Polarographic and Coulometric Studies of Tropolone

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Polarographic behavior of tropolone and its derivatives has been studied by several authors[1-5]. James and Speakman[2] studied the polarographic behavior of tropolone, but they used a supporting electrolyte which contained borate ions. It has been confirmed that borate ions form complexes with tropolone. Neish and Müller[3] studied the polarographic behavior of β-methyltropolone and the related compounds and discussed the reduction mechanism, but they did not include tropolone itself in their study. Moreover, no coulometric analysis has been made as far as tropolone and the related compounds are concerned. The mechanisms of the electrode processes of tropolone so far proposed were analogized from those of benzaldehyde.

It seems worth-while, this being the case, to reinvestigate the polarographic behavior of tropolone in buffer solutions containing no borate ion and to determine the number of electron involved in the reduction from the coulometric analysis.

Experimental

Materials.—Tropolone was purified by recrystallization from mixed solvent of petroleum ether and benzene and by successive sublimation. A white needle-like crystalline compound of a melting point of 51°C (uncorrected) was obtained. The buffer solutions used in this study are listed in Table I. All electrolytic solutions contained

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1) F. Šantavý, *Collection Czechoslov. Chem. Communs.*, **14**, 145 (1949).

2) J. C. James and J. C. Speakman, *Trans. Faraday Soc.*, **48**, 474 (1952).

3) W. J. P. Neish and O. H. Müller, *Rec. trav. chim.*, **72**, 301 (1953).

4) T. Murayama, Presented at the 7th Annual Meetings of Chem. Soc. Japan in Tokyo (1954).

5) F. Šantavý, B. Jámbor, A. Němečkova, J. Mollin and J. Bartek, *Collection Czechoslov. Chem. Communs.*, **22**, 1655 (1957).

TABLE I

BUFFER SOLUTIONS USED

pH	Buffer solutions
2.2~ 8.0	Citric acid—disodium phosphate
8.9~11.4	Sodium carbonate —sodium bicarbonate
11.0~12.0	Sodium hydroxide —disodium phosphate
13.0	0.1 M Potassium hydroxide

0.1 M of potassium nitrate as an indifferent electrolyte and also contained 0.01% of gelatin as a maximum suppressor. Commercial guaranteed reagents were used for the buffer and supporting electrolyte without further purification.

pH measurements.—The pH of the solution was measured before and after the measurements with a Hitachi pH meter Model EHP-1 with a glass electrode.

Polarography.—Current-voltage curves were recorded with a Shimadzu photo-recording polarograph Model SH-UI and with a Yanagimoto pen-recording Galvarecorder Model 2 with an automatically scanning applying potentiometer attached.

The dropping mercury electrode used had an m value of 0.893 mg./sec. and a drop time t of 3.94 sec., being measured in 0.1 M potassium chloride solution at 55 cm. of mercury height at 25°C with open circuit. An H-type cell with a saturated calomel electrode was used. Pure nitrogen gas was bubbled through the solution for about 30 minutes to remove oxygen dissolved in the solution. All measurements were carried out in a thermostat of 25.0±0.1°C.

Coulometry.—For the coulometric measurements[6], the solutions whose constituents were the same as those subjected to the polarographic measurement were employed. The potentials of the working electrode were controlled against a saturated calomel electrode during the electrolysis with a Yanagimoto automatic potentiostat. The electrolytic current was recorded with a Yanagimoto pen-recording Galvarecorder Model 2 connected to the circuit in series. The potentials of the working electrode were adjusted to be −1.15 volts vs. S.C.E. at pH 3.0, −1.35 volts at pH 5.35 and −1.55 volts at pH 8.0.

The electrolysis cell was of a beaker type, the diameter being 4.8 cm. and the height, 5.5 cm., which is shown in Fig. 1b. A mercury pool was used for the working electrode and a spiral platinum wire whose effective area was approximately 1 cm² was used for the auxiliary anode. The latter was connected to the electrolytic solution through a Hickling-type salt bridge of potassium nitrate. The dropping mercury electrode was also placed in the electrolysis cell, which made it possible to measure the current-voltage curve at any moment during the controlled potential electrolysis. The electrical circuit of the equipment was designed for the purpose, as shown in Fig. 1a. The electrolytic solution was stirred by bubbling pure nitrogen gas and by means of a magnetic stirrer.

