of 0.005 ml. were used. The β-alcohol had a longer retention time than the α-isomer.

A. **($Me_3SiC_2H_4$)$_3$B.**—In one run the alcohol mixture resulting from the oxidation of the triorganoborane was distilled, giving an 88% yield of mixed α- and β-$Me_3Si(C_2H_4)$-OH, b.p. 62–75° (42 mm.).

Anal. Calcd. for $C_5H_{14}OSi$: C, 50.78; H, 11.93. Found: C, 50.83; H, 12.06.

The results of a number of representative runs are summarized below

Conditions of hydroboration	α-Alcohol, mole %	β-Alcohol, mole %
$NaBH_4$–$AlCl_3$, 20 hr. at room temp.	37	63
$NaBH_4$–$AlCl_3$, 2 hr. at room temp., 1 hr. at 60°	33	67
$NaBH_4$–$AlCl_3$, 3 hr. at room temp., 8 hr. at 150°	37	63
$Me_3N \cdot BH_3$, 22 hr. at 70–80°	34	66

The similar ratios of α- to β-trimethylsilylethanol obtained in these reactions, in which the thermal history of the reactions covers a fairly wide range, makes the possibility that thermal rearrangements occurred in the direction $Me_3SiCHMe$–B → $Me_3SiCH_2CH_2$–B, similar to those reported by Hennion, *et al.*,[17] and by Brown and Rao[18], seem unlikely.

B. **1:1.6 Hydroboration Reaction Products.**—Oxidation of the products of the 1:1.6 hydroboration reaction described above are summarized below.

The $(Me_3SiC_2H_4)_2BOC_2H_5$ obtained, 12.8 g. (0.0495 mole), was oxidized in the usual manner using 1.6 g. NaOH in 50 ml. of ethanol and 14 g. of 30% hydrogen peroxide to give 10 g. of mixed alcohols. Gas chromatographic analysis showed the mixture to consist of 70.4% α-trimethylsilylethanol and 29.7% β-trimethylsilylethanol. The $(Me_3SiC_2H_4)_3B$, 8.8 g. (0.028 mole), was oxidized using 1.5 g. of NaOH in 50 ml. of ethanol and 13 g. of 30% H_2O_2 to give 8.1 g. of a mixture containing 42.8% of the α-alcohol and 57.1% of the β-alcohol. Similarly, the $[(Me_3SiC_2H_4)_2B]_2O$, 6.3 g. (0.014 mole), was oxidized in solution with 1.0 g. of NaOH in 35 ml. of ethanol by 8 g. of 30% H_2O_2, yielding 5 g. of mixed alcohols (40.5% α-alcohol and 59.4% β-alcohol).

Thus the boron compounds obtained in this experiment contained a total of 0.128 mole of $Me_3SiCHMe$- groups and 0.112 mole of $Me_3SiCH_2CH_2$–groups, giving an over-all distribution of 53.4% α-trimethylsilylethyl groups and 46.6% of the β-isomer.

Hydroboration of Trimethylvinyltin.—Attempted hydroboration of trimethylvinyltin with the $NaBH_4$–$AlCl_3$ reagent gave a product having a characteristic organoborane-like odor that caused ignition when poured on cloth or paper. Attempted distillation resulted in decomposition. Oxidation of the crude trimethylvinyltin hydroboration product by the usual procedure also resulted in decomposition and no organotin-alcohol could be isolated.

Acknowledgments.—This work was supported in part by the United States Office of Naval Research and may be reproduced in whole or in part for any purpose of the United States Government. The author is indebted to Professor J. S. Waugh and Dr. S. Castellano for determination and interpretation of the NMR spectra, and to Mr. Harold Ward for carrying out gas chromatographic analyses.

CAMBRIDGE 39, MASS.

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[17] G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, THIS JOURNAL, **79**, 5190 (1957).

[18] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

The Hammett Acidity Function H_0 for Trifluoroacetic Acid Solutions of Sulfuric and Hydrofluoric Acids[1]

BY HERBERT H. HYMAN AND RONALD A. GARBER

RECEIVED OCTOBER 17, 1958

The H_0 values of mixtures of H_2SO_4 and trifluoroacetic acid, as well as HF and trifluoroacetic acid, have been measured over the entire range of compositions. The values found are related to those found for aqueous systems, displaced as expected due to the higher acid strength of trifluoroacetic acid.

