantitative significance should be placed on such values. In considering the $AlBr_3$ data in i-C_5, the k_{iso} value is certain to be much larger than 0.6 and $(I/E)_{i\text{-}C_5}$ much larger than 35, the problem being that the shortest interval used to estimate the kinetics was twice as long as in the other experiments and the conversion too high to permit a more useful determination. The $AlBr_3$ data in MCP offer a much better idea of its acidity relative to the other acids.

The isomerization rate constants should reflect the steady-state ion concentrations developed in the MX_n–HB_r solutions:

$$R^+ \rightleftharpoons H^+ + R^= \quad (1)$$

or


(2)

$$HBr + MX_n \overset{K_1}{\rightleftharpoons} \underbrace{H^+{\cdot}MX_nBr^-}_{B} \overset{K_2}{\rightleftharpoons} \underbrace{H^+||MX_nBr^-}_{C} \quad (3)$$

The ions should be in equilibrium with olefins or alkylcyclopropanes with the proton activity being governed by the equilibria of eq 3. Presumably, the solvated proton may exist in either a tight ion pair, B, or solvent separated ion pair, C, no distinction being made in this work. The concentration of *B and C* ought to measure the Brønsted acidity of HBr–MX_n but since K_2 may be a function of the anion as well as of the solvent, and B and C may react at different rates, it seems unwarranted to take the relative isomerization rates as more than a qualitative indication of acidity. Nevertheless, it is interesting to analyze the isomerization and exchange data to search for inherent changes in ion stability with acid strength. This may be done by assuming the isomerization rates are proportional to the total ion concentration in HBr and normalizing the data in Table I, to obtain the relative concentration of ions formed with the various Lewis acids. From these values and the measured exchange rates the relative rates of exchange or deprotonation per ion can be calculated. These values are given in the last column of Table II and when they are compared with the ion concentrations in column 3 it is clear that ion stability is proportional to the total ion concentration or the acid strength.

The ordering of TiF_4, BF_3, and HfF_4 is less certain than the other Lewis acids in HBr. One might attempt to place these in accord with the decreasing exchange rate but as acidity decreases one expects two opposing factors to become important. These are that the ion concentration should decrease as acidity drops, suggesting a lower exchange rate, but the basicity of the medium simultaneously increases and this should augment the exchange. It is difficult to decide which is most significant and hence ordering solely on the HBr exchange data is unreliable.

(B) Relative Strength in HF. Consideration of the HF solutions enables one to order the metal fluorides. Again, some of the mixtures are heterogeneous while others may be homogeneous. The 2 *M* mixture of TaF_5 far exceeds its solubility which is *ca.* 0.5 *M* but the 2 *M* SbF_5 solution should be homogeneous. As noted previously, the presence of excess TaF_5 led to a reversal of the ion stabilizing capability of SbF_5 and TaF_5 which was deduced from *I/E* values on more dilute and fully homogeneous solutions. The list which follows is thus subject to limitations imposed by the presence of more than one phase and the selectivity parameter is subject to the unknown influence of the excess Lewis acid.

Table III
Apparent Acidity Deduced from Ion Stabilizing Ability of Lewis Acids in HBr and HE[a]

HBr	$(I/E)_{MCP}$	HF	$(I/E)_{MCP}$
$AlBr_3$	>3.8		
$GaBr_3$	0.9		
TaF_5	0.11	TaF_5	2.1–2.8
BBr_3	0.0005	SbF_5	>1.5?
$\left\{\begin{matrix}BF_3\\TiF_4\\HfF_4\end{matrix}\right\}$		BF_3	(0.01–0.07)
		TiF_4	0.002
		HfF_4	0.0009

[a] 2 *M* mixtures or solutions.

The ion stabilizing ability of the metal fluorides decreases in the series TaF_5, SbF_5? > BF_3 > TiF_4 > HfF_4. The list is again gleaned primarily from the $(I/E)_{MCP}$ and $(I/E)_{i\text{-}C_5}$ ratings of the acids. If the HF data in Table I are probed as was done with HBr to relate isomerization activity to the rate of exchange per ion one finds that the exchange is again inversely proportional to the ion concentration. The relative ion stability in HF–TaF_5 as opposed to HF–SbF_5 is uncertain and changes between the isopentane and methylcyclopentane systems, but carbonium ions appear to be much more stabilized in these solutions than in BF_3, TiF_4, or HfF_4–HF.

