JOURNAL OF CATALYSIS **134**, 126–133 (1992)

Evaluation of Acidity of Strong Acid Catalysts

II. The Strength of Boron Trifluoride–Water Systems

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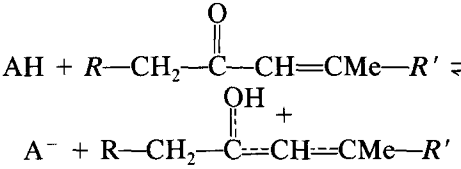
Received August 16, 1991

The method of determining a thermodynamic acidity function from the chemical shift changes of ^{13}C signals of unsaturated ketones at infinite dilution in the investigated acid established by the authors was applied to the system boron trifluoride–water (**III**) ranging from the monohydrate ($BF_3 \cdot H_2O$) to the trihydrate ($BF_3 \cdot 3H_2O$). The indicators used were mesityl oxide and 4-hexen-3-one. It was found that **III** is significantly stronger than indicated by earlier measurements conducted by the classical Hammett method based on UV-visible spectroscopy. The mixtures with about 1.25 mol of water per mol of BF_3 or less are stronger than pure sulfuric acid and are therefore superacidic. The stronger acidity of **III** can be understood because boron trifluoride is a much stronger Lewis acid than sulfur trioxide; therefore the complex with a hydroxyl anion of the former (hydroxytrifluoroborate anion) should have a lower affinity for a hydron than the corresponding complex of sulfuric anhydride (bisulfate anion). Preliminary experiments indicate that the ^{13}C NMR method can be applied successfully to working catalysts based on **III**, which are colored and contain dissolved organic materials.

INTRODUCTION

The preceding paper (*1*) has discussed the shortcomings and limitations of the methods currently used for the measurement of acidity of strong acid catalysts, liquid and solid. A new approach, applicable both for derivation of an acidity function and for comparison and ranking of protonating abilities of practical catalysts, has been introduced in the same work. It is based on the determination of changes in the ^{13}C chemical shifts of unsaturated ketones, such as mesityl oxide (**I**) upon partial protonation (*1*). An isomer of **I**, 4-hexene-3-one (**II**), behaves similarly, but requires an acid stronger by about two H_0 units than that needed by **I** for half-protonation (Eq. (1)) (*2*). Introduction of electron-donating and electron-attracting substituents, as well as other structural changes in **I** and **II** is bound to expand greatly the acidity range measurable with this type of indicator bases.



$$AH + R{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH{=}CMe{-}R' \rightleftharpoons A^- + R{-}CH_2{-}\overset{\overset{\displaystyle OH}{\|}}{C}{=}CH{=}CMe{-}R'^{\,+} \qquad (1)$$

I $R = H$, $R' = Me$
II $R = Me$, $R' = H$

We report here on the application of our method to the measurement of acidity of mixtures of boron trifluoride and water, $BF_3 \cdot xH_2O$ (**III**). Two stoichiometric compounds, the monohydrate ($x = 1$) and the dihydrate ($x = 2$), first described by Meerwein and Pannwitz (*3*), are known. Only the dihydrate can be distilled under vacuum with no (*3*) or very little (*4*) decomposition. One can obtain, however, solutions of varying concentrations of BF_3 in water, which are strong acids. Examples of reactions of practical importance for which use of **III** as

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0021-9517/92 $3.00

catalyst has been extensively reported are oligomerization of 1-alkenes for the manufacture of lubricating oils (*5*), alkylation of aromatics with alkenes (*6*), and carbonylation of carbocations derived from alkenes or alcohols to carboxylic acids (*7*). Applications of **III** to petroleum refining for removal of S, N, O, and unsaturated compounds (*8*), to conversion of alkenes to formamides by the Ritter reaction (*9*), and to reduction of naphthalenes to tetralins and of ketones to alkanes by hydride transfer from alkylsilanes (*10*) have also been disclosed.

