

the ferrocene nucleus. Values for σ_p were originally derived from the ionization constants of benzoic acid and its substitution products, and, in a *p*-substituted benzoic acid, there exists a resonance interaction between substituent and carboxyl group as relayed through the ring. Values of σ_m and σ^* do not include a resonance contribution of this type. Thus, it may be concluded that the resonance interactions between substituents and the ferrocene nucleus parallel those between substituents and the carboxyl group in *p*-substituted benzoic acids.

In Fig. 4 there is shown a plot of $E_{1/4}$ values vs. σ_p -values for a series of *p*-substituted phenylferrocenes. The equation of the line is

$$E_{1/4} = 0.132\sigma_p + 0.361 \quad (4)$$

with a correlation coefficient of 0.998. These results are in substantial agreement with the findings of Mason and Rosenblum,² who have determined formal oxidation potentials for the same compounds¹⁵ by titration with dichromate ion in aqueous acetic acid containing perchloric acid. Calculation of the equation for the regression line from the data of Mason and Rosenblum in the form employed in this study gives

$$E_{0.4^*} = 0.151\sigma_p + 0.255 \quad (5)$$

From eq. 4 and 5 it is evident that the slope for the line based upon chronopotentiometric data is less than the slope for the line obtained by the titrimetric method. The difference in slopes is probably due in large part to the difference in solvation effects between acetonitrile (the solvent employed in our study) and aqueous acetic acid.

The linearities of the plot of $E_{1/4}$ values vs. $\Sigma\sigma^*$ values (except for the values of acetylferrocene and the trimethylsilylferrocenes) and of the plot of $E_{1/4}$ values vs. $\Sigma\sigma_p$ permit the calculation of substituent constants which are unknown for one system but known for the other. From eq. 1 and

(15) We are indebted to Professor Rosenblum for his gift of samples of these compounds.

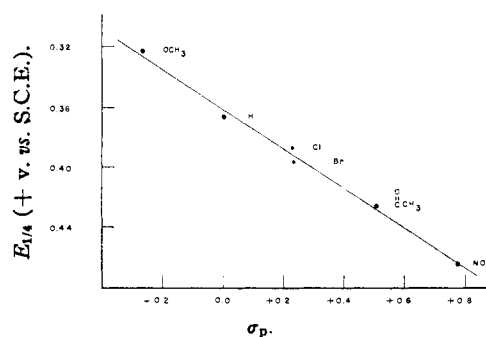


Fig. 4.—Plot of $E_{1/4}$ vs. σ_p for *p*-substituted phenylferrocenes.

3 the following relationships are derived

$$\Sigma\sigma^* = 4.406\Sigma\sigma_p - 5.156 \quad (6)$$

$$\Sigma\sigma_p = 0.227\Sigma\sigma^* + 1.170 \quad (7)$$

It should be emphasized that eq. 6 and 7 are applicable only in those instances in which there cannot be significant overlap between the h_a molecular orbital of the ferrocene nucleus and a suitable p or d orbital of an atom of the substituent group. It must also be remembered that the $\Sigma\sigma^*$ term in eq. 1 includes proper values for the weighting of hydrogen as well as the substituents.

Finally, the values of substituent constants calculated by use of eq. 6 and 7 must be regarded as tentative ones and must be tested in other systems before their validity can be considered to be established.

Acknowledgment.—This research was supported by grants from the Petroleum Research Fund administered by the American Chemical Society, and the Office of Ordnance Research, U. S. Army. Grateful acknowledgment is made to the donors of these funds. We are indebted to Dr. Marvin D. Rausch and to Dr. D. E. Bublitz for their gifts of samples of several ferrocenes, and to Dr. Theodore Kuwana and to Dr. Ralph N. Adams for helpful discussions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

The Kinetics and Mechanism of the Reaction of Borohydrides with Weak Acids¹

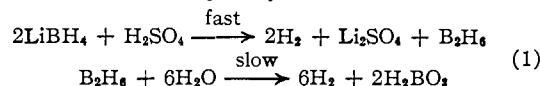
BY RAYMOND E. DESSY AND EDWARD GRANNEN, JR.

RECEIVED DECEMBER 6, 1960

The mechanism of the reaction of NaBH_4 and $\text{C}_6\text{H}_5\text{OH}$ in diglyme to yield hydrogen plus sodium phenoxyborohydride has been investigated, and found to obey the rate law $d(\text{H}_2)/dt = (k(\text{C}_6\text{H}_5\text{OH})^2(\text{NaBH}_4)/(\text{C}_6\text{H}_5\text{ONa}))$. Evidence indicates that $\text{C}_6\text{H}_5\text{OH}_2^+$ is the attacking species; k_H/k_D ($\text{C}_6\text{H}_5\text{OH}$) is 1.7. The reaction of LiBH_4 with CH_2OH is similar in character. k_H/k_D (LiBH_4) is 0.63. These isotope effects, along with the fact that the rate of reaction of LiBH_4 with HA increases along the series C_6H_6 , $\text{C}_4\text{H}_5\text{N}$, *t*-BuOH, CH_3OH , as HA is varied, while the K_a 's of the acids increase along the series C_6H_6 , *t*-BuOH, CH_3OH , C_6H_6 , suggests a four-center transition state for the reactions.

