[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Kinetics of the Reaction of Aluminum Borohydride Vapor with Olefins[1]

BY RICHARD S. BROKAW AND ROBERT N. PEASE

In the course of experiments on the oxidation of butene-1 induced by aluminum borohydride[2] it was found that these substances undergo a slow reaction with one another, even in the absence of oxygen. It was also noted that no reaction occurred between aluminum borohydride and the saturated hydrocarbon, *n*-butane.

In the research described in this paper the kinetics of the reactions between aluminum borohydride and ethylene, propylene and butene-1 have been studied. Also, products of the reaction of aluminum borohydride with ethylene have been isolated.

Experimental

In the apparatus used for kinetic studies reactions were carried out in a spherical reaction bulb of 6.6 cm. inside diameter. A clean flask was employed from time to time, but this did not affect the rate of reaction. The reaction bulb was immersed in a thermostat which held temperature constant to within ±0.1°. The reaction bulb was connected to a vacuum system through a mercury cut-off-manometer which served both as a cut-off to ensure constant volume during the reaction and as a manometer for observing pressure changes. Attached to the vacuum system was a reservoir flask for the olefin being studied and an ampule containing aluminum borohydride. The ampule was closed off by a mercury cut-off which protected the bulk supply of aluminum borohydride from stopcock grease with which it reacts slowly.

Aluminum borohydride vapor was run into the reaction flask at the desired temperature, and the pressure was measured. Then the olefin vapor was allowed to enter the external system from the reservoir flask. The mercury in the cut-off was then lowered, the olefin admitted to the reaction flask, and the clock started. The mercury was raised again, a vacuum applied to the external system, and observations of the pressure as a function of time were made.

The apparatus used to isolate the products of the aluminum borohydride–ethylene reaction consisted of a 500-cc. reaction flask connected through a mercury cut-off manometer to a vacuum system with a reservoir flask for ethylene storage, an ampule for aluminum borohydride, and a series of ampules into which reaction products could be distilled. In carrying out an experiment, aluminum borohydride was run into the reaction flask. About thirteen times as much ethylene was then added, the cut-off closed and the temperature raised to 140° and held there until the pressure ceased falling. The products were then cooled and fractionated.

Aluminum borohydride was obtained from the Naval Research Laboratory. The propylene and butene-1 used were obtained from the Matheson Company, and ethylene from U. S. Industrial Chemicals, Inc.

Results and Discussion

The Reaction between Aluminum Borohydride and Ethylene.—Experiments on the kinetics of the reaction between aluminum borohydride and ethylene were carried out in the temperature range of 40–90°. A typical pressure *versus* time curve at 70° is shown in Fig. 1. The initial slopes of such plots were found to be proportional to the pressure of aluminum borohydride and independent of the ethylene pressure. In runs in which an excess of aluminum borohydride was present, the curves showed sharp breaks attributable to the exhaustion of the ethylene. These facts suggest that the reaction is first order with respect to the aluminum borohydride.

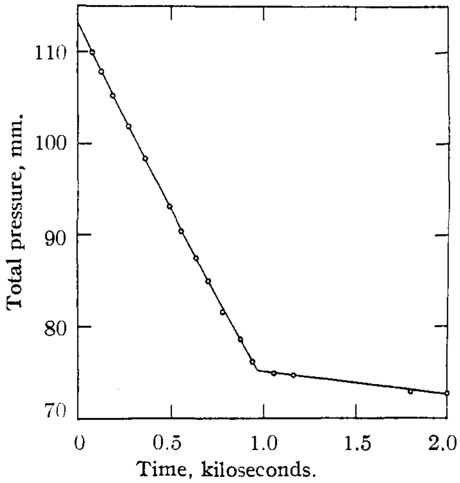

Fig. 1.—Pressure–time curve for a mixture of 63.6 mm. of aluminum borohydride and 49.7 mm. of ethylene at 70°.

