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S. I. ZHDANOV and Academician A. N. FRUMKIN

![Fig. 1](image)

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Fig. 1

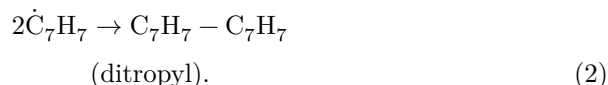
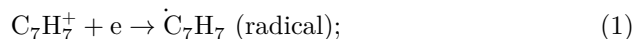
Figure 1: Fig. 1

Abstract**Full Text****PHYSICAL CHEMISTRY****S. I. ZHDANOV and Academician A. N. FRUMKIN****POLAROGRAPHY OF THE TROPYLIUM ION**

The polarogram of the tropylium ion ($C_7H_7^+$) against a LiCl background contains three waves (Figs. 1, 3), of which the third, with $\varphi_{1/2} \approx -1.5$ V (N.C.E.), corresponds to the discharge of H^+ ions arising from hydrolysis of the tropylium salt ⁽¹⁾. In the present communication the nature of the remaining waves is considered. Tropylium perchlorate was used as the starting material in the work.

Fig. 1. Polarization and electrocapillary curves of the tropylium ion. Composition of solutions: LiCl = 0.1 M; $[C_7H_7ClO_4]$: 1—0, 2— $2 \cdot 10^{-4}$, 3— $5 \cdot 10^{-3}$ M; [gelatin]: 1—3—0, 4— $1.48 \cdot 10^{-3}$, 5— $1 \cdot 10^{-3}\%$. Curve 6 was measured in 0.1 M $HClO_4$ solution, curve 7 in 0.1 M $HClO_4 + 0.01$ M $C_7H_7ClO_4$ solution; $t = 25^\circ$. Curve 5 is located below curve 4 because of dilution of the tropylium solution with gelatin solution.

At $[C_7H_7^+] < 3 \cdot 10^{-4}$ M, the polarogram contains only the first wave (Figs. 1, 2) with $\varphi_{1/2} \approx -0.30$ V, whose limiting current is proportional to \sqrt{h} (h is the height of the mercury column above the drop), indicating its diffusion nature. The slope of this wave is ~ 80 mV. According to microcoulometric data, 1 faraday of electricity is consumed per 1 mole of $C_7H_7^+$ during reduction. In the studied interval (10^{-4} — $1M$), $\varphi_{1/2}$ is independent of $[H^+]$. Thus, the most probable mechanism for the reduction of $C_7H_7^+$ is the following:



This conclusion is confirmed by the data of Doering and Krauch ⁽²⁾, who prepared ditropyl by reduction of a tropylium salt with zinc dust.

Fig. 2. Effect of KJ on the polarization curves of tropylium. Composition of solutions: 0.1 M LiCl + 10^{-3} M C₇H₇ClO₄ + KJ. [KJ]: 1—0, 2— $5 \cdot 10^{-5}$, 3— $5 \cdot 10^{-4}$ M. 4—0.1 M KJ + 10^{-3} M C₇H₇ClO₄ + $5 \cdot 10^{-3}$ % gelatin; $t = 25^\circ$

Figure 2: Fig. 2. Effect of KJ on the polarization curves of tropylium. Composition of solutions: 0.1 M LiCl + 10^{-3} M C₇H₇ClO₄ + KJ. [KJ]: 1—0, 2— $5 \cdot 10^{-5}$, 3— $5 \cdot 10^{-4}$ M. 4—0.1 M KJ + 10^{-3} M C₇H₇ClO₄ + $5 \cdot 10^{-3}$ % gelatin; $t = 25^\circ$

Fig. 3. Effect of β -naphthol on the polarization curve of tropylium.

Composition of solutions: 1—0.1 M KCl + 10^{-3} M C₇H₇ClO₄ ($t = 25^\circ$), 2—0.1 M KCl + 10^{-3} M C₇H₇ClO₄ + saturated β -naphthol ($t = 25^\circ$), 3—0.1 M KCl + 10^{-3} M C₇H₇ClO₄ + saturated β -naphthol ($t = 50^\circ$)

Figure 3: Fig. 3. Effect of β -naphthol on the polarization curve of tropylium. Composition of solutions: 1—0.1 M KCl + 10^{-3} M C₇H₇ClO₄ ($t = 25^\circ$), 2—0.1 M KCl + 10^{-3} M C₇H₇ClO₄ + saturated β -naphthol ($t = 25^\circ$), 3—0.1 M KCl + 10^{-3} M C₇H₇ClO₄ + saturated β -naphthol ($t = 50^\circ$)

From comparison of the polarization and electrocapillary* curves of tropylium (Fig. 1), it follows that the C₇H₇⁺ ions are reduced in the adsorbed state. In this connection it may be imagined that the adsorbed radical \dot{C}_7H_7 is bound to the metal surface by means of an electron. With such an interpretation, the discharge of the tropylium ion proves analogous to the dis-

* The electrocapillary curves were measured by **M. A. Gerovich** and N. S. Polyanovskaya at the Department of Electrochemistry of Moscow University.

a series of metal cations, which attach themselves to the metal lattice, replacing the water molecules of the hydrate shell by the electrons of the metal.

