SOLVENT EFFECTS ON THE MECHANISM OF POLAROGRAPHIC REDUCTION OF NITROALKANES

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The polarographic reduction of nitroalkanes has been studied in dimethylformamide, acetonitrile, ethyl alcohol and in aqueous buffered media (2 < pH < 11).

It has been shown that different reduction mechanisms take place in the different solvents. In dimethylformamide and in acetonitrile evidence has been obtained for a multi-step nucleophilic mechanism. The reaction mechanism in aqueous solutions is always determined by a single (but not the same) protonation step. At pH < 7 the electrochemically active form is the protonated nitroderivative, while at higher pH the reduction of the neutral form is prevalent, and so the determining step turns out the protonation of RNO_2^-. This behaviour is quite similar to that observed in acetonitrile and dimethylformamide with phenol and in ethyl alcohol. The above discussed reaction mechanisms are supported by the values (and signs) of the calculated reaction constants.

Polarographic reduction of nitroalkanes has been studied by many authors[1-6] in various media. All the authors have found, that the first wave is always an irreversible wave with four electrons, and that the reduction product is hydroxylamine. But the relevant bibliographical data lead to different reaction mechanisms and to kinetic parameters which cannot always be compared with one another.

Suzuki and Elving[4], who studied the reaction kinetics of nitroalkanes in McIlvaine's buffers, established that $E_1/_2$ depends on the pH of the solution, and Koutecký's analysis applied to the polarographic wave indicated that the process is nearly always controlled by a single step.

The analysis carried out by Lee and DeVries[5] in non-aqueous media revealed a wide variety of behaviour patterns according to the solvents examined. And finally the results reported by Mairanovskii[7] show that in an aqueous acid medium the electrochemically active form is the protonated nitroderivative, while in alkaline solutions the neutral form is reduced.

Thus, because of the variety of experimental results obtained by the various authors under different experimental conditions, and which therefore cannot successfully be related or compared with one another, it was thought worthwhile to conduct a systematic investigation into the influence which the solvent, the pH, and the com-

position of the base electrolyte have on the reduction kinetics, in order to establish which is the electrochemically active form, and the reduction mechanism to hydroxylamine.

Therefore dimethylformamide and acetonitrile were the aprotic media chosen; and ethyl alcohol and buffer solutions with variable protonic activity $(1 < \text{pH} < 11)$ were the protic environments. The influence of the protonating agent (phenol or water) on the reduction mechanism in dimethylformamide and acetonitrile was also examined.

The analysis of polarographic behaviour was carried out by examining the dependence of the values of i and of $E_{1/2}$ on the properties of the solution, and determining the kinetic parameters by means of Koutecký's method[8]. This method consists of calculating for each potential value the corresponding value $k_{f,h}$, using the parameter $\lambda = k_{f,h} t^{1/2} / D^{1/2}$ (which is obtained from the ratio i/i_d) where D is the coefficient of diffusion and t the drop-time. When the process is controlled by a single reaction step, the $\log k_{f,h}$ vs E plot is straight, and it is possible to calculate the electronic transfer coefficient (αn_a) and the reaction constant $k_{f,h}^0$, from the slope of the line and by extrapolation at $E(\text{NHE}) = 0$, respectively. When the plot is not a straight line, providing adsorption does not affect the current and potential values unduly[9], the presence of a broken line indicates that the reaction mechanism is complex, and that it consists of several successive steps with fairly similar kinetic constants and reduction potentials.

Moreover, from the Hammett–Taft–Zuman[10] correlation $\Delta E_{1/2} = \varrho^* \sigma^*$ (which is valid when the steric and mesomeric effects are constant or negligible) the values and the signs of the reaction constant ϱ^*, which depends on the experimental conditions but is independent of the substituent, were calculated.

EXPERIMENTAL

Nitroethane, 1-nitropropane, 1-nitrobutane, and 1-nitropentane produced by high-purity analyses in the concentration $5 \cdot 10^{-4}$ mol/l, were examined for their polarographic behaviour in high-purity dimethylformamide, spectroscopically pure CH_3CN, anhydrous C_2H_5OH, and buffered aqueous solutions prepared with double-distilled water also in Na_2HPO_4–citric acid for pH 2—8 (McIlvaine's buffers), and $NaHCO_3$–NaOH for pH 9—11.

