[A CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Polarographic Behavior of Organic Compounds. IV. Some Ethers and Esters of 2-Nitro-1-butanol

BY WILLIAM J. SEAGERS AND PHILIP J. ELVING

This paper is an extension of the investigation of the polarographic reduction of the hydroxynitrobutanes[1] to the ethers and esters of 2-nitro-1-butanol. The object is to remove one possibility from the several for hydrogen bonding present during the reduction of the hydroxynitrobutanes, which bonding may stabilize the N-hydroxyalkylhydroxylamine to further polarographic reduction in the potential range available. The hydrogen bonding could involve either a hydrogen of the hydroxylamine group and the oxygen of the alcoholic hydroxyl group, or the hydrogen of the latter group and the oxygen of the former group. In the esters and ethers studied herein the hydrogen of the alcoholic hydroxyl group has been replaced with an acyl or alkyl group and hence is not available for hydrogen bonding.

Experimental

Nitrobutyl Ethers.—The preparation, composition and physical constants of the ethers investigated have been reported.[2]

Nitrobutyl Esters.—These were prepared by standard methods using sulfuric acid as catalyst and benzene for the removal of water by azeotropic distillation. Physical constants were: 2-nitro-1-butyl formate, b. p. (10 mm.) 98–98.5°, n^{25}D 1.4366; and 2-nitro-1-butyl acetate, b. p. (10 mm.) 102.5–103.5°, n^{25}D 1.4280.

Apparatus.—The apparatus and methodology were essentially that used previously[1] except that the current-potential curves were obtained with a Sargent Model XXI Polarograph and a different capillary was used with an $m^{2/3}t^{1/6}$ constant of 1.60 mg.$^{2/3}$sec.$^{-1/2}$ in 1 *M* potassium chloride at open circuit (h = 73 cm.).

Results and Discussion

Nitrobutyl Ethers.—In Fig. 1 the diffusion current–pH relations are plotted for the methyl, ethyl and propyl ethers of 2-nitro-1-butanol as well as that for the alcohol itself.[1] The polarographic waves at zero time were obtained as soon as was practicable after mixing the buffer and solution of reducible material, and the removal of oxygen; in all cases, in less than fifteen minutes. The slight drop of the curve in basic solution indicates the speed with which the aci ion of the nitro group forms since the diffusion current is due to the reduction of the nitro group.[1]

The behavior of the three ethers after twenty-four hours is much the same as that of the hydroxynitrobutanes,[1] in that the diffusion current–pH relation remains essentially constant in acid solution but the diffusion current decreases to zero in basic solution due to formation of the aci ion of the nitro group. The position of the curves with respect to the diffusion current axis is expected since the methyl ether being the smallest molecule of the three ethers would be expected to have the largest diffusion coefficient and hence the largest diffusion current; the ethyl and propyl ethers should follow with decreasing magnitude of diffusion current in that order, as is found experimentally. The approximate ratio of the diffusion coefficients of the alcohol and of the methyl, ethyl and propyl ethers in the pH interval of 2 to 6 is 1.00:0.98:0.90:0.75.

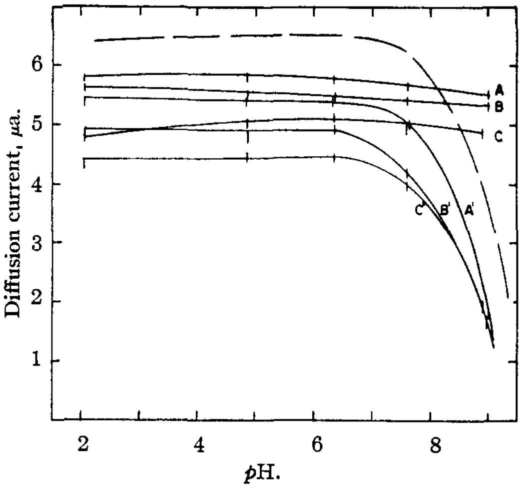

Fig. 1.—Diffusion current *vs.* pH relation for the ethers of 2-nitro-1-butanol: methyl ether, A at zero time, A′ after 24 hours; ethyl ether, B at zero time, B′ after 24 hours; propyl ether, C at zero time, C′ after 24 hours; 2-nitro-1-butanol, dashed line.