The observed data could be fitted, assuming the reaction to be first order with respect to aluminum borohydride, with the following stoichiometry

$$\mathrm{Al(BH_4)_3} + 4\mathrm{C_2H_4} \longrightarrow \mathrm{A} + \mathrm{B} \text{ (two gaseous products)} \quad (1)$$

Assuming this stoichiometry, it is possible to calculate the pressure of aluminum borohydride from the pressure of the system at any time, using the following formula

$$P_{\mathrm{Al(BH_4)_3}} = P_{0\mathrm{Al(BH_4)_3}} - (P_0 - P)/3 \quad (2)$$

where

$P_{\mathrm{Al(BH_4)_3}}$ = the pressure of aluminum borohydride at time t

$P_{0\mathrm{Al(BH_4)_3}}$ = the initial pressure of aluminum borohydride

P = the total pressure at time t

P_0 = the initial total pressure

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[2] Brokaw, Badin and Pease, THIS JOURNAL, **72**, 1793 (1950).

Plots of the logarithm of the aluminum borohydride pressure so calculated against time gave good straight lines. A typical plot is shown in Fig. 2. As can be seen, the points lie on the straight line to a time at which the pressure of aluminum borohydride has diminished from an initial pressure of 23.9 mm. to a pressure of 3.9 mm. The deviation of the last two points arises from the fact that the olefin supply has been exhausted.

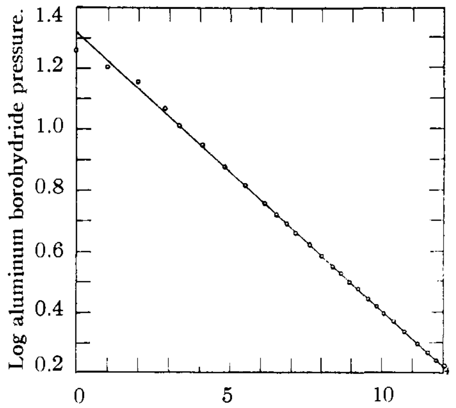

Fig. 2.—Plot of logarithm aluminum borohydride pressure against time for a mixture of 23.9 mm. of aluminum borohydride and 84.3 mm. of ethylene at 70°.

From the slope of the log $P_{(\mathrm{AlBH_4})_3}$ *versus* time plot the rate constant may be determined. This has been done for mixtures at a variety of temperatures, and the results are shown in Table I.

Assuming that equation (1) represents the correct stoichiometry for the reaction, and that the reaction is first order with respect to aluminum borohydride, it would be expected that the pressure–time curves of mixtures containing an excess of aluminum borohydride should show "curve-breaks." The last two columns of Table I compare observed "curve-break" pressure with values calculated assuming equation (1) to be correct. The agreement seems very good.

The variation of the rate constant k with temperature is given by the expression[3]

$$k = BTe^{-E/RT} \qquad (3)$$

where

T = absolute temperature
E = activation energy
R = gas constant
B = a constant

Therefore, if log k/T is plotted against reciprocal temperature, the result should be a straight line of slope $E/2.303R$. Such a plot is shown in Fig. 3 in which the data of Table I have been plotted. From the slope of the line the activation energy is found to be 30.5 kilocalories.

Table I

Rate Constants for the Reaction of Aluminum Borohydride with Ethylene. Comparison of Observed and Calculated "Curve Breaks"

Temp., °C.	Initial press., mm. Al-$(\mathrm{BH_4})_3$	$\mathrm{C_2H_4}$	Rate constant, sec.$^{-1}$	Curve break pres. (obs.), mm.	(calcd.), mm.
40.6	66.8	86.8	2.89×10^{-6}	...	...
	81.0	54.0	2.96×10^{-6}	...	...
	Average value		2.92×10^{-6}		
49.9	42.0	59.1	1.23×10^{-5}	...	...
	80.2	23.1	1.29×10^{-5}	85.6	86.0
	Average value		$1.26 > 10^{-5}$		
60.0	34.0	71.8	5.18×10^{-5}	...	...
	48.0	71.1	5.09×10^{-5}	65.5	65.8
	69.0	50.8	5.29×10^{-5}	82.0	81.7
	87.9	39.6	5.50×10^{-5}	97.5	97.8
	87.5	72.4	5.36×10^{-5}	105.5	105.6
	Average value		5.28×10^{-5}		
69.2	47.0	60.5	1.96×10^{-4}	61.8	62.1
70.2	14.2	104.4	2.12×10^{-4}	None	None
	23.9	83.4	2.11×10^{-4}	44.1	44.7
	40.2	62.8	2.01×10^{-4}	55.4	55.9
	40.2	98.0	2.16×10^{-4}	63.5	64.7
	63.6	50.1	2.28×10^{-4}	75.2	76.1
	Average value		2.14×10^{-4}		
80.5	31.8	65.2	8.31×10^{-4}	48.4	48.1
	38.8	126.4	8.05×10^{-4}	70.7	70.6
	47.9	108.8	8.19×10^{-4}	76.3	75.1
	Average value		8.18×10^{-4}		
89.4	27.9	88.9	2.53×10^{-3}	50.4	50.1
	41.3	138.5	2.42×10^{-3}	76.5	76.1
	Average value		2.48×10^{-3}		