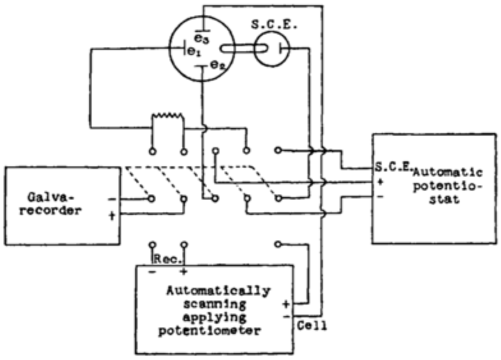

Fig. 1a. Schematical diagram of the circuit for the electrolysis: e_1, working electrode (Hg pool); e_2, auxiliary anode (Pt wire); e_3, dropping mercury electrode.

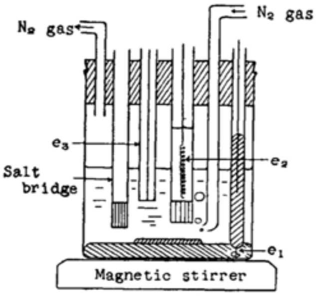

Fig. 1b. Electrolysis cell: e_1, e_2 and e_3, the same as in Fig. 1a.

The concentration of tropolone was varied in the range from 2×10^{-4} M to 1×10^{-3} M. The temperature of the solution was kept at 20°C. The maximum current in the coulometry was 5 milliamperes.

Results

Current-voltage curves.—The current-voltage curves obtained with the solution containing 1×10^{-3} M of tropolone at various pH's are shown in Fig. 2. One wave was observed in the media of pH lower than 4.0, two waves in the pH range from 5 to 7 and one wave in the pH range from 8 to 10. Only an indistinct wave was observed in the pH region higher than 11.

The half-wave potentials of all waves except the second wave at the intermediate pH's were observed to shift to negative potential with the increase of pH. The wave height except that of the second wave decreased with the increase of pH. The half-wave potential and the wave height of the second wave were observed

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[6] J. J. Lingane, "Electroanalytical Chemistry", Interscience Publishers, Inc., New York (1953), p. 347.

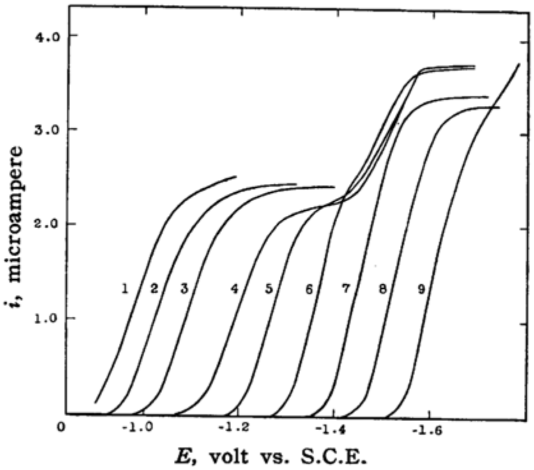


Fig. 2. Current-voltage curves of 1×10^{-3} M tropolone obtained with dropping mercury electrode: 1, pH 2.2; 2, pH 3.0; 3, pH 4.0; 4, pH 5.0; 5, pH 6.0; 6, pH 7.0; 7, pH 8.0; 8, pH 9.0; 9, pH 10.0.

to be almost independent of pH. The variation of half-wave potential $E_{1/2}$ of the first wave with pH was given by

$$E_{1/2}=-0.837-0.07\,\text{pH}$$

volt vs. S.C.E. at 25°C.

As seen in Fig. 3, a linear relation was obtained between the concentration and the wave height of the first wave in the pH region of 3.0 to 6.0.

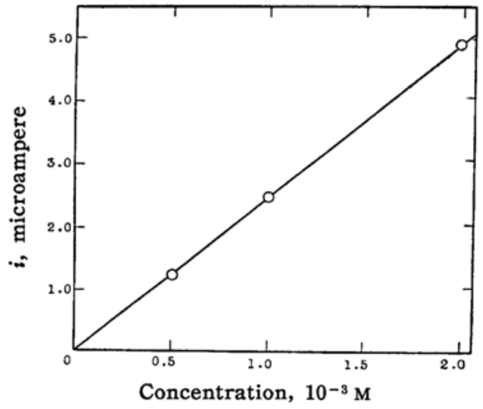


Fig. 3. Relation between the concentration of tropolone and the limiting current obtained at pH 4.0 at 25°C.