Since SbF_5 leads to a much more active isomerization catalyst than TaF_5 the data raise the question of why the ion stability in TaF_5–HF appears as high as it does. This might be because *I/E* is artificially high due to the unsuspected trapping of intermediates by the excess solid which could otherwise enter exchange reactions or alternatively because *I/E* in SbF_5–HF is too low. This could be caused by a rapid proton displacement reaction on the paraffins but it is difficult to assess this possibility at this time.

The BF_3–HF system appears to be substantially weaker than TaF_5–HF. In the experiments with isopentane, isomerization and exchange both appeared to proceed at very high rates. However, the apparent isomerization is very likely due to the occurrence of fast polymerization and cracking reactions of C_6 ions and C_6 olefins rather than to a unimolecular ionic rearrangement. The polymerization–cracking or disproportionation reactions are known to occur in this acid.[4] Their existence is indicated by the fact that large amounts of isobutane were formed along with the isomeric hexanes.

The relatively acidity of HF–BF_3 is better assessed from $(I/E)_{MCP}$ and the isomerization rate in this system. $(I/E)_{MCP}$ is very low and k_{iso} is about two orders of magnitude lower than TaF_5–HF. The BF_3–HF system provides an example of earlier predictions, namely, that low values of the selectivity parameter would be conducive to destabilization of ions, formation of olefins or alkylcyclopropanes, and subsequent coupling of these products with carbonium ions. The apparent acidities of the Lewis acids in HBr and HF as deduced from $(I/E)_{MCP}$ are shown in Table III.

TaF_5 offers the most important overlap between *I/E* determinations in HBr and HF. The general behavior of these systems is also shown by a comparison of the $(k_{iso})_A$ data in Table I of BF_3, TiF_4, and HfF_4 in HF and HBr.

Table IV
Some Physical Properties of the Liquid Hydrogen Halides

Property	HCl	Ref	HBr	Ref	HF	Ref
Mp, °C	−114.25	*a*	−86.92	*a*	−89.37	*g*
Bp, °C	−85.09	*a*	−66.78	*a*	19.51	*h*
Entropy of vaporization, eu	20.5	*a*	20.4	*a, d*	6.117	*g*
Dielectric constant	14.3 at 158.9°K 11.3 at 188.1°K	*b*	7.33 at 187.1°K	*e*	175 at 200°K 134 at 231°K 111 at 246°K	*i*
Specific conductance, ohm^{-1} cm^{-1}	3.5 × 10^{-9} at −85°C	*c*	1.4 × 10^{-10} at −83.6°C	*f*	1.4 × 10^{-5} at −15°C	*j*

[a] W. F. Giaugue and R. Wiebe, *J. Amer. Chem. Soc.*, **50**, 101 (1928). [b] R. W. Swenson and R. H. Cole, *J. Chem. Phys.*, **22**, 284 (1954). [c] G. Glocker and R. E. Peck, *J. Chem. Phys.*, **4**, 658 (1936). [d] J. R. Bates, J. O. Halford, and L. C. Anderson, *J. Chem. Phys.*, **3**, 531 (1935). [e] N. L. Brown and R. H. Cole, *J. Chem. Phys.*, **21**, 1920 (1953). [f] M. E. Peach and T. C. Waddington, *J. Chem. Chem. Soc.*, 2702 (1963). [g] J. H. Hu, D. White, and H. L. Johnston, *J. Amer. Chem. Soc.*, **75**, 1232 (1953). [h] R. L. Jarry and W. J. Davis, *J. Phys. Chem.*, **57**, 600 (1953). [i] K. Fredenhagen and J. Dahmlos, *Z. Anorg. Chem.*, **178**, 272 (1929). [j] K. Fredenhagen and G. Cadenbach, *Z. Anorg. Chem.*, **178**, 289 (1929).

The isomerization activity of TaF_5 is markedly lower in HBr than in HF. Thus, $(k_{iso})_{i\text{-}C_5}$ is 0.028 hr^{-1} in HBr and 0.58 hr^{-1} in HF. Similarly, $(k_{iso})_{MCP}$ is 0.024 hr^{-1} in HBr and (0.55–0.72) hr^{-1} in HF. This behavior suggests that it is more difficult for a Lewis acid to function as an acid in HBr than in HF. One reason might be that HBr is more acidic and less nucleophilic than HF, thus rendering it more of a discriminating solvent than HF. Another and perhaps more important factor is that there is a large difference in solvation properties of liquid HBr and HF primarily because of differences in the dielectric constant. Table IV contains some of the physical properties of the liquid hydrogen halides.