Introduction

Some interest has been shown in this and other laboratories in non-aqueous highly acid media. Trifluoroacetic acid has rather good solvent properties for many organic molecules, is readily available as a rather pure anhydrous chemical and is completely miscible in all proportions with some stronger acids such as H_2SO_4, $HClO_4$ and HF. The Hammett acidity function has been correlated with other phenomena of interest involving proton mobility.[2] The H_2SO_4–trifluoroacetic acid system has been used to investigate the effect of increasing acidity on the hexamethylbenzene spectrum, and values were given for a Hammett function H_0 calculated using hexamethylbenzene as the indicator.[3] This hydrocarbon is a different type of proton acceptor than is usually used as a Hammett indicator and as would be true of any indicator, is useful only in a narrow acidity range. This paper gives the acidity of the entire trifluoroacetic acid, sulfuric acid system obtained by using the conventional Hammett indicators. Since systems exist in which the sulfonating behavior of sulfuric acid systems is undesirable, the HF–trifluoroacetic acid system was also investigated. Mixtures containing high concentrations of perchloric acid are too oxidizing to be useful as simple acidic solvents and were not investigated.

The data of Dallinga and Kok discussed by Mackor, *et al.*,[4] were not known to us at the time this program was initiated. Over the range of concentrations reported, the results are in good agreement.

Experimental

Materials.—The indicators used were Aldrich Chemical Company products sold for use as Hammett indicators. They were used as received. Trifluoroacetic acid is now

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] L. P. Hammett, *Chem. Revs.*, **16**, 67 (1935); "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.

[3] M. Kilpatrick and H. H. Hyman, THIS JOURNAL, **80**, 77 (1958).

[4] E. L. Mackor, P. J. Smit and J. H. van der Waals, *Trans. Faraday Soc.*, **53**, 1309 (1957).

available from Matheson Coleman & Bell. It was freshly distilled before making up the solutions used in this work. Similar material has been shown to contain less than 0.01% H_2O.

Reagent grade concentrated sulfuric acid was mixed with similar grade fuming sulfuric acid to give approximately 100% acid. The concentration was checked by titration with standard base and readjusted to give anhydrous material.

Distilled hydrogen fluoride was kept over cobalt trifluoride but handled in a metal vacuum line so that the water content is probably somewhat higher than that described by Hyman, Kilpatrick and Katz.[5] The H_0 found for this material, -9.97 corresponds to less than 0.01 mole of H_2O/liter.

Optical Equipment.—Conventional glass stoppered silica cells were used for all solutions not containing HF. Cells suitable for optical measurements with HF have been described previously.[6] The ones used in this research employed polychlorotrifluoroethylene bodies and windows and external metal fittings. A length of Kel-F tubing and a valve machined from Kel-F stock were used to connect the cell to the vacuum line used in preparing these solutions.

All spectra were obtained using the Beckman DK 1 recording spectrophotometer equipped with a secondary container to prevent damage in the case of leaky cells. The instrument was in a constant temperature room and all measurements were made at 24 ± 2°.

Solution Preparation.—The trifluoroacetic acid, sulfuric acid solutions were prepared by volume in conventional graduated glass equipment. The required amount of indicator was weighed on a micro-balance and dissolved in a 100-ml. sample of trifluoroacetic acid. 100% sulfuric acid was added to this stock solution to make up 5 to 10 ml. of the required solution for spectral observation. The reference solution was a similar trifluoroacetic sulfuric acid mixture containing no indicator.

The solutions containing hydrogen fluoride were prepared and handled in a totally enclosed system as follows. The empty spectrophotometer cell and attached Kel-F valve were weighed on an analytical balance. From 0.2 to 0.7 ml. of a trifluoroacetic acid solution of the indicator being used was placed in the cell, and the cell and valve were weighed again. The cell and valve were then connected to the vacuum line containing HF but not evacuated. A portion of HF sufficient to give the desired solution was distilled into a receiver just above the valve. This receiver was then closed, the valve between the receiver and cell opened, the HF warmed and allowed to flow into the cell. The valve was then closed and the cell removed from the line and weighed. The reference cell in this case was filled with pure trifluoroacetic acid.

Observations and Discussion

Typical values for the acidity function for trifluoroacetic acid, sulfuric acid mixtures are in Table I and plotted in Fig. 1. The H_0 value is plotted against the concentration in moles/l. In the absence of accurate density determinations for the solutions, it is not possible to convert accurately the concentration scale to weight per cent. or moles per 1000 grams, although the deviation from additivity on mixing is probably smaller for these solutions than for the sulfuric acid–water system.