In Fig. 2 the half-wave potential–pH relations for the same three ethers and for the alcohol are plotted. In all cases the ethers are more easily reduced than the parent alcohol, the ease of reduction increasing with the size of the alkyl

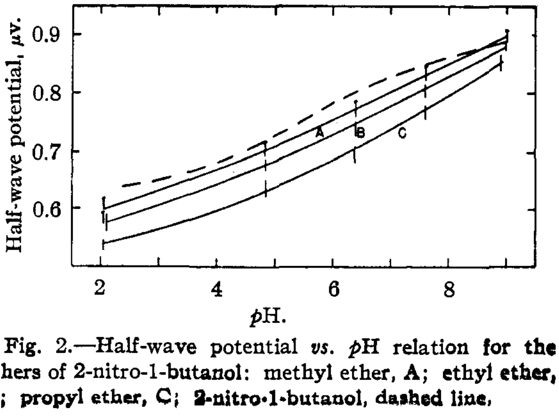

Fig. 2.—Half-wave potential *vs.* pH relation for the ethers of 2-nitro-1-butanol: methyl ether, A; ethyl ether, B; propyl ether, C; 2-nitro-1-butanol, dashed line.

---

(1) W. J. Seagers and P. J. Elving, THIS JOURNAL, 72, 3241 (1950).

(2) W. J. Seagers and P. J. Elving, *ibid.*, 71, 2947 (1949).

group, due probably to the inductive effect since the increasing electronegativity of a substituent group usually increases the ease of reduction.

Coulometric studies[3] show that at *p*H 4.2 the reduction of all three ethers involves four electrons. Presumably, the reduction of the nitro group proceeds to the hydroxylamine group since chemical tests[4] of the reduced solutions indicate that an N-alkylhydroxylamine is present.

Nitrobutyl Esters.—In Fig. 3 the diffusion current-*p*H relations for the formyl and acetyl esters of 2-nitro-1-butanol are plotted. The behavior of these esters is complicated by the ease with which they lose the elements of the respective acid[5] in weakly acid and basic media to form 2-nitro-1-butene which in turn hydrates to form 2-nitro-1-butanol.[6] At zero time in basic solution the decrease in diffusion current is due to this cause. The 2-nitro-1-butene formed is reduced at more positive potentials than either ester and causes the appearance of a small wave (designated as wave I in Figs. 3 and 4) preceding that of the ester. The diffusion current of this small wave is plotted at the bottom of the figure and then added to the curve for the ester as the dashed line.

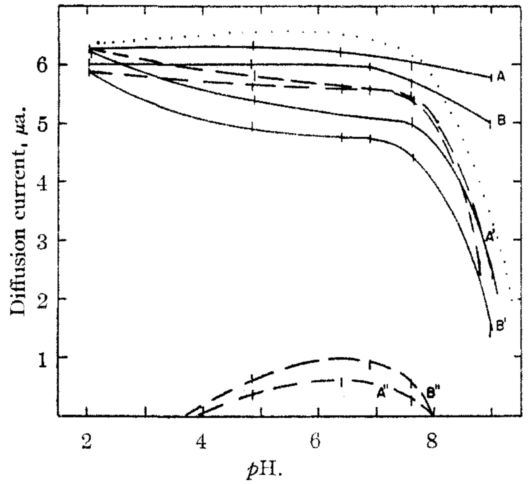

Fig. 3.—Diffusion current *vs.* *p*H relation for the esters of 2-nitro-1-butanol: formate, A at zero time, A′ after 24 hours, A″ wave I after 24 hours; acetate, B at zero time, B′ after 24 hours, B″ wave I after 24 hours; 2-nitro-1-butanol, dotted line.

