Journal of Organometallic Chemistry, 150 (1978) 101—113

THE KINETICS AND MECHANISM OF THE PROTODEBORONATION OF FERROCENEBORONIC ACID IN MODERATELY CONCENTRATED SULFURIC ACID *

BARBARA FLORIS AND GABRIELLO ILLUMINATI

Centro C.N.R. dei Meccanismi di Reazione, c/o Istituto di Chimica Organica, Università di Roma, 00185 Roma (Italy)

(Received November 28th, 1977)

Summary

Ferroceneboronic acid has been characterized by its UV and NMR spectrum and its dissociation constant in water/ethanol solvents has been determined. The kinetics of protodeboronation have been studied in the same solvents containing moderate concentrations of sulfuric acid; the H_0 acidity function has been evaluated throughout the range of the reaction media used. The log of the rate of reaction of ferroceneboronic acid depends linearly with unit slope on H_0. The solvent hydrogen isotope effect, the temperature dependence and the nature of acid catalysis have also been investigated. The reaction probably proceeds by an A-S_E2-type mechanism.

Introduction

Electrophilic substitution at the Cp rings of ferrocene is one of the outstanding features of the chemistry of this compound. The structure of ferrocene suggests the possibilities of special paths for this reaction, involving participation of the metal in the initial stages of the electrophilic attack [1,2]. Surprisingly, there has been relatively little physical organic investigation of this topic and, in spite of an accumulation of evidence to the contrary in a number of cases, the idea of metal participation, though not adequately supported, has become fairly popular, and so before describing new work on the reaction, we briefly summarize the available information about the mechanism.

The participation of the nonbonding 3*d* electrons of iron in the reactions of ferrocene has been a subject of continued interest. The metal atom has been

---

* Presented at the EUCHEM Conference on Oxidative-Addition and Reductive-Elimination Processes, Bressanone, 5—10 September, 1977.

suggested to be the site of protonation [3,4] and of hydrogen bonding [5—8], and has been considered to have a role as a neighbouring group in internal electron-transfer reactions of α-ferrocenylcarbonium ions [9] and in solvolyses of α-ferrocenylcarbinyl acetates [6,10—12]. The role of iron was first questioned by Ware and Traylor [13] for the latter reaction. Later on, we showed that weak proton—ring interactions readily occur under mild acid conditions [14], whereas the complex in which a proton is bound to the metal is formed only under very strong acid conditions [4,15].

For electrophilic acylation, Richards [16] proposed a mechanism in which the metal plays an essential role, a fast, reversible addition of the electrophile on the iron atom being followed by a rate-determining rearrangement of the cation thus formed to yield a σ-adduct analogous to that assumed for aromatic benzenoid substitutions. Fast removal of proton then leads to the substituted ferrocene. A similar scheme was proposed by Sorokin and Domrachev [17].

However, deficiencies in this mechanism were revealed by a study of the stereochemistry of acetylation of certain bridged ferrocenes [18] and examination of steric effects on the rate of protodesilylation of alkyl-substituted trimethylsilylferrocenes [19]. Rosenblum et al. have reconsidered their earlier suggestions [8,20], and found that in intramolecular acylation the participation of iron is not an essential assumption for the reaction mechanism [21—23]. In acylation the alternative mechanism involves direct attack of the electrophile on the 5-membered Cp ring without any kinetically significant metal participation. Either one or the other of these mechanisms has been assumed in discussions by other groups [24,25].

A number of familiar substitutions such as nitration and halogenation cannot be easily investigated with ferrocene because of competing oxidation to give ferricenium ion. Quantitative studies on the ferrocene system have been carried out for mercuration [26,27], protodesilylation [28,29], protodeboronation [29], and hydrogen isotope exchange [30—32]. Use of the proton as the electrophile requires special care in the choice of the reaction conditions if concurrent oxidation is to be avoided. Substitutions involving this electrophile give clear evidence against iron participation [14,15,29]. For example, the metal participation theory [31,32] cannot be easily reconciled with the fact that metal-protonated species can inhibit the reaction, the exchange slowing down as metal-protonation becomes more extensive [15]. Furthermore, the low basicity of the iron atom of ferrocene rules out any effective participation by the metal-protonated species when the substitutions by H^+ occur under mildly acidic conditions [15,29].

When our study on protodeboronation was undertaken few data were available for ferroceneboronic acid. Some reactions were known in which the $B(OH)_2$ group is displaced by other groups under various conditions [33]. As like benzeneboronic acid [34], we found that ferroceneboronic acid undergoes protodeboronation in Brønsted acid media [29]. Our rate studies on protodesilylation and protodeboronation [29] allow a comparison of the reactivity of the ferrocene and the benzene systems, and provided further information of mechanistic significance. We now describe the results of further work on the protodeboronation of ferroceneboronic acid which has given an extended picture of the kinetics and enabled a more thorough comparison to be made with the behavior of benzeneboronic acid.

Results and discussion

The characterization of ferroceneboronic acid

Accurate IR and mass spectra for this compound are available [35], and we have obtained new data for its characterization, viz., the electronic and PMR spectra and the acid dissociation constant.