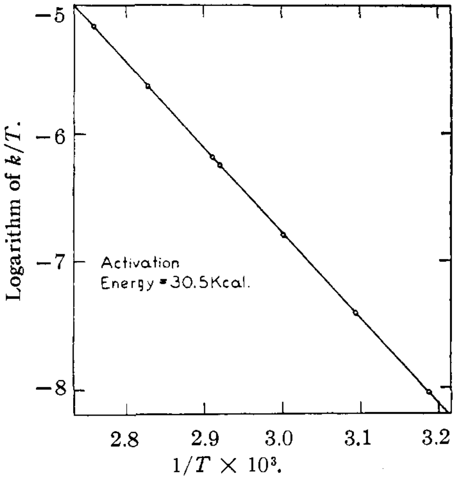

Fig. 3.—Activation energy plot for the aluminum borohydride–ethylene reaction.

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[3] This form of the equation has been adopted in conformity with the equation for the variation of the unimolecular rate constant with temperature given by the theory of absolute reaction rates

$$k = \frac{\mathbf{k}T}{h} e^{\Delta S^{\ddagger}/R}\, e^{-\Delta H^{\ddagger}/RT}$$

Using a form in which the coefficient of the exponential has no temperature term raises slightly the value of the activation energy.

The Reaction between Aluminum Borohydride and Propylene.—The kinetics and stoichiometry of this reaction were found to be the same as in the case of the aluminum borohydride–ethylene reaction.

$$\mathrm{Al(BH_4)_3} + 4\mathrm{C_3H_6} \longrightarrow \mathrm{C} + \mathrm{D} \text{ (two gaseous products)} \quad (4)$$

In Table II the rate constants observed at a variety of temperatures are recorded, and observed "curve-break" pressures are compared with calculated values.

In order to determine the effect of surface area on the rate constant, some runs were made in a bulb packed with glass beads so that the area–volume ratio was increased by a factor of about twelve. These runs are indicated by [a] in Table II. It can be seen that surface plays no role in the reaction. Also, the rate constants determined in clean flasks were found to be the same as those observed in a bulb used in several previous runs.

TABLE II

RATE CONSTANTS FOR THE REACTION OF ALUMINUM BOROHYDRIDE WITH PROPYLENE. COMPARISON OF OBSERVED AND CALCULATED "CURVE BREAKS"