We became particularly interested in boron fluoride hydrates for two reasons. First, in connection to our studies of alkylation of aromatics by alkenes with and without anion-stabilizing solvents (*11*), we examined **III** as a catalyst and wanted to correlate the decrease in activity during a run with the change in acidity. Traditional Hammett acidity measurements (*12*) were out of the question because the catalyst became black from the early stages of the reaction.

On the other hand, acidities determined by UV-visible spectroscopy with Hammett indicators had been reported for **III** (*12, 13*), but the protonation curves presented for the indicators studied were not always overlapping, and each indicator was useful over a rather narrow acidity range (*13*). Moreover, when one considers the reported H_0 values (*13*), the catalytic activity of **III** appears much higher than that of other acids. Thus, maximum yields of C_7 trialkylacetic acids in the Koch reaction with **III** as catalyst were obtained for $x = 2.5$ (*14*), which had been claimed (*13*) to be of the same strength as 66% sulfuric acid (*12*). Attempts at using sulfuric acid, however, of concentration below 90% as catalyst in the alkene carbonylation by the Koch reaction were unsuccessful or gave poor yields (*15*).

We decided, therefore, to examine the acid strength of BF_3–water mixtures by the ^{13}C NMR method (*1*).

EXPERIMENTAL

Materials. Commercial A.R. grade **I** and **II** were dried as indicated (*1*). Boron trifluoride dihydrate (**III**, $x = 2$) was a complimentary sample from BASF–Wyandotte. The monohydrate was obtained (*3, 4*) by bubbling BF_3 through the dihydrate in a Teflon FEP bottle at 0°C, until a copious amount of white fumes began escaping. Other compositions were obtained by mixing appropriate proportions of monohydrate with dihydrate or of the latter with water.

Chemical analysis of III (*16*). The acid (ca 0.25 ml) was added to $CaCl_2 \cdot 2H_2O$ (12 g) and distilled water (75 ml) in a 250-ml Erlenmeyer flask with ground joint, which was weighed stoppered before and after sample addition. Methyl orange solution (2–3 drops), 1-octanol (3–4 drops), and a magnetic stirring bar were added. The flask was fitted to a water-cooled wide-bore Liebig condenser and brought to boiling with vigorous stirring. The HCl liberated in solution was titrated with 1 *N* NaOH from a microburet (0.02 ml markings) through the condenser. When the color changed, boiling continued for 20 min, adding more NaOH if needed to reach the end point. The flask was stoppered and cooled to room temperature in a water bath. Mannitol (9 g) and phenolphthalein indicator solution were added and the solution was titrated with the same NaOH solution. For the analysis of the monohydrate, four samples (0.25 ml each) were added to preweighed glass vials with screw caps provided with Teflon-lined rubber septa, inside a dry box. The caps were secured tightly, the vials were taken out of the box, weighed, and placed over dry ice until the acid froze. Water (2 ml) was injected from a plastic syringe with a stainless-steel needle through the septum into each vial. The vials were then kept in an ice bath until the fumes cleared. Each sample was transferred quantitatively with distilled water to the 250-ml Erlenmeyer flask and analyzed as above. The monohydrate results were always low ($x = 1.03$ to 1.05), irrespective of the length of time that BF_3 gas bubbling was continued after fumes started to emerge during preparation. All these samples gave the same chemical shift values.

These samples were, therefore, taken as "monohydrate" ($x = 1$). We recognize the approximate nature of this assignment.

NMR analysis of F content in III. For a less accurate but quicker evaluation of samples of **III**, trifluoroacetic acid (0.3–0.75 ml) was weighed in a vial with Teflon-lined screw cap, then **III** (0.25–0.5 ml) was added and weighed as well. For best results, two samples, in which the ratios TFA/**III** were (1.5..2) : 1 and 1 : (1.5..2) were prepared. Dioxane (ca. 0.1 ml) was added and the vial was heated in a 60° bath until the content was homogeneous. The sample was transferred to an NMR tube and analyzed by ^{19}F NMR, integrating the signals for TFA and **III** (−76 and −149 ppm from $CFCl_3$, respectively).

Acidity determination by ^{13}C NMR was conducted as described before (*1*).