The electronic spectrum was recorded in several solvents and displays two maxima, at 325 and 442 nm, respectively (see Experimental). The PMR spectrum in hexadeuteroacetone displays a singlet at δ 4.10 ppm and a complex signal in the range of δ 4.30 to 4.50 ppm, due to the ferrocenyl protons of the unsubstituted and substituted rings, respectively, a slightly broad singlet at δ 2.97 ppm and a singlet at δ 6.53 ppm. The area ratios are 5/4/1/1. The signals at δ 2.97 and 6.53 ppm disappear after shaking with D_2O, while both the chemical shifts and the area ratio of the other signals remain unchanged. In $CDCl_3$ the ferrocenyl protons resonances appear at δ 4.17 ppm for the unsubstituted ring and at δ 4.33—4.67 ppm for the substituted one; there is also a broad signal centered at δ 1.27 ppm, which disappeares after shaking with D_2O.

Benzeneboronic acid has different properties in that it gives only a singlet at δ 7.2 ppm in deuterated acetone, which disappears on shaking the solution with D_2O and which can be attributed to the equivalent protons of the $B(OH)_2$ group (area ratio of benzene protons to this singlet, 5/2). Presumably the special geometry of the ferrocene system makes such protons non-equivalent due to their diverse electronic environments, in the vicinity of the Cp rings and of the metal. Also, the solvent may play a role by affecting the expectedly weak interactions of the $B(OH)_2$ group protons and the environment around each of them, but we did not investigate this point any further.

The acid dissociation constant at 25°C was determined by the method described by Kuivila et al. [36] for benzeneboronic acid, but ethanol/water mixtures were used rather than water because of the low solubility of ferroceneboronic acid in water. The "pK_a" values thus obtained are really equilibrium concentration quotients, $-\log Q_a$ [37]. They are as follows (% ethanol given in parenthesis): 10.92 (33), 11.32 (47), 11.48 (53), 11.59 (60), 11.71 (67). In spite of the greater basicity of ethanol relative to water, the dissociation constant decreases on increasing the ethanol content [38]. This is interpreted as a dielectric constant effect [39,40].

The "pK_a" of benzeneboronic acid under conditions nearest to those used by Kuivila, i.e., 40% ethanol/water, was found to be 9.82. Thus, ferroceneboronic acid is a weaker acid than benzeneboronic acid by more than a pK unit, which is in agreement with the higher electron donor ability of the ferrocenyl group as compared to the phenyl group. A similar trend has been observed with the corresponding carboxylic acids, the "pK_a" values being 5.52 for benzoic acid [41] and 6.11 for ferrocenoic acid [42] in 50% ethanol/water. The dissociation constant of ferrocenoic acid also decreases on increasing the ethanol content of the solvent ("pK_a", 6.67 in 80% ethanol/water and 6.94 in 95% ethanol/water [43]).

Acid catalysis and medium effects

The acid-catalyzed protodeboronation of ferroceneboronic acid was complicated by oxidation. This was the case for reactions in formic acid/aqueous

(continued on p. 106)

TABLE 1

RATE CONSTANS FOR THE PROTODEBORONATION OF FERROCENEBORONIC ACID AT VARIOUS SULFURIC ACID CONCENTRATIONS AND DEPENDENCE ON THE H_0 ACIDITY FUNCTION, AT 47.7°C

% H_2SO_4 [a]	$-H_0$	$10^3 \times k_{obs}$ (s^{-1})	% H_2SO_4 [b]	$-H_0$	$10^3 \times k_{obs}$ (s^{-1})	% H_2SO_4 [c]	$-H_0$	$10^3 \times k_{obs}$ (s^{-1})
13.0	0.39	0.66	12.5	0.37	0.82	12.1	0.43	1.40
19.7	0.96	1.36	19.0	0.91	1.89	18.4	0.88	2.77
22.2	1.17	2.47	21.5	1.12	3.34	20.8	1.05	6.04
23.3	1.27	2.92	22.5	1.20	4.52	21.9	1.13	7.62
25.0	1.41	4.20	24.2	1.34	6.08	23.4	1.25	8.82
26.2	1.56	5.85	25.3	1.46	7.91	24.6	1.36	9.29
26.5	1.58	6.08	25.6	1.48	8.16	24.9	1.39	10.7
29.6	1.96	14.5	28.6	1.81	15.7	27.8	1.71	20.9
31.5	2.22	32.0	30.5	2.05	49.6	29.6	1.88	48.8
35.8	2.73	95.5	34.7	2.48	83.0			

[a] In 1/2 v/v H_2O/EtOH. [b] In 1/1 v/v H_2O/EtOH. [c] In 2/1 v/v H_2O/EtOH.