Polarographically pure $10^{-1}M$-$(C_4H_9)_4NI$ was used as the base-electrolyte in the non-aqueous solutions. The potential values given, referring to the saturated calomel electrode, were corrected for the interliquid potential. The drop time was kept constant (4 s) and the temperature maintained to within $25° \pm 0.5°C$ using a water jacket.

RESULTS AND DISCUSSION

Aprotic Solvents

Fig. 1a shows the results obtained by analysing the polarographic wave of n-nitropropane with Koutecký's method: the $\log k_{f,h}$ vs E that is broken line which becomes

straight in the presence of phenol in concentrations $> 10^{-4}$ mol/l and of water in higher concentrations (Table I).

These results confirm the reduction mechanism proposed by Hoijtink[11] for organic substances in aprotic solvents

$$R \; + e \; \rightleftarrows \; R^-,$$

$$R^- \; + e \; \rightarrow \; R^{2-}.$$
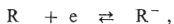
The reduction potential of the anion R^- is more negative than that of R. If the difference is large enough (> 100 mV) then the polarogram shows two distinct waves, if it is small enough a single wave is recorded; but Koutecký's analysis yields a broken line. The addition of a protonating agent to the solution causes the anion R^- to protonate according to the reaction $R^- + HA \rightarrow RH\cdot + A^-$, yielding the radical $RH\cdot$ whose reduction potential is more positive than that of R. Thus the plot becomes a straight line, and different values are obtained for the kinetic parameters, since the overall process is determined by the new protonating step. Moreover, the protonating agent makes its influence felt in very low concentrations, and this supports Peover's hypothesis that it acts in the undissociated form and that the reaction is controlled by its diffusion to the electrode. In order to confirm this hypothesis the treatment of Given and Peover[12] was extended to a reduction wave of n electrons applying Nernst's equation to the following reaction mechanism:
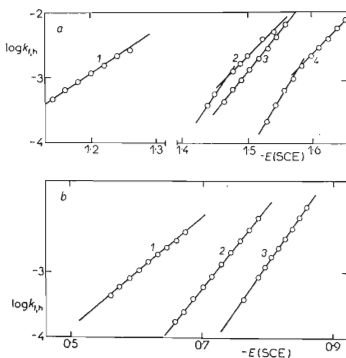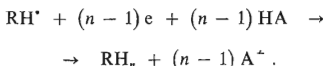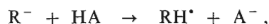
$$R \; + e \; \rightleftarrows \; R^-,$$

$$R^- \; + HA \; \rightarrow \; RH\cdot + A^-,$$

$$RH\cdot + (n-1)\,e + (n-1)\,HA \; \rightarrow$$

$$\rightarrow \; RH_n + (n-1)\,A^-.$$

Fig. 1

Plots of log $k_{f,h}$ vs E for the 1-Nitropropane a Non aqueous solvents: 1 C_2H_5OH, 2 CH_3CN, 4 dimethylformamide, 3 dimethylformamide + phenol; b aqueous buffered solutions: 1 pH 2; 2 pH 5·1; 3 pH 7·1.

TABLE I

Effect of Phenol and Water Concentration (c) on the $E_{1/2}$ Values and Kinetic Parameters of the 1-Nitropropane

c, mol/l[a]	$-E_{1/2}$ V	αn_a	$-\log k_{f,h}^0$ cm^{-1} s	$-E_{infl.}$ V	m
			Dimethylformamide + phenol		
0	1·560	0·65	17·2	1·545	—
2 . 10^{-6}	1·557	0·65	17·2	1·553	4 . 10^{-3}
10^{-5}	1·551	0·67	17·5	1·543	2 . 10^{-2}
10^{-4}	1·555	0·65	17·1	—	2 . 10^{-1}
5 . 10^{-4}	1·550	0·71	18·2	—	1
2 . 10^{-3}	1·540	0·75	18·6	—	4
4 . 10^{-3}	1·523	0·76	19·0	—	8
5 . 10^{-3}	1·516	0·75	18·7	—	10
8 . 10^{-3}	1·489	0·78	19·1	—	16
10^{-2}	1·489	0·78	19·1	—	20
1·2 . 10^{-2}	1·489	0·76	18·7	—	24
			Dimethylformamide + water		
0	1·560	0·65	16·8	1·561	—
10^{-3}	1·556	0·64	16·4	1·563	2
10^{-2}	1·550	0·65	16·8	1·545	20
5 . 10^{-2}	1·540	0·67	17·3	—	100
10^{-1}	1·532	0·69	17·5	—	200
5 . 10^{-1}	1·520	0·67	16·7	—	1 000
5·5 . 10^{-1}	1·528	0·55	14·3	—	1 110
1·65	1·480	0·51	13·2	—	3 340
2·75	1·460	0·51	12·9	—	5 600

[a] Concentration of 1-nitropropane 5 . 10^{-4} mol/l.