Although reactions of the alkali borohydrides with acids have been investigated, relatively few systematic surveys have been undertaken. Kilpatrick² measured the rate of reaction of LiBH_4

with H_2SO_4 in water by a manometric method involving a pressure transducer. He suggested that the mechanism of hydrolysis was

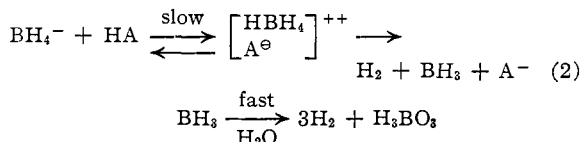


(1) The Research reported in this paper was partially supported by the Air Force Office of Scientific Research, Air Research and Development Command, under contract AF 49(638)-824 with the University of Cincinnati. The paper is identified as AFOSR TN-60-1467.

(2) M. Kilpatrick and C. D. McKinney, *J. Am. Chem. Soc.*, **72**, 5474 (1950).

The rate constant for removal of the first hydrogen under these conditions was $0.79 \text{ l. m.}^{-1} \text{ sec.}^{-1}$, although it has been suggested that he was measuring rate of H_2 dissolution.⁴

Pecsok³ has investigated the rate of hydrolysis of NaBH_4 in buffered aqueous solution ($\text{pH } 7.7\text{--}9.5$) by a polarographic method and found that $d(\text{BH}_4^-)/dt = k(\text{BH}_4^-)(\text{H}^+)$, with $k^{25\text{H}_2\text{O}} = 2.5 \times 10^5 \text{ l. m.}^{-1} \text{ sec.}^{-1}$. He postulated as an intermediate $\text{HBH}_4 \cdot x\text{H}_2\text{O}$. This agrees with the recent work of Davis,⁴ who has studied the same system titrimetrically ($\text{pH } 7.6\text{--}14.8$) and found $k^{25\text{H}_3\text{O}^+} = 1.10^6$ and $k^{25\text{H}_2\text{O}} = 2 \pm 1 \times 10^{-9} \text{ l. m.}^{-1} \text{ sec.}^{-1}$. General acid catalysis was found. The mechanism suggested was



All of the other work reported^{5,6} has been qualitative in nature; however, the latter papers indicate that $\text{BH}_3(\text{B}_2\text{H}_6)$ is indeed an intermediate in the reaction.

Hawthorne⁷ has measured the rate of hydrolysis of the diaryl borane-pyridine adducts in acetonitrile, and Ryschkewitsch⁸ has studied the kinetics of the reaction of trimethylamineborane with aqueous HCl .

None of these investigations has been conducted in non-aqueous solutions where the structure of the attacking acid can be changed systematically, and where the cation of the borohydride is intimately connected to it. The purpose of this paper is therefore to present some data on: (1) the mechanism of the reaction of sodium borohydride with phenols in diglyme; (2) the reaction of lithium borohydride with various weak acids in diglyme; (3) deuterium isotope effects in these systems.

Experimental

Materials.—The solvent diglyme (diethylene glycol dimethyl ether) was distilled from LiAlH_4 immediately before use.

Sodium borohydride and lithium borohydride (Metal Hydrides, Inc.) were used as received; LiBH_4 was also prepared from B_2H_6 and LiH following the procedures described by Brown.^{9a} The two types of LiBH_4 gave the same kinetic results indicating that any impurity in the commercial material did not affect the reaction. Stock solutions of the appropriate borohydride were made up in diglyme, allowed to stand at least 24 hours, filtered in a nitrogen atmosphere and standardized by analysis for active hydrogen.

Phenol was purified by two distillations from aluminum turnings (0.05% by wt.) at atmospheric pressure. The material which distilled at $179\text{--}180^\circ$ was stored in a desiccator over P_2O_5 .

The substituted phenols were all commercially available (Distillation Products unless otherwise stated) and were

purified by distillation or recrystallization. *m*-Chlorophenol, b.p. $93\text{--}95^\circ$ (6 mm.); *p*-chlorophenol, b.p. $212\text{--}214^\circ$ (745 mm.); 98° (8 mm.); *m*-methoxyphenol, b.p. $106\text{--}108^\circ$ (6 mm.); *p*-methoxyphenol, m.p. 54° ; *m*-fluorophenol (Pierce Chemical Co.) b.p. $40\text{--}41^\circ$ (1 mm.). The liquids were stored in the refrigerator in sealed ampoules under nitrogen. The solids were stored in a desiccator over P_2O_5 .

Methanol (Fisher analyzed reagent) was used as received. Cyclopentadiene was prepared by thermal cracking of the dimer, b.p. 42° (745 mm.). Both pyrrole, b.p. 131° , and *t*-butyl alcohol, b.p. $82\text{--}82.5^\circ$ (745 mm.), were distilled immediately before use.

Sodium phenoxide was prepared according to the method of Kornblum.¹⁰ The solid was heated for 35 hours at 100° (2 mm.) to ensure complete removal of phenol.