After twenty-four hours, there are relatively flat portions to the curves in the *p*H range 4 to 7, rather than a decrease as expected from the transformation of ester to olefin, which are due to the production of 2-nitro-1-butanol through the hydration of 2-nitro-1-butene. The alcohol, since it has a half-wave potential very close to that of the ester, does not give rise to a separate wave but increases the height of the wave due to the ester. In neutral solution the hydration rate of the olefin is slow so that its wave is relatively high.

After twenty-four hours in basic solution only one wave, that of the esters, appears. This effect may be due to either of two reasons; the rate of formation of the aci ion of the nitrobutyl ester may be faster than the loss of the acid to form the olefin so that little olefin is formed, or the rate of this last reaction may be faster than the former but the rate of hydration of the olefin to the alcohol is also increased so that no wave for the olefin appears.

Coulometric studies of the reduction of the esters at *p*H 4.2 indicate that the nitro group in these compounds is also reduced to the hydroxylamine group through the addition of four electrons. Chemical tests confirm the presence of an N-alkylhydroxylamine in the reduced solutions.

In Fig. 4 the half-wave potential-*p*H relations for the esters and the alcohol are plotted. The error in the lowest curve (wave I), that of 2-nitro-1-butene,[6] is large, due to the small values

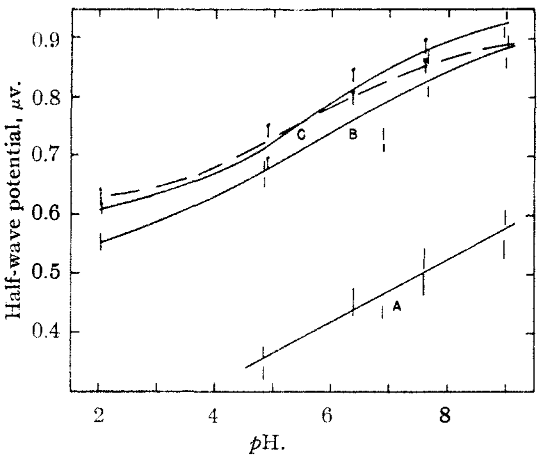

Fig. 4.—Half-wave potential *vs.* *p*H relation for the esters of 2-nitro-1-butanol: 2-nitro-1-butene (wave I), A; acetate, B; formate, C; 2-nitro-1-butanol, dashed line.

Table I

Ease of Reduction of 1- and 2-Nitrobutane and their Derivatives

Compound	Half-wave potential, $E_{0.5}$, v. at *p*H 5.0	at *p*H 7.0
1-Nitrobutane	0.73	0.83
1-Nitro-2-butanol	.69	.82
2-Nitrobutane	.79	.85
2-Nitro-1-butanol	.73	.81
2-Nitro-1-butyl formate	.69	.82
2-Nitro-1-butyl acetate	.66	.75
1-Methoxy-2-nitrobutane	.71	.81
1-Ethoxy-2-nitrobutane	.69	.80
1-Propoxy-2-nitrobutane	.65	.74

---

(3) J. J. Lingane, This Journal, 67, 1916 (1945).

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

(5) H. B. Hass and E. Riley, *Chem. Revs.*, 32, 408 (1943).

(6) W. J. Seagers and P. J. Elving, This Journal, accepted for publication.

of the diffusion current. In all cases, the esters are more easily reduced than the parent alcohol, the effect of the formyl group being less than that of the acetyl group as would be expected from the consideration previously indicated for the ethers.

