TABLE II

SUMMARY OF KINETIC DATA

Benzazide in ligroin, 63.9°

P (atm.)	68	340	610	880	1220	1360
k (hr.$^{-1}$)	0.051	0.049	0.048	0.045	0.041	0.041

Benzazide in 50% alcohol–50% water, 50.3°

P (atm.)	68	1440
k (hr.$^{-1}$)	0.208	0.194

p-Cresyl allyl ether in benzene, 186.4°

P (atm.)	68	680	1440
k (hr.$^{-1}$)	0.062	0.091	0.113

p-Cresyl allyl ether in 65% alcohol–35% water, 167.5°

P (atm.)	68	750	1440
k (hr.$^{-1}$)	0.136	0.181	0.240

p-Cresyl allyl ether in 65% alcohol–35% water, 147.0°

P (atm.)	68	750	1440
k (hr.$^{-1}$)	0.0267	0.0346	0.0443

p-Cresyl allyl ether in cyclohexane, 176.4°

P (atm.)	68	750	1440
k (hr.$^{-1}$)	0.0249	0.0337	0.0430

m-Methoxyphenyl allyl ether in 65% alcohol–35% water, 155.9°

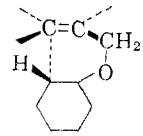
P (atm.)	68	405	750	1440
k (hr.$^{-1}$)	0.125	0.148	0.178	0.214

Vinyl allyl ether, neat, 130.4°

P (atm.)	68	405	750	1080	1470
k (hr.$^{-1}$)	0.307	0.394	0.446	0.510	0.525

Experimental

Benzazide was prepared by the method of Barrett and Porter.[18]



Allyl *p*-cresyl ether was prepared by the method of Kincaid and Tarbell.[19]

Allyl *m*-methoxyphenyl ether was prepared by the method of Mauthner.[20]

Allyl vinyl ether was prepared by the method of Watanabe and Conlon.[21]

Rearrangement of Benzazide.—A 2 ml. sample of 0.1 *M* solution was allowed to react in an inverted glass bell, and the volume of nitrogen was measured by the method developed for the decomposition of diazonium salts.[8]

Rearrangement of Allyl Aryl Ethers.—A 6 ml. sample of 0.333 *M* solution reacted for approximately one half-life and then was added to 15 ml. of 10% potassium hydroxide solution. The mixture was steam-distilled until approximately 20 ml. of distillate containing unreacted ether was collected. The residue then was acidified and another 20 ml. of distillate containing rearranged phenol was collected. Each distillate was diluted to 50 ml. with ethanol and a portion of each was again diluted tenfold with ethanol. The maximum optical densities of the *p*-cresyl ether at 277 mμ, its phenolic product at 281 mμ, the *m*-methoxyphenyl ether at 273 mμ and its phenolic product at 279 mμ were measured, and the concentrations were calculated from the optical densities of known solutions.

Rearrangement of Allyl Vinyl Ether.—Samples of the pure liquid reacted for approximately one half-life and were injected into a gas chromatograph. The concentrations of ether and rearranged aldehyde were calculated from the areas under the recorder trace.

High Pressure Apparatus and Thermostat Bath.—The equipment has been described in a previous paper.[5]

Acknowledgment.—The author is indebted to Mr. Jack Fiskness of Braun Chemical Co., Albuquerque, New Mexico, for the use of a Beckman GC-2 gas chromatograph.

(18) E. W. Barrett and C. W. Porter, *J. Am. Chem. Soc.*, **63**, 3434 (1941).

(19) J. F. Kincaid and D. S. Tarbell, *ibid.*, **61**, 3085 (1939).

(20) F. Mauthner, *J. prakt. Chem.*, **102**, 41 (1921).

(21) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

The Influence of Solvent and Metal Ion on the Rate of Reaction of Alkali Metal Borohydrides with Acetone[1]

BY HERBERT C. BROWN AND KATSUHIKO ICHIKAWA[2]

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In water, ethanol and isopropyl alcohol the rate of reaction of sodium borohydride with acetone exhibits second-order kinetics, first order in each of the two reactants. The rate constants at 0° are (10^{-4} l. mole^{-1} sec.$^{-1}$) 93 in water, 97 in ethanol and 15.1 in isopropyl alcohol. The addition of lithium chloride in water has no effect upon the rate, whereas in isopropyl alcohol the rate constant increases by a factor of three, to 50.3. Moreover, the rate constant increases with increasing concentrations of lithium halide. These results indicate that in water the reaction involves the dissociated borohydride ion, whereas in isopropyl alcohol the reacting species must be the ion pair, $M^+ BH_4^-$. In aprotic solvents, such as acetonitrile, pyridine, dimethylformamide and diglyme, no detectable reaction of sodium borohydride with acetone was observed at 0°. Consequently, the ability of the solvent to ionize must be involved in the mechanism of the reaction between the borohydride and the ketone.