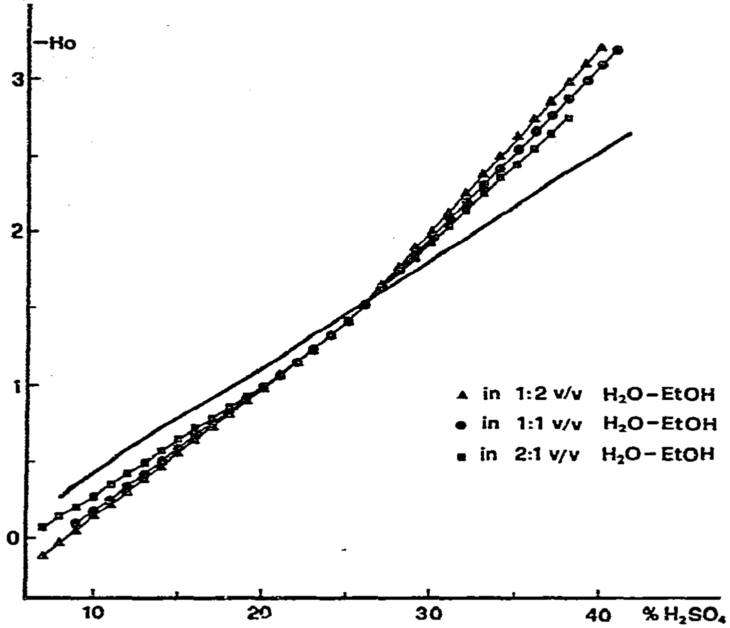

Fig. 1. —H_0 vs. H_2SO_4 diagram in ethanol/water mixtures.

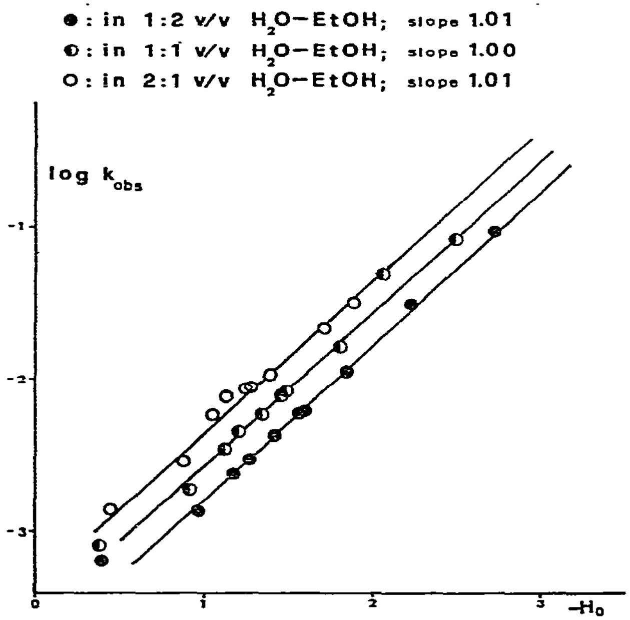

Fig. 2. Plot of the log of the rate constant against the H_0 acidity function in various ethanol/water mixtures.

ethanol or hydrochloric acid/aqueous ethanol. Conditions avoiding oxidation were obtained by using sulfuric acid in aqueous ethanol under nitrogen (see Experimental); product analyses confirmed that in the medium ferroceneboronic acid gave ferrocene in practically quantitative yield, as reported for 1/2 v/v water/ethanol [29]. Rates were determined spectrometrically at 440 nm and 50°C. The rate constants in diverse H_2SO_4/ethanol/water mixtures are listed in Table 1.

The H_0 values for sulfuric acid in the ethanol/water mixtures used for the kinetic measurements were obtained by the Hammett method [44]. A plot of these values against % H_2SO_4 and, for comparison, of the corresponding data in water [44] (Fig. 1) shows that the smaller is the content in water of the solvent the more pronounced is the deviation of the H_0 value from the line for water. Curves resulting from the three mixtures used, i.e., 2/1, 1/1, and 1/2 by volume, cross the water line at the same point, corresponding to 25.9% H_2SO_4 and lie below that line for concentrations below that value.

The H_0 values for the acid percentages used in the kinetic experiments, as evaluated from the above plot, are listed in Table 1. They are linearly correlated with the free energies of activation as shown in Fig. 2, the slopes of the lines being practically unity. Although the relative proton donor abilities of the three investigated media, at a given H_2SO_4 percentage, depend on the H_2SO_4 concentration, and is inverted above 26.5% H_2SO_4 (Fig. 1), the three straight lines in Fig. 2 are parallel to each other and show that the rates are always higher the higher the water content. Thus, the proton availability and solvent effects both influence the reaction rate. Apparently water solvates the transition state relative to the reactants more effectively than does ethanol. The rate effect is small, however, and it involves a factor of 3.2 in going from 1/2 to 2/1 water/ethanol mixtures.

In order to find out whether the reaction is subject to general acid catalysis, the kinetic behavior was examined in phosphoric acid/dihydrogen phosphate buffers in 1/1 v/v water/ethanol. The test was made in the usual way [45] by changing the H_3PO_4 and NaH_2PO_4 concentrations while keeping their concentration ratio constant. The observed rate constants were unaffected by the overall concentration of the buffer, as shown in Table 2, as so there is no evidence for general acid catalysis.