As may be seen from the sulfuric acid–water curve drawn for comparison, there is nothing surprising in the general shape of the curve given by this system. The very sharp rise in acidity on the addition of the first amount of sulfuric acid is undoubtedly accompanied by the shift in the acid base pair in equilibrium with the indicator from the trifluoroacetate ion-neutral acid combination in the pure solvent to the neutral acid-protonated species in the system containing the stronger acid. In the middle range of sulfuric acid concentration, no qualitative changes are taking place and the acidity rises slowly until one is well into the region where the sulfuric acid is the major component. The effect of adding trifluoroacetic acid at this point is that of a base competing with the indicator and, therefore, reducing the acidity at a proportionately greater rate.

TABLE I

TYPICAL H_0 VALUES FOR SULFURIC ACID SOLUTIONS IN TRIFLUOROACETIC ACID

H_2SO_4, M	$-H_0$	Indicator[a]
0	3.03	a
0.019	5.20	b
.075	5.72	b
.19	6.01	b
.94	7.33	c
1.87	8.07	c
3.74	8.86	d
5.61	9.25	e
9.35	9.33	e
14.96	9.61	e
16.83	9.85	e
18.70	11.10	e

[a] (a) 2,4-Dichloro-6-nitroaniline, $pK = -3.32$; (b) 2,4-dinitroaniline, $pK = -4.53$; (c) 6-bromo-2,4-dinitroaniline, $pK = -6.71$; (d) anthraquinone, $pK = -8.27$; (e) trinitroaniline, $pK = -9.41$.

TABLE II

TYPICAL H_0 VALUES FOR HYDROFLUORIC ACID SOLUTIONS IN TRIFLUOROACETIC ACID

Wt. %	$-H_0$	Indicator[a]
0	3.03	
10.9	6.04	a
12.5	6.63	a
22.5	8.40	b
35.1	8.42	b
43.7	8.43	b
49.8	8.39	c
64.1	8.71	b
74.1	8.40	c
76.5	8.73	c
83.8	8.94	c
100.0	9.97	c

[a] (a) 6-Bromo-2,4-dinitroaniline, $pK = -6.71$; (b) anthraquinone, $pK = -8.27$; (c) trinitroaniline, $pK = -9.41$.

The numbers reported by Mackor as obtained by Dallinga and Kok are not strictly comparable. They were obtained for solutions prepared by weight and, while the indicator constants specified are not given, the absence of a reference to the recent review paper of Paul and Long[7] suggest that they used the older indicator constants of Paul and Hammett.[2] A few points calculated on the basis of additive densities and using the newer indicator constants are shown on the curve in Fig. 1. The agreement is excellent, although the small correction for the newer constants lifts the D and K points consistently above the curve. For some reason they report no value using an aniline type indicator for pure trifluoroacetic acid. They quote the Van Dyke Tiers value of -4.4 using benzalacetophenone as indicator. This is in poor agreement with our value of -3.1 obtained by using

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(5) H. H. Hyman, M. Kilpatrick and J. J. Katz, THIS JOURNAL, **79**, 3668 (1955).

(6) J. J. Katz and H. H. Hyman, *Rev. Sci. Instr.*, **24**, 1066 (1953).

(7) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

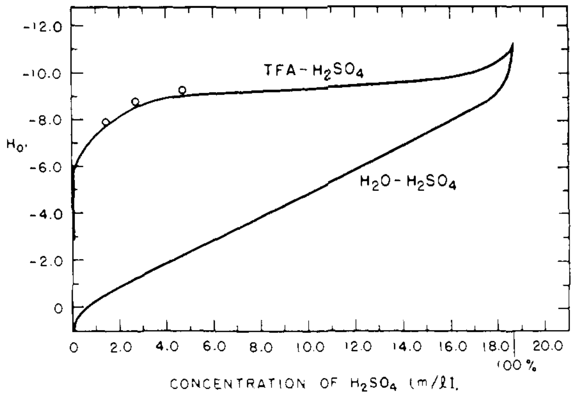

Fig. 1.—The H_0 function for sulfuric acid solutions in water and trifluoroacetic acid. O, D and K points from ref. 4, see text.

