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.

PRINCETON, NEW JERSEY RECEIVED DECEMBER 31, 1949

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

Polarographic Behavior of Organic Compounds. II. The Hydroxynitrobutanes

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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°, $n^{20}\text{D}$ 1.439; 3-nitro-2-butanol, b. p. (9 mm.) 91°, $n^{20}\text{D}$ 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°, $n^{20}\text{D}$ 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).

before and after the addition of the sample, usually two drops. In most of the experiments the cell was conditioned prior to reduction at −1.2 volts *vs.* the S. C. E. and the reduction carried out at −1.1 volts *vs.* the S. C. E.

Buffer Solutions.—All components of the buffers were analytical grade chemicals and were dissolved in water distilled from permanganate in an all-glass apparatus. Stock solutions of McIlvaine[8] citric acid–disodium hydrogen phosphate (*p*H 2–8) and Sørensen[9] boric acid–sodium hydroxide buffers were prepared double the usual strength and 1 *M* in potassium chloride.

Medium.—Cell solutions were prepared by mixing 20 ml. of the stock buffer solution with 20 ml. of a 1.0 mM. solution of the nitro compound, giving a final cell solution 0.5 mM. in nitro compound, 0.5 *M* in potassium chloride and the usual concentration (about 0.2 *M*) for both buffering constituents. It was found by preliminary experiments that the ionic strength of such a cell solution was sufficiently high so that a variation of 10% in concentration of the buffering components had a negligible effect on the polarographic wave. The *p*H of all solutions was measured, after bubbling with nitrogen, using a Beckman Model G *p*H meter. All cell solutions were allowed to stand 12 hours before polarographing, which was sufficient time for the conversion of the nitro group to the aci-form to reach equilibrium.

Results and Discussion

In Fig. 1 the diffusion current–*p*H curves are plotted for four nitrobutanols. The shape of the curves is that expected from the results of previous workers with nitroparaffins, *i.e.*, a decrease in diffusion current in alkaline solution. The diffusion current in all cases appears to be the result of the reduction of the nitro group. In the acidic region, *p*H has little effect on the diffusion current since the nitro group is not affected. In neutral and basic solution there is partial conversion of the nitro group to the ion of the aci-form which is not reducible at the most negative potential obtainable with the buffers used; the height of the wave thus represents the equilibrium concentration of the molecules with the normal nitro group.

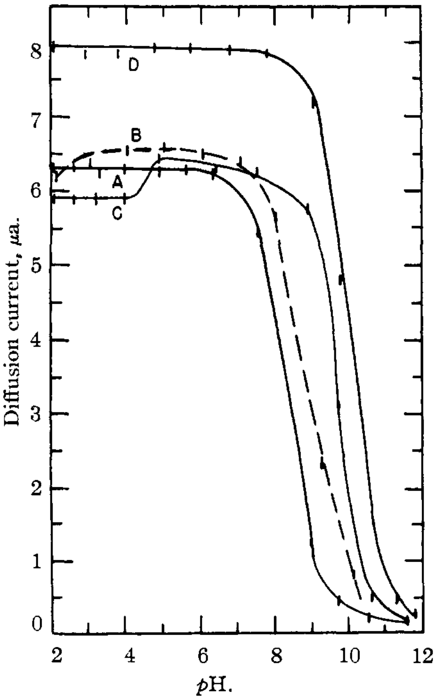

Fig. 1.—Diffusion current–*p*H curves for 0.5 mM. solutions: A, 3-nitro-2-butanol; B, 2-nitro-1-butanol; C, 1-nitro-2-butanol; D, 2-methyl-1-nitro-2-propanol.

The relation of the decrease in diffusion current to *p*H indicates the relative acidities of the hydrogen atoms on the carbon atom holding the nitro group. Thus, the secondary nitro group (curves A and B) form the ion of the aci-form at a lower *p*H than does the primary nitro group (C and D); this behavior is in conformity with the fact that 2-nitropropane is a stronger acid than 1-nitropropane.[10] The increased diffusion current exhibited by D is due to the greater symmetry of the isobutyl structure, resulting in a larger diffusion current. The increase in curve C at *p*H 5 may be due to a change from a four-electron reduction to a six-electron one; at higher *p*H, conversion to the ion of the aci-form overshadows this effect.

In Fig. 2 the half-wave potential is plotted *vs.* *p*H for the same four nitrobutanols. The combination of a primary nitro group and a secondary hydroxyl group (C) is more easily reduced than any of the other three combinations. In basic solution, the primary nitro group (C and B) is easier to reduce than the secondary nitro group (A and B).