RESULTS AND DISCUSSION

The ^{13}C NMR spectra of **I** in solutions of **III** between the trihydrate ($x = 3$) and monohydrate were recorded at three concentrations for each acid (between 0.06 and 1.08 mol/liter **I**). The chemical shift for the carbonyl, C-2, and the olefinic carbons, C-3 and C-4, and the chemical shift differences $\Delta\delta$ between C-4 and C-3 (*1*) are presented in Table 1.

There are two ways in which one could compare acidities from data like those in Table 1. The first involves matching the $\Delta\delta$ values obtained at the same concentration of **I**, for example 0.50 *M*, which can be obtained by interpolation between the experimentally determined numbers. In this way we can match the strength of solution of **III** with sulfuric acid solutions (*1*) exhibiting the same $\Delta\delta$ (0.5 *M*) values. The more rigorous approach consists of extrapolating the $\Delta\delta$ vs concentration straight line to $c = 0$, to determine a quantity $\Delta\delta^0$, which can be used to derive a thermodynamic acidity function. Sulfuric acid, studied in Part I, is the reference against which the $\Delta\delta^0$ values are calibrated (*1*).

As discussed already, to determine the $\Delta\delta^0$ parameter, $\Delta\delta$ can be plotted either against the molar concentration of base or against the molar ratio of base to acid. The latter approach is preferred when intending to study protonation in the range of base to acid ratios close to stoichiometric (*1*). For the current investigation, however, the actual nature and molar quantities of acid species in solution is difficult to ascertain because hydrolysis of BF_3 occurs for systems with $x > 2$.

$$BF_3 + H_2O \rightleftharpoons HO\text{–}BF_2 + HF \quad (2)$$

$$HO\text{–}BF_2 + H_2O \rightleftharpoons F\text{–}B(OH)_2 + HF \quad (3)$$

$$F\text{–}B(OH)_2 + H_2O \rightleftharpoons B(OH)_3 + HF. \quad (4)$$

An early NMR study of **III** with $x > 3$ had evidenced three signals, which coalesced upon heating (*17*). We have confirmed these findings, and we also found that no boric acid was present in solution (^{11}B NMR) or precipitated from the trihydrate in the course of 2 months. Thus, the three ^{19}F signals correspond to **III** and the products of reactions (*2*) and (*3*), complexed with the HF formed in the same reactions (*17*). In fact, when we mixed the monohydrate (**III**, $x = 1$) with increasing quantities of 36% aqueous HF, no ^{19}F signal for free HF was observed until HF in excess over BF_3 was present, and no hydrolysis products were observed, even though the final mixture had a water to BF_3 ratio of at least 3.

We noted, however, that the number of moles of HF liberated in reactions (*2*)–(*4*) will normally not match the number of moles of boron-containing species; that is, the BF_3 and the hydroxyfluoroboranes will be only partially converted to fluoroboric and hydroxyfluoroboric acids. It follows, therefore, that the molar composition of the so-called **III** for $x > 2$ is ill-defined. For this reason, in the present work we obtained the $\Delta\delta^0$ values by correlating $\Delta\delta$ with the molar concentration of indicator.

A comparison of $\Delta\delta^0$ values for various compositions of **III** with the same parameter for sulfuric acid (*1*) allows us to compare the strength of the two acids and assign H_0

