too insoluble even in tetrahydrofuran (pale violet solution) for a satisfactory spectrum to be obtained although some evidence for the presence of a broad peak around −420 to −460 cycles relative to internal $(CFCl_2)_2$ was obtained.

Anal. Calcd. for $C_{18}H_{10}F_{12}S_4Cr_2$: C, 31.5; H, 1.5; F, 33.2; S, 18.7; Cr, 15.1. Found (two independent preparations): C, 31.7, 32.0; H, 1.7, 2.0; F, 33.6; S, 19.3; Cr, 14.9.

The molybdenum compound was prepared in an analogous manner using $[C_5H_5Mo(CO)_3]_2$ in place of $C_5H_5V(CO)_4$. After a single sublimation at ~ 175° (0.25 mm.), a 48% yield of purple-brown crystalline $[C_5H_5MoC_4F_6S_2]_2$ was obtained; infrared spectrum: C—H bands at 3130(vw) cm.$^{-1}$; C=C bands at 1650(w), 1630(m) and 1420(vw) cm.$^{-1}$; C—F bands at 1245(s), 1169(s), and 1135(s) cm.$^{-1}$; cyclopentadienyl bands at 1009(w) and 813(m) cm.$^{-1}$; other $C_4F_6S_2$ bands at 861(w), 840(w), 701(m) and 685(m) cm.$^{-1}$; F^{19} n.m.r. spectrum: resonance at −385 cycles relative to internal $(CFCl_2)_2$ in dichloromethane solution (deep purple).

Anal. Calcd. for $C_{18}H_{10}F_{12}S_4Mo_2$: C, 27.9; H, 1.3; F, 29.5; S, 16.5; Mo, 24.8. Fonnd: C, 28.1; H, 1.7; F, 29.7; S, 16.8; Mo, 25.6.

Reaction between Cyclopentadienylcobalt Dicarbonyl and Bis-(trifluoromethyl)-dithietene.—A mixture of 1.0 ml. (~1.4 g., ~8 mmoles) of cyclopentadienylcobalt dicarbonyl, 0.5 ml. (~0.8 g., ~3.5 mmoles) of bis-(trifluoromethyl)-dithietene and 50 ml. of methylcyclohexane was refluxed 5.5 hr. under nitrogen with magnetic stirring. The reaction mixture became a dark purple. After cooling to room temperature and then in a −78° bath for several hours, the black crystals were filtered. They were purified by recrystallization from a mixture of dichloromethane and hexane to give a total of 930 mg. (76% yield) of dark violet crystals of $C_5H_5CoC_4F_6S_2$, m.p. 150°, isolated in two crops; infrared spectrum: C—H band at 3140(vw) cm.$^{-1}$; C=C bands at 1480(w), and 1417(w) cm.$^{-1}$; C—F bands at 1262(sh), 1240(s), 1176(s) and 1145(s) cm.$^{-1}$; cyclopentadienyl bands at 1015(w), 1007(w) and 849(m) cm.$^{-1}$; other $C_4F_6S_2$ bands at 930(w), 727(w) and 695(w) cm.$^{-1}$; F^{19} n.m.r. spectrum: resonance at −710 cycles relative to internal $(CFCl_2)_2$ in dichloromethane solution (very deep purple). The compound $C_5H_5CoC_4F_6S_2$ is the only new compound described in this paper that exhibits a definite melting point on heating in a closed capillary.

The compound $C_5H_5CoC_4F_6S_2$ may also be purified by sublimation at 80° (0.1 mm.). A significant amount of decomposition occurs during this process.

Anal. Calcd. for $C_9H_5F_6S_2Co$: C, 30.9; H, 1.4; F, 32.6; S, 18.3; Co, 16.8; mol. wt., 350. Found (sublimed sample): C, 31.2; H, 1.7; Co, 16.9. Found (recrystallized sample): C, 31.5; H, 1.5; F, 32.5; S, 18.4; Co, 16.6; mol wt., 360 (isopiestic in dichloromethane), 354 (Mechrolab vapor pressure osmometer in benzene).