In an earlier study we examined a number of solvents for sodium borohydride and their utility as reaction media for the reduction of ketones by the reagent.[3] We observed that methyl alcohol reacted very rapidly with the borohydride, ethyl alcohol somewhat slower, whereas the reaction of isopropyl and *t*-butyl alcohols was almost negligible, so that these solvents could be considered as suitable media for kinetic studies.[4] Diglyme[5] and triglyme[5] were also excellent solvents for

(1) Addition Compounds of the Alkali Metal Hydrides. XII.

(2) Post-doctorate research assistant on Contract DA-33-008-ORD-992, supported by the Office of Ordnance Research, U. S. Army.

(3) H. C. Brown, E. J. Mead and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

(4) H. C. Brown, O. H. Wheeler and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957).

sodium borohydride, but the rate of reaction of sodium borohydride with ketones in these aprotic solvents was too slow for them to be considered as useful reduction media. We also demonstrated that the addition of lithium or magnesium bromide to a diglyme solution of sodium borohydride greatly increased the reducing power of the solution.

These early studies utilized hydrogen evolution from acidified borohydride solutions as a means of following the reaction of borohydride with ketones. The development of a precise kinetic procedure,[3] based upon the accurate iodometric determination of borohydride,[6] encouraged us to re-examine and to extend our earlier observations.

Results and Discussion

Reaction with Solvents.—At 0° the reaction of sodium borohydride with methyl alcohol is quite rapid, with more than 80% of the available "hydride" being lost in 1 hr. (Table I). The results follow a first-order kinetic expression.

TABLE I

SOLVOLYSIS OF SODIUM BOROHYDRIDE AT 0°

Methanol			Water		
Time, min.	$NaBH_4$, M	$k_1 \times 10^4$, sec.$^{-1}$	Time, min.	$NaBH_4$, M	$k_1 \times 10^5$, sec.$^{-1}$
0	0.01011		0	0.0236	
16	.00593	5.5	60	.0222	16.5
27	.00381	6.0	80	.0218	16.0
41	.00255	5.5	460	.0185	8.7
52	.00195	5.3	1140	.0151	6.5
66	.00128	5.5	23900	.0107	5.3

The reaction of sodium borohydride with water is considerably slower. In this case the calculated first-order rate constants decrease with time, corresponding to the effect of the increasing *p*H of the solution on the rate.[7]

It was concluded that the reaction of sodium borohydride with methanol was too rapid to permit following rates of reaction with ketones in this solvent. However, the reaction with water was considered to be sufficiently slow to permit rate measurements.

The reaction of sodium borohydride with ethyl alcohol at 0° is much slower than either of the two above cases. Thus, in a similar rate experiment, the initial concentration of 0.0224 M sodium borohydride had decreased by only 5%, to 0.0215 M, after 42 hr. at 0°. This leads to an approximate first-order constant of 2.8×10^{-7} sec.$^{-1}$, in contrast with the value of 5.5×10^{-4} sec.$^{-1}$ observed for methyl alcohol.

Solutions of sodium borohydride in isopropyl alcohol and *t*-butyl alcohol were quite stable, with no detectable change being observed in several weeks at 0 or 25°.

In view of the high reactivity of sodium borohydride toward methanol, it is unfortunate that this solvent continues to be widely used for organic reductions. Ethyl alcohol or ethyl alcohol–water mixtures would appear to be preferable.

(5) Diglyme:diethyleneglycol dimethyl ether; triglyme:triethyleneglycol dimethyl ether.

(6) D. A. Lyttle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

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

No reaction with acetonitrile, pyridine, dimethylformamide or diglyme was observed.

Kinetic Studies.—The reaction of sodium borohydride with acetone in water solution at 0° followed second-order kinetics, first order in each component, analogous to the corresponding reaction in isopropyl alcohol.[4] However, the rate constant was considerably larger, 93×10^{-4} l. mole^{-1} sec.$^{-1}$, as compared to the value 15.1×10^{-4} l. mole^{-1} sec.$^{-1}$ observed in isopropyl alcohol. In ethyl alcohol the rate constant is 97×10^{-4} l. mole^{-1} sec.$^{-1}$.