The assumption according to which, in the adsorbed tropylium radical, the ionic structure is preserved to some extent makes it possible to explain the relative stability of this adsorbed radical, which should contribute to an increase in its stationary surface concentration during the electrode process and, consequently, to the dimerization reaction. As is known, in the case of halogen derivatives reduction usually proceeds with the addition of two electrons and leads to replacement of the halogen by hydrogen without doubling the number of carbon atoms in the molecule⁽³⁾.

Fig. 2. Effect of KJ on the polarization curves of tropylium. Composition of solutions: 0.1 M LiCl + 10^{-3} M C₇H₇ClO₄ + KJ. [KJ]: 1—0, 2— $5 \cdot 10^{-5}$, 3— $5 \cdot 10^{-4}$ M. 4—0.1 M KJ + 10^{-3} M C₇H₇ClO₄ + $5 \cdot 10^{-3}$ % gelatin; $t = 25^\circ$

Fig. 3. Effect of β -naphthol on the polarization curve of tropylium. Composition of solutions: 1—0.1 M KCl + 10^{-3} M C₇H₇ClO₄ ($t = 25^\circ$),

- 2—0.1M KCl + $10^{-3}M$ C₇H₇ClO₄ + saturated β-naphthol ($t = 25^\circ$),
 3—0.1M KCl + $10^{-3}M$ C₇H₇ClO₄ + saturated β-naphthol ($t = 50^\circ$)

At $[C_7H_7^+] \sim 3 \cdot 10^{-4}M$ the growth of the first wave ceases. A further increase in $[C_7H_7^+]$ leads to the appearance of a second wave with $\varphi_{1/2} \sim -0.7$ V (Figs. 1, 3). Under these conditions i_{pr} of the first wave becomes proportional to h , which indicates the adsorption nature of the wave. The sum i_{pr} of the two waves is proportional to $\sqrt{h^*}$ and $[C_7H_7^+]$, i.e., it is determined by diffusion of C₇H₇⁺. Microcoulometric measurements showed that at the potentials of the second wave the process remains one-electron.

After the well-known work of Brdička (4), in which the theory of adsorption waves for reversible systems was developed using methylene blue as an example, a large number of organic and inorganic compounds were found that also exhibit adsorption waves. In most cases, sometimes without proof of the reversibility of the process, the appearance of an adsorption prewave is associated, as in Brdička's theory, with an energy gain upon adsorption of the reduction product.

The adsorption wave of tropylium has properties that substantially distinguish it from the Brdička wave:

1. According to Brdička's theory, from i_{pr} of the adsorption wave one can calculate the maximum number of molecules adsorbed per unit surface of the electrode, and the area occupied by one molecule. The same calculation, carried out for our case, leads to too small a value

* As a result of this, the height of one second wave decreases with increasing h , which was taken in (1) as an indication of the kinetic nature of the wave.

—5.6 Å² per C₇H₇ radical. Lower values have also been obtained by other authors (5,6).

2. Brdička waves disappear with increasing temperature as a result of a decrease in adsorbability (4,7). The adsorption wave of tropylium increases with increasing temperature; moreover, the temperature coefficient i_{pr} in the range 25–95° is approximately 1.5% per degree.
3. When surface-active substances that are adsorbed on mercury more strongly than the reduction product are added, the Brdička wave disappears (4,8,9). Surface-active substances exert the opposite effect on the adsorption wave of tropylium. The addition of surface-active anions leads to an increase in i_{pr} of the adsorption wave, over a limited or even over the entire range of potentials of the adsorption wave, up to the value i_{pr} of the second wave (Fig. 2). The activity of anions in this respect increases in the series Br[−], CNS[−], J[−].