Provided that the limiting current is controlled by diffusion, it must be proportional to the square root of the effective height of mercury. The relation was examined with the first and the second waves at three different mercury heights, i. e., 55 cm., 45 cm. and 40 cm. in the pH range of 3.0 to 7.0. The results obtained are listed in Table II, which indicate that the ratio, $i_l/h_{eff.}^{1/2}$, is nearly constant and that the limiting current is of diffusion control.

TABLE II

RELATION BETWEEN THE LIMITING CURRENT AND THE MERCURY HEIGHT

pH	Mercury height*	$i_l/h_{eff.}^{1/2}$ μ amp. cm$^{-1/2}$ 1st wave	2nd wave
	I	0.346	
3.0	II	0.344	
	III	0.347	
	I	0.337	
4.0	II	0.330	
	III	0.332	
	I	0.302	0.213
5.0	II	0.320	0.227
	III	0.341	0.206
	I	0.330	0.209
6.0	II	0.335	0.214
	III	0.341	0.202
	I	0.519	
7.0	II	0.478	
	III	0.456	

* I, h=55 cm.; II, h=45 cm.; III, h=40 cm. The concentration of tropolone was 1×10^{-3} M.

Coulometric measurements. — Before and after the electrolysis, the polarograms were recorded with the sample solution, so that the initial and the final concentration of tropolone could be estimated from the wave heights. However, the polarogram which was recorded when a half quantity of tropolone was reduced showed two new waves appearing at the potentials more positive than that of the reduction wave of tropolone. A typical example of the polarograms is given in Fig. 4. The first wave is anodic and the second is cathodic, the latter appearing at somewhat more positive potentials than the reduction wave of tropolone. The third wave is consipered to be the wave of tropolone because the potentials are identical with those of tropolone.

The height of the first wave was observed to decrease with the lapse of time; it decreased to nearly a half of the original height after some twenty minutes. The height of the second wave, on the other hand, increased with the lapse of time. This was observed with all solutions whose pH's were between 3 and 8. The half-wave potentials of those new waves were found to depend on pH of the

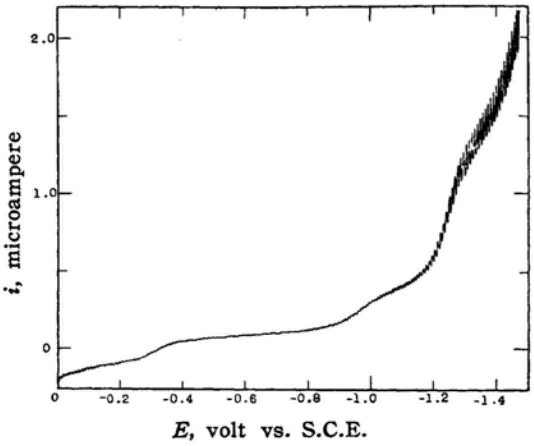


Fig. 4. Current-voltage curve recorded at pH 5.35, at 20°C, with the solution in which a half of tropolone was reduced by controlled potential electrolysis. The initial concentration of tropolone was 3.53×10^{-4} M.

solution and both waves shifted to more negative potentials by 40 to 80 mV. with the increase of one unit of pH.

The quantity of electricity required in the controlled potential electrolysis was determined by integrating graphically the recorded current-time curve. The quantity due to the residual current which was measured separately with the same procedure was subtracted. The values thus obtained naturally included the electricity that was consumed in the reduction of the substance which had been produced as a result of the electro-reduction of tropolone followed by the chemical conversion, because the substance is easily reduced at the potential where tropolone is reduced. Moreover, the concentration of tropolone after a certain period of the electrolysis could not be determined accurately from the polarogram, because of the occurrence of the ill-defined reduction wave whose potentials are close to those of the reduction wave of tropolone. On account of those two unavoidable causes of error, the electricity required for the reduction of the unit concentration of tropolone could not be determined accurately in the usual way.