The order of magnitude difference in the dielectric constant would be expected to facilitate the separation of ion pairs in HF whereas dissociation in HBr is highly unlikely except within polar cavities that might exist like micelles in solution. Thus, the apparent loss of acidity in HBr may be related to differences in degree of dissociation due to the bulk solvent properties.

The solvent properties of liquid HBr are similar to those of liquid HCl. In view of this and even though we have no direct comparison of Lewis acids in HBr and HCl it seems reasonable to compare the *I/E* values within these acids directly. On this basis we conclude that $GaCl_3$–HCl, $(I/E)_{MCP}$ = 5.6, is an exceptionally strong acid system.

The *I/E* values also indicate that BBr_3–HBr is more acidic than BCl_3–HCl or BF_3–HBr from which we infer the Lewis acidity of BBr_3 is greater than BCl_3 or BF_3, but the relative strengths of the latter are uncertain. The results are consistent with other qualitative estimates of the acidity of the boron halides.[5]

(C) $(I/E)_{i\text{-}C_5}$ and $(I/E)_{MCP}$ Rank Acid Systems. It has already been observed that the exchange rates are a product of competing factors, changing concentration, and changing reactivity, and thus are not simply related to acid strength. Nevertheless, there are some important points to be learned from the changes in both the isomerization and exchange rates found in *i*-C_5 and MCP.

With the stronger acids, $AlBr_3$–HBr, TaF_5–HBr, TaF_5–HF, and SbF_5–HF one generally finds an increase in $(k_{ex})_{MCP}$ *vs.* $(k_{ex})_{i\text{-}C_5}$. One also finds equivalent or slightly accelerated isomerization rates, $(k_{iso})_{MCP} \geq (k_{iso})_{i\text{-}C_5}$. This behavior had previously been found with SbF_5–HSO_3F and TaF_5–HSO_3F,[1] and had been explained by assuming that reaction with methylcyclopentane leads to the formation of a higher concentration of ions than is obtained with isopentane. The cations are assumed to be intermediates in isomerization and hence a high rate is found in spite of the fact forming a high salt concentration necessarily lowers the acidity. The effect of the latter should be to accelerate the exchange.

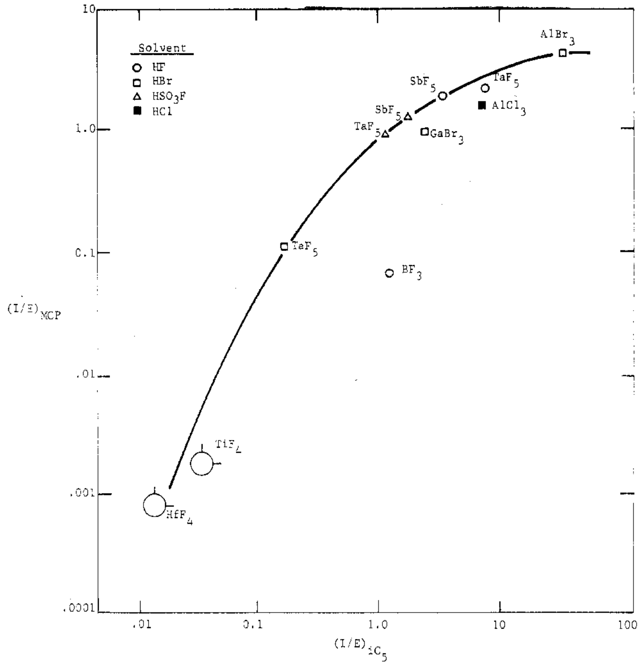


Figure 1. Correlation between the selectivity parameter in MCP and *i*-C_5.

These effects are found with the stronger acids. In the weaker acids, BF_3–HF, TiF_4–HF, and HfF_4–HF, the major effect of using MCP is to lower both the isomerization and exchange rates, the isomerization rate being most depressed. This implies that although these acids are strong enough to support the relatively stable MCP^+ ion, they are too weak for less stable tertiary alkyl cations. The observations are consistent with the view that the rate-determining step shifts from ion formation *via* hydride transfer to ionic rearrangement processes as acidity increases.

