stages of the present work, Dr. Sol Weller of the Houdry Corporation suggested to the authors that the hydrogenation of silver acetate might involve a similar heterolytic fission process with silver ions and acetate ions engaging opposite ends of the hydrogen molecule in a concerted attack.

The relatively small pre-exponential factor, $10^{7.64}$ (mole/l.)$^{-1}$ sec.$^{-1}$, offers support for this model of the activated complex, since it is consistent with the low values frequently obtained in four center reactions.[10] The observed correlation of rate with both basicity of anion and basicity of the ammine liquid would also be understandable. Increased basicity of the anion would tend to favor reaction rate, since proton extraction is occurring at the transition state; alternately, decreased basicity of the ammine would render the silver ion more electronegative and facilitate hydride ion extraction by the silver ion.[13]

While the conclusion reached above regarding the instability of second silver–hydrogen bond is probably correct, the structure cannot be completely ignored for the energy-rich activated complex. Judging from the considerable stability of $(H_3)^+$, $(AgH_2)^+$ might well exist as a stable ion in the gas phase.[14] Unfortunately little can be said about the stability of the ion when associated with acetate ion and pyridine in the solution phase.

The kinetics of hydrogenation of mercuric acetate[15] and cupric acetate[16] have recently been studied in aqueous solution; activation energies of 20.7 and 24.6 kcal., respectively, were observed for the two salts.

In a review of this work Halpern and Peters have summarized their views regarding the mechanism of hydrogenation of cations in aqueous solution. In a mechanism consistent with the rate law discussed above, their formulation of the structure of the intermediate is somewhat different than ours. However, they also conclude that the metal ions which readily hydrogenate will be characterized by having a strong attraction for electrons. While from our viewpoint high electronegativity is a prerequisite for rapid hydrogenation, of perhaps even greater importance is the ability of the metal ion to make use of an unoccupied orbital in forming a bond with a hydrogen atom or hydride ion. In this regard the dicoördinate silver and cuprous ions are especially favored, since they contain low-lying, non-bonding, p-orbitals which can be utilized in the activated complex. In cupric ion, and probably even in mercuric ion, the corresponding orbitals are used for bonding in the ground state, and the activated complex under consideration can be formed only at the expense of a considerable loss in solvation energy.

---

(13) In a solution where the anion is a very poor base it is to be expected that the hydrogenation will proceed by an alternate path less sensitive to anion basicity, if such a path exists. In a private communication A. H. Webster and J. Halpern of the University of British Columbia indicate that they have found this situation to occur in aqueous solutions of silver perchlorate. Here the rate of the relatively slow hydrogenation varies with the second power of the silver ion concentration. In the work summarized in Table IV, especially in those experiments where the rate is very slow, it is possible that alternate paths are contributing to the hydrogenation, and we are overestimating the contribution to the reaction by the path under consideration.

(14) Only semiquantitative information is available regarding the stability of $(H_3)^+$. A calculation by Joseph O. Hirschfelder, *J. Chem. Phys.*, **6**, 795 (1938), yields a value of approximately −80 kcal. for the heat of formation from molecular hydrogen and the proton.

(15) J. Halpern, G. K. Korinek and E. Peters, *Research (London)*, **7**, S61 (1954).

(16) J. Halpern and E. Peters, *J. Chem. Phys.*, **23**, 605 (1955).

LOS ANGELES, CALIFORNIA

[CONTRIBUTION NO. 962 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Kinetics of the Reaction of Lithium Aluminum Hydride with Some Primary Alkyl Bromides[1]

BY D. J. MALTER, JOHN H. WOTIZ AND C. A. HOLLINGSWORTH[2]

RECEIVED JULY 12, 1955

The kinetics of the reaction of lithium aluminum hydride, $LiAlH_4$, with *n*-butyl or *n*-amyl bromide in ether solutions was found to be second order for the reaction of the first hydride. Subsequent reaction is very slow; a precipitate, likely $(AlH_3)_x$, separates and redissolves.

Introduction

Substitution reactions with lithium aluminum hydride are usually believed to be SN2 reactions. This belief is supported by the following evidence: the reactivity of organic halides decreases in the order primary > secondary > tertiary.[3,4] Inversion occurs in the reduction of bicyclic epoxides.[4]

Conductivity measurements[5] indicate that lithium aluminum hydride is ionized in ethereal solutions, and Raman and infrared spectra give evidence of the presence of a tetrahedral AlH_4^- ion.[6] It is often assumed that this ion is the reacting species. However, Paddock[5] suggests that the increase in reactivity with increasing basicity of solvent is evidence for the equilibrium

$$AlH_4^- \rightleftharpoons H^- + AlH_3$$

and that the reactivity entity is the H^- ion.