Temp., °C.	Initial press., mm. Al-$(BH_4)_3$	Initial press., mm. C_3H_6	Rate constant, sec. $^{-1}$	Curve break pres. (obs.), mm.	Curve break pres. (calcd.), mm.
42.4	86.7	92.3	4.39×10^{-6}	..	..
	112.9	140.8	4.44×10^{-6}	..	..
	Average value		4.41×10^{-6}		
49.6	107.3	135.8	[a]1.28×10^{-5}	..	..
50.2	57.2	97.8	1.31×10^{-5}	..	..
	62.0	85.0	[a]1.36×10^{-5}	..	..
	80.9	52.6	1.35×10^{-5}	94.0	94.0
	80.9	85.8	1.31×10^{-5}	..	..
	84.4	124.2	1.36×10^{-5}	..	..
	84.9	70.3	1.35×10^{-5}	..	..
	89.6	91.5	[a]1.35×10^{-5}	..	..
	111.5	113.5	[a]1.35×10^{-5}	..	..
	123.5	71.1	1.33×10^{-5}	..	..
	Average value		1.34×10^{-5}		
60.4	57.1	108.0	5.72×10^{-5}	..	..
68.1	50.6	161.4	[a]1.69×10^{-4}	..	..
69.0	24.4	78.5	1.81×10^{-4}	42.4	44.0
	50.3	49.4	1.91×10^{-4}	63.1	62.7
	51.7	66.8	1.83×10^{-4}	69	68.4
	54.5	97.7	1.90×10^{-4}	78.4	78.9
	73.3	41.6	1.88×10^{-4}	84.3	83.7
	82.0	29.1	1.91×10^{-4}	89.9	89.4
	Average value		1.87×10^{-4}		
69.6	41.5	135.5	2.07×10^{-4}	75.0	75.3
	64.7	99.3	2.11×10^{-4}	..	..
	Average value		2.09×10^{-4}		
71.0	64.9	101.7	2.53×10^{-4}	89.0	90.3
79.9	23.8	42.7	7.37×10^{-4}	35.5	34.5
	37.9	154.0	7.61×10^{-4}	..	..
	59.0	116.1	8.54×10^{-4}	88.0	88.0
	Average value		7.8×10^{-4}		

[a] Indicates run with packed reaction bulb.

The reaction of aluminum borohydride with propylene is different from the reaction with ethylene in that after the "curve-break" the rate of pressure drop may either increase or decrease, possibly due to secondary reaction.

The plot of log *k/T versus* reciprocal temperature yields a straight line from whose slope the activation energy is found to be 30.4 kilocalories.

The Reaction between Aluminum Borohydride and Butene-1.—The kinetics of this reaction is also first order with respect to aluminum borohydride. The stoichiometry is given by the equation

$$\mathrm{Al(BH_4)_3} + 4\mathrm{C_4H_8} \longrightarrow \mathrm{E_{gas}} + \mathrm{F_{liquid}} \text{ (one gaseous product)} \quad (5)$$

so that the pressure of aluminum borohydride at any time is given by

$$P_{\mathrm{Al(BH_4)_3}} = P_{0\mathrm{Al(BH_4)_3}} - (P_0 - P)/4 \qquad (6)$$

in which the symbols have the same significance as in equation (2).

In Table III rate constants and "curve break" pressures observed under a variety of conditions are tabulated. The liquid product showed an appreciable vapor pressure at higher temperatures, and observed "curve break" pressures have been corrected for this.

TABLE III

RATE CONSTANTS FOR THE REACTION OF ALUMINUM BOROHYDRIDE WITH BUTENE-1: COMPARISON OF OBSERVED AND CALCULATED "CURVE BREAKS"

Temp., °C.	Initial press., mm. $Al(BH_4)_3$	Initial press., mm. C_4H_8	Rate constant, sec. $^{-1}$	Curve break pres. (obs.), mm.	Curve break pres. (calcd.) mm.
49.9	84.9	88.6	[a]1.31×10^{-5}	83.8	84.9
	91.0	93.2	1.27×10^{-5}	..	..
	93.4	125.2	[a]1.33×10^{-5}	..	..
	109.8	95.0	1.33×10^{-5}	..	..
	Average value		1.31×10^{-5}		
60.8	64.0	44.7	6.07×10^{-5}	65.1	64.0
	77.9	31.2	6.40×10^{-5}	77.4	77.9
	82.0	23.4	6.49×10^{-5}	82.4	82.0
	Average value		6.32×10^{-5}		
69.0	32.0	66.8	1.89×10^{-4}	[b]32.1	32.0
	40.0	55.4	1.84×10^{-4}	[b]39.4	40.0
	63.9	43.7	1.96×10^{-4}	[b]63.7	63.9
	74.8	23.2	1.92×10^{-4}	[b]74.8	74.8
	Average value		1.90×10^{-4}		
79.9	32.6	95.0	7.25×10^{-4}	[b]32.5	32.6
80.1	29.4	76.6	7.76×10^{-4}	[b]29.5	29.4
	37.0	86.4	8.37×10^{-4}	[b]37.4	37.0
	44.2	67.2	8.06×10^{-4}	[b]43.7	44.2
	Average value		8.04×10^{-4}		
91.5	41.9	65.7	2.86×10^{-3}	..	..