The $(I/E)_{i\text{-}C_5}$ and $(I/E)_{MCP}$ values are compared in Figure 1 where the logarithms of the ratios obtained in HBr, HF, HCl, and HSO_3F solutions are plotted against one another. The nonlinearity of the graph indicates that although some relationship exists it is not a simple free-energy relationship. This is not surprising since the change from isopentane to methylclopentane has already been surmized to change a number of factors. More important is that the graph indicates that I/E in any acid may be compared with I/E in any other acid as an index of the relative strength and ion stabilizing capacity of the system. In other words, the graph supports the proposal that I/E be used to rank acid systems.

***I/E* and H_0: A Limited Correlation.** How do acidity scales determined by H_0 compare with the ranking of the same acids *via* the selectivity parameter? In Table V and Figure 2 comparative data for homogeneous HF, HSO_3F, and CF_3SO_3H systems are shown. It would obviously be desirable to have a more extensive set of data to better establish the relationships but it seems clear that I/E is a complex function of H_0 and the specific acid medium. Conversely, H_0 is also not a unique function of I/E.

Table V

	$-H_0$[a]	$(I/E)_{i\text{-}C_5}$
HF	11.2–11.7	0
2 *M* SbF_5–HF	15.3	3.5
2 *M* TaF_5–HF, sat.	13.5	8.29
HSO_3F	14.5–15	0.42
2 *M* SbF_5–HSO_3F	>18	1.80
2 *M* TaF_5–HSO_3F	16.7	1.16
CF_3SO_3H[c]	13	0
2 *M* SbF_5–CF_3SO_3H	>18	4.25
2 *M* TaF_5–CF_3SO_3H	16.5	1.03
2 *M* NbF_5–CF_3SO_3H		<0.58
0.5 *M* SbF_5–HF	15.1	2.60
0.5 *M* TaF_5–HF	13.5	1.35
0.5 *M* NbF_5–HF, sat	~13.5[b]	0.54

[a] H_0 values were determined using indicators proposed by R. J. Gillespie and T. E. Peel, *Advan. Phys. Org. Chem.*, **9**, 1 (1971); *J. Amer. Chem. Soc.*, **93**, 5083 (1971); **95**, 5173 (1973). [b] From conductivity: H. H. Hyman, L. A. Quarterman, M. Kilpatrick, and J. J. Katz, *J. Phys. Chem.*, **65**, 123 (1961). [c] The CF_3SO_3H used was an aged acid.

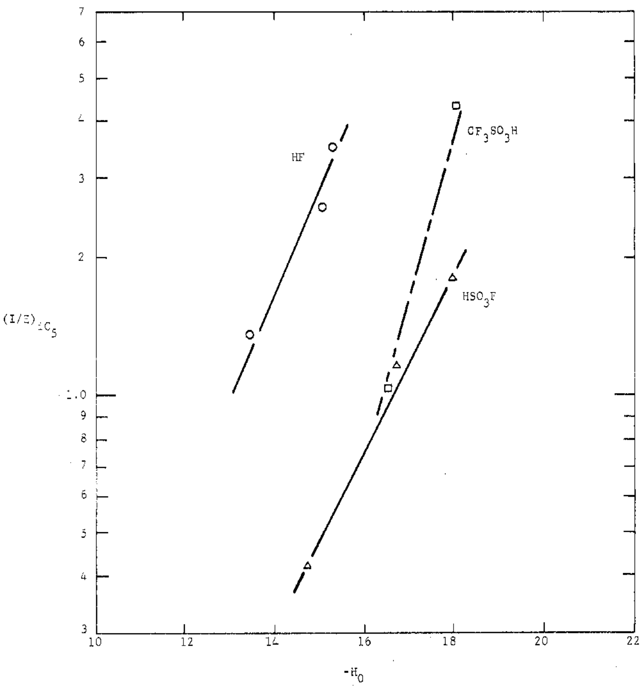


Figure 2. The selectivity parameter follows H_0 in a given acid.

Figure 2 suggests that in a given medium the selectivity parameter is linearly related to acidity measured by H_0 and hence a linear free-energy correlation exists. The main point, however, is that we now have an added scale to use in evaluating acidic systems. The two scales do not correlate in such a way as to permit measurements on one scale to uniquely define those on the other. This raises the immediate question of which scale is best suited for evaluating catalytic systems and which scale is best suited for evaluating acid strength. The apparent correlation of $(I/E)_{i\text{-}C_5}$ with $(I/E)_{MCP}$ described in the last section suggests that the I/E scales may provide a more consistent means of characterizing different acid systems than H_0, but they have the drawback of not being easily related to proton activity.