Solvent hydrogen isotope effects

Deboronation rates of ferroceneboronic acid have been measured in solutions

TABLE 2

RATE CONSTANTS FOR THE PROTODEBORONATION OF FERROCENEBORONIC ACID IN 1/1 v/v H_2O/EtOH AND PHOSPHATE BUFFERS. AT 52.2°C (NaH_2PO_4/H_3PO_4 0.46. pH 3.48)

NaH_2PO_4 (*M*)	H_3PO_4 (*M*)	Buffer	$10^5 \times k_{obs}$ (s^{-1})
0.020	0.043	0.063	4.46
0.032	0.069	0.101	4.72
0.040	0.087	0.127	4.67
0.050	0.108	0.158	4.55
0.50	1.08	1.58	4.55

TABLE 3

SOLVENT ISOTOPE EFFECT IN THE DEBORONATION OF FERROCENEBORONIC ACID, AT 47.7°C

% H_2SO_4	$10^3 \times k_H$ (s^{-1})	% D_2SO_4	$10^3 \times k_D$ (s^{-1})	k_H/k_D
19.7	1.36 [a]	19.9	0.88 [d]	1.55
19.0	1.89 [b]	19.2	1.15 [e]	1.64
19.5	4.16 [c]	19.5	2.59 [f]	1.61

[a] In 1/2 v/v H_2O/EtOH. [b] In 1/1 v/v H_2O/EtOH. [c] In 2/1 v/v H_2O/EtOH. [d] In 1/2 v/v D_2O/EtOD. [e] In 1/1 v/v D_2O/EtOD. [f] In 2/1 v/v D_2O/EtOD.

of D_2SO_4 in deuterium oxide/ethanol-d_1 mixtures. The values of the solvent hydrogen isotope effect, k_H/k_D, for a given acid percentage and different D_2O/EtOD mixtures are listed in Table 3.

The k_H/k_D values are somewhat lower than those observed [46] for *p*-methoxybenzeneboronic acid (k_H/k_D 2.0) and other substituted areneboronic acids, e.g., *p*-F, k_H/k_D 2.2; *m*-F, k_H/k_D 2.5, and are similar to the effects observed [47] for the protodesilylation of trimethylsilylbenzene (k_H/k_D 1.55 at 50°C). Such values can be attributed [47] to a balance of the isotope effects in the bond-breaking of the acid HA and in the bond-making of the aromatic C—H in the rate-determining step. It is worth noting that markedly greater effects have been observed in other protonation reactions: thus, the protodeiodination of *p*-iodoaniline, a reaction which involves a rate-determining protonation, is six times faster in H_2O than in D_2O [48].

TABLE 4

RATE CONSTANTS AT SEVERAL TEMPERATURES AND ACTIVATION PARAMETERS FOR THE PROTODEBORONATION OF FERROCENEBORONIC ACID WITH H_2SO_4

T (°C)	$10^3 \times k_{obs}$ (s^{-1}) [a]	$10^3 \times k_{obs}$ (s^{-1}) [b]	$10^3 \times k_{obs}$ (s^{-1}) [c]
57.2	12.70	16.70	22.90
52.1	8.33	11.50	16.50
48.4	6.38	9.50	12.70
40.5	3.57	4.87	7.07
36.6	2.60	3.45	4.73
29.5	1.42	1.86	3.14
E_a (kcal/mol)	15.4 ± 0.5 [a]	15.7 ± 0.5 [b]	15.0 ± 0.5 [c]
$\Delta S^{\ddagger}$ (e.u.)	—22.8 ± 1.5 [a]	—21.2 ± 1.5 [b]	—22.6 ± 1.5 [c]
T (°C)	$10^3 \times k_{obs}$ (s^{-1}) [d]	$10^3 \times k_{obs}$ (s^{-1}) [e]	$10^3 \times k_{obs}$ (s^{-1}) [f]
59.9	3.60	4.60	—
56.1	2.75	3.57	5.06
52.1	2.00	2.68	3.87
42.6	0.92	1.28	1.90
37.0	0.59	0.85	1.26
30.5	0.32	0.49	1.06
E_a (kcal/mol)	15.6 ± 0.5 [d]	15.3 ± 0.5 [e]	15.2 ± 0.5 [f]
$\Delta S^{\ddagger}$ (e.u.)	—38.5 ± 1.5 [d]	—38.0 ± 1.5 [e]	—38.0 ± 1.5 [f]

[a] 26.5% H_2SO_4 in 1/2 v/v H_2O/EtOH. [b] 25.6% H_2SO_4 in 1/1 v/v H_2O/EtOH. [c] 24.9% H_2SO_4 in 2/1 v/v H_2O/EtOH. [d] 19.7% H_2SO_4 in 1/2 v/v H_2O/EtOH. [e] 19.0% H_2SO_4 in 1/1 v/v H_2O/EtOH. [f] 18.4% H_2SO_4 in 2/1 v/v H_2O/EtOH.

The activation parameters

Activation parameters were obtained for two acid concentration ranges, 18.4—19.7% and 24.9—26.5% sulfuric acid in the three water/ethanol mixtures from rate measurements over a range of about 30°C at six different temperatures, which yielded good Arrhenius plots. The activation parameters are listed in Table 4. The energies of activation all lie in the range 15.0—15.7 kcal/mol, i.e., are independent of acid concentration and solvent, whereas the entropies of activation depend on the acid concentration but not on the solvent. The $\Delta S^{\ddagger}$ values are markedly negative, —21.2 to —22.8 and —38.0 to —38.5 e.u., the lower values applying to the lower acid concentration range.