Since no kinetics studies for lithium aluminum hydride reactions were found in the literature, and since the evidence cited above does not indicate the order of the rate-determining step, it seemed desirable to determine the kinetics of a simple substitution reaction. Accordingly, the kinetics

---

(1) Abstracted from a portion of the M.S. thesis of D. J. M., University of Pittsburgh, 1955.

(2) The authors wish to thank the Research Corporation for partial support of this work.

(3) J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948).

(4) L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

(5) N. L. Paddock, *Nature*, **167**, 1070 (1951).

(6) E. R. Lippincott, *J. Chem. Phys.*, **17**, 1351 (1949).

of the reaction of lithium aluminum hydride with *n*-butyl bromide and with *n*-amyl bromide in diethyl ether at 25° was investigated and is reported in this paper. It is known that in this reaction it is the reaction of the first hydride only that is of importance as a reduction reaction; the reaction of the remaining three hydrides is too slow.[7]

Experimental

Lithium aluminum hydride was obtained from the Metal Hydrides Co. The ether solutions were prepared by refluxing for six to eight hours.

***n*-Butyl bromide** was purified by distillation, b.p. 99-100°.

***n*-Amyl bromide** was purified by distillation, b.p. 123-127°, n^{20}D 1.4440.

The reactions were followed by determining the hydride remaining as a function of the time. The concentration of hydride was determined by measuring the volume of hydrogen liberated from aliquots of the reacting mixture upon the addition of butanol (in benzene). Titration of the hydride using N-phenyl-*p*-aminoazobenzene as indicator[8] was also investigated but was found to be unsatisfactory because the end-point was destroyed by the products of the reaction.

During the reaction the temperature was kept at 25 ± 1°. Six runs were made with *n*-butyl bromide and two with *n*-amyl bromide. The initial concentrations in these runs are summarized in Table I, where *a* and *b* are the concentrations of lithium aluminum hydride and alkyl bromide, respectively, in moles per liter. The values of *a* were obtained from aliquots taken both before and immediately after the addition of the alkyl bromide; satisfactory checks were obtained in this way.

Table I

Initial Concentrations of Reactants

Run	*a* = moles $LiAlH_4$/l.	*b* = moles *n*-C_4H_9Br/l.	Run	*a* = moles $LiAlH_4$/l.	*b* = moles *n*-$C_5H_{11}Br$/l.
1	0.40	1.03	A	0.50	2.52
2	.42	1.08	B	.62	0.63
3	.35	1.89			
4	.54	2.12			
5	.36	2.26			
6	.44	3.08			

The reactions were carried out under a cover of sulfuric acid-washed nitrogen, and the aliquots were obtained by forcing the solution under nitrogen pressure into an automatic pipet. Blank runs were made in which solutions of lithium aluminum hydride alone were given the same treatment that the reaction mixture was given in a regular run. It was found from these blank runs that the concentration of the hydride decreased, but so slowly that the error thus introduced should not have become serious in less than 10 or 12 hours. The only data which were used in the kinetic calculations and which were obtained after times greater than 12 hours were some from run B.

The reaction became very slow and a precipitate formed soon after the first hydride in lithium aluminum hydride had reacted. No data obtained after the appearance of the precipitate were used in the kinetic treatment. Run A (and the corresponding blank) was followed for approximately one month. The precipitate was observed to form during the interval from the seventh to the ninth hour after mixing. At this time the reaction had gone slightly beyond the point where one-fourth of the equivalents of hydride had reacted. The amount of precipitate appeared to be nearly constant for about 15 days, but after 30 days much of the precipitate had disappeared. At various times while the precipitate was present, two aliquots, one without and one with precipitate, were analyzed for hydride. The ratio of the hydride in the aliquot without precipitate to that with precipitate is designated α and is shown as a function of the extent of reaction P/a in Fig. 1; here P represented the moles of hydrocarbon product.

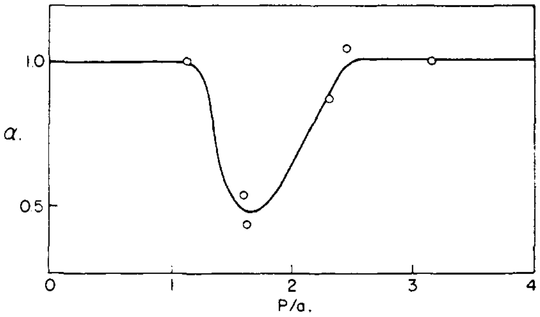

Fig. 1.—*a versus P/a* (run A).