[a] Indicates run with packed reaction bulb. [b] Value corrected for apparent vapor pressure of liquid product (2.8 mm. at 69°, 4.3 mm. at 80°).

The activation energy for this reaction is found to be 30.3 kilocalories.

A sample of the liquid reaction product from the aluminum borohydride–butene-1 reaction was removed from the system by distillation, and was analyzed for carbon and hydrogen. The results of the analysis, along with percentages expected if the product were boron tributyl, are: Calcd.: C, 79.1; H, 14.9. Found: C, 78.0; H, 14.7.

The constants of the rate expression (equation (3)) are summarized in Table IV. In the last two columns the rate constants at 50° and 80° calculated by substituting values for B and for the activation energy into equation (3) are shown. The constants are the same for all three reactions, within experimental error.[4]

TABLE IV

VALUES OF LOG B AND ACTIVATION ENERGY FOR ALUMINUM BOROHYDRIDE–OLEFIN REACTIONS. CALCULATED RATE CONSTANTS AT 50 AND 80°

Olefin	Activation energy, kcal.	Log B	Rate constant (sec.$^{-1}$) 50°	80°
Ethylene	30.5	13.215	1.24×10^{-5}	7.94×10^{-4}
Propylene	30.4	13.193	1.28×10^{-5}	7.98×10^{-4}
Butene-1	30.3	13.094	1.29×10^{-5}	7.89×10^{-4}

The similarities in the values of the rate constants suggest that the reaction whose rate is being measured is the same in all three cases, and that the products are analogous, differing only in the nature of their organic substituents. The fact that the rate is first order with respect to the aluminum borohydride pressure suggests that the rate measured is the rate of a dissociation reaction of aluminum borohydride. This may be indicated as shown

$$Al(BH_4)_3 \underset{k_b\ \text{(fast)}}{\overset{k_f\ \text{(slow)}}{\rightleftharpoons}} Al(BH_4)_2H + BH_3 \qquad (7)$$

In the absence of an olefin, an equilibrium is set up, and at any time the concentrations of $Al(BH_4)_2H$ and BH_3 are so minute as to be undetectable. When an olefin is present, however, the following rapid reactions are assumed to take place

$$BH_3 + 3CH_2{=}CHR \xrightarrow{\text{very fast}} B(C_2H_4R)_3 \qquad (8)$$

$$Al(BH_4)_2H + CH_2{=}CHR \xrightarrow{\text{very fast}} Al(BH_4)_2C_2H_4R \qquad (9)$$

Equations (7), (8) and (9) satisfactorily account for the kinetics and stoichiometry observed in the aluminum borohydride–olefin reactions, and explain the presence of boron tributyl among the products of the butene-1–aluminum borohydride reaction. Equation (8) is in agreement with the mechanism proposed by Hurd[5] to explain the formation of boron trialkyls through the reaction of olefins with diborane (B_2H_6).

It must be borne in mind that the evidence for the compound $Al(BH_4)_2C_2H_4R$ is indirect, and its existence has not been established with any certainty. In fact, it might be suspected that in the presence of an excess of olefin and at a higher temperature this compound would further react. To test this hypothesis runs were made in which a thirteen-fold excess of ethylene was mixed with aluminum borohydride and the temperature raised to 140° and held there until the pressure became constant. Approximately eleven molecules of ethylene combined with each molecule of aluminum borohydride. Excess ethylene was pumped off at −78°, and the vapor pressure curve of the products suggested that a mixture of at least two substances was present. The more volatile constituent was distilled into an ampule at 0°, and the remaining heavy fraction was distilled at about 100° into an ampule affixed to the reaction flask. Products from several runs were collected and fractionated.