Experience shows that neutral molecules of organic substances act similarly, for example, β-naphthol (Fig. 3), camphor, hydroquinone, paratoluidine, and

Fig. 4. Polarization curves of tropylium at various concentrations.
 Composition of solutions: 1 $-0.1 \text{ M LiCl} + 10^{-3} \text{ M C}_7\text{H}_7\text{ClO}_4$, 2 $-0.35 \text{ M HCl} + 0.011 \text{ M C}_7\text{H}_7\text{ClO}_4$, 3 $-1 \text{ M HCl} + 0.05 \text{ M C}_7\text{H}_7\text{ClO}_4$, 4 $-1 \text{ M HCl} + 0.1 \text{ M C}_7\text{H}_7\text{ClO}_4$

Figure 4: Fig. 4. Polarization curves of tropylium at various concentrations.
 Composition of solutions: 1 $-0.1 \text{ M LiCl} + 10^{-3} \text{ M C}_7\text{H}_7\text{ClO}_4$, 2 $-0.35 \text{ M HCl} + 0.011 \text{ M C}_7\text{H}_7\text{ClO}_4$, 3 $-1 \text{ M HCl} + 0.05 \text{ M C}_7\text{H}_7\text{ClO}_4$, 4 $-1 \text{ M HCl} + 0.1 \text{ M C}_7\text{H}_7\text{ClO}_4$

gelatin (Fig. 1), and even cations, for example, the tropylium ions themselves at sufficiently high concentration (Fig. 4). Similar effects have also been observed by other investigators (¹⁰⁻¹³).

Fig. 4. Polarization curves of tropylium at various concentrations. Composition of solutions:

- 1 $-0.1 \text{ M LiCl} + 10^{-3} \text{ M C}_7\text{H}_7\text{ClO}_4$,
- 2 $-0.35 \text{ M HCl} + 0.011 \text{ M C}_7\text{H}_7\text{ClO}_4$,
- 3 $-1 \text{ M HCl} + 0.05 \text{ M C}_7\text{H}_7\text{ClO}_4$,
- 4 $-1 \text{ M HCl} + 0.1 \text{ M C}_7\text{H}_7\text{ClO}_4$.

Thus, the nature of the adsorption wave of tropylium differs from that of the Brdička waves. It is evident that the appearance of the adsorption wave of tropylium is a consequence of the retardation of the electrode process by an adsorption film of ditropylium*. The height of the adsorption wave is determined by the number of C_7H_7^+ ions whose reduction is necessary in order to cover the electrode surface with a continuous film of ditropylium, increased by the number of C_7H_7^+ ions whose reduction product is desorbed from the surface. Desorption is evidently accelerated with temperature, which accounts for the presence of a positive temperature coefficient of i_{pr} .

It is interesting that in the irreversible reduction of halogen derivatives of cyclohexane, as shown by Kemula and Ciecak (¹⁵), adsorption of the depolarizer leads to the appearance of an adsorption prewave, i.e., to facilitation of the process, and not to retardation, as follows from Brdička's theory for reversible processes.

The strength of adsorption of ditropylium, which, according to the ideas of M. A. Gerovich (¹⁶), occurs through interaction of the π -electrons with the metal, weakens with increasing negative potential; this leads to removal of the retardation and to the appearance of the second wave (Fig. 1).

Surface-active substances adsorbed more strongly than ditropylium hinder the formation of an adsorption layer of ditropylium, but themselves

* A similar interpretation of the causes of the appearance of an adsorption prewave in the irreversible reduction of sodium vanadate was recently given by Schmidt and Reilley (¹⁴).

in the cases studied by us they do not exert such a substantial influence on the kinetics of the electrode process. Experience shows that complete elimination of inhibition by additions of surface-active substances is not always achieved. In such cases, on the first tropylium wave a current minimum is observed (Fig. 2, 2 and 3; Fig. 3 and 4).

In the absence of surface-active substances, on the second tropylium wave a polarographic maximum of complex shape develops (Fig. 1, 3), readily suppressed by gelatin (curves 4 and 5). Near the desorption potential of ditropylium the current of the maximum increases and then drops sharply. This drop in current was initially incorrectly interpreted⁽¹⁾ as termination of process (1) upon desorption. Further investigation is necessary.

In the presence of J^- ions and gelatin, which was added to suppress the maximum, it was possible to determine the shape of the tropylium wave not distorted by adsorption of ditropylium. Under these conditions the tropylium wave is not symmetrical: its upper part is less steep than its lower part. Such a wave shape corresponds to the concepts of reversibility of the electrode stage (1) with subsequent rapid dimerization of the reduction product (2)*⁽¹⁷⁾.

The product of complete hydrolysis of the tropylium salt—tropylium oxide⁽²⁾—exhibits one one-electron irreversible (slope 87 mV) reduction wave with $\varphi_{1/2} = -2.09$ V.

The authors take this opportunity to express their gratitude to M. E. Vol' pin for providing the preparation of tropylium perchlorate.

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CITED LITERATURE

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* The solution of the problem for this case was carried through to completion by V. S. Krylov and B. M. Grafov. For the lower and upper portions of the wave,

two different wave equations were obtained which describe the experimental curve well.

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

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