TABLE 1

^{13}C Chemical Shifts[a] of Mesityl Oxide (**I**) in $BF_3 \cdot xH_2O$

No.	x	Conc. **I**[b] mol/liter	Chemical shift				$\%H_2SO_4$ of equivalent strength (*1*)	H_0	
			C-2	C-3	C-4	(C-4)–(C-3)		[c]	[d]
1	3.05	1.01	210.44	122.51	183.72	61.21			
	±0.03	0.51	210.67	122.23	186.35	64.12			
		0.275	210.83	122.23	186.35	65.44			
		0.0				67.04[e]	64.3	−5.1	−4.42
						$s = -5.8$			
2	2.55	0.98	211.03	122.03	190.71	68.73			
	±0.11	0.55	211.06	121.93	192.45	70.52			
		0.081	211.03	121.81	194.14	72.33			
		0.0				72.69[e]	71.8	−6.2	−5.25
						$s = -4.1$			
3	2.08	1.02	211.09	121.80	195.40	73.60			
	±0.06	0.51	210.99	121.68	196.73	75.05			
		0.077	210.86	121.61	197.86	76.25			
		0.0				76.47[e]	76.7	−7.0	−6.59
						$s = -2.8$			
4	1.75	1.05	210.87	121.58	199.16	77.58			
	±0.03	0.53	210.70	121.48	200.29	78.81			
		0.060	210.57	121.42	201.13	79.71			
		0.0				79.88[e]	91.8	−9.3	−7.46
						$s = -2.2$			
5	1.43	1.05	210.67	121.45	201.78	80.33			
	±0.01	0.52	210.51	121.35	202.48	81.13			
		0.068	210.38	121.26	203.04	81.78			
		0.0				81.89[e]	—	ca. −12.5	−8.34
						$s = -1.5$			
6	1.38[f]	1.06	210.57	121.42	202.65	81.23			
		0.51	210.44	121.32	203.20	81.88			
		0.056	210.38	121.26	203.62	82.36			
		0.0				82.43[e]	—	ca. −14	−8.49
						$s = -1.1$			
7	1[g]	1.08	210.51	121.38	203.65	82.27			
		0.48	210.38	121.29	204.01	82.72			
		0.06	210.25	121.22	204.23	83.01			
		0.0				83.06[e]	—	<-14	−11.5
						$s = -0.73$			

[a] From external CDCl (77.00 ppm).

[b] Moles of total base (**I** + IH^+) per liter of solution.

[c] This work.

[d] Literature values (*13*).

[e] $\Delta\delta^0$ (See Ref. (*1*)).

[f] F analysis only.

[g] See Experimental.

values to **III** in Table 1. We find an acidity of **III** higher than concluded from UV-visible spectroscopic measurement with Hammett indicators. The H_0 parameter values for BF_3 hydrates with $x < 1.4$ are only estimates because these solutions are found by NMR to be stronger than 100% sulfuric acid.

The results of the study of protonation of the other indicator, 4-hexen-3-one (**II**) are presented in Table 2. The protonation shifts

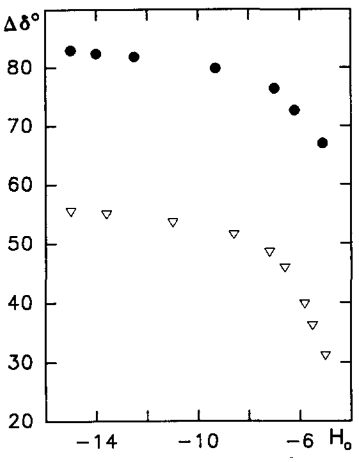

FIG. 1. Chemical shift differences between C-4 and C-3 of mesityl oxide (**II**, ●) and between C-5 and C-4 of 4-hexen-3-one (**III**, ▽) at infite dilution ($\Delta\delta^0$) as a function of acidity of $BF_3 \cdot xH_2O$.

for **II** were calibrated in sulfuric acid (*2*). The acidities deduced for **III** from the experiments with **II** (Table 2) are in agreement with the values deduced from the experiments with **I** (Table 1), and these values are again significantly higher than the literature values (*13*).

A correlation of $\Delta\delta^0$ determined for **I** and **II** with the acidity (H_0) of **III** is presented in Fig. 1. It is seen that **I** is well over 50% protonated in the weakest composition of **III** ($x = 3$). Nonetheless, the NMR method is quite sensitive, with $\Delta\delta^0$ (**I**) varying from about 67 for the trihydrate to 83 for the monohydrate. The observation of continuing variation rather than leveling off in the high acidity region is due to the onset of a second protonation of the carbonyl group (*18*). Figure 1 also suggests that the acid strength needed for half-protonation of **II** is higher than the strength of boron fluoride trihydrate (**III**, $x = 3$).