Reaction between Cyclopentadienylnickel Carbonyl Dimer and Bis-(trifluoromethyl)-dithietene.—A mixture of 1.5 g. (~5 mmoles) of $[C_5H_5NiCO]_2$, 1.0 ml. (~1.6 g., ~7 mmoles) of bis-(trifluoromethyl)-dithietene and 50 ml. of hexane was stirred for 16 hr. at room temperature under nitrogen. The reaction mixture became dark green and much black solid separated. After cooling to −78°, the black crystals were filtered. They were purified by two recrystallizations from dichloromethane–hexane mixtures. After one recrystallization the yield was 1.2 g. (48%); infrared spectrum: C—H band at 3150(w) cm.$^{-1}$; C=C bands at 1520(m), 1440(w) and 1405(m) cm.$^{-1}$; C—F bands at 1248(s), 1170(s) and 1132(s) cm.$^{-1}$; cyclopentadienyl bands at 1020(m), 993(w), 848(m), 830(m), and 816(s) cm.$^{-1}$; other $C_4F_6S_2$ bands at 921(m), 724(m) and 695(m) cm.$^{-1}$; F^{19} n.m.r. spectrum: no resonance could be observed even in what appeared to be a fairly concentrated tetrahydrofuran solution (deep green) as would be expected due to the paramagnetism of this compound.

Anal. Calcd. for $C_9H_5F_6S_2Ni$: C, 30.9; H, 1.4; F, 32.6; S, 18.3; Ni, 16.8. Found: C, 31.1; H, 1.8; F, 31.4; S, 18.7; Ni, 16.8.

Reaction between Dicobalt Octacarbonyl and Bis-(trifluoromethyl)-dithietene.—A mixture of 2.0 g. (5.9 mmoles) of dicobalt octacarbonyl, 0.5 ml. (~0.8 g., ~3.5 mmoles) of bis-(trifluoromethyl)-dithietene and 50 ml. of methylcyclohexane was refluxed 3 hr. 15 min. under nitrogen with magnetic stirring, the reaction mixture becoming black. The reaction mixture was allowed to cool to room temperature and finally in a −78° bath and the black precipitate filtered. In some experiments the precipitate was pyrophoric. The product was isolated from the precipitate by sublimation at 170° (0.5 mm.) and purified by resublimation at 100–135° (0.25 mm.). A highly erratic yield of black crystals of empirical formula $C_4F_6S_2CoCO$ was obtained; infrared spectrum: carbonyl bands at 2110(s) and 2080(s) cm.$^{-1}$; C=C bands at 1560(m) and 1530(m) cm.$^{-1}$; C—F bands at 1245(vs), 1185(s), and 1160(s) cm.$^{-1}$; other $C_4F_6S_2$ bands at 1012(w), 900(m), 890(m), 716(m), 693(w) and 689(w) cm.$^{-1}$.

Anal. Calcd. for $C_5F_6OS_2Co$: C, 19.2; H, 0.0; F, 36.4; S, 20.4; Co, 18.8. Found: C, 19.3; H, 0.6; F, 36.2; S, 20.8; Co, 17.8.

Reaction between Nickel Tetracarbonyl and Bis-(trifluoromethyl)-dithietene.—A mixture of 1.0 ml. (~1.6 g., ~7 mmoles) of bis-(trifluoromethyl)-dithietene and 50 ml. of hexane was prepared under nitrogen and treated with 2.0 ml. (~2.6 g., ~15 mmoles) of nickel tetracarbonyl, the reaction mixture turning black. The reaction mixture was refluxed 2 hr. under nitrogen with magnetic stirring, becoming a dark brown-black in color, much solvent being lost. The reaction mixture was allowed to cool to room temperature, diluted to 50 ml. with pentane, and cooled in a −78° bath. The resulting black solid was filtered and sublimed at 150° (0.2 mm.) for 24 hr., 50 mg. (2.5% yield) of brown-black crystals being obtained; infrared spectrum: C=C band at 1590(m) cm.$^{-1}$; C—F bands at 1240(s) and 1170(s) cm.$^{-1}$; other bands at 1010(w), 897(m), 720(m) and 692(m) cm.$^{-1}$.