The Arrhenius plots for the lower acid concentrations enabled evaluation of the rate constants at 40°C, which allows fairly direct comparison to be made with Kuivila's rate constants for areneboronic acids at this temperature (Table 5). Ferroceneboronic acid is shown to be markedly more reactive than benzene- and *p*-methoxybenzene-boronic acids; the reported relative rates are in fact lower limits for the ferrocenyl derivative since they refer to water/ethanol mixtures in which the reaction is slower than in water.

The reaction mechanism

Despite the complexity of the protodeboronation of areneboronic acids, the work by Kuivila et al. [34,46] has shown that the reaction over a fairly wide range of structures involves a rate-determining proton transfer (A-S_E2) rather than a fast protonation followed by a slow decomposition of the conjugate acid of the substrate (A-1 or A-2) [49]. The reactivity of ferroceneboronic acid, however, is much greater than that of any of the structures studied by Kuivila (Table 5), and even greater than that of 2-thiopheneboronic acid [50], which reacts 8.5 × 10^5 times as fast as benzeneboronic acid at 70°C. Such a high reactivity and the special structure of the ferrocenyl group demand some care in comparing the diverse systems.

It should be first noted that because of its high reactivity ferroceneboronic acid was studied under relatively moderate acidic conditions. Under our conditions, its rate variation on change of the H_0 acidity function is more regular than that for areneboronic acid, the log k vs. $-H_0$ correlation being linear with a slope value virtually equal to 1. Although this is consistent with both types of mechanism above, the fast protonation mechanism implies a linear log k vs. $-H_0$ correlation only when the concentration of the conjugate acid remains much smaller than that of the substrate [49]. Under the latter conditions, the solvent hydrogen isotope effect, k_H/k_D, is expected to be clearly less than one [49,51], which

TABLE 5

RATE CONSTANTS FOR THE PROTODEBORONATION OF SOME BORONIC ACIDS, AT 40°C

Compound	% H_2SO_4	Solvent	k (s^{-1})	Relative rate
$PhB(OH)_2$	20.1	Water	5.0×10^{-10}	1
p-$MeOC_6H_4B(OH)_2$	20.1	Water	1.35×10^{-5}	2.7×10^4
$FcB(OH)_2$	19.7	1/2 v/v $H_2O/EtOH$	7.47×10^{-4}	1.5×10^6
$FcB(OH)_2$	19.0	1/1 v/v $H_2O/EtOH$	1.06×10^{-3}	2.1×10^6
$FcB(OH)_2$	18.4	2/1 v/v $H_2O/EtOH$	1.56×10^{-3}	3.1×10^6

is in contrast with our results. Although the solvent isotope effect found for areneboronic acids is somewhat higher (1.60—2.99) [46] than that in the present work (1.55—1.64), the difference may be explained in terms of the different reactivities of the substrates [46]. The activation parameters of ferroceneboronic acid also display a general overall pattern similar to that for the areneboronic acids and the thiopheneboronic acids, in that they are characterized by low entropies of activation. In view of the relative reactivities, it follows that the energy of activation is markedly lower than that for the areneboronic acids.

Unfortunately, we were unable to detect any general acid catalysis, probably because we could not vary the buffer concentration by a factor >25. This result is thus not an unequivocal proof that there is specific acid catalysis [52, 53]. In spite of this uncertainty, the reaction of ferroceneboronic acid is likely to proceed by an $A\text{-}S_E2$ mechanism as in the case of areneboronic acids. However, the complexities introduced by the presence of the $B(OH)_2$ function may well lead to changes in the detail of the mechanism. For example, the strong electron release by ferrocenyl conjugation [35] will reduce the Lewis acid strength at the boron atom and thus lower the probability of an $A\text{-}S_Ei$ mechanism involving attack of the bisulfate ion on boron [34,54].

A noticeable difference between ferrocene and areneboronic acids is the greater sensitivity of $\Delta S^{\ddagger}$ of the former to the sulfuric acid concentration (Table 4) and the particularly low $\Delta S^{\ddagger}$ value in 18.4—19.7% acid (—38.5 e.u.). These $\Delta S^{\ddagger}$ changes generally reflect the state of solvation of the reactants and of the transition state and the changing structure of the acidic medium. However, there may be a superposition of specific effects such as intramolecular H-bonding of the $B(OH)_2$ group with the iron lone pair. Hydrogen bonding of this kind is not important in the ground state [35] but may become significant in the σ-adduct-like transition state, and such interaction can be seen to be possible in models. Intramolecular H-bonding would more effectively compete at lower acid concentrations by providing an intramolecular solvation [55]. Further investigations are required to test this hypothesis.

To sum up, we note that for the reaction of ferroceneboronic acid in aqueous sulfuric acid there is no indication that the metal participates in the electrophilic attack by proton in the early stages of the protodeboronation, in keeping with our previous conclusions on this problem.