The following relations were obtained:

$$E = \text{const.} + (RT/F) \ln \left[(i_d - i)/i\right] \left[(mi_d/n) - i\right], \qquad (1)$$

$$E_{1/2} = \text{const.} + (RT/F) \ln (i_d/2n) + (RT/F) \ln (2m - n), \qquad (2)$$

where the standard potentials, the diffusion coefficients and the rate constant of the slowest protonating step are subsumed in the constant; m is the ratio between the concentration of the protonating agent and that of the reducible form.

The experimental results, reported in Fig. 2, verify equation (1) and confirm the validity of the proposed mechanism. The data given in Table I show that for concentrations above the minimum required to completely protonate the nitroalkane, the values of the kinetic parameters are independent of m. Therefore the step which determines the process remains as before, while the variation of $E_{1/2}$ is described by equation (2).

A similar behaviour has been observed using water as the protonating agent, but very high concentrations are required since the protonating action of water is lower than that of phenol. Thus it is clear that under these conditions $(Eq. (2))$ no longer describes completely the variations of $E_{1/2}$, which is considerably influenced by the solvent effect of the water and by the dielectric constant of the solution (Table I).

Protic Solvents

The variations of $E_{1/2}$ in relation to the pH of the solution are given in Fig. 3. The initial value of i_1 is constant in all the solutions examined, while $E_{1/2}$ depends heavily on the pH. This behaviour can be explained by supposing that two electroreducible forms[13] (the neutral form and the protonated form) are present on the electrode at the same time, and that their ratio depends on the protonation kinetics. At pH < 3, when the protonation rate is very high, the value of $E_{1/2}$ is independent of the pH. Increasing the pH (3 < pH < 8) the protonation is slower, $E_{1/2}$ becomes progressively more negative, and, since the reduction potentials of the two electroreducible forms differ very little under these conditions, they are reduced at the same time. At very high pH (pH > 8), since protonation is virtually nil, only the neutral form is reduced, and $E_{1/2}$ assumes a new constant value.
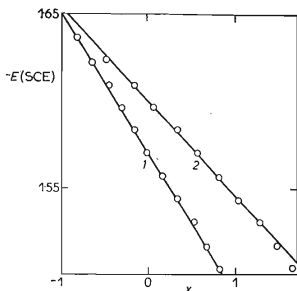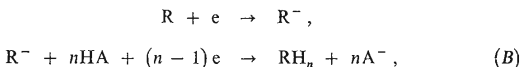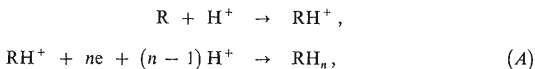

Fig. 2

Logarithmic Analysis of Wave of 1-Nitropropane with Phenol in mol Ratio $m = 4.0$ in Dimethylformamide

$1\ X = \log [(i_d - i)/i]$, $2\ X = \log [(i_d - i) : i]\ [(mi_d/n) - i]$.

In aqueous solutions the overall reduction mechanism may be described by the following schemes:

$$R + H^+ \rightarrow RH^+,$$

$$RH^+ + ne + (n-1)H^+ \rightarrow RH_n, \qquad (A)$$

$$R + e \rightarrow R^-,$$

$$R^- + nHA + (n-1)e \rightarrow RH_n + nA^-, \qquad (B)$$

where processes (A) and (B) are contemporaneous and the number of electrons necessary for the reduction is the same, as is the reduction product.

Determinations carried out in alkaline media are complicated by the tautomeric equilibrium which holds between the nitro form and the aci form of the nitroalkane[14-16]

$$RCH_2NO_2 \rightleftarrows RCH=NO_2^-H^+,$$
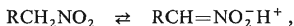
the latter being irreducible. As i_1 decreased in time, it was possible to follow the tautomerization kinetics, the rate of which increases the higher is the pH of the solution. The value of i_1 extrapolated at zero time is constant at any pH (Fig. 4). At pH < 11 the values of $E_{1/2}$ and i_1 cannot be accurately determined.