The phenol-O-*d* was prepared by placing 12 g. (0.104 mole) of sodium phenoxide in a previously dried 300-ml. three-necked flask fitted with a stopper, stirring bar, gas inlet and gas outlet. The outlet was connected to a CaCl_2 drying tube; 100 ml. of dry dioxane was added to the flask which was then flushed with nitrogen. Phenolphthalein was added and DCl (Merck and Co., Ltd.) was bubbled through the stirred mixture until the color had changed from purple to light pink. The flask was cooled in an ice-bath during the addition of the DCl . The solvent was removed at reduced pressure. The deuterated phenol, 8 g. (84%), had a boiling point of $66\text{--}69^\circ$ (3 mm.). Infrared spectra indicated the presence of less than 5% phenol as a contaminant.

The LiBD_4 was prepared from LiD and B_2D_6 . All of the glassware used was dried overnight in an oven at 110° . Oil-pumped nitrogen was used to sweep out the system prior to the reaction. The B_2D_6 was generated from LiAlD_4 and BF_3 .¹¹

Lithium aluminum deuteride (2.35 g., 0.058 mole, 98%, Metal Hydrides, Inc.) was placed in a 100-ml. three-necked flask fitted with a stopper, a dropping funnel and a delivery tube. Stirring was accomplished by means of a magnetic stirrer; 50 ml. of dry ether (distilled from LiAlH_4) was placed in the reaction vessel. A delivery tube connected this flask with a 300-ml. flask containing 0.723 g. (0.0775 mole) of LiD (Metal Hydrides, Inc., 96.5%) suspended in 200 ml. of diglyme. Exit gases were passed into an acetone wash bottle.

Boron trifluoride etherate (5.26 g., 0.0776 mole, 10 ml.) in 50 ml. of dry ether was added slowly to the LiAlD_4 . Total addition time was 90 minutes. The LiD suspension was cooled in an ice-bath during the absorption of B_2D_6 . The suspension was stirred for 48 hours. It was then filtered in a dry-box. Any ether which was carried over from the B_2D_6 generating flask was removed during the filtration. The solution then was standardized by analysis for active hydrogen. The yield was 70% based on LiAlD_4 .

Apparatus.—A modified Thomas-Van Slyke-Folch manometric apparatus was used in our work. The reaction vessel was a 100-ml. round-bottom flask to which an addition tube had been sealed. Stirring of the solutions in the flask was accomplished by a magnetic stirrer. The gas chamber was thermostated by means of a circulating pump operating from the constant temperature bath. The maximum temperature variation was 0.1° .

Analysis of Borohydride Solutions.—The amount of borohydride solution taken for analysis varied from 2 to 5 ml. depending upon the concentration of the solution. A given amount of the borohydride solution was transferred to the reaction vessel by means of a syringe. The vessel was attached to the manometric apparatus and evacuated, using a Dry Ice-acetone-bath around the reaction flask. The constant temperature bath was assembled and the reaction vessel was connected with the gas chamber. After the bath had come to temperature, the system was allowed to equilibrate for at least 30 minutes. Then 2 ml. of concentrated HCl was added and the change in pressure observed. The concentration was obtained from the equation $PV = nRT$, corrections being applied for the pressure exerted by excess HCl . Duplicate analyses agreed to within 1% or better.

Kinetic Runs.—The apparatus was the same as described above. In all kinetic runs 10 ml. of the borohydride solu-

- (3) R. L. Pecsok, *J. Am. Chem. Soc.*, **75**, 2862 (1953).
- (4) R. E. Davis and C. G. Swain, *ibid.*, **82**, 5949 (1960).
- (5) V. I. Mikeheeva and E. M. Fedneva, *Doklady Akad. Nauk, SSSR*, **101**, 99 (1955).
- (6) (a) H. G. Weiss and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 6167 (1959); (b) H. Schlesinger and H. Brown, *ibid.*, **82**, 3429 (1960).
- (7) M. F. Hawthorne and E. S. Lewis, *ibid.*, **80**, 4296 (1958).
- (8) G. Ryschkewitsch, *ibid.*, **82**, 3290 (1960).
- (9) (a) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *ibid.*, **75**, 199 (1953); (b) I. Shapiro, H. G. Weiss, M. Schmick, S. Skolnik and G. E. L. Smith, *ibid.*, **74**, 901 (1952).

(10) N. Kornblum and A. P. Lurie, *ibid.*, **81**, 2705 (1959).

(11) W. S. Koski, J. J. Kaufman, C. F. Pachucki and F. J. Shipko, *ibid.*, **80**, 3202 (1958).

tion was placed in the reaction vessel and allowed to come to equilibrium. Then 10 ml. of the appropriate acid solution (previously equilibrated) was added. An initial pressure change due to the volume of added acid solution usually was noted and suitable corrections for this were made. Pressure readings were taken at appropriate time intervals along 75% of the total reaction path. The kinetic runs all were made in duplicate and agreed to within 5%.

Interpretation of Data.—Attempted fits to a second-order rate expression were made plotting $1/(a-x)$ vs. t or $\ln(b/a)/((a-x)/(b-x))$ vs. t , where a and b represent initial concentrations and x the extent of reaction determined by hydrogen evolution.

Fits to a third-order rate expression were made plotting $1/2(a-x)^2$ vs. t .