Experimental

Preparation of ferroceneboronic acid

Several methods of preparing ferroceneboronic acid were tried, with the aim of improving the yield and quality of the product. Previously [33,56] ferroceneboronic acid has been synthesized from ferrocenyllithium and tributylborate in anhydrous diethyl ether at —75°C. However, 1,1′-ferrocenediboronic acid, which is obtained as a side-product, could not be completely removed. Another route was to treat bromomercuriferrocene [57] with boron tribromide, under conditions similar to those reported for the synthesis of ferrocenyldichloroborane [58]. Hydrolysis of the obtained ferrocenyldibromoborane gave ferroceneboronic acid in only 17% yield. We tried to use diferrocenylmercury as starting material, since benzeneboronic acid can be obtained from diphenylmercury [59]. Boron tribromide (0.38 ml in 20 ml of 80—100°C petroleum ether) was added dropwise to a stirred suspension of diferrocenylmercury [60] (950 mg, 2.07×10^{-2} mol) in 30 ml of 80—100°C petroleum ether. As soon as the reagent was added, the suspension disappeared and the solution became dark red. After refluxing half an hour, the mixture was hydrolyzed with 5% aqueous NaOH. The aqueous layer was separated, neutralized with 10% aqueous H_2SO_4, and extracted with diethyl ether. The solid obtained after evaporation of the solvent was repeatedly washed with 30—50°C petroleum ether to remove the ferrocene formed in the reaction. 90 mg of ferroceneboronic acid were obtained (18% yield).

Finally, a modification of a patent by Sollott et al. [61] gave the best results, especially with respect to purity. 17.5 *g* (0.06 mol) of boron tribromide in 30 ml of anhydrous heptane were added under nitrogen to a stirred mixture of 39.2 g (0.21 mol) of ferrocene and 9.3 g (0.07 mol) of $AlCl_3$ in 200 ml of anhydrous heptane. After the addition the mixture was refluxed for 4 h, then treated with 15% aqueous NaOH, neutralized with 10% H_2SO_4, and shaken with diethyl ether. After evaporation of the ether extract a yellow orange solid was recovered, which was repeatedly washed with 30—50°C petroleum ether in order to remove unchanged ferrocene. Ferroceneboronic acid was obtained in a 23% yield (3.2 g, 0.014 mol).

Characterization of ferroceneboronic acid

Electronic spectra were recorded with Beckman DB-GT and Perkin—Elmer 402 spectrophotometers. The absorptivities and wavelengths of the maxima (given in parentheses, nm) in various solvents are as follows: 170 (325, s) and 160 (442), in dichloromethane; 170 (325, s) and 145 (440), in *N,N*-dimethylformamide; 180 (327) and 165 (444), in methanol; 170 (328) and 165 (444), in ethanol; 175 (325) and 165 (441), in 75% v/v ethanol/water; 195 (327) and 165 (440), in 50% v/v ethanol/water.

PMR spectra were carried out with Jeol C60-HL and Varian 60 spectrometers using TMS as internal standard.

The "pK_a" of ferroceneboronic acid was determined by potentiometric titrations with 0.01 *N* NaOH, using a Radiometer 22 pH-meter, equipped with glass and saturated calomel electrodes, and a thermostatted cell. Since ferroceneboronic acid is almost insoluble in water, titrations were performed in ethanol/water mixtures prepared by adding water to known volumes of 95% ethanol.

Product analysis

Ferroceneboronic acid (0.24 g, 1.05 mmol) was brought into reaction with 500 ml of sulfuric acid solution in 1/2 v/v water/ethanol. The solutions of reactants were saturated with nitrogen before use, and a nitrogen atmosphere was maintained during the reaction. After 5 minutes the mixture was cooled, extracted with 30—50°C petroleum ether, and worked up as usual to yield a yellow solid, which was identified as ferrocene, m.p. 172—174°C (lit. [8] 174°C); the PMR spectrum in CCl_4 shows a sharp singlet at δ 4.0 ppm. Similar analyses were obtained for reactions in 1/1 v/v and 2/1 v/v H_2O/EtOH solutions.

Kinetic measurements

The rate measurements were made by recording the absorbance decrease of the reaction solutions at 440 nm. A thermostatted Beckman DB-GT self-recording spectrophotometer was used with a tenfold expansion scale and zero suppression, to allow sufficiently accurate measurements, despite the small overall spectral change. All the solvents were saturated with nitrogen before mixing and a nitrogen atmosphere was maintained in the cell compartment during the kinetic experiments. Under those conditions there was no apparent oxidation up to 75% reaction, but it became apparent in the later stages of the reaction as a slight absorbance at 620 nm, and this prevented recording of infinity absorbances. Therefore, absorbance data were treated by Mangelsdorf's [62a] and Guggenheim's [62b] methods, which gave results in good agreement.

The rate constants reported in Table 1 with 19.7 and 26.5% H_2SO_4 (1/2 v/v H_2O/EtOH), 19.0 and 25.6% H_2SO_4 (1/1 v/v H_2O/EtOH), 18.4 and 24.9% H_2SO_4 (2/1 v/v H_2O/EtOH) are mean values from several runs carried out with substrate concentrations in the range 1.0×10^{-3}—1.0×10^{-2} *M*. The standard deviation was 5% or less. The measurements in the other H_2SO_4 media were carried out in duplicate.