From the careful observation of the current-voltage curves obtained after the controlled potential electrolysis, it was found that the rate of formation of the new reducible substance was not extremely great. This indicates that a shorter period of electrolysis is more favorable for determining the quantity of electricity required for the reduction of tropolone itself. In an extreme case, at a zero time, only tropolone must be reduced. In the present investigation, therefore, the following procedure was employed. The controlled potential electrolyses were carried out in varied electrolysis periods with the solutions in which the initial concentration of tropolone and the pH were the same. The quantity of electricity was obtained from each current-time curve recorded. With the same solution as was subjected to the electrolysis the limiting current was measured, before and immediately after the electrolysis, with the dropping mercury electrode at potential where tropolone gives the diffusion current. The apparent amount of tropolone which was reduced in the given period was calculated from the difference of the limiting current by assuming the limiting current obtained immediately after the electrolysis to be caused by tropolone only. The apparent number of electrons required in the reduction was calculated by dividing the quantity of electricity with the product of the Faraday constant and the apparent molar amount of tropolone reduced in the period. The apparent numbers of electrons thus obtained for various electrolysis periods were found to have the tendency to decrease with the decrease of the electrolysis period. Thus, the true value of n could be obtained by plotting the apparent value of n against the electrolysis period and by extrapolating the curve to a zero time. An example of such a plotting is given in Fig. 5. The values

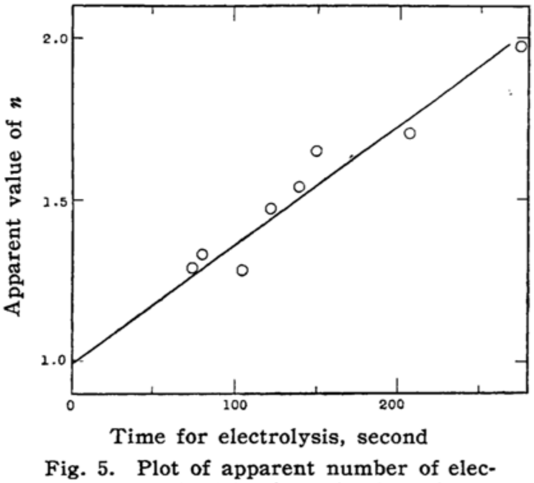


Fig. 5. Plot of apparent number of electrons involved in the reduction of tropolone against electrolysis period, measured at pH 5.35 at 20°C. The initial concentration of tropolone was 3.53×10^{-4} M.

of *n* obtained are given in the third column of Table III. Using the revised Ilkovič equation⁷⁾, the diffusion coefficients of tropolone were calculated from the limiting currents obtained at various pH's, which are given in the fourth column of Table III.

TABLE III
NUMBER OF ELECTRONS REQUIRED IN THE REDUCTION OF TROPOLONE AND DIFFUSION COEFFICIENT AT 25°C

pH	Wave used in the calculation	*n*	D, cm²/sec.
3.0	1st wave	1.0	9.0×10^{-6}
5.0	〃	1.0	7.6×10^{-6}
8.0		2.0	5.0×10^{-6}

Discussion

The diffusion coefficient of organic compounds can be evaluated with the aid of Oeholm's law⁸⁾,

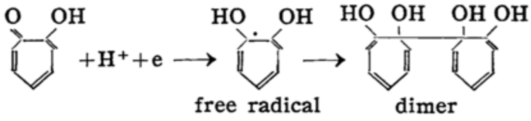
$$M^{1/2}D \fallingdotseq 7 \quad (\text{at } 20^\circ\text{C})$$

where M is molecular weight and D, the diffusion coefficient expressed in cm²/day. The value calculated for tropolone is 0.63 cm²/day, i. e., 7.4×10^{-6} cm²/sec. The diffusion coefficient of benzoic acid which is the isomer of tropolone was observed to be 9.2×10^{-6} cm²/sec. at 25°C⁹⁾ and is calculated to be 8.7×10^{-6} cm²/sec. at 25°C from the conductance data¹⁰,¹¹⁾. Comparing with those referred values, the diffusion coefficients of tropolone obtained in this study (Table III) seem to be reasonable.

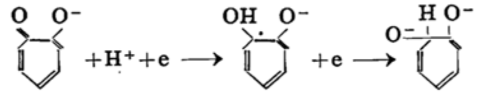
Tropolone molecules dissociate to form anions in an alkaline medium, the dissociation constant being 1.2×10^{-7} at 25°C¹²⁾. Since the degree of interaction between the anion and the solvent molecules would be greater than that between undissociated tropolone and solvent molecules, the diffusion coefficient of the former is expected to be smaller than that of the latter, and, therefore, a smaller coefficient is expected in an alkaline medium. The experimental results given in Table III coincide with the above expectation.