In all cases good third-order fits were obtained to about 50–60% of the first hydrogen. Beyond this point reaction of the alcohol with the product, an alkali alkoxyborohydride, complicated the kinetic picture.

Preparation of $\text{NaBH}_3\text{OC}_6\text{H}_5$.—a. Sodium borohydride (1.90 g., 0.05 mole) was dissolved in 150 ml. of diglyme. To this solution was added 4.70 g. (0.05 mole) of phenol. The mixture was allowed to stand overnight.

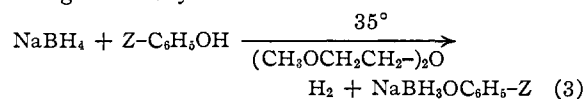
b. Diborane was generated by the method suggested by Brown and Tierney.¹² To 1.56 g. (0.0413 mole) of NaBH_4 in 100 ml. of diglyme was added 7.0 ml. (3.73 g., 0.055 mole) of BF_3 etherate. The diborane produced was passed into 5.8 g. (0.05 mole) of sodium phenoxide in diglyme cooled to -80° . The solution was permitted to warm to room temperature over 4 hours. The infrared spectra of the materials produced by methods a and b were identical from 2 to 15 μ .

Reaction of Products with Hexene-1.—Stock solutions of NaBH_4 (0.1 M), hexene-1 (0.35 M) and LiBH_4 (0.1 M) hexene-1 (0.35 M) were made up. To an aliquot of each solution was added an aliquot of the acid, phenol or methanol respectively. Analysis by v.p.c. on the stock solution and the sample solutions showed that the hexene content decreased in the latter, indicating reduction. The amount of reduction was directly proportional to the amount of added acid.

Reaction of Products with Triethylamine.—Sodium borohydride (1.90 g., 0.05 mole) was suspended in 50 ml. of ether. Seven grams (0.07 mole) of triethylamine was added to the ether slurry. Then 4.7 g. (0.05 mole) of phenol in 50 ml. of ether was added over 3 hours. A solid which formed was filtered off and the clear solution was distilled. There was obtained 5 g. (88%) of the amine-borane adduct, b.p. 66–69° (3 mm.).

Discussion and Results

The reaction of NaBH_4 with phenol, and substituted phenols, in diglyme (dimethyl ether of diethylene glycol) may be followed manometrically using a Van Slyke–Folch manometer.



Although no $\text{BH}_3(\text{B}_2\text{H}_6)$ could be detected in the reacting media, or in the gases above it, the addition of a 1:1 reaction mixture at the end of a kinetic run to a solution of hexene-1 in diglyme resulted in reduction of the hexene as evidenced by vapor phase chromatography of the products. The addition of triethylamine to a similar reaction mixture gave excellent yields of the triethylamine–borane adduct (b.p. 66–69° (3 mm.)) indicating that although free BH_3 was not present, it was potentially available. The postulation of $\text{NaBH}_3\text{OC}_6\text{H}_5\text{-Z}$ as the other product was confirmed by comparing the infrared spectra of a 1:1 reaction mixture with a sodium phenoxide– B_2H_6 adduct. Equation 3 is therefore stoichiometrically correct. Disproportionation of the $\text{NaBH}_3\text{OC}_6\text{H}_5$ may occur over

(12) H. C. Brown and P. Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958).

long time periods, but this does not seem to be important over periods of ~ 24 hours at room temperature.

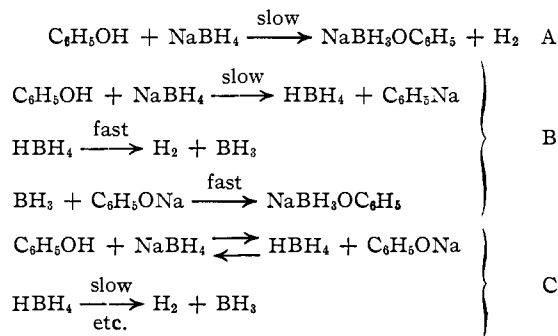
Table I shows the kinetic results employing various ratios of NaBH_4 and $\text{C}_6\text{H}_5\text{OH}$, assuming second-order kinetics, first-order in $\text{C}_6\text{H}_5\text{OH}$ and NaBH_4 . Higher $\text{C}_6\text{H}_5\text{OH}/\text{NaBH}_4$ ratios could not be employed because they favored secondary reactions of the sodium phenoxyborohydride with phenol, and led to a complex pattern of hydrogen evolution.

TABLE I
35°
 $\text{NaBH}_4 + \text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{diglyme}} \text{H}_2 + \text{NaBH}_3\text{OC}_6\text{H}_5$

NaBH_4 , M	$\text{C}_6\text{H}_5\text{OH}$, M	$\text{C}_6\text{H}_5\text{ONa}$, M	k_2^{35} , sec. ⁻¹ (M) ⁻¹	k_3^{35} , sec. ⁻¹ (M) ⁻²
0.10	0.10	..	0.0011	0.013
.20	.10	..	.0011	.012
.10	.20	..	.0019	.012
.10	.10	0.010045
.10	.20	.040038
.10	.10	.10	N.R.	N.R.
.10	.10 ^a	0.013

^a 0.1 M *t*-butyl alcohol added.