Anal. Calcd. for $C_4F_6S_2Ni$: Ni, 20.6. Found: Ni, 20.8.

Magnetic Susceptibility Measurements.[8]

1. $[C_5H_5MoC_4F_6S_2]_2$: $\chi^{25°} = -124 \times 10^{-6}$ cm.^{3}/molybdenum atom
2. $[C_5H_5VC_4F_6S_2]_2$: $\chi^{25°} = 0.00 \times 10^{-6}$ cm.^{3}/vanadium atom (sample I); $\chi^{25°} = +140 \times 10^{-6}$ cm.^{3}/vanadium atom (sample II), corresponding to a magnetc moment of 0.58 B. M. for sample I and 0.62 B. M. for sample II after making the necessary correction for the diamagnetism of the cyclopentadienyl ring and the $C_4F_6S_2$ residue.[9]
3. $C_5H_5NiC_4F_6S_2$: $\chi^{25°}_{mole} = +1030 \times 10^{-6}$ cm.^{3}/mole corresponding to a magnetic moment of 1.67 B.M. after making the necessary correction for the diamagnetism of the ligands.[9]

(8) The author is indebted to Dr. L. Vaska of the Mellon Institute for carrying out these magnetic measurements.

(9) The total diamagnetism of the cyclopentadienyl ring and of the $C_4F_6S_2$ residue was estimated at -140×10^{-6} cm.^{3}/metal atom.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

On the Purported Tetraphenylboric Acid

BY JOHN N. COOPER AND RICHARD E. POWELL

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The kinetics of the reaction of H^+ with $B(C_6H_5)_4^-$ shows no evidence for a molecular species $HB(C_6H_5)_4$. A decomposition mechanism involving attack of the proton on one of the aromatic rings is consistent with the observed acidity dependence, deuterium isotope effect, salt effect and activation parameters.

In his original work on the salts of tetraphenylborate anion, Wittig[1] stated that the corresponding acid is formed on addition of mineral acids to cold aqueous solutions of the salts, and that it can be back-titrated with base (reaction 1), although he also reported that in warm solutions decomposition takes place according to reaction 2. We were interested in preparing the

$$H^+ + B(C_6H_5)_4^- \rightleftharpoons HB(C_6H_5)_4 \quad (1)$$

$$H^+ + B(C_6H_5)_4^- \longrightarrow C_6H_6 + B(C_6H_5)_3 \quad (2)$$

substance $HB(C_6H_5)_4$, with the idea of investigating the physical properties of this apparently 5-coördinated boron compound.

Preliminary experiments showed, first, that the addition of mineral acid to cold sodium tetraphenylborate produced no acidic solid (although reaction 2

(1) G. Wittig, G. Keicher, A. Rückert and P. Raff, *Ann.*, **563**, 110 (1949).

began to occur), and, second, that the potentiometric titration curve of 0.01 M HCl into sodium tetraphenylborate solution was indistinguishable from that of a like amount of HCl into distilled water. Accordingly, $HB(C_6H_5)_4$, if it exists, is water soluble and a comparatively strong acid. To pursue this question further, we have studied the kinetics of reaction 2 into as acidic a range as we could. It is clear that, if the equilibrium constant for reaction 1 is K, the rate law for reaction 2 will contain a factor $[H^+]/(K + [H^+])$; *i.e.*, that the pseudo-first-order rate constant k_1, plotted as a function of acid concentration, will curve toward the horizontal axis as the acid concentration becomes comparable to K.

We regret to report that we observe no evidence for a molecular species $HB(C_6H_5)_4$, up to an acidity of $h_0 = 15$.