A test of the validity of the acidities obtained from chemical shift differences $\Delta\delta^0$ is offered by the slopes of the $\Delta\delta$ vs concentration plot (the *s* parameter), which was shown to vary with the acid strength, reaching a minimum (most negative) in the acid that half-protonates the indicator (*1*). The *s* values determined for the protonation of indicators **I** and **II** in the acid **III** are given in Tables 1 and 2, and they are compared with the *s* values obtained in sulfuric acid solutions for both **I** (*1*) and **II** (*2*) in Fig. 2 and 3, respectively. This comparison shows again that the weakest solution **III** studied ($x = 3$) is stronger than the acid that half-protonates ketone **I**. On the other hand, the more weakly basic ketone **II** is half-protonated in an acid **III** with x about 2.67; the H_0 value for this acid matches the strength of 70.1% sulfuric acid, which half-protonates ketone **II**. Thus, the parameter *s* substantiates the conclusions based on $\Delta\delta^0$ values about the acid strength of **III**.

The acidity function H_0 for **III** between $x = 3$ and $x = 1$ is plotted as a function of x in Fig. 4. The filled points in Fig. 4 represent values beyond the sulfuric acid range, and as such the H_0 values are considered mere estimates. Whatever the uncertainty of the actual numbers, a conservative estimate is that for $x = 1.25$ or less **III** is a superacid.

The higher acidity of **III** ($x = 1$) than that of H_2SO_4 can be rationalized. Ionization of the two acids gives the hydroxytrifluoroborate (**IV**) and bisulfate anion (**V**), respectively. The former is the Lewis acid–Lewis base complex of BF_3 and hydroxyl, the latter of the much weaker Lewis acid SO_3 and

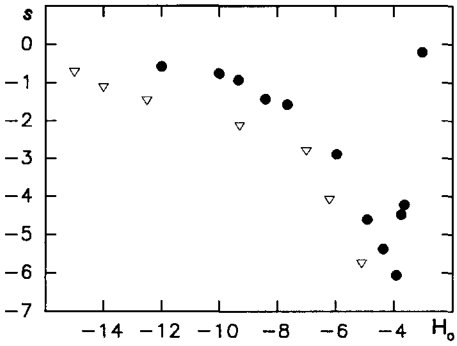

FIG. 2. Variation of slope, *s*, of the linear correlation $\Delta\delta$ vs total concentration (*1*) of mesityl oxide (**I**) with acidity of H_2SO_4 (●) and $BF_3 \cdot xH_2O$ (▽).

TABLE 2

^{13}Chemical Shifts[a] of 4-Hexen-3-one (**II**) in $BF_3 \cdot xH_2O$

No.	x	Conc. **II**[b] mol/liter	Chemical shift				$\%H_2SO_4$ of equivalent strength (*1*)	H_0
			C-3	C-4	C-5	(C-5)–(C-4)		
1	2.95	0.93	213.07	128.89	156.00	27.11		
	±0.03	0.49	213.91	128.63	157.55	28.92		
		0.156	214.55	128.37	158.78	30.41		
		0.0				31.09[c]	63.5	−5.0
						$s = -4.3$		
2	2.76	0.95	214.49	128.37	159.17	30.80		
	±0.03	0.49	215.39	127.98	161.17	33.19		
		0.172	216.17	127.72	162.92	35.20		
		0.0				36.15[c]	67.1	−5.5
						$s = -5.6$		
3	2.67	0.95	215.65	127.92	161.98	34.06		
	±0.07	0.50	216.56	127.57	164.22	36.65		
		0.170	217.27	127.27	166.03	38.76		
		0.0				39.74[c]	69.2	−5.8
						$s = -6.0$		
4	2.25	0.99	217.79	127.08	167.71	40.63		
	±0.06	0.51	218.50	126.75	169.97	43.22		
		0.161	218.95	126.56	171.53	44.97		
		0.0				45.84[c]	74.3	−6.6
						$s = -5.2$		
5	2.03	0.92	218.82	126.69	171.08	44.39		
	±0.06	0.48	219.28	126.43	172.88	46.45		
		0.181	219.54	126.30	173.92	47.62		
		0.0				48.47[c]	78.0	−7.2
						$s = -4.4$		
6	1.80	1.04	219.73	126.37	174.70	48.33		
	±0.06	0.51	220.05	126.17	176.12	49.95		
		0.165	220.18	126.04	176.96	50.92		
		0.0				51.43[c]	87.0	−8.6
						$s = -3.0$		
7	1.54	1.02	220.38	126.17	177.67	51.50		
	±0.06	0.53	220.51	126.04	178.58	52.54		
		0.143	220.57	125.98	179.16	53.18		
		0.0				53.49[c]	99.7	−11.0
						$s = -1.9$		
8	1.36	1.05	220.76	126.11	179.81	53.70		
	±0.04	0.51	220.83	125.98	180.33	54.35		
		0.181	220.83	125.91	180.58	54.67		
		0.0				54.89[c]	—	ca. −13.6
						$s = -1.1$		
9	1[d]	1.04	220.96	125.98	180.97	54.99		
		0.67	220.96	125.98	181.10	55.12		
		0.173	220.89	125.91	181.23	55.32		
		0.0				55.38[c]	—	<-14
						$s = -0.4$		