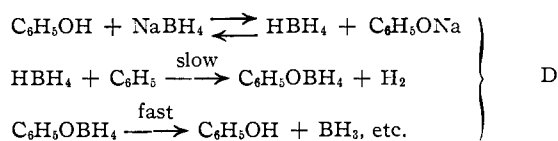
The increase in k_2 as the $\text{C}_6\text{H}_5\text{OH}/\text{NaBH}_4$ ratio increases indicates a higher order in phenol since added *t*-butyl alcohol did not affect the rate. Table I also shows the results of assuming a third-order reaction, second order in $\text{C}_6\text{H}_5\text{OH}$, first order in NaBH_4 . The constancy of k_3 indicates that the postulated mechanism must somehow include two molecules of $\text{C}_6\text{H}_5\text{OH}$ before the rate-determining step. This fact therefore automatically excludes mechanisms A, B and C and indicates that removal of



the three hydrogens from $\text{NaBH}_3\text{OC}_6\text{H}_5$ occurs at a lower rate than removal of the first. Although complete conversion to $\text{NaB}(\text{OC}_6\text{H}_5)_4$ is possible under forcing conditions (large excesses of phenol) the kinetics are "good" to about 60% of the first hydrogen.

The addition of an equivalent amount of sodium phenoxide to the reaction reduces the rate to the point where it is not measurable (Table I).

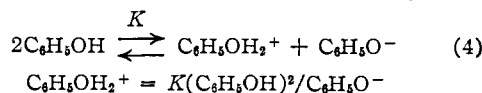
Mechanism D, or its equivalent, would fit the observed facts, but involves the highly unstable



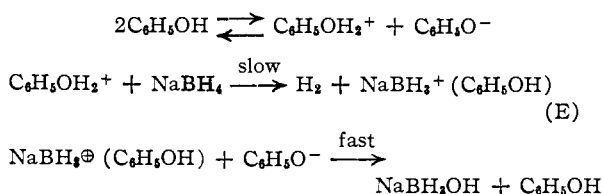
HBH_4 as an *intermediate*, an unlikely possibility.

It is interesting to note that reactions run with different amounts of C_6H_5OH and C_6H_5ONa , but with the same $(C_6H_5OH)^2/(C_6H_5ONa)$ ratio (Table I) have approximately the same calculated k_3 . Considering the salt effects in such solutions the agreement is good.

Such results are compatible with $C_6H_5OH_2^+$ as an attacking species since we may write



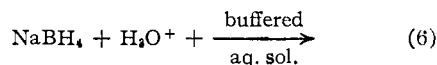
indicating a mechanism consistent with all of the available facts



where $NaBH_3^+(C_6H_5OH)$ is meant to indicate some type of complex. The structure of this complex and the nature of the last fast step will be discussed in succeeding paragraphs. The rate law is therefore

$$\frac{d(H_2)}{dt} = k_2(C_6H_5OH_2^+)(NaBH_4) = (k_2K = k_3) \frac{k_2K (C_6H_5OH)^2(NaBH_4)}{(C_6H_5O^-)} \quad (5)$$

A simple calculation of K indicates a value of roughly 10^{-3} for the autoprotolysis of phenol in diglyme, making $k_2C_6H_5OH_2^+$ about $11 \text{ sec.}^{-1} M^{-1}$ at 35° . It is interesting to compare this with the values reported by Pecsok³ and Davis⁴ for the reaction



where values of $k^H_{H_3O^+}$ of $\sim 1 \times 10^6 \text{ sec.}^{-1} M^{-1}$ are reported at 25° .

Substitution of deuterium for hydrogen in the phenol (C_6H_5OD) reduces the observed k_3 ³⁵ to $0.0072 \text{ sec.}^{-1} M^{-2}$, yielding a k_H/k_D ratio of 1.7, indicating a rate-determining proton transfer. This value of k_H/k_D is a maximum value for the rate-determining process since any isotope effect in the equilibrium step prior to the rate-determining step should also favor the protium compound over the deuterium compound.

A series of substituted phenols has been investigated and the results are displayed in Table II. The series follows the expected order, electron withdrawers facilitating reaction, electron donors impeding reaction. However, a Hammett plot is not obeyed probably because of the complex nature of the protonated species in solution and the fact that in the autoprotolysis those substituents which increase the acidity of one molecule of phenol, the donor, will decrease the basicity of another molecule, the acceptor.

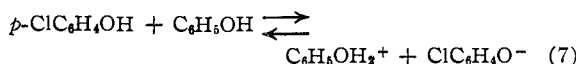
If this suggested mechanism is correct, the phenol must serve two functions as indicated above—a donor of a proton and an acceptor—functions that are in a sense mutually exclusive, and that one

TABLE II
 $NaBH_4 + Z-C_6H_5OH \xrightarrow[35^\circ]{\text{diglyme}} H_2 + NaBH_3OC_6H_5-Z$

Z	M	k_3^{35} sec. ⁻¹ (M) ⁻²	pKa ^a
<i>p</i> -MeO	0.110	0.0023	10.2
H	.101	.013	9.94
<i>m</i> -MeO	.110	.015	9.65
<i>p</i> -Cl	.110	.21	9.38
<i>m</i> -Cl	.098	.75	9.02
<i>m</i> -F	.098	1.13	9.28

^a See H. C. Brown, D. H. McDaniel, and O. Haffinger in "Determination of Organic Structures by Physical Methods," edited by E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1955.