Discussion

Kinetics.—The results show that the rate of the reaction depends upon the concentrations of both reactants and thus a second-order mechanism is suggested. Accordingly, in order to explain the rate up to and slightly beyond the reaction of one-fourth of the equivalents of hydride, the following mechanism is proposed

$$A_0 + X \xrightarrow{k_1} A_1 + P$$
$$A_1 + X \xrightarrow{k_2} A_2 + P \qquad (1)$$

where A_0 represents lithium aluminum hydride; X, the alkyl bromide; A_1 and A_2 the lithium aluminum hydride after one and two hydride ions, respectively, have reacted; and P, the hydrocarbon product.

We define a time variable θ by $d\theta = X\,dt$, or

$$\theta = bt - \int_0^t P\,dt' \qquad (1)$$

where X and P represent the concentrations of the alkyl bromide and hydrocarbon products, respectively; b is the initial value of X; and t is the time.

The rate law can then be expressed

$$\frac{P}{a} = \frac{1}{k_1 - k_2}\,[(2k_2 - k_1)\,e^{-k_1\theta} - k_1e^{-k_2\theta}] + 2 \qquad (2)$$

where a is, as previously defined, the initial concentration of the hydride. When $k_1 >> k_2$, as it is in the present case, eq. 2 simplifies to

$$P/a = 2 - e^{-k_1\theta} - e^{k_2\theta} \qquad (3)$$

By a simple graphical integration of curves of P as a function of the time, the variable θ was found as a function of t for the various runs and is shown in Fig. 2.

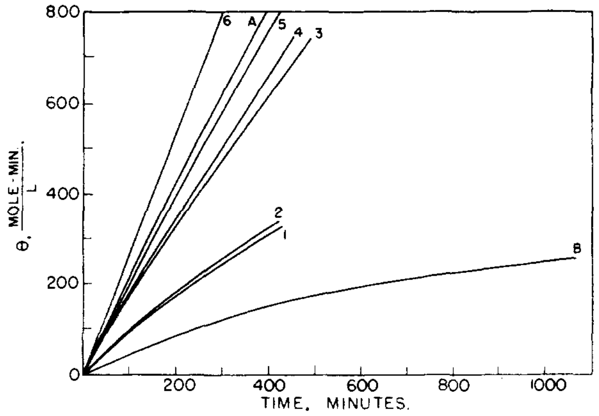

Fig. 2.—θ *versus* time (runs 1-6, A and B).

It will be noted that according to eq. 2 or 3 the

---

(7) R. F. Nystrom, This Journal, **77**, 2544 (1955).

(8) T. Higuchi and D. A. Zuck, *ibid.*, **73**, 2676 (1951).

value of θ for which $P/a = \beta$, where β is some arbitrarily chosen constant, is independent of a and b; that is, θ_β should have the same value for all runs with a given alkyl bromide. On the other hand, t_β, *i.e.*, the time corresponding to $P/a = \beta$, would depend upon the values of a and b. Figure 3 shows θ_β and t_β for $\beta = {}^4/_5$ as a function of b. Within experimental error, $\theta_{4/5}$ is a constant, whereas $t_{4/5}$ increases with decreasing b.[9] The reaction is, therefore, second order and consistent with I.

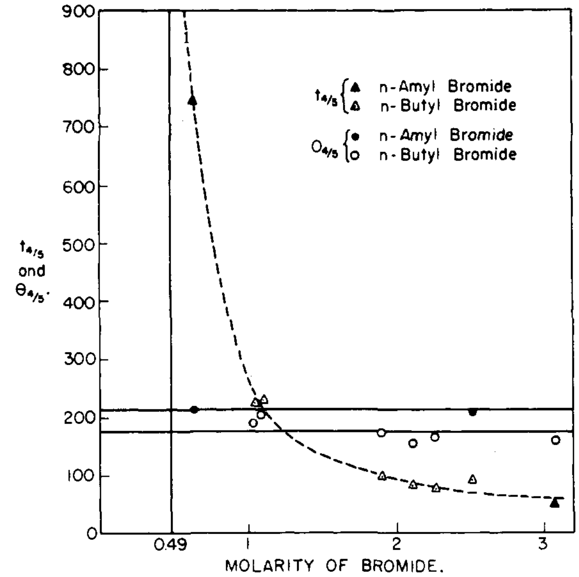

Fig. 3.—$\theta_{4/5}$ and $t_{4/5}$ *versus* molarity of alkyl bromide (runs 1–6, A and B).