Table VI
Lewis Acidity Orders

Order	Method	Ref
$BF_3 > TaF_5 > NbF_5 > TiF_4 > PF_5 > SbF_3 > WF_6 >> SiF_4 \sim CrF_3$	Solvent extraction of $ArH^+MF_{n+1}^-$	6
$AsF_5 \sim BF_3 > PF_3 \sim WF_6 > NbF_5 \sim TaF_5 > SiF_4 \sim CrF_3$	Solubility of Lewis acid	7
$SbF_5 > AsF_5 > BF_3 > PF_5$	Decomposition of complex	8
$AsF_5 > PF_5 > BF_3$	Displacement reaction	9
$BF_3 = SbF_5 = AsF_5 = PF_5 > GeF_4 > TeF_6 > InF_5 > SeF_4$	Salt formation	10
$AsF_3 > BF_3 > SiF_4 > AsF_5 > PF_3$	F^- transfer from SF_6^-	11
$AsF_5 > PF_5 > BF_3 > SiF_4 > AsF_3 > SF_4, SF_5$	Ion cyclotron spectroscopy	3
$SbF_5 > TaF_5 > NbF_5; BF_3 > TiF_4 > HfF_4$	Selectivity parameter	1
$SbF_5 > TaF_5 \simeq NbF_5$	Conductivity	12
$SbF_5 \sim PF_5 > BF_3$	Solvolysis constants salt formation	13
$SbF_5 > AsF_5 = BF_3 > PF_5 = SnF_4 = ReF_6 = WF_6 = MoF_6 = VF_5 > IF_5 = TeF_6 = GeF_4 = TaF_5 = NbF_5 > SeF_4 = SiF_4 = TiF_4 > SbF_3 = AlF_3 = CrF_3 = BeF_2$	Solubility, salt formation	14

The relative acidities of metal fluorides determined in these studies may be compared with Lewis acidity orders from previous investigations. This is done in Table VI.

The data indicate a general agreement in the ranking to be deduced from a large variety of techniques. It is not our intention to review these studies but simply to indicate that the selectivity parameter is quite consistent with a large body of information.

Summary

Selectivity parameter measurements have been made on a series of 2 M mixtures of metal bromides and fluorides in HBr and HF. The Lewis acids have been ranked in the order $AlBr_3 > GaBr_3 > TaF_5 > BBr_3 > BF_3$, TiF_4, and HfF_4 in HBr and TaF_5 SbF_5? $> BF_3 > TiF_4 > HfF_4$ in HF. The order is based on the ability of the system to support isomerization relative to proton exchange. It is subject to the unknown effect of comparing homogeneous with heterogeneous systems, and the fact that the selectivity parameter for SbF_5 and TaF_5 in HF inverts as the concentration of the Lewis acid increases is an unresolved puzzle.

The Lewis acids tend to exhibit a higher selectivity parameter in HF than in HBr. This is attributed mainly to the enormous difference in dielectric constant and hence dissociative tendencies in the solvents. This overcomes the fact that HBr is more acidic than HF and therefore is a more discriminating rather than a leveling solvent.

The $(I/E)_{i\text{-}C_5}$ scale was found to be related to $(I/E)_{MCP}$, with measurements being compared in different Brφnsted acids. This suggests that these scales may provide a basis for comparing the acidity or at least the catalytic activity of Lewis acids in varied media like HBr, HF, and HSO_3F.

The I/E scale in any one acid appears to correlate with H_0 but since the correlation depends on the solvent one cannot use I/E to predict H_0 in an unknown solvent or, *vice versa,* one cannot use H_0 to infer the ion stabilizing properties of the acid.

Registry No.—HBr, 11035-10-6; $AlBr_3$, 7727-15-3; $GaBr_3$, 13450-88-9; TaF_5, 7783-71-3; BBr_3, 10294-33-4; TiF_4, 7783-63-3; BF_3, 7637-07-2; HfF_4, 13709-52-9; HF, 7664-39-3; SbF_5, 7783-70-2; HCl, 7647-01-0; $GaCl_3$, 13450-90-3; $AlCl_3$, 7446-70-0; BCl_3, 10294-34-5; HSO_3F, 7789-21-1; CF_3SO_3H; 1493-13-6; NbF_5, 7783-68-8.