No significant reaction was observed in acetonitrile, pyridine, dimethylformamide and diglyme at 0°. This confirms our earlier conclusion that the ability of the solvent to ionize must be involved in the transfer of hydride from the borohydride ion to the carbonyl group.[3]

We had previously observed that the addition of triethylamine to a diglyme solution of sodium borohydride and acetone brought about an apparent loss of 25% of the available hydride with a concurrent loss of 25% of the acetone. We concluded that triethylamine caused the transfer of one of the four "hydrides" in the borohydride ion, simultaneously forming triethylamine–borane.

Repetition of the experiment utilizing the present analytical procedure (iodometric titration) revealed that triethylamine does not catalyze the reaction between sodium borohydride and acetone in diglyme solution.

Apparently, in the earlier experiments the triethylamine decreased the rate of hydrolysis of the borohydride during the analytical procedure, and thereby permitted a partial reduction of the acetone during the hydrolysis step of the analysis.

Addition of lithium chloride to the aqueous reaction mixture resulted in no change in the observed rate constant (Table II). On the other hand, addition of lithium chloride to the reaction

TABLE II

KINETIC DATA FOR THE REACTION OF LITHIUM AND SODIUM BOROHYDRIDE WITH ACETONE[a] IN VARIOUS SOLVENTS AT 0°

Solvent	Metal borohydride	Concn., M	Added material	Concn., M	Rate constant (10^4 l. mole^{-1} sec.$^{-1}$
Water	$NaBH_4$	0.0194			93
Ethanol	$NaBH_4$	.0224			97
Isopropyl alc.	$NaBH_4$	.0159			15.1
Acetonitrile	$NaBH_4$	.0176			0[b]
Pyridine	$NaBH_4$	.0172			0[b]
Dimethylformamide	$NaBH_4$	.0240			0[b]
Diglyme	$NaBH_4$	.0221			0[b]
Water	$NaBH_4$	.0224	Et_3N	0.050	89
Isopropyl alc.	$NaBH_4$	.0200	Et_3N	.050	15.2
Diglyme	$NaBH_4$	.0240	Et_3N	.050	0[a]
Isopropyl alc.	$LiBH_4$	.0176			50.3
Isopropyl alc.	$LiBH_4$	.0200	Et_3N	.050	50.6
Isopropyl alc.	$LiBH_4$	.0196	LiCl	.050	76
Water	$NaBH_4$	.0200	LiCl	.050	93
Isopropyl alc.	$NaBH_4$	.0162	NaI	.097	15.7
Isopropyl alc.	$NaBH_4$	.0178	LiI	.010	26.2
Isopropyl alc.	$NaBH_4$	.0178	LiI	.030	40
Isopropyl alc.	$NaBH_4$	.0178	LiI	.060	67
Isopropyl alc.	$NaBH_4$	.0178	LiI	.100	81
Isopropyl alc.	$NaBH_4$	.0213			1.87[c]
Isopropyl alc.	$LiBH_4$	.0176			4.94[c]

[a] Initial concentration of acetone, 0.160 M. [b] No detectable reaction in 24 hr. [c] Benzophenone; initial concentration, 0.0800 M.

mixture in isopropyl alcohol resulted in a precipitation of sodium chloride and a marked increase in the second-order rate constant. A similar increase in rate constant was observed for the reaction of benzophenone with lithium borohydride.

Addition of sodium iodide (soluble in isopropyl alcohol) to the reaction mixture of sodium borohydride and acetone in isopropyl alcohol did not influence the rate significantly. This indicates that the reaction is not very sensitive to general salt effects. However, the addition of lithium iodide results in an increase in rate which rises linearly with the amount of lithium iodide.

It therefore appears that in aqueous solution there is no difference in the rate of reaction of lithium or sodium borohydride with acetone, whereas in isopropyl alcohol there is a major difference in rates. These results suggest that in water the reaction of borohydride with acetone involves the dissociated ion, and the positive ion present does not influence the rate of reaction. In a solvent such as isopropyl alcohol the alkali metal borohydride must be largely present as undissociated ion-pairs. Consequently, the reactivity of the ion-pair would be expected to depend somewhat on the precise cation present in the reaction mixture.