Figure 4 shows the experimental points for P/a as a function of θ for the six n-butyl bromide runs and the theoretical curve given by eq. 3 with $k_1 = 7.8 \times 10^{-3}$ and $k_2 = 2.7 \times 10^{-4}$ (liter mole^{-1} min.$^{-1}$). Values of k_1 and k_2 obtained from individual runs range from 6.6×10^{-3} to 8.8×10^{-3} and 2.4×10^{-4} to 2.9×10^{-4}, respectively. Figure 5 shows the experimental values of P/a as a function of θ for the two n-amyl bromide runs and the theoretical curve with $k_1 = 7.4 \times 10^{-3}$ and $k_2 = 1.6 \times 10^{-4}$. The data from run B are not so good as those from the other runs, since the value of b was so low in this case that the reaction was very slow; this resulted in greater errors.

The values given above for the rate constants were obtained by a method of successive approximation in fitting eq. 3 to the experimental points.

From these results it can be concluded that n-butyl bromide and n-amyl bromide react with the first hydride of lithium aluminum hydride in ethyl ether by way of a second-order reaction. The kinetics of the second step in the reaction is less certain since the appearance of a precipitate causes a complication. However, the data up to the time at which the precipitation occurs are consistent with a second-order mechanism for the second step.

This result does not allow one to decide between AlH_4^- and H^- as the reactive species but merely shows that the dissociation of AlH_4^-, if it occurs, cannot be the rate-determining step.

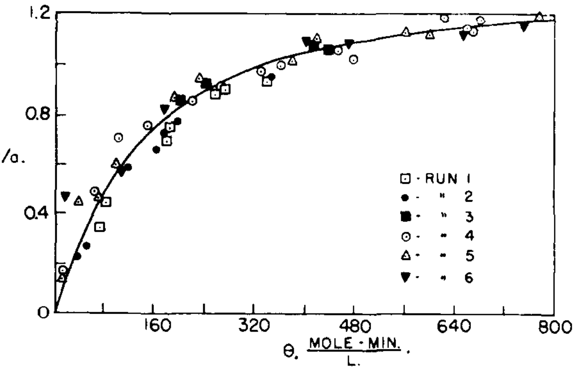

Fig. 4.—Theoretical curve and experimental points for P/a *versus* θ for n-butyl bromide and lithium aluminum hydride.

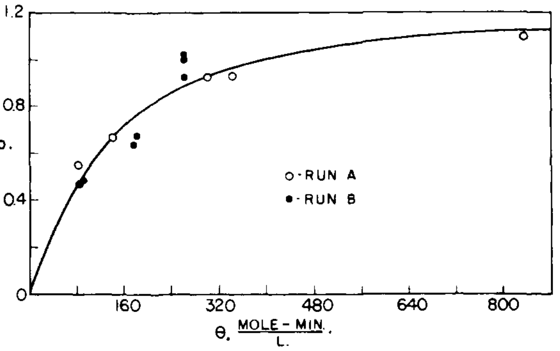

Fig. 5.—Theoretical curve and experimental points for P/a *versus* θ for n-amyl bromide and lithium aluminum hydride.

The Nature of the Reaction beyond the First Step.—It was found in this work that k_1 is approximately 35 times larger than k_2. Also, in run A, as an example, a value of unity for P/a was reached in about six hours, while it took two days (50 hours) to reach a value of 1.63, and after 40 days the value of P/a was only 3.24. In this run there was excess amyl bromide so that the reaction could have gone to completion for the hydride, *i.e.*, to $P/a = 4$.

There is some evidence that the precipitate which formed soon after the first step is the polymer $(AlH_3)_x$. In the first place, the curve of α as a function of P/a (Fig. 1) can be shown to be consistent with the assumption that the precipitate is A_1; on the other hand, only by assuming a very unlikely increase in the solubility of A_2 with the extent of reaction can one obtain the observed behavior of α from the assumption that the precipitate is A_2. The fact that about the usual amount of precipitate was formed in run B, where the reaction should have reached completion at about $P/a = 1$, is further evidence that the precipitate is A_1. In agreement with these facts is the observation of Finholt, Bond and Schlesinger[10] that aluminum hydride produced in ether does not form a stable solution in the ether; rather, it polymerizes and precipitates as $(AlH_3)_x$.

PITTSBURGH, PA.

---

(9) Although a smooth curve has been drawn through the $t_{4/5}$ points, these do not theoretically lie on the same curve, since the value of a is not constant. The vertical asymptote at 0.49 applies exactly only to the curve which would go through the point $t_{4/5} = 750$, $b = 0.629$ (run B).

(10) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, THIS JOURNAL, **69**, 1199 (1947).