Acidity functions

These were determined with the H_2SO_4/water/ethanol media used for the kinetic study. Some primary anilines were used as indicators, the log C_{BH^+}/C_B ratio being determined for each of them in several sulfuric acid solutions. The actual concentration of sulfuric acid in the various water/ethanol mixtures was determined accurately by weight, whereas the concentrations reported previously [29] were determined approximately by volume.

The p*K*a's of *p*-nitroaniline were determined with HCl in water/ethanol mixtures while the pK_a's of the other anilines were obtained from these values in the usual manner [44]. The values obtained were as follows (the solvent composition is given in parentheses, as v/v H_2O/EtOH ratios): *p*-nitroaniline: +0.01 (1/2), +0.17 (1/1), +0.40 (2/1); *o*-nitroaniline: —1.56 (1/2), —1.31 (1/1), —0.91 (2/1); 3,5-dinitroaniline: —0.89 (1/2), —0.54 (1/1), —0.23 (2/1); 2-nitro-4-methylaniline: —0.94 (1/2), —0.69 (1/1), —0.31 (2/1); 2-methyl-4-nitroaniline: —0.14 (1/2), +0.02 (1/1), +0.27 (2/1).

Kinetics in buffer solutions

The determination of reaction rates in H_3PO_4/NaH_2PO_4 buffer solutions was carried out by procedures reported in refs 34 and 45. Silica cells with septums were used to follow the absorbance decrease at 440 nm. To avoid oxidation an argon atmosphere was provided over the solutions in the cell before mixing. The pH's of the kinetic solutions were measured with a Radiometer 22 pH-meter equipped with glass and saturated calomel electrodes.

Kinetics in deuterated media

Ethanol-d_1 was prepared according to the literature [63], by hydrolyzing tetraethoxysilane with an equivalent amount of deuterium oxide. Commercial D_2O and 96% D_2SO_4 were used. The actual percentage of deuterium sulfate in the various D_2O/EtOD mixtures was determined by weight. The rate measurements were carried out as previously described with H_2SO_4 and all runs were duplicated. Oxidation caused trouble, and particular care had to be taken to exclude oxygen.