The more volatile fraction, believed to be boron triethyl, had a vapor pressure of 12.9 mm. at 0° in good agreement with the value of 12.5 mm. reported by Stock and Zeidler.[6] The sample was analyzed for carbon, hydrogen, and boron, and the following percentages were found: C, 71.3 (73.5); H, 16.3 (15.4); B, 11.6 (11.0). The results are in fair agreement with expected values, indicated in parentheses.

The less volatile fraction, a colorless viscous liquid, had a vapor pressure of 12 mm. at 100°. This value is lower than the vapor pressure of aluminum triethyl at the same temperature as calculated from the data of Bamford, Levi and Newitt.[7] Analysis of this fraction showed its composition to be: C, 54.6; H, 12.2; Al, 32.3. These figures correspond approximately to the compound $Al_2H_2(C_2H_5)_4$ (C, 55.8; H, 12.9; Al, 31.3). An analogous methyl compound of aluminum has been reported by Wiberg and Stecher,[8] a viscous liquid of lower volatility than aluminum trimethyl. It is possible that the heavy fraction may also contain some other ethyl aluminum compounds. The over-all reaction might therefore be written

$$Al(BH_4)_3 + 11C_2H_4 \xrightarrow{140°} 3B(C_2H_5)_3 + {}^1/_2Al_2H_2(C_2H_5)_4 \qquad (10)$$

Thus the reaction between aluminum borohydride and ethylene must occur in at least two steps

$$Al(BH_4)_3 + 4CH_2{=}CHR \longrightarrow B(C_2H_4R)_3 + Al(BH_4)_2C_2H_4R \qquad (11)$$

$$Al(BH_4)_2C_2H_4R + 7CH_2{=}CHR \longrightarrow 2B(C_2H_4R)_3 + {}^1/_2Al_2H_2(C_2H_4R)_4$$

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[4] A few runs were made on the reaction between aluminum borohydride and butadiene-1,3. While the rates of pressure decrease were of the same order of magnitude as those observed in the reactions between aluminum borohydride and ethylene, etc., they did not fit into the same kinetic scheme. Possibly aluminum borohydride is capable of initiating a polymerization of butadiene.

[5] D. T. Hurd, THIS JOURNAL, **70**, 2053 (1948).

[6] Stock and Zeidler, *Ber.*, **54**, 531 (1921).

[7] Bamford, Levi and Newitt, *J. Chem. Soc.*, 468 (1946).

[8] Wiberg and Stecher, *Angew. Chem.*, **52**, 372 (1939); *Ber.*, **75**, 2003 (1942).

Summary

1. The kinetics of the reactions between aluminum borohydride vapor and ethylene, propylene and butene-1 have been studied, have been found to be first order with respect to the aluminum borohydride pressure and independent of the olefin concentration. All three reactions occur at the same rate. The activation energy has been determined and a reaction mechanism is proposed. Boron alkyls are among the reaction products.

2. The reaction between aluminum borohydride vapor and an excess of ethylene at 140° yields boron triethyl and an ethyl-aluminum compound.

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[A CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, AND THE PURDUE RESEARCH FOUNDATION]

Polarographic Behavior of Organic Compounds. II. The Hydroxynitrobutanes

BY WILLIAM J. SEAGERS AND PHILIP J. ELVING[1]

The object of this investigation was to determine the polarographic behavior of certain hydroxynitro aliphatic compounds, in particular, the butanes with hydroxyl and nitro groups on adjacent carbon atoms. Polarographic measurements were supplemented by chemical tests and coulometric analysis.

Aromatic nitrohydroxy compounds have been extensively investigated.[2] The results for the nitrophenols have been interpreted in terms of hydrogen bonding since it was found that, in general, the *ortho* compounds are more easily reduced than the corresponding *meta* and *para* compounds. Furthermore, in acid solution, a six-electron reduction is observed for the *meta* and *para* compounds, indicating conversion to the amine, while a four-electron reduction is found for the *ortho* compound, indicating conversion to the hydroxylamine which is stabilized to further reduction by hydrogen bonding. In basic solution, a six-electron reduction is observed for all three isomers. Discrepancies in experimental results and in interpretation between different investigators are apparent. Hydrogen bonding has been similarly postulated as the explanation for the polarographic behavior shown by the other nitrohydroxy aromatic compounds and by the amidines.[3] In acid solution the simple nitroparaffins including *n*- and isonitrobutane are apparently reduced to the amine.[4] It was postulated that the aci-form of the nitro group present in basic solution is not polarographically reduced at the most negative potentials possible with the various buffers used. Two waves were observed[4c] in the *p*H range 4.5 to 6; one was attributed to the reduction of the nitro group to the hydroxylamine and the other to the reduction of the latter to the amine. The kinetics of conversion of the nitro group to the ion of the aci-form have been investigated.[4b]

