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BEHAVIOR AT THE DROPPING MERCURY ELECTRODE OF CERTAIN POLYNITROALKANES

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The study of the polarographic behavior of aliphatic polynitro compounds is still at an early stage. Thus, there are only reports on the behavior of dinitro compounds at the dropping mercury electrode. Stock, Masui, and Sayo recently reported on the peculiar polarographic reduction of 2,2-dinitropropane, dinitromethane, and 1,1-dinitroethane ([1–3]). It is undoubtedly of considerable interest to study the behavior, at the dropping mercury electrode, of compounds with a larger number of nitro groups at one carbon atom. Kruse and Howell ([4]) obtained polarograms of tetranitromethane; however, they did not give a satisfactory interpretation of these polarograms*. We investigated the polarographic behavior of polynitro compounds at the dropping mercury electrode, $t = 4.1$ sec, $m = 1.038$ mg/sec, in 10% methanol–water buffer solutions at 25° and a nitro compound concentration of $5 \cdot 10^{-4}$ mole/liter.

In a very acidic solution (pH 2) the nitroform wave splits into two; in weakly acidic and neutral solutions there is one well-defined wave. In alkaline solutions two waves are observed, the first of which is considerably more pronounced. The height of the first wave in alkaline solutions decreases with increasing pH, while the height of the second wave increases. The total height of the waves remains practically constant over the pH range studied (Fig. 1).

With increasing pH of the solution, the half-wave potential of the first nitroform wave shifts toward more negative potentials. The value of the coefficient $dE_{1/2}/d\text{pH}$ is 56 mV/pH. In alkaline solutions (pH 9–12) the half-wave potential does not depend on the pH of the solution (Fig. 2); since the second wave is difficult to measure, its $E_{1/2}$ values are not given.

The dependence of the wave height on the pressure on the dropping mercury and on temperature in weakly acidic and weakly alkaline solutions indicates its diffusion character. The temperature coefficient of the wave is 1.5%/deg. The half-wave potential of nitroform depends on the buffer capacity of the solution. A tenfold increase in the concentration of acetic acid in a solution with pH 4.2 causes a shift of the half-wave potential by 26 mV toward positive potentials. In an unbuffered solution, three waves appear on the nitroform polarogram. The

Fig. 1. Polarograms of nitroform in solutions with pH (2-12)

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sum of the heights of these waves is equal to the wave height in buffered solutions. The dependence of the half-wave potential of nitroform on the buffer capacity of the solution, and also on the pH of the solution, indicates that reduction of nitroform in the region pH < 9 proceeds through a protonated complex.

To study the influence of the structure of the electrical double layer on the polarographic wave of nitroform, sodium chloride was introduced into the solution.

* After the present work had been completed, a report by Masui and Sayo ([5]) appeared in print on the polarographic behavior and electrolysis at controlled potential of certain gem-polynitroalkanes, including trinitromethane, trinitroethane, and tetranitromethane. The material presented in the present article is in agreement with the data of the Japanese authors and supplements them.

With a tenfold increase in the concentration of salt in the solution, the half-wave potential of nitroform shifts in the negative direction by 20 mV. Since, in a certain pH region, the reduction of nitroform proceeds with the participation of protons, the substantial influence on the half-wave potential is exerted by the change in the structure of the electrical double layer due to the associated change in pH in the surface reaction layer of the electrode, as compared with its value in the bulk of the solution. The small magnitude of this shift indicates that protonation takes place not only in the surface reaction layer but also in the bulk of the solution.

The half-wave potential of nitroform depends on the concentration of the depolarizer. The limiting-current value changes linearly with the concentration of nitroform in the solution.