Experimental

Reagents.—J. T. Baker sodium tetraphenylboron was dissolved in distilled water and filtered repeatedly through aluminum hydroxide until the turbidity was removed. A benzalkonium solution was prepared by diluting a commercial 12.8% solution of Zephiran[2] 100-fold. Deuterium oxide (99.5%, General Dynamics Corp.) was redistilled under vacuum. Other chemicals used were reagent grade

Stoichiometry.—The stoichiometry of reaction 2 was verified, within the uncertainty of our methods of analysis of the products (±3%); benzene was determined spectrophotometrically in isooctane solution following vacuum distillation of the volatile products of reaction, and triphenylborine was determined by the addition of mercuric chloride in methanol and titration of the resulting strong acid.[1]

Side Reaction.—When a vigorous current of O_2 was bubbled through the reaction mixture, it was rapidly saturated with biphenyl ($C_{12}H_{10}$) in a reaction of approximately half the rate of the desired decomposition. When the reaction was carried out under N_2, no biphenyl was produced. While the reaction of tetraphenylborate with O_2 does not appear to have been studied in aqueous media, Geske[3] has reported it to take place in acetonitrile solution. Under the conditions of our kinetic study, the exclusion of air was not necessary; only a trace of biphenyl was formed, and within experimental error the rates in N_2 and in air were the same (Table I).

TABLE I
EFFECT OF ATMOSPHERIC OXYGEN

Temp., °C.	k_2, mole^{-1} liter hr.$^{-1}$ Under N_2	Under air
0.0	0.426 ± 0.02	0.434 ± 0.02
29.8	14.7 ± 0.6	14.0 ± 0.6
39.7	46.6 ± 2	44.6 ± 2

Kinetics.—Since we were unable to devise a satisfactory method for following the reaction continuously, aliquots were taken and analyzed for residual tetraphenylborate, either by precipitating thallous tetraphenylborate from a known volume of thallous nitrate and titrating the excess thallous ion with a known iodate solution,[4] or by precipitating the benzalkonium tetraphenylborate to the Titan Yellow end point with a standardized benzalkonium solution.[5] The temperature was controlled to ±0.1°. Although the rate was generally followed only for about 20% decomposition, a few runs were made with different initial concentrations of tetraphenylborate to verify the assumption that the reaction is kinetically first order with respect to tetraphenylborate (Fig. 1).

Results and Discussion

At low acidities reaction 2 is kinetically first order with respect to H^+ concentration, and at somewhat higher acidities first order with respect to the Hammett acidity h_0 (Fig. 2). The lack of curvature in the plot indicates that no significant quantity of $HB(C_6H_5)_4$ has been formed at the highest acidity studied. Moreover, the fact that the rate does not follow the h_- function[6,7] implies that even in the activated complex the

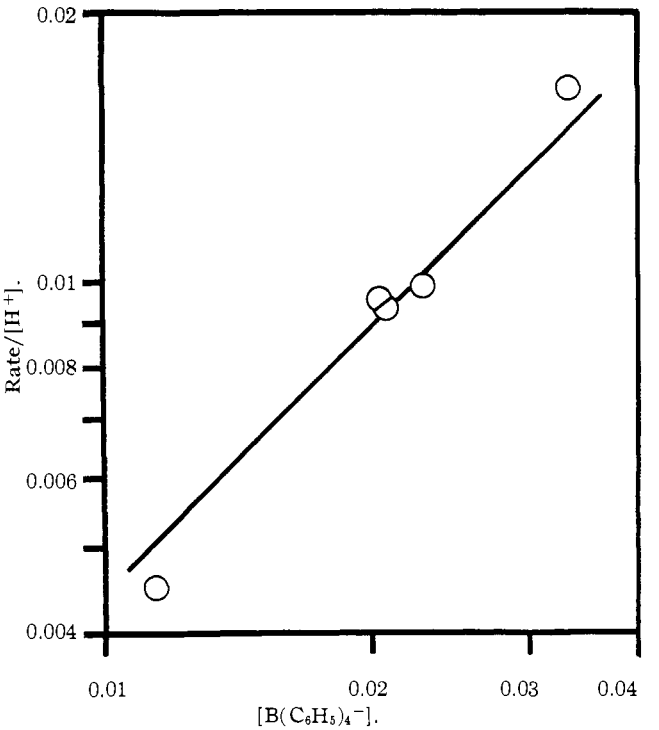
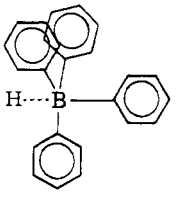
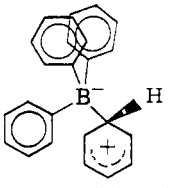