References and Notes

(1) G. M. Kramer, *J. Org. Chem.*, preceding paper.
(2) D. P. N. Satchell and R. S. Satchell, *Chem. Rev.*, **69**, 251 (1969).
(3) J. C. Haartz and D. H. McDaniel, *J. Amer. Chem. Soc.*, **95**, 8562 (1973).
(4) A. V. Topchiev, S. V. Zargorodnii, and Ya. M. Paushkin, "Boron Fluoride and Its Compounds as Catalysts in Organic Chemistry," Pergamon Press, Elmsford, N.Y., 1959, p 310.
(5) M. E. Peach and T. C. Waddington in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press, New York, N.Y., 1965, p 83.
(6) (a) D. A. McCauley and A. P. Lien, *J. Amer. Chem. Soc.*, **73**, 2013 (1951); (b) D. A. McCauley, W. S. Higley, and A. P. Lien, *ibid.*, **78**, 3009 (1956).
(7) J. M. S. Henis and C. A. Mabie, *J. Chem. Phys.*, **53**, 2999 (1970).
(8) S. Brownstein, *Can. J. Chem.*, **47**, 605 (1969).
(9) J. D. McDonald, C. H. Williams, J. C. Thompson, and J. L. Margrave, *Advan. Chem. Ser.*, **No. 72**, 265 (1968).
(10) A. F. Clifford and A. G. Morris, *J. Inorg. Nucl. Chem.*, **5**, 71 (1957).
(11) T. C. Rhyne and J. G. Dillard, *Inorg. Chem.*, **10**, 730 (1971).
(12) H. H. Hyman, L. A. Quarterman, M. Kilpatrick, and J. J. Katz, *J. Phys. Chem.*, **65**, 123 (1961).
(13) A. F. Clifford and S. Kongpricha, *J. Inorg. Nucl. Chem.*, **20**, 147 (1961).
(14) A. F. Clifford, H. C. Beachell, and W. M. Jack, *J. Inorg. Nucl. Chem.*, **5**, 57 (1957).

Solvolysis in Dipolar Aprotic Media.[1] I. Production of Water-Extractable Bromide *vs.* Olefin Distribution in the Course of the Solvolysis of 2-Bromo-2-methylpentane in Dimethylformamide

Marc Anteunis*

Department of Organic Chemistry, State University of Gent, Gent B-9000, Belgium

Hendrik L. Peeters

Hoger Rijksinstituut voor Kernenergiebedrijven, Mol B-2400, Belgium

Received December 19, 1973

An investigation about the kinetics of the solvolysis of 2-bromo-2-methylpentane (1) in DMF was conducted using different titration procedures, following distributive extraction between CCl_4 and water, and gas chromatography. The reaction picture allowed division into distinct phases. The last of these is dominated by an autocatalytic second-order elimination with a notable Saytzeff character (94%) for which kinetic parameters could be estimated. The initial phase shows a remarkable instantaneous release of titrable bromide until a given level is reached; this is attributed largely to the formation of un-ionized species, probably ion pairs. Elimination in this phase has a less pronounced Saytzeff orientation (40–50% terminal olefin) and is thought to be mostly a secondary process, probably succeeding to the formation of a cationic intermediate $(RDMF)^+$ by solvent substitution. Radiobromide experiments showed a rapid incorporation of ^{82}Br into a CCl_4-extractable form, which was completely inhibited by growing C_{Br^-}, and a slower one which remained unaffected.

Solvolysis in aprotic media of alkyl halides and related compounds, carrying good leaving groups, has, on the whole, received only little attention. With a few exceptions, the scanty data available[2,3] have been obtained in view of an extension of solvent–reactivity correlations. In view of the well-established properties of DAS[4] (substantial ionizing power, high nucleophilicity and basicity, etc.) a more probing investigation was justified.

In 1957 Ross and Labes[3b] determined some first-order rate constants for the hydrogen halide production from t-BuCl, dimethylneopentylcarbinyl chloride, and t-BuBr in DMF (and N-methylpropionamide). Kornblum and Blackwood[3a] had already noted a halide ion production by several alkyl halides in DMF. Among these was t-BuBr, but also there were MeI and benzyl bromide, the latter two being unable to decompose by elimination. In neither study has an elucidation of the elimination or of the salt-forming mechanism been attempted.

In this paper the decomposition of 2-bromo-2-methylpentane (1) in dimethylformamide (DMF; ϵ_{25} 36.7) is described, as studied by (a) different distributive extraction procedures, using carbon tetrachloride and water, and (b) gas chromatography. Radiobromide incorporation has been followed under comparable conditions.