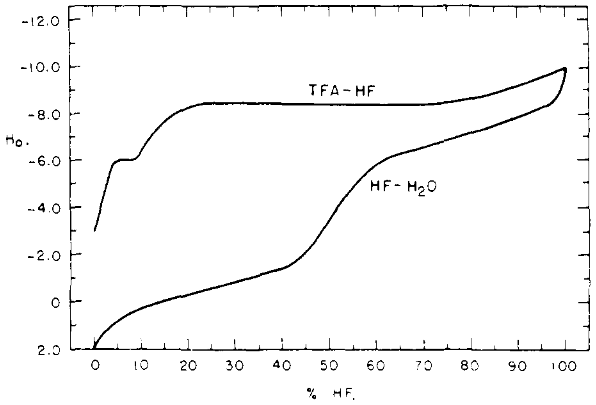

Fig. 2.—The H_0 function for hydrogen fluoride solutions in water and trifluoroacetic acid.

the 2,4-dichloro-6-nitroaniline indicator which has been reported by Kilpatrick and Hyman[3] and reconfirmed in this study. The values of H_0, the function for some sulfuric-trifluoroacetic acid mixtures suggested by Kilpatrick and Hyman using hexamethylbenzene as an indicator, are also in poor agreement with the values shown in Fig. 1.

Similar lack of agreement between indicators has been noted by other workers, especially, Bates and Schwarzenbach,[8] and Paul and Long[7] have discussed this to some extent. In the case of the hexamethylbenzene, it is perhaps not unreasonable to observe that the rearrangement needed in order to place a proton on the organic molecule makes this reaction somewhat different from the addition of a proton to the nitrogen in an amine group. Great care must be exercised in extrapolating pure proton transfer measurements given by H_0 values using Hammett indicators to problems where the important reaction is not entirely proton transfer.

The hydrogen fluoride-trifluoroacetic acid system also shows no surprises if compared with the hydrogen fluoride-water system. Since these solutions were prepared by weight, the data in Table II and Fig. 2 are given on a weight per cent. basis. The rise in acid strength with the first addition of HF is somewhat steeper than in the water case. This may be associated with the lower dielectric constant of the trifluoroacetic acid and, therefore, the greater increase in such constant on the addition of HF.

Acknowledgments.—Much of the special equipment has been fabricated by J. R. Pickhardt. The authors would like to acknowledge gratefully the continued interest in this program of Drs. M. Kilpatrick and J. J. Katz and the stimulating discussions resulting.

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(8) R. S. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, **38**, 699 (1955).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE UNIVERSITY]

Paramagnetic Resonance Spectra of Adsorbed Manganese(II), Copper(II) and Oxovanadium(IV)[1]

BY ROGER J. FABER[2] AND MAX T. ROGERS

RECEIVED AUGUST 18, 1958

Paramagnetic resonance spectra were obtained for Mn(II), Cu(II) and oxovanadium(IV) adsorbed on cation- and anion-exchange resins, activated charcoal, zeolite and silica gel. Essentially ionic bonding was found for the Mn(II) samples except when adsorbed on an anion exchanger, where a large amount of covalent bonding was indicated. The electrostatic field symmetry was largely cubic with a small component of lower symmetry. The spectrum of Cu(II) was sensitive to the nature of the active group in the adsorbent, and values of $g_{\|}$, $g_{\perp}$ and A were measured for most adsorbents. Increasing covalent character is to be expected in bonds between adsorbent and adsorbed ion in going from sulfonic acid-type exchangers through carboxylic acid-type to the amine-type; g-values, hyperfine structure intervals and line widths all changed in a manner consistent with this hypothesis. Values of $g_{\|}$, $g_{\perp}$, A and B were obtained for oxovanadium(IV); g-values were nearly isotropic and close to the free electron value. The hyperfine structure was very anisotropic and the intervals decreased in going from sulfonic acid-type to amine-type adsorbents; this behavior is consistent with the theoretical prediction that the intervals should decrease with increase in covalent bonding.

Introduction

The large amount of data on the paramagnetic resonance spectra of transition metal ions in crystals of known structure makes it possible to draw conclusions concerning the bonding and the environment of transition ions in unknown surroundings on the basis of their paramagnetic resonance spectra.

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[1] Taken from a thesis submitted by Roger J. Faber to the School of Advanced Graduate Studies of Michigan State University in partial fulfillment of the requirements for the Ph.D. degree. Presented in part before the Physical and Inorganic Division of the 139th National Meeting of the American Chemical Society, San Francisco, California, April, 1958.

[2] Union Carbide Corp. Fellow for 1956–1957.