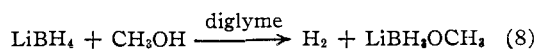
molecular structure cannot perform equally well. If, however, one chooses the combination of a good proton donor, say *p*-ClC₆H₄OH, and a good proton acceptor, say C₆H₅OH, then these together should serve as a better attacking system, because of the increased concentration of C₆H₅OH₂⁺.



When 0.1 M NaBH₄ is allowed to react with a mixture of 0.05 M *p*-ClC₆H₄OH and 0.05 M C₆H₅OH it is found that the initial rate is 3 times faster than that of *p*-ClC₆H₄OH alone at 0.1 M concentrations. This would seem to confirm the proposed mechanism.

One other factor in the rate-determining step of the reactions needs to be considered. Essentially the transition state involves the interaction of a hydride donor and a proton donor, an action which would leave one donor molecule electron deficient. In the present case the proton donor has available lone pair electrons, and it is meaningful to ask how much interaction between B and O occurs in the transition state. To aid in answering this question another reaction system has been studied.

The reaction of LiBH₄ with methanol in diglyme was investigated, and a similar picture found, *i.e.*,



inhibition by methoxide ion, second order in methanol, over a sixfold span in borohydride concentration. The reaction order could not be investigated at high CH₃OH/LiBH₄ ratios because of the tendency for the kinetic plots to deviate after the first half-life. With a CH₃OH/LiBH₄ ratio of 0.15 the reaction follows a third-order plot for at least 85% of the reaction. At a ratio of 1.0, the plot falls off at about 60%. All of the deviations were positive in the sense that the reaction appeared to proceed more rapidly than expected on the basis of the assumed kinetics. On the basis of Brown's¹³ work on the disproportionation of NaBH(OCH₃)₃ to NaBH₄ and NaB(OCH₃)₄, it is possible that the LiBH₃OCH₃ disproportionates, or symmetrizes, leading to species that augment the rate; on the other hand, it is known that NaBH(OCH₃) is a more powerful reducing agent than NaBH₄,¹⁴ suggesting that the rate of reaction

(13) H. C. Brown, E. J. Mead and P. Tierney, *J. Am. Chem. Soc.*, **79**, 5400 (1957).

(14) H. C. Brown and E. J. Mead, *ibid.*, **75**, 6263 (1953).

of $\text{LiBH}_3\text{OCH}_3$ with a proton donor might be more rapid than LiBH_4 . The fact that when large excesses of borohydride are used, good kinetics are observed for over 85% of the reaction indicates that the latter fact is the correct source of the explanation for kinetic deviations, and that disproportionation is not a serious problem during the lifetime of the present reaction. It is interesting to compare the two systems, since in non-aqueous solution the cation of the borohydride markedly affects its reactivity, and to contrast all this with the work of Davis⁴ and Pecsok⁸ in aqueous solution. In aqueous solution LiBH_4 and NaBH_4 react with H_3O^+ with similar rate constants in the neighborhood of $10^6 \text{ sec.}^{-1} (M)^{-1}$. In diglyme k_3 ³⁵ for the $\text{LiBH}_4/\text{CH}_3\text{OH}$ system is $0.015 \text{ sec.}^{-1} M^{-2}$, while the $\text{NaBH}_4/\text{C}_6\text{H}_5\text{OH}$ system has a k_3 ³⁵ of $0.012 \text{ sec.}^{-1} M^{-2}$. The change in cation from sodium to lithium requires a change in the strength of the attacking acid of about 6 pK_a units.¹⁶ This is of course in line with the observed greater reducing power of LiBH_4 compared to NaBH_4 .

Because of the conclusions regarding transition states that can be drawn from primary and secondary isotope effects, a comparison of LiBH_4 and LiBD_4 was made. Table III shows the results.

TABLE III
 $\text{LiBH}_4 + \text{HA} \xrightarrow[35^\circ]{\text{diglyme}} \text{H}_2 + \text{LiBH}_2\text{A}$

Boro- hydride	M	HA	M	pK_a	$k_3, \text{sec.}^{-1}$ (M) ⁻²
a. LiBH_4	0.101	CH_3OH	0.101	16	0.015
LiBH_4	.645	CH_3OH	.100	16	.016
LiBD_4	.276	CH_3OH	.270	16	.024
b. LiBH_4	.101	CH_3OH	.101	16	.015
LiBH_4	.255	$\text{C}_6\text{H}_5\text{N}$.255	19	3.3×10^{-6}
LiBH_4	.239	$t\text{-C}_4\text{H}_9\text{OH}$.239	19	2.1×10^{-4}
LiBH_4	.190	C_6H_6	.190	15 ^b	N.R.