Hydrogen Bonding.—Astle[7] has postulated that the cessation, at the hydroxylamine stage, of the polarographic reduction of *o*-nitrophenol in acidic media is due to hydrogen bonding between the phenolic hydrogen and the hydroxylamine oxygen; in basic solution such bonding is not possible and hence reduction is direct to the amine; in the intermediate *p*H region the current increases from that due to a four-electron process to that due to a six-electron process. Pearson[8] does not agree with this explanation since he found that *o*-nitrophenol gave two polarographic waves in acid media; the second due, presumably, to the reduction of the hydroxylamine. Pearson explains his results on the assumption that the neutral molecule is reducible in two steps to the amine up to about *p*H 5, but beyond this value reduction of the neutral molecule is possible only to the hydroxylamine; in alkaline media, the anionic or quinoid form present permits reduction direct to the amine; the total amount of reduction will therefore increase as hydrogen-ion concentration decreases. This explanation is supported by more recent work.[9] In the aliphatic series, the α-nitrobutanols,[1] the aliphatic analogs of *o*-nitrophenol, exhibit only a four-electron reduction wave, representing reduction to the hydroxylamine stage. The hydroxylamine group is not reducible within the potential range available presumably because activation of the type present in aromatic nitro compounds, due to the phenyl group, is absent in the aliphatic series. Since both the alcohol and the esters and ethers of the alcohol show the same behavior in exhibiting only a four-electron reduction wave, it would appear that hydrogen bonding has no effect on the degree of reduction possible with these compounds.

Astle[7] has also postulated for *o*-nitrophenol in acidic media, that interference with the normal resonance of the nitro group through hydrogen bonding causes the reduction of the nitro group to occur more readily, *i.e.*, at a more positive potential, ,than in the case of the *meta* and *para* isomers. Pearson's results[8] agree with this explanation but he points out that the electron-donating effect of the hydroxyl group would tend to make the nitro group more difficult to reduce, as is observed for the *meta* and *para* isomers, this tendency being opposed and overcome by the hydrogen bonding possible in the *ortho* isomer. This latter explanation is supported by other work[9] on the nitrophenols as well as on the nitroanisoles. The electron donating and withdrawing tendencies of substituent groups in aromatic nitro compounds have been used to explain the polarographic behavior of aromatic nitro compounds.[10,11] An explanation along similar lines is postulated to explain the ease of reduction of the compounds reported in the present work.

The α-nitrobutanols (Table I) are reduced at less negative potentials than the corresponding nitro paraffin, presumably, because the hydrogen bonding possible overcomes the electron-donating property of the hydroxyl group which would tend to make the alcohols more difficult to reduce. In the compounds where the alcoholic hydrogen is replaced, as in the ethers and esters, the electron-withdrawing property of the substituent group makes the nitro group easier to reduce by decreasing the electron density on the nitro group thus making electron capture easier. As the length of the alkyl portion of the substituent group increases, the ease of reduction increases.

The polarographic behavior of the nitrobutanols and their derivatives is thus explicable on the basis that while hydrogen-bonding is apparently a factor in determining the ease of reduction of the nitro group, it is not necessary to assume that hydrogen-bonding is the cause of the cessation of the reduction at the hydroxylamine stage; the latter is probably due to the likely situation that the reduction of the hydroxylamine to the amine occurs at a considerably more negative potential than that of the parent nitro group to the hydroxylamine.

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 esters and ethers of 2-nitro-1-butanol are polarographically reduced in acid solution to the corresponding N-alkylhydroxylamine, as evidenced by coulometric studies and chemical tests. The behavior of the esters is complicated by their easy loss of the elements of the acid to form 2-nitro-1-butene and its subsequent hydration to 2-nitro-1-butanol.

It is suggested that the hydroxylamine stage is not reducible within the potential range available because of the absence of activation of the type present in the aromatic series resulting from conjugation with the phenyl group.

Evidence is presented that the ease of reduction of the hydroxynitrobutanes and derivatives is explicable on the basis of inductive effects and hydrogen bonding.

STATE COLLEGE, PENNSYLVANIA RECEIVED APRIL 3, 1950

---

[7] M. J. Astle and W. V. McConnell, THIS JOURNAL, **65**, 35 (1943).

[8] J. Pearson, *Trans. Faraday Soc.*, **44**, 692 (1948).

[9] J. E. Page, J. W. Smith and J. G. Waller, *J. Phys. Colloid Chem.*, **53**, 545 (1949).

[10] J. Pearson, *Trans. Faraday Soc.*, **44**, 683 (1948); **45**, 199 (1949).

[11] S. F. Dennis, A. S. Powell and M. J. Astle, THIS JOURNAL, **71**, 1484 (1949).