Experimental

Materials.—Nitrobutanols obtained from the Commercial Solvents Corporation had the following melting points after recrystallization from the solvent indicated: 2-methyl-2-nitro-1-propanol, 87–88°, (petroleum ether); 2-methyl-2-nitro-1,3-propanediol, 145°, (1-butanol); tris-(hydroxymethyl)-nitromethane, 150°, (chloroform–ethyl acetate). Two nitrobutanols, prepared by the method of Hass and Vanderbilt,[5] had the following physical properties: 2-nitro-1-butanol, b. p. (10 mm.) 106°, $n^{20}\mathrm{D}$ 1.439; 3-nitro-2-butanol, b. p. (9 mm.) 91°, $n^{20}\mathrm{D}$ 1.4430. The method of Lambert and Lowe[6] was used to prepare 2-methyl-1-nitro-2-propanol: b. p. (10 mm.) 76–77°, $n^{20}\mathrm{D}$ 1.4427.

Apparatus.—Potential–current curves were obtained on a manually operated Fisher Elecdropode. The capillary used was prepared from marine barometer tubing and had an $m^{2/3}t^{1/6}$ constant of 1.701 mg.$^{2/3}$sec.$^{-1/2}$ (open circuit) in 1 *M* potassium chloride at 25° (h = 75 cm.). The cell used was of the conventional water-jacketed H-type with saturated calomel electrode. The resistance of the cell and dropping mercury electrode was 90 ohms measured with a Kohlrausch bridge employing a 1000-cycle oscillator. The cell was maintained at 25 ± 0.1° by means of an external water-bath equipped with a centrifugal circulating pump.

Oxygen was removed from all cell solutions by bubbling for five minutes with nitrogen which had previously been bubbled through alkaline pyrogallol solution, water and a sample of the cell solution. Bubbling in such a manner up to thirty minutes caused negligible further decrease in wave height.

Coulometric apparatus similar to that described by Lingane[7] was used with a sheet silver anode, 6″ × 2.25″ × 0.010″, approximately double the area of Lingane's anode. The Elecdropode was used to measure the potential between the saturated calomel electrode and the mercury cathode. The potential across the cell was adjusted manually using a 12-ohm wire-wound rheostat as the potential divider. The supporting electrolyte was 0.5 *M* in potassium chloride and 0.1 *M* in disodium hydrogen phosphate with sufficient solid citric acid added to adjust the *p*H to the value desired. Since most of the materials reduced were liquids, a dropper and homeopathic vial were used as weighing bottle; the vial and dropper were weighed

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[2] (a) Astle and McConnell, THIS JOURNAL, **65**, 35 (1943); (b) Astle and Cropper, *ibid.*, **65**, 2395 (1943); (c) Astle and Stephenson, *ibid.*, **65**, 2399 (1943); (d) Page, Smith and Waller, *J. Phys. Colloid Chem.*, **53**, 545 (1949); (e) Pearson, *Trans. Faraday Soc.*, **44**, 692 (1948).

[3] Runner, Kilpatrick and Wagner, THIS JOURNAL, **69**, 1406 (1947).

[4] (a) DeVries and Ivett, *Ind. Eng. Chem., Anal. Ed.*, **13**, 339 (1941); (b) Miller, Arnold and Astle, THIS JOURNAL, **70**, 3971 (1948); (c) Petrů, *Coll. Czech. Chem. Commun.*, **12**, 620 (1947).

[5] Vanderbilt and Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

[6] Lambert and Lowe, *J. Chem. Soc.*, 1517 (1947).

[7] Lingane, THIS JOURNAL, **67**, 1916 (1945).