References

1 M. Cais, Aromaticity Problems in Metallocenes, in E.D. Bergmann and B. Pullman (Eds.), Aromaticity, Pseudoaromaticity, Antiaromaticity, The Israel Academy of Sciences and Humanities, 1971.
2 Gmelin Handbuch der Anorganischen Chemie, 14, Eisen-Organische Verbindungen, Teil A, Ferrocen 1, Springer-Verlag, Berlin, 1974.
3 M. Rosenblum and J.O. Santers, J. Amer. Chem. Soc., 81 (1959) 5517.
4 T.J. Curphey, J.O. Santers, M. Rosenblum and J.H. Richards, J. Amer. Chem. Soc., 82 (1960) 5249.
5 D.S. Trifan, J.L. Weinmann and L.P. Kuhn, J. Amer. Chem. Soc., 79 (1957) 6566.
6 D.S. Trifan and R. Bacskai, J. Amer. Chem. Soc., 82 (1960) 5010.
7 E.A. Hill and J.H. Richards, J. Amer. Chem. Soc., 83 (1961) 4216.
8 M. Rosenblum, Chemistry of the Iron Group Metallocenes, Interscience, New York, N.Y., 1965.
9 K.L. Rinehart, C.J. Michejda and P.A. Krittle, J. Amer. Chem. Soc., 81 (1959) 3162.
10 E.A. Hill and J.H. Richards, J. Amer. Chem. Soc., 83 (1961) 3840.
11 J.H. Richards and E.A. Hill, J. Amer. Chem. Soc., 81 (1959) 3484.
12 D.S. Trifan and R. Bacskai, Tetrahedron Lett., (1960) 1.
13 J.C. Ware and T.G. Traylor, Tetrahedron Lett., (1965) 1295.
14 B. Floris, G. Illuminati and G. Ortaggi, Tetrahedron Lett., (1972) 269.
15 G. Cerichelli, A.M. Giuliani, G. Illuminati and G. Ortaggi, J. Organometal. Chem., 127 (1977) 357.
16 J.H. Richards, Abstr. 135th Nat. Meeting Amer. Chem. Soc., April 1959, p. 86—90.
17 Yu.A. Sorokin and G.A. Domrachev, Trudy po Khim. i Khim. Teckhnol., 4 (1961) 665; Chem., Abstr. 58 (1963) 2349c.
18 K.L. Rinehart, D.E. Bublitz and H.D. Gustafson, J. Amer. Chem. Soc., 85 (1963) 970.
19 R.A. Benkeser, Y. Nagai and J. Hooz, J. Amer. Chem. Soc., 86 (1964) 3742.
20 M. Rosenblum, J.O. Santer and W.G. Howells, J. Amer. Chem. Soc., 85 (1963) 1450.
21 M. Rosenblum and F.W. Abbate, J. Amer. Chem. Soc., 88 (1966) 4178.
22 M. Rosenblum and F.W. Abbate, Advan. Chem. Ser., 62 (1967) 532.
23 E.G. Perevalova and T.V. Nikitina, in F.I. Becker and M. Tsutsui (Eds.), Organometallic Reactions, Vol. 4, Wiley-Interscience, New York, 1972.
24 J.A. Mangravite and T.G. Traylor, Tetrahedron Lett., (1967) 4461.
25 T.E. Bitterwolf and A.C. Ling, J. Organometal. Chem., 40 (1972) 197.
26 B. Floris, G. Illuminati, P.E. Jones and G. Ortaggi, Coord. Chem. Rev., 8 (1972) 39.
27 B. Floris and G. Illuminati, Coord. Chem. Rev., 16 (1975) 107.
28 G. Marr and D.E. Webster, J. Chem. Soc., B, (1968) 202.
29 G. Cerichelli, B. Floris, G. Illuminati, and G. Ortaggi, J. Org. Chem., 39 (1974) 3948.
30 J.A. Mangravite and T.G. Traylor, Tetrahedron Lett., (1967) 4457.
31 F.S. Yakushin, V.N. Setkina, E.A. Yakovleva, A.N. Shatenstein and D.N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1967) 206; Chem. Abstr., 66 (1967) 94426f.
32 M.N. Nefedova, V.N. Setkina, E.G. Perevalova, D.N. Kursanov and A.N. Nesmeyanov, Reaktzionnaya Sposobnost Org. Soedin., Tartu Gos. Univ., SSSR, 2 (1965) 69; Chem. Abstr., 67 (1967) 107870u.
33 A.N. Nesmeyanov, V. Sazonova and V.N. Drodz, Dokl. Akad. Nauk SSSR, 126 (1959) 1004; Chem. Abstr. 54 (1960) 6673q.
34 H.G. Kuivila and K.V. Nahabedian, J. Amer. Chem. Soc., 83 (1961) 2159.
35 E.W. Post, R.G. Cooks and J. Kotz, Inorg. Chem., 9 (1970) 1670.
36 H.G. Kuivila and T.G. Muller, J. Amer. Chem. Soc., 84 (1962) 377.
37 E.J. King, Acid-Base Equilibria, Pergamon Press, London, 1965.
38 A.K. Covington and T. Dickinson, Physical Chemistry of Organic Solvent Systems, Plenum Press, London and New York, 1973.
39 L.P. Hammett, Physical Organic Chemistry, 1st ed., McGraw-Hill, New York and London, 1940, p. 261.
40 L.G. van Vitert and C.G. Haas, J. Amer. Chem. Soc., 74 (1953) 451.
41 H.H. Jaffé, Chem. Rev., 53 (1953) 161.
42 W.F. Little and R. Eisenthal, J. Org. Chem., 26 (1961) 3609.
43 B. Floris, unpublished results.
44 H.C. Rochester, Acidity Functions, Academic Press, London, 1970, and ref. therein.
45 A.A. Frost and R.G. Pearson, Kinetics and Mechanism, John Wiley and Sons Inc., New York, 1965.
46 K.V. Nahabedian and H.G. Kuivila, J. Amer. Chem. Soc., 83 (1961) 2167.
47 R.O.C. Norman and R. Taylor, Electrophilic Substitution in Benzenoid Compounds, Elsevier, Amerdam, 1965, and ref. therein.
48 H.S. Choguill and J.H. Ridd, J. Chem. Soc., (1961) 822.
49 M. Liler, Reaction Mechanisms in Sulfuric Acid, Academic Press, London, 1971.
50 R.D. Brown, A.S. Buchanan and A.A. Humffray, Aust. J. Chem., 18 (1965) 1521.
51 T.A. Modro and K. Yates, J. Amer. Chem. Soc., 98 (1976) 4247.
52 E.S. Gould, Mechanism and Structure in Organic Chemistry, Holt, Rinehart and Winston, London, 1959, p. 112.

53 W.P. Jencks, Catalysis in Chemistry and Enzymology, McGraw-Hill, New York, 1969, p. 175.
54 R. Taylor, in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 13, Reactions of Aromatic Compounds, Elsevier, Amsterdam, 1972, and ref. therein.
55 J.F. Bunnett and R.J. Morath, J. Amer. Chem. Soc., 77 (1955) 5051, 5055.
56 H. Schecter and J.F. Helling, J. Org. Chem., 29 (1964) 1034.
57 R.W. Fisch and M. Rosenblum, J. Org. Chem., 30 (1965) 1253.
58 J.C. Kotz and E.W. Post, Inorg. Chem., 9 (1970) 1661.
59 A. Michaelis and P. Becker, Ber., 13 (1880) 58; ibid., 15 (1882) 180.
60 M.D. Rausch, M. Vogel and M. Rosenblum, J. Org. Chem., 22 (1957) 900.
61 G.P. Sollott, J.L. Sneap, S. Portnoy, N.R. Petersen and H.E. Mertnoy, U.S. Department of Commerce, Office Tech. Serv., A.A. 611869; Chem. Abstr. 63 (1965) 18147d.
62 (a) C. Bamford and C.F.H. Tipper (Eds.), Chemical Kinetics, Vol. 1, Elsevier, London, 1969, p. 390; (b) ibid., p. 380.
63 J.P. Pasto and G.R. Meyer, J. Org. Chem., 33 (1968) 1257.