The reactivity of lithium borohydride in isopropyl alcohol is increased by dissolved lithium chloride. Similarly, the presence of lithium iodide increases the reactivity of sodium borohydride somewhat. The increase with the smaller concentrations of lithium iodide is moderate, suggesting that the exchange to form lithium borohydride in solution cannot be complete—we are evidently dealing with an equilibrium system of sodium and lithium borohydrides.

The data do not permit a definite explanation of the effect of excess lithium chloride or iodide on the rate. Conceivably, the excess salt modifies the nature of the ionic clusters in the solvent, or conceivably the lithium ion may serve two functions. On the one hand, it may serve to activate the borohydride ion in the ion-pair (or ionic cluster) through its polarizing influence. On the other, it may also serve to activate the carbonyl group of the ketone through its known ability to coördinate with such groups.

Experimental Part

Materials.—Sodium borohydride, acetone, diglyme and isopropyl alcohol were purified as previously described.[3,4] Methanol, ethanol and pyridine were dried over calcium hydride and distilled through a packed column: methanol, b.p. 63.5° at 740 mm., $n^{20}D$ 1.3288; ethanol, b.p. 78.0° at 740 mm., $n^{20}D$ 1.3610; pyridine, b.p. 115.0° at 745 mm., $n^{20}D$ 1.5102. The other materials were dried over Drierite and distilled: acetonitrile, b.p. 81.0° at 743 mm., $n^{20}D$ 1.3460; dimethylformamide, b.p. 151–151.5° at 743 mm., $n^{20}D$ 1.4297; triethylamine, b.p. 88.5° at 740 mm., $n^{20}D$ 1.4003.

Sodium iodide, lithium chloride and magnesium chloride were reagent grade chemicals. Lithium iodide was a sample previously prepared by Dr. B. C. Subba Rao.

The following procedure was utilized to prepare lithium borohydride in isopropyl alcohol solution. To 200 ml. of sodium borohydride solution (0.02124 *M*) was added 0.1801 g. of lithium chloride. Sodium chloride precipitated. The fine precipitate could not be removed by filtration, so it was removed by centrifugation. The solution exhibited no change in activity over 3 hr. at 0°. This was ample time to complete a typical kinetic run.

Kinetic Determinations.—The procedures followed were those previously developed and utilized in a detailed study of the kinetics of reaction of sodium borohydride with representative aldehydes and ketones.[4] With each solvent, standard solutions of sodium borohydride in the solvent were prepared, and it was established that the analytical procedure was operative in the presence of the solvent in question and that the concentration of the borohydride did not change significantly over the time required to complete a kinetic study. The kinetic results are summarized in Table II.

Acknowledgment.—It is a pleasure to acknowledge the assistance provided by Contract DA-33-008-ORD-992, supported by the Office of Ordnance Research, U. S. Army.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF UNION CARBIDE CONSUMER PRODUCTS COMPANY, DIVISION OF UNION CARBIDE CORPORATION, PARMA 30, OHIO]

An Experimental Study of Energy Transfer between Unlike Molecules in Solution

BY WILLIAM R. WARE

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The transfer or excitation between polynuclear aromatic hydrocarbons has been studied using fluorescence lifetime measurements. Second order rate constants three to twelve times greater than predicted by diffusion theory have been observed, and correlation has been obtained between the experimental results and the theory of weak resonance interaction.

Introduction

While the subject of energy transfer between unlike molecules in solution through a resonance interaction has received considerable theoretical attention,[1-3] there have been relatively few critical experiments reported.[3,4] One of the contributing factors to this situation is the difficulty of unambiguously interpreting fluorescence intensity measurements. This arises from the following circumstances: (a) conditions for resonance transfer favor the trivial process of fluorescence absorption; (b) the acceptor frequently exhibits some absorption in the region where the sensitizer ab-

(1) Th. Förster, "Fluoreszenz Organisher Verbindungen," Vandenhoeck and Ruprecht, Göttingen, 1951.

(2) Th. Förster in "Comparative Effects of Radiation," ed. by M. Burton, J. S. Kirby-Smith and J. L. Magee, John Wiley and Sons, Inc., New York, N. Y., 1960.

(3) Th. Förster, *Discussions Faraday Soc.*, 27 (1959).

(4) E. J. Bowen and Robert Livingston, *J. Am. Chem. Soc.*, **76**, 6300 (1954).