As already indicated, one anodic wave and two cathodic waves were observed on the polarogram which was recorded with the solution subjected to the controlled potential electrolysis. The first wave which was anodic decreased with the lapse of time and the second which was cathodic increased. This showed that an oxidizable substance which is produced upon the electro-reduction of tropolone to give the anodic wave is unstable and converted gradually into a reducible substance which gives a cathodic wave at potentials more positive than tropolone.

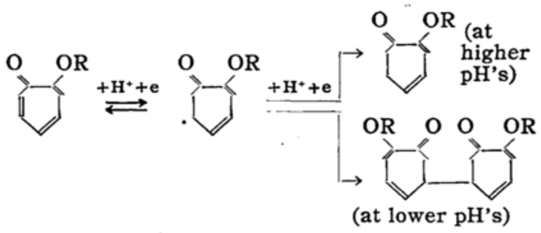
The mechanism of the electro-reduction of tropolones has been inferred from that of benzaldehyde²,³⁾. Neish and Müller³⁾ gave the following to the first wave in the acid region:



The double wave in the intermediate pH region was assumed to appear according to the mechanism³⁾,



Recently Šantavý et al.⁵⁾ proposed the following processes for the reduction of tropolone and its ethers:



One-electron reduction followed by the dimerization was assumed at lower pH's, while two-electron reduction was assumed at higher pH's. In both cases the reduction of tropone nucleus was assumed.

In this study, the number of electrons involved in the electro-reduction of tropolone was determined from the coulometric measurement at constant potential. One-electron reduction at lower pH's and two-electron reduction at higher pH's were confirmed. This supports partly the reduction mechanism of tropolone previously proposed. However, the observation of current-voltage curves which were obtained with the solution preliminarily subjected to the controlled potential electrolysis strongly suggests that the chemical

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7) M. von Stackelberg, *Z. Elektrochem.*, **57**, 338 (1953); etc.

8) L. W. Oeholm, *Z. physik. Chem.*, **70**, 378 (1910).

9) H. Freundlich and D. Krüger. *Biochem. Z.*, **205**, 186 (1929).

10) F. G. Brockman and M. Kilpatrick, *J. Am. Chem. Soc.*, **56**, 1483 (1934).

11) B. Saxton and H. F. Meiner, ibid., **56**, 1918 (1934).

12) N. Yui, *Sci. Repts. Tohoku Univ. First Ser.*, **40**, 102 (1956).

processes following on the electro-reduction are not so simple as has been proposed. The half-life period of the substance which formed upon the controlled potential electrolysis and gave the anodic wave would not indicate this substance to be the free radical described above, but a secondary substance produced therefrom. It is also unlikely that the dimer which Šantavý et al. assumed in their mechanism corresponds to the substance which gives the anodic wave, because the dimer seems not to be easily oxidizable. However, the difficulty in preparation of the substance because of chemical conversion, at present, seems to make it impossible to identify the substance. It would be desirable to carry out more elaborate studies for the precise explanation of the reduction mechnism.

Summary

The current-voltage curves of tropolone were recorded at the dropping mercury electrode in buffer solutions of various pH's containing no borate. One reduction wave was observed in the pH region of 2.2 to 4.0, two waves with nearly equal heights, in the pH region of 5 to 6 and one wave, in the solution of pH higher than 8. All waves except the second in the intermediate pH region were found to shift to negative potentials with the increase of pH of the solution by approximately 70 mV./pH. The number of electrons involved in the reduction was determined by the controlled potential coulometric method. One-electron reduction was confirmed for the first wave at lower pH's, two-electron reduction for the two-step waves at the intermediate pH region and two-electron reduction for the wave at higher pH's. The current-voltage curves which were recorded with the solution preliminarily subjected to the controlled potential electrolysis gave two new waves; one is anodic and the other, cathodic. The former decreased with time and the latter increased. This indicates that the reduction product of tropolone is unstable and changed gradually to the substance which gives the reduction wave. The diffusion coefficients of tropolone were calculated from the limiting current using the revised Ilkovič equation.

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