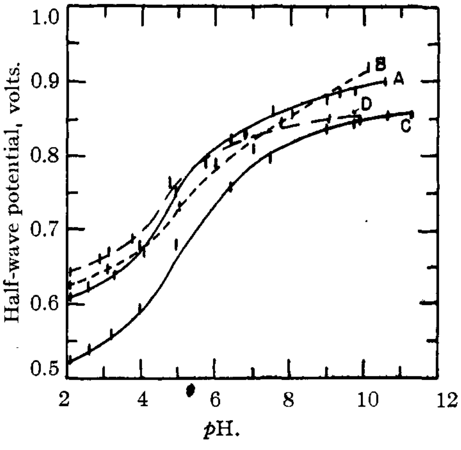

Fig. 2.—Half-wave potential–*p*H curves for 0.5 mM. solutions: A, 3-nitro-2-butanol; B, 2-nitro-1-butanol; C, 1-nitro-2-butanol; D, 2-methyl-1-nitro-2-propanol.

To investigate the tertiary nitro group and the effect of additional hydroxyl groups in the molecule on the behavior of this nitro group, 2-methyl-2-nitro-1-propanol and its di- and trihydroxy homologs were studied (Fig. 3). The decrease in diffusion current in alkaline solution is un-

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(8) Clark, "The Determination of Hydrogen Ions," 3rd ed., Williams and Wilkins Co., Baltimore, Md., 1928, p. 214.

(9) Ref. 8, p. 208.

(10) Wheland and Farr, THIS JOURNAL, **65**, 1433 (1943).

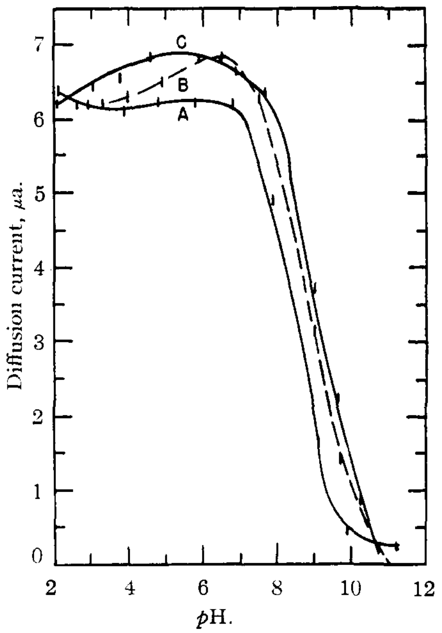

Fig. 3.—Diffusion current–pH curves for 0.5 mM. solutions: A, 2-methyl-2-nitro-1-propanol; B, 2-methyl-2-nitro-1,3-propanediol; C, tris-(hydroxymethyl)-nitromethane.

expected since the tertiary nitro group cannot form the aci-form or its ion. A possible reason for this decrease is the cleavage of the tertiary nitro group.[11] Additional hydroxyl groups cause this cleavage to take place at higher *p*H. The expected result,[2c] that of making the nitro group more easily reduced through hydrogen bonding as additional hydroxyl groups are added, is seen in Fig. 4; the effect is, however, slight.

Coulometric studies of 2-nitro-1-butanol show that reduction at *p*H 4.2 involves four electrons, indicating reduction to the hydroxylamine; the reduced solution gave a positive hydroxamic acid test,[12] proving the presence of an N-alkylhydroxylamine as a reduction product. Similar results were obtained with the other three simple

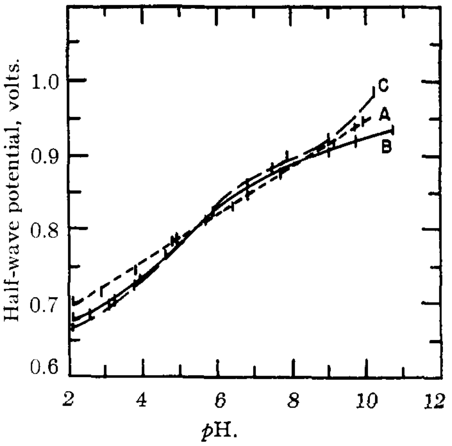

Fig. 4.—Half-wave potential–pH curves for 0.5 mM. solutions: A, 2-methyl-2-nitro-1-propanol; B, 2-methyl-2-nitro-1,3-propanediol; C, tris-(hydroxymethyl)-nitromethane.

nitrobutanols studied. It would appear from this evidence that the reduction proceeds to the hydroxylamine and that the hydroxylamine so formed is not reducible within the potential range (−1.6 volts *vs.* the S.C.E.) possible with the buffers used.

Acknowledgment.—This work was supported by a Frederick Gardner Cottrell Grant made by the Research Corporation to whom the authors wish to express their gratitude.

Summary

The hydroxynitrobutanes with hydroxyl and nitro groups on adjacent carbon atoms are polarographically reduced in acidic solution to the corresponding N-hydroxyalkylhydroxylamines. It is suggested that the latter are stabilized to further reduction by hydrogen bonding. In alkaline solution, conversion of the nitro group to the non-reducible ion of the aci-form prevents an interpretation of the reduction mechanism. Some evidence is presented, in the case of 1-nitro-2-butanol, that in alkaline solution the reduction proceeds to the amine.

WEST LAFAYETTE, INDIANA RECEIVED JULY 5, 1949

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(11) Kleinfeller, *Ber.*, **62B**, 1582 (1929).

(12) Davidson, *J. Chem. Education*, **17**, 81 (1940).