[a] From external $CDCl_3$ (77.00 ppm).

[b] Moles of total base (**I** + $\mathbf{IH}^+$) per liter of solution.

[c] $\Delta\delta^0$ (see Ref. (*1*)).

[d] See Experimental.

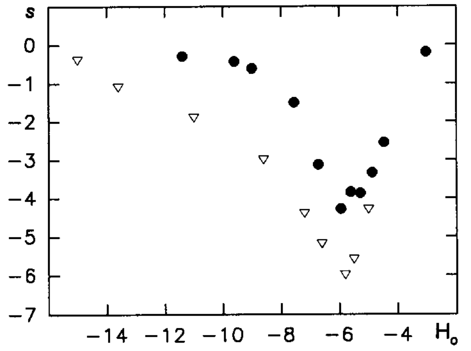

FIG. 3. Variation of slopes of the linear correlation Δδ vs total concentration (*1*) of 4-hexen-3-one (**II**) with acidity of H_2SO_4 (●) and $BF_3 \cdot xH_2O$ (▽).

hydroxyl. The complex of the stronger Lewis acid should have a lower tendency to accept a hydron from the counterion (Eq. (5)) than the complex of the weaker acid in Eq. (6), which means that Eq. (5) is displaced farther to the left than Eq. (6).

$$HO\text{-}BF_3^- + HB^+ \rightleftharpoons H_2O \cdot BF_3 + B \quad (5)$$

$$HO\text{-}SO_3^- + HB^+ \rightleftharpoons HO\text{-}SO_2\text{-}OH + B \quad (6)$$

CONCLUSIONS

The ^{13}C NMR spectroscopic method of acidity measurement (*1*) was applied sucessfully to the study of a practically important catalyst, the family of boron fluoride–water solutions (**III**) between the monohydrate and the trihydrate. It is found that **III** is significantly stronger than indicated by earlier measurements conducted by the classical Hammett method (*13*). The mixtures with about 1.25 mol of water per mol of BF_3 or less are superacidic. Preliminary experiments indicate that our method can be applied successfully to working catalysts based on **III**, which are colored and contain dissolved organic materials (*2*).

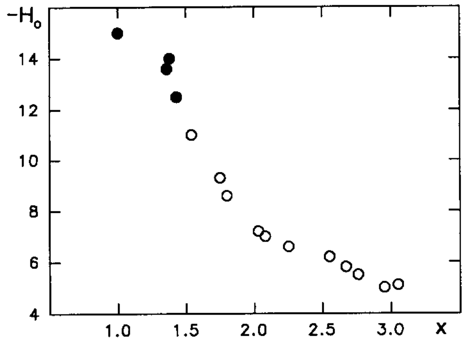

FIG. 4. Variation of acidity of boron fluoride hydrates with the ratio water/BF_3 (*x* in $BF_3 \cdot xH_2O$). See text for the discussion on the filled points in the diagram.

ACKNOWLEDGMENTS

This work was supported by a grant from the Exxon Education Foundation.

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