Fig. 1.—Dependence of rate on tetraphenylborate concentration at 0°; rate in mole liter^{-1} hr.$^{-1}$.

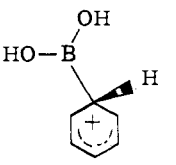
H^+ does not attack the charge-bearing boron atom, but some other point in the molecule. The difference between a reaction which follows h_0 and one which follows h_- lies primarily in the fact that in the former there is comparatively little change in solvation between the reactants and the activated complex, whereas in the latter the charges are so nearly neutralized as to produce a comparatively large change in solvation of the activated complex. If reaction 2 were to proceed through the rate-determining formation of



followed by rapid rearrangement to C_6H_6 and $B(C_6H_5)_3$, more extensive changes in solvation would be expected than if the proton were to attack a benzene ring to produce a zwitterion activated complex



Accordingly, the data on acidity-dependence favor the latter structure for the activated complex, and reaction 2 can be regarded as an example of a protodeboronation reaction similar to those studied by Kuivila and Nahabedian.[8]



(2) Zephiran is the Winthrop Laboratories trade name for a buffered aqueous solution of benzalkonium chlorides.
(3) D. H. Geske, *J. Phys. Chem.*, **63**, 1062 (1959).
(4) B. R. Sant and A. K. Mukherji, *Talanta*, **2**, 154 (1959).
(5) F. B. Martinez and M. G. Borl, *Chemist Analyst*, **49**, 69 (1960).
(6) R. H. Boyd, *J. Am. Chem. Soc.*, **83**, 4288 (1961).
(7) J. N. Phillips, *Australian J. Chem.*, **14**, 183 (1961).
(8) H. G. Kuivila and K. V. Nahabedian, *J. Am. Chem. Soc.*, **83**, 2159, 2164, 2167 (1961).

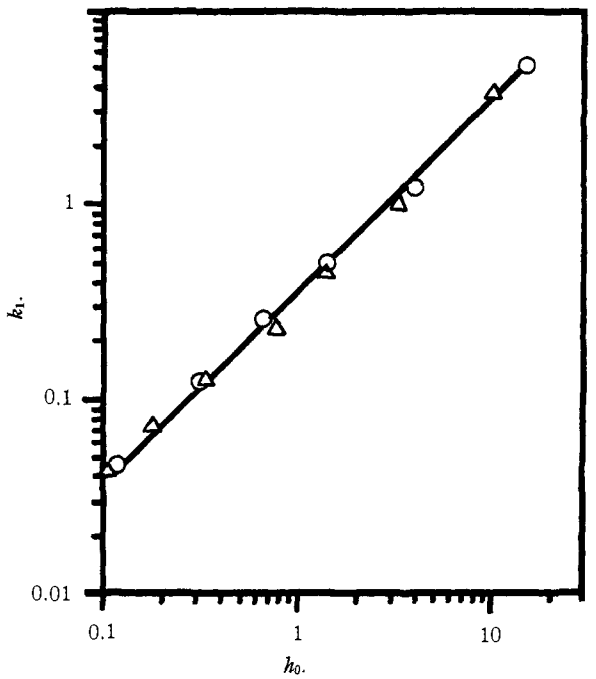


Fig. 2.—Dependence of rate on acidity function; pseudo-first-order rate constant k_1 (*viz.*, rate/$[B(C_6H_5)_4^{-1}]$) in hr.$^{-1}$, at 0°: O, $HClO_4$; Δ, HCl.