^a Ref. 10. ^b R. E. Dessy and Y. Okazumi, unpublished observations. The rate of deuterium exchange, k , in the system, $\text{RH} \xrightarrow[\text{D}_2\text{O}]{\text{DMF}} \text{RD}$, for some 35 weak acids has been

measured. Log k vs. pK_a for a number of compounds where the latter has been determined relatively¹⁰ is linear. From this plot a rough value for the pK_a of cyclopentadiene can be derived, 15. This is confirmed by the fact that sodium methoxide metalates cyclopentadiene, indicating that its acidity is greater than CH_3OH , pK_a 16.

The deuterated compound reacts 1.6 times more rapidly than does the hydrogen analog ($k_H/k_D = 0.63$).

Such inverse secondary isotope effects have been noted before, notably by Robertson,¹⁶ in the solvolysis of tosylates and halides, where k_H/k_D had values from 1–0.9. More recently Davis^{4,17} has reported on the hydrolysis of NaBH_4 and NaBD_4 in aqueous buffered solution, where a k_H/k_D of 0.7 was found.

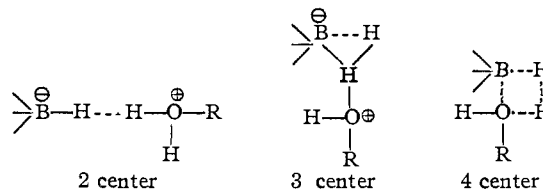
(15) W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1125 (1936), and Table II.

(16) (a) J. A. Llewellyn, R. E. Robertson and J. M. Scott, *Chemistry & Industry*, 732 (1959); (b) K. T. Leffek, J. A. Llewellyn and R. E. Robertson, *ibid.*, 588 (1960); (c) J. A. Llewellyn, R. E. Robertson and J. M. Scott, *Can. J. Chem.*, **38**, 222 (1960).

(17) R. B. Davis, C. L. Kibby and C. G. Swain, *J. Am. Chem. Soc.*, **82**, 5950 (1960).

Many explanations for inverse (and normal) secondary deuterium isotope effects have been postulated. Halevi¹⁸ believes that many of the secondary isotope effects observed can be attributed to a ground state inductive effect of D vs. H, a "differential inductive electron release which is greater for C–D than C–H bonds." Tiers¹⁹ has found some evidence for this concept in the n.m.r. spectra of fluorohydrocarbons. However, Weston²⁰ has provided an alternate explanation for such effects and Ropp²¹ has evidence which contradicts Halevi's data on the effect of α -deuterium substitution on the acidity of carboxylic acids. On the other hand, Robertson¹⁶ and others²² feel that inverse isotope effects arise from bond stiffening in the transition state. Unfortunately the experimental verification of these concepts is hindered by difficulties such as solvation effects.

If inverse isotope effects are attributable to bond stiffening, it is obvious that bulky entering and leaving groups in a given reaction will be expected to stiffen out-of-plane bending modes. In the present reactions several possible arrays of the reacting hydrogen atoms are conceivable



It will be recalled that in the $\text{C}_6\text{H}_5\text{OH}/\text{NaBH}_4$ reaction k_H/k_D ($\text{C}_6\text{H}_5\text{OH}$) is 1.7, while in the $\text{CH}_3\text{OH}/\text{LiBH}_4$ case the k_H/k_D (LiBH_4) was 0.63.

On the basis of the calculated maximum deuterium isotope effects [$(k_H/k_D)_{\text{max}} = 8.8$]²³ the k_H/k_D ($\text{C}_6\text{H}_5\text{OH}$) ratio is small, leading one to the conclusion that the 3-center model is incorrect,⁷ since one would expect a large loss of OH stretching character in this transition state, and a subsequently large k_H/k_D . The 2-center model, on the other hand, has no steric repulsions in the transition state which would lead to the small k_H/k_D (LiBH_4) found, an effect which must be due to a bulky transition state in which the smaller "effective volume" of the deuterium is important.

If a 4-center model were more nearly correct, then the structure of the attacking acid should influence the reactivity in a predictable manner. The rates of reaction of a series of acids with LiBH_4 should be an ordered function based on (a) acidity, (b) ability of an adjacent atom to donate a lone pair. Such a series has been investigated, and the results are shown in Table III. It is obvious that both acidity and lone-pair availability must

(18) E. A. Halevi, *Tetrahedron*, **1**, 174 (1957). For recent references cf. A. J. Kresge, N. N. Rao and N. N. Lichtin, *Chemistry & Industry*, 53 (1961); H. S. Klein and A. Streitwieser, Jr., *ibid.*, 180 (1961).

(19) G. Van Dyke Tiers, *J. Am. Chem. Soc.*, **79**, 5585 (1957).

(20) R. E. Weston, *Tetrahedron*, **6**, 31 (1950).

(21) G. A. Ropp, *J. Am. Chem. Soc.*, **82**, 4253 (1960).

(22) C. G. Swain and R. F. W. Bader, *Tetrahedron*, **10**, 182 (1960), and C. G. Swain, R. F. W. Bader and E. R. Thorton, *ibid.*, **10**, 200 (1960).