Addition of surface-active substances (camphor) to nitroform solutions causes splitting of the polarographic wave. As the concentration of camphor is increased, the ratio of the heights of the first and second waves changes, but at camphor concentrations above $1.7 \cdot 10^{-3}$ mole/liter it becomes constant, equal to $1 : 5$. The total height remains practically constant as the camphor concentration is increased. To clarify the features of the reduction of nitroform formed as a result of the preceding electrode reaction, we recorded polarograms of the following halotrinitromethanes: $CJ(NO_2)_3$, $CBr(NO_2)_3$, $CCl(NO_2)_3$.

Fig. 1. Polarograms of nitroform in solutions with pH (2-12)

The reduction waves of the C—Hal bonds in these compounds were studied by Mairanovskii and co-workers ([6]), who showed that the presence of nitro groups in halotrinitromethane molecules facilitates the electrochemical cleavage of the C—Hal bond, and the corresponding wave appears before the reduction wave of the nitro group.

Fig. 2. Dependence of $E_{1/2}$ of nitroform on the pH of the solution

Figure 2: Fig. 2. Dependence of $E_{1/2}$ of nitroform on the pH of the solution

In weakly alkaline and alkaline solutions, halotrinitromethanes give two waves on the polarograms, corresponding to analogous waves on the polarogram of unsubstituted nitroform. In acidic and weakly acidic solutions, features of their polarographic behavior are observed. Under these conditions, halotrinitromethanes are reduced at potentials more negative than those of nitroform (Fig. 3).

In addition, on the polarogram of trinitrochloromethane in acidic solutions two waves are clearly observed over a broader pH range (2-5), gradually merging into one wave with the total height; on the polarogram of nitroform at pH 2 only a weak inflection is observed. The limiting current of chloronitromethane is considerably smaller than the limiting current of nitro-

form.

Compound	$CH(NO_2)_3$	$CJ(NO_2)_3$	$CBr(NO_2)_3$	$CCl(NO_2)_3$
i, μA	12.78	13.68	12.35	7.17

The peculiarities are probably associated with different conditions of protonation and reduction for nitroform formed at the electrode as a result of the preceding reaction, and for nitroform delivered into the reaction layer by diffusion. During reduction of the C—Hal bond the halotrinitromethane molecule is oriented in a definite way at the electrode surface (corresponding to the polarity of the C—Hal bond), and some additional amount of energy must be expended so that the arrangement at the electrode surface of the nitroform molecule formed after reduction of the C—Hal bond is the same as that of unsubstituted nitroform. The nitro-group wave in halotrinitromethanes is diffusion-controlled. The temperature coefficients of the halotrinitromethanes, calculated for pH 3.00, do not exceed 1.5-2%.

Fig. 2. Dependence of $E_{1/2}$ of nitroform on the pH of the solution

In order to clarify the influence of accumulation of nitro groups at one carbon atom on polarographic reduction, we studied the behavior of tetranitromethane in methanol-water solutions in the pH range 2-12. The study was complicated by the fact that the height of the tetranitromethane wave decreases rapidly with time; therefore the polarograms were recorded almost immediately after addition of the nitro compound to a supporting electrolyte previously freed from oxygen. The behavior of tetranitromethane and nitroform at the dropping mercury electrode is in principle analogous. The waves obtained on the polarograms of tetranitromethane in the pH range 2-12 coincide in their potentials with the waves of nitroform; however, in acidic solutions some deviations are observed.

Fig. 3. Half-wave potentials of halotrinitromethanes as a function of solution pH

Figure 3: Fig. 3. Half-wave potentials of halotrinitromethanes as a function of solution pH

In addition, in acidic solutions (pH 2 and 2.6) a third wave is clearly observed on the polarogram of tetranitromethane with $E_{1/2} \approx 1.1$ V, which with increasing pH merges with the background decomposition wave. However, the wave height of tetranitromethane is considerably smaller than the wave height of nitroform. The tetranitromethane wave is diffusion-controlled. The value of the coefficient

$$\frac{dE_{1/2}}{d\text{pH}}$$

is 57 mV/pH. The half-wave potential of tetranitromethane, beginning at a concentration of about $4 \cdot 10^{-4}$ mol/liter, depends on the concentration of the depolarizer. A change in the buffer capacity of the solution leads to a shift of $E_{1/2}$ of $C(NO_2)_4$; moreover, a tenfold increase in the concentration of acetic acid in the solution causes a shift of $E_{1/2}$ toward positive potentials the same as for nitroform, 28 mV.