Deuterium Isotope Effect.—The decomposition rate was measured in D_2O (Table II), and k_H/k_D found to be 2.8, in agreement with expectation for a protodeboronation mechanism, but not for a preliminary formation of $HB(C_6H_5)_4$.

TABLE II

THE SOLVENT HYDROGEN ISOTOPE EFFECT

H_2O	k_2 = 14.0 ± 0.06 mole^{-1} l. hr.$^{-1}$
D_2O	5.2 ± 0.2

Rate measured at 29.8°, ionic strength of 0.115 *M*.

General Acid Catalysis.—The addition of chloroacetic acid up to 0.327 *M* gave no observable catalytic effect (Table III). Kuivila and Nahabedian[8] observed general acid catalysis. A possible explanation for

TABLE III

THE EFFECT OF CHLOROACETIC ACID

$[ClCH_2CO_2H]$ = 0.065 *M*	k_2 = 16.1 mole^{-1} l. hr.$^{-1}$
0.196	15.5
0.327	15.5

Rate measured at 29.8°, ionic strength of 0.237 *M*, acidity of 0.036 *M*.

its absence here may be that the steric hindrance is greater in tetraphenylborate. An alternative, and perhaps more plausible, explanation is that the general acid catalysis in Kuivila's reaction involved a pre-equilibrium attack by the conjugate base on the leaving group–$B(OH)_2$, followed by rate-determining proton transfer to the benzene ring. The loss of the leaving group $-B(OH)_2$ would be facilitated considerably by attachment of a base; on the other hand, the loss of the group $-B(C_6H_5)_3^-$ would be hardly affected by base, both because the attachment of a base is sterically hindered and because the negatively-charged group repels an anionic base.

Salt Effect.—The anticipated salt effect for the protodeboronation mechanism above, in which the activated complex is a zwitterion, is in the same direction as, but smaller than, the conventional Debye–Hückel effect for a +1, −1 combination. Our data (Table IV) are consistent with this expectation, although the experimental error is great enough that we would hesitate to draw conclusions from these data alone.

TABLE IV

EFFECT OF IONIC STRENGTH AND TEMPERATURE

Temp., °C.	Ionic strength, *M*	k_2, mole^{-1} l. hr.$^{-1}$
0.0	0.122	0.434
	.187	.446
	.305	.466
19.8	.026	5.44
	.113	5.00
	.255	5.70
29.8	.013	18.9
	.038	14.8
	.064	13.4
	.114	14.0
	.171	14.2
	.214	14.1
39.7	.013	52.5
	.114	44.6
44.7	.013	92.5
	.114	73.6

Activation Parameters.—From the rate data at various temperature (Table IV) one calculates $\Delta H^{\ddagger}$ = 18 ± 1 kcal. mole^{-1} and $\Delta S^{\ddagger}$ = −10 ± 4 cal. deg.$^{-1}$ mole^{-1} at ionic strength 0.11. The activation energy is about the same as those observed by Kuivila. The entropy of activation is consistent with the formation of a zwitterion activated complex; as Jordan[9] has found, the entropy of ionization is remarkably sensitive to the polar nature of the molecule involved, acetic acid having an entropy of ionization of −22 ± 1 and trichloroacetic acid −2 ± 5 cal. deg.$^{-1}$ mole^{-1}. In terms of structural properties, we interpret this observation to indicate that the solvation in a highly polar species is not greatly different from that in the separated ions; and, as applied to reaction 2, that no significant changes in solvation have taken place between the initial state and the activated complex.[10]

Acknowledgment.—J. N. C. is pleased to acknowledge the tenure of fellowships of the National Science Foundation (1960–1961), California Research Corporation (Summer 1962), and Texaco, Inc. (1962–1963).

(9) J. Jordan and W. H. Dumbaugh, *Anal. Chem.*, **31**, 210 (1959).

(10) NOTE ADDED IN PROOF.—It has come to our attention that this same problem has been investigated by Verne Allen Simon (dissertation, Flordia State Unverisity, 1962; *Dissertation Abstr.*, **23**, 1534 (1962)).