The tautomeric equilibrium in alkaline solutions (pH > 8) considerably influences the values of E and i, and makes it impossible to apply Koutecký's analysis to the
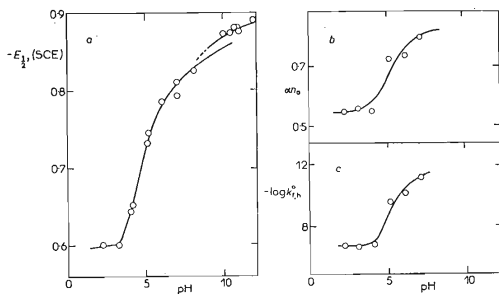

Fig. 3

pH Effect on $E_{1/2}$ (a), αn_a (b) and log $k_{f,h}^0$ (c)

reduction wave, but in the whole range of solution of lower pH the log $k_{f,h}$ vs.E plot is a straight line whose slope depends on the properties of the base solution (Fig. 1b). The examination of the values of αn_a and $k_{f,h}^0$, obtained from the plots, indicates the easier the protonation, the easier the reduction (Fig. 3).

To complete the analysis of the polarographic behaviour of nitroalkanes and to confirm the schemes proposed, the Hammett–Taft–Zuman correlation was used. The values and the signs of the reaction constant ϱ^* were obtained using the values of $E_{1/2}$ for the four nitroalkanes studied. (Table II, Fig. 5). In aqueous media the sign of ϱ^* is always negative, and its value depends on the pH at pH < 8 but remains constant
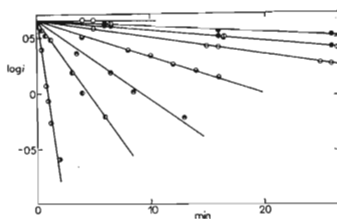

FIG. 4

Plot of log i vs Time at Different pH
○ 2·3, ⊗ 4·2, ● 6·0, ⊙ 7·0, ◉ 8·0, ⊖ 9·6, ◓ 10·0, ◐ 10·4, ◑ 10·8, ◗ 11·4.

TABLE II

$E_{1/2}$ and ϱ^* Values of the Nitroalkanes in Different Media[a]

Solvents	$-E_{1/2}$, V				ϱ^* V
	$C_2H_5NO_2$	n-$C_3H_7NO_2$	n-$C_4H_9NO_2$	n-$C_5H_{11}NO_2$	
pH 2·1	0·642	0·600	0·551	0·492	−3·0
pH 5	0·762	0·730	0·698	0·640	−2·3
pH 8	0·841	0·824	0·787	0·757	−1·7
pH 9·2	0·894	0·883	0·857	0·829	−1·3
pH 10	0·900	0·880	0·848	0·832	−1·3
Dimethylform-amide	1·561	1·571	1·568	1·572	+0·2
10^{-1}M Phenol in dimethylformamide	1·525	1·522	1·516	1·510	−0·3
CH_3CN	1·424	1·458	1·480	1·514	+1·6
C_2H_5OH	1·206	1·210	1·201	1·196	−0·2

[a] Concentration of nitroalkanes $5 . 10^{-4}$ mol/l.

for higher pH values. This shows that in aqueous media the step which determines the process is always electrophilic. This conclusion, which is in perfect agreement with the hypothesis put forward, does not agree completely with the results reported by Zuman[17]. This discrepancy may be attributed to the different choice of nitroalkanes examined, and in fact the values of $E_{1/2}$ obtained for the 1-nitroalkanes and the 2-nitroalkanes are not comparable with one another, for the latter display a not inconsiderable steric effect.

An equally valid agreement was found between the values of the reaction constant ϱ^* (Table II) and the results obtained from Koutecký's analysis as applied to nitroalkanes in aprotic medium with and without phenol (Table I). ϱ^* is positive in CH_3CN and dimethylformamide, but its sign changes with the addition of phenol until it reaches a negative value which is constant and comparable with that obtained in aqueous alkaline media. This confirms that the phenol added affects the reduction mechanism, and that when it is present in sufficient concentration the step determining the whole process is electrophilic.