Fig. 3. Half-wave potentials of halotrinitromethanes as a function of the pH of the solution:
1 —$CBr(NO_2)_3$, 2 —$CCl(NO_2)_3$, 2′ —first wave of $CCl(NO_2)_3$, 3 —$CJ(NO_2)_3$

The great analogy in the behavior of tetranitromethane and nitroform at the dropping mercury electrode suggests that the waves appearing in water-alcohol solutions on the polarograms of tetranitromethane belong to nitroform. This is also indicated by the UV spectrum of the alcohol-water solution, in which an absorption band appears very rapidly

with a maximum at 350 mμ, characteristic of nitroform. For a more detailed analysis of the reduction of nitroform and tetranitromethane, the effect of experimental conditions on the kinetic parameters of the electrode reaction αn_a and K° was studied.

In the pH range 4-9, plots of $\log K_f$ versus E give good straight lines, but at pH 2.7 the plot $\log K_f$—E is a curved line. Apparently, in this case the electrode process is limited by two or several successive reactions.

With increasing pH the values of $\log K^\circ$ increase, while the values of αn_a remain constant, equal to 0.53 (Fig. 4). As can be seen from Fig. 4, the values of the kinetic parameters for the waves of nitroform and tetranitromethane are close to one another. The mechanism of the electrode reaction for the reduction of $CH(NO_2)_3$ and $C(NO_2)_4$ remains constant over a fairly wide pH range (3.8-9.2). The potential-determining stage of the process of their reduction evidently consists in the addition of one electron to the molecule.

Fig. 4. Dependence of K° on pH for the waves of nitroform (a) and tetranitromethane (b)

Figure 4: Fig. 4. Dependence of K° on pH for the waves of nitroform (a) and tetranitromethane (b)

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The same is indicated by the addition of surface-active substances to solutions of trinitro compounds. The wave of the nitro group decreases, in all probability, to the value of a one-electron wave, determined by the primary potential-determining stage. The secondary processes completing the reduction are retarded and proceed at more negative potentials, where neutral dipolar inhibitor molecules are desorbed and displaced by cations.

Table 1

No.	Alcohol concentration, %	pH	$E_{1/2}$ relative to saturated calomel electrode	i_d, μA	$-\log K^\circ$	αn_a
1	2.5	8.8	−0.516	14.30	7.64	0.53
2	4.5	–	−0.528	13.92	7.74	–
3	6.5	–	−0.544	13.72	7.90	–
4	8.5	–	−0.560	13.72	7.98	–
5	14.5	–	−0.596	11.96	8.34	–
6	18.5	–	−0.616	10.78	8.50	–
7	26.5	–	−0.654	9.02	8.70	–

With increasing methanol concentration, the values of K° decrease. The limiting current of nitroform decreases with increasing alcohol content; $E_{1/2}$ shifts linearly in the negative direction.

The dependence of the kinetic parameters of nitroform reduction on the concentration of methyl alcohol in solution is given in Table 1.

The change in $\log K^\circ$ with methanol concentration has the character of an adsorption isotherm. The adsorption of methanol on the electrode surface is confirmed by the form of the electrocapillary curves recorded for nitroform at different methanol contents in solution. Addition of methanol at a concentration of 0-26% does not change the mechanism of the electrode reaction ($\alpha n_a = 0.53$). We calculated, by the Ilkovič equation, the number of electrons taking part in

the reduction of nitroform at the dropping mercury electrode. We obtained $n \approx 12$. However, the value of n found experimentally by the microcoulometric method is half this value.

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Note: Figure translations are in progress. See original paper for figures.