(23) Calculated from the O–H and O–D stretching frequencies given by V. v. Keussler and G. Rossmly, *Z. Elektrochem.*, **60**, 136 (1956), and the equations $E_0 = 1/2 h\nu$, $(k_H/k_D)_{\text{max}} = \exp[-(E_0^H - E_0^D)/RT]$ given by K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

be considered; pyrrole, one of the weakest acids, reacts rapidly, its donating ability being strong because of the N lone pair. Cyclopentadiene, the strongest acid,²⁴ shows no reactivity apparently because of its lack of donor properties.

One can conclude then that a 4-center transition state is in agreement with all of the available facts.

It is interesting that in Hawthorne's investigation⁷ of the acid hydrolysis of $(C_6H_5)_2BH \cdot NC_6H_5$ where boron is already coordinated with a donor, a 3-center transition state has been suggested. Similarly, Shore and Parry²⁵ have shown that NH_4X salts react slowly with many borohydrides, the reaction being *strongly* catalyzed by ammonia.

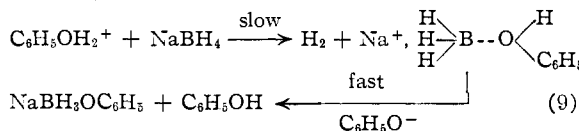
Obviously, both a proton donor and an electron donor seem to be necessary for such reactions to

(24) One referee has correctly pointed out that the greater reactivity of pyrrole or alcohols compared to that of cyclopentadiene might be due to the fact that in general N-H and O-H bond-breaking processes are rapid compared to C-H bond breaking. As indicated in the footnote to Table III we are currently measuring the rates of deuterium exchange in a series of weak acids, and cyclopentadiene exchange has been studied. If the N-H systems prove amenable to the same treatment this question may be answered.

(25) S. S. Shore and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 8 (1958).

take place easily. These may be in one molecule of the attacking reagent (present work), in separate attacking reagent molecules (Shore and Parry²⁵) or distributed between the substrate (borohydride) and the attacking reagent (Hawthorne⁷).

Returning then to the problem of the detailed mechanism of the reaction between C_6H_5OH and $NaBH_4$, we can write



Whether the attack of phenoxide is on the B, followed by displacement, or involves proton abstraction is not known.

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n-Alkyl Perchlorates: Preparation, Study and Stabilization

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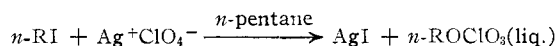
The previously unreported normal pentyl, hexyl, heptyl and octyl perchlorates were prepared from the corresponding alkyl iodide and silver perchlorate. The pure esters of perchloric acid were stabilized as the endocycle of a urea inclusion compound. The infrared spectra and some physical properties are reported for the *n*-alkyl perchlorates.

Introduction

Covalent esters of perchloric acid have been reported² in the literature. These alkyl perchlorates are extremely unstable and treacherous to prepare. Because of the explosion hazard associated with these compounds, we undertook to stabilize these covalent perchlorates by trapping them as the endocycle in a urea inclusion compound. This approach was used because the highly oxidized urea molecule would be expected to act as a protective cover for the strongly oxidizing *n*-alkyl perchlorates.

Discussion

The alkyl perchlorates were prepared by the reaction



Commercially available "anhydrous" silver perchlorate required dehydration. This dehydration is necessary because covalent perchlorates are

(1) From the Frankford Arsenal and from whom reprints may be obtained.

(2) C. Hare and M. H. Boyle, *Phil. Mag.*, **19** (3), 370 (1841); K. A. Hofmann, A. Zedtwitz and H. Wagner, *Chem. Ber.*, **42**, 4390 (1909); L. Birckenbach and J. Goubeau, *Naturwissenschaften*, **18**, 530 (1930); J. Meyer and W. Spormann, *Z. anorg. u. allgem. Chem.*, **228**, 341 (1936); R. D. Stewart in J. C. Schumacher, "Perchlorates," Reinhold Publishing Corp., New York, N. Y., 1960, pp. 67, 214.

thermodynamically unstable to hydrolysis.³ All of the alkyl perchlorates prepared were explosive. The lowest molecular weight alkyl perchlorate was most sensitive to shock. Although the highest molecular weight alkyl perchlorate was least sensitive to shock after isolation, the higher temperatures required for distillation introduced a compensatory hazard.

The isolated perchlorates were treated with a urea-methanol solution. Crystalline urea inclusion compounds formed for the normal pentyl, hexyl, heptyl and octyl perchlorates.

The ease of formation of the urea inclusion compound was proportional to the chain length of the alkyl perchlorate. The resulting crystalline complexes had no apparent shock sensitivity in small quantities (*ca.* 0.5 g.). The formation of the urea inclusion compound was unequivocally verified by the X-ray powder diffraction data in Table I. The pentyl perchlorate inclusion compound is the least stable and most highly dissociated. The following spacings characteristic of urea inclusion compounds are consistently present for all of the perchlorates except the pentyl: 7.05–7.10, 4.09–

(3) J. Radell and J. W. Connolly, Papers and Summaries, International Symposium on Macromolecular Chemistry, The International Union of Pure and Applied Chemistry, Moscow, U.S.S.R., June, 1960, Section I, pp. 292–295; *J. Polymer Sci.*, **XLVIII**, 343 (1960).