The polarographic reduction of nitroalkanes in alcoholic media is similar to that which occurs in aqueous alkaline media and in aprotic media with phenol, since the log $k_{f,h}$ vs E plot is a straight line and ϱ^* is weakly negative (Table II, Fig. 1a, Fig. 5).
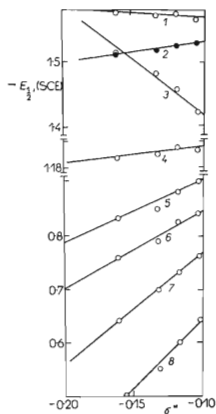

Fig. 5

Taft's Correlations of $E_{1/2}$ for the Studied Nitroalkanes

1 Dimethylformamide, 2 dimethylformamide + phenol; 3 CH_3CN; 4 C_2H_5OH; aqueous buffered solutions: 5 pH 10; 6 pH 8; 7 pH 5; 8 pH 2·1.
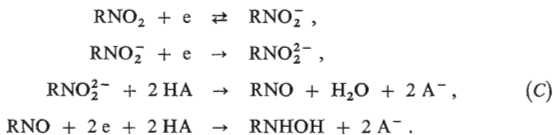
CONCLUSIONS

The analysis of the results leads therefore to the conclusion that the polarographic reduction of nitroalkanes is heavily influenced by the solvent and by the nature and concentration of the base electrolyte. Three basic types of mechanism can be distinguished: reduction in aprotic media, in protic media with low protonating activity
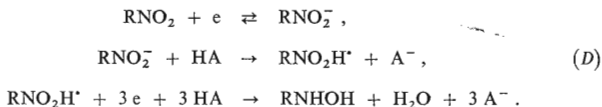
(alkaline aqueous solutions, alcoholic solutions, and aprotic solvents with the addition of a protonating agent) and in acid media.

Reduction in dimethylformamide and acetonitrile takes place according to the scheme suggested by Hoijtink for the reduction of organic molecules in aprotic media:
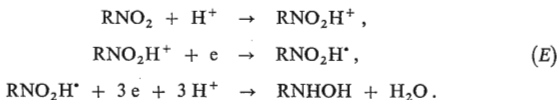
$$RNO_2 + e \rightleftarrows RNO_2^- ,$$

$$RNO_2^- + e \rightarrow RNO_2^{2-} ,$$

$$RNO_2^{2-} + 2\,HA \rightarrow RNO + H_2O + 2\,A^- , \qquad (C)$$

$$RNO + 2\,e + 2\,HA \rightarrow RNHOH + 2\,A^- .$$

The presence of traces of RNO, found by Hoffmann and coworkers[18] among the products determined in CH_3CN, seems to confirm the hypothesis that, because of its high protonic affinity, the anion RNO_2^{2-} protonates at the expense of the solvent and is subsequently reduced to RNO, which in turn is quickly reduced to hydroxylamine.

The addition of a protonating agent to the solution or reduction in a medium with low protonic activity leads to protonation on the electrode of the anion RNO_2^- (the presence of which in solution was made evident in non aqueous media and aqueous weakly alkaline media[18-20]) to RNO_2H, the reduction potential of which is more positive than that of RNO_2; this causes its immediate reduction to RNO_2H^- and the slowest step is therefore protonation. The reaction scheme proposed is thus the following:

$$RNO_2 + e \rightleftarrows RNO_2^- ,$$

$$RNO_2^- + HA \rightarrow RNO_2H^{\cdot} + A^- , \qquad (D)$$

$$RNO_2H^{\cdot} + 3\,e + 3\,HA \rightarrow RNHOH + H_2O + 3\,A^- .$$

Finally, in acid medium reduction of the protonated form of the nitro alkane (which is present even in solutions with a relatively high pH) prevails, for the electric field[21] generates a substantial difference of protonic activity between the electrode and the solution, leading to protonation on the electrode even in solutions in which it is not supported by the value of the basic constant of the nitroalkane[22-24].

In this case the reduction kinetics are controlled by the protonation kinetics, thus by the pH, by the buffering capacity and by the nature of the solution itself. The scheme of the reduction mechanism which is proposed is therefore the following:

$$RNO_2 + H^+ \rightarrow RNO_2H^+ ,$$

$$RNO_2H^+ + e \rightarrow RNO_2H^{\cdot} , \qquad (E)$$

$$RNO_2H^{\cdot} + 3\,e + 3\,H^+ \rightarrow RNHOH + H_2O .$$

Of course in solutions in which complete protonation of the nitroalkane is impossible, the two mechanisms (D) and (E) occur simultaneously. Nevertheless, in both cases the slowest step which determines the rate of the process is the protonation which precedes or is preceded by the transfer of the first electron; so the sign of the reaction constant ϱ^* is always negative.

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