

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

## Electrooxidation of Tropilidene to Tropylium Ion

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An electrochemical study was made of the electrooxidation of tropilidene to tropylium ion on a platinum electrode using acetonitrile as solvent. The nature of the electrode reaction was established on the basis of coulometric, titrimetric and spectrophotometric data. Ditropyl also is oxidized to tropylium ion in the same potential region. A reaction mechanism, which is consistent with experimental data, is presented for the tropilidene oxidation. This non-aqueous electrooxidation has succeeded where conventional chemical oxidations have failed.

Recent characterization of the tropylium ion (cycloheptatrienyl ion)<sup>1</sup> has verified the prediction of relative stability made for those conjugated unsaturated cycles having six  $\pi$ -electrons in the ring. (The other two members of the triad are benzene and cyclopentadienyl ion.) It was of interest to consider the formation of tropylium ion by electrooxidation of the "parent" hydrocarbon tropilidene (cycloheptatriene). Acetonitrile was used as the electrolysis medium because it is a good solvent for all of the species involved and because it has a large range available for study of anodic electrode reactions. Acetonitrile is far superior to aqueous solutions on both of these counts.

## Experimental Part

**Chemicals.**—Tropilidene was kindly furnished by Shell Development Company, Emeryville, California. The material was labeled 91.4% tropilidene with toluene as the major impurity. Our analysis by vapor phase chromatography, the same analytical method used by Shell, gave an estimate of 92.4% tropilidene. A portion of this material was fractionated through a 40 cm. column of glass helices. Since the resulting heart cut, boiling at 114–115° at 760 mm., discolored slowly the compound was redistilled immediately before use. Analysis by vapor phase chromatography gave a purity of at least 99%. This purified material was used in the voltammetric and chronopotentiometric measurements.

Tropylium perchlorate,  $C_7H_7^+ClO_4^-$ , was prepared by the method of Dauben, *et al.*<sup>1d</sup> Dihydroheptafulvalene (bitropyl) was prepared by zinc reduction of tropylium perchlorate. The melting point, 60–61°, agreed with the literature value.<sup>1e</sup> Samples of 1,4-cyclohexadiene (K and K Laboratories) and bicyclo[2.2.1]hepta-2,5-diene (Shell Chemical) were used without further purification. Purification of acetonitrile has been described previously.<sup>2</sup>

**Apparatus.**—Electrochemical measurements were made using the same electrodes and apparatus as previously described.<sup>2</sup> Solutions investigated by chronopotentiometry and voltammetry were thermostatted at 25.0°. Controlled potential electrolyses were done at ambient temperatures. As before, all potential measurements were made using an aqueous saturated calomel reference electrode, but the data are reported on the silver, silver nitrate (acetonitrile) scale.<sup>3</sup> All solutions were 0.1 *M* in lithium perchlorate.

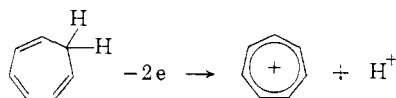
## Results and Discussion

Acetonitrile solutions of tropilidene show a well-defined oxidation wave at a rotating platinum electrode. The half-wave potential is  $+1.13 \pm 0.03$  v. *vs.* Ag, AgNO<sub>3</sub>. The limiting current constant,  $i_l/C$ , where  $i_l$  is the limiting current and  $C$  is the concentration of tropilidene, is  $11.3 \mu\text{a. mM}^{-1}$ . Using the same electrode and stirring conditions, hydroquinone is oxidized, presumably in a two-electron

process, with a current constant of  $10.9 \mu\text{a. mM}^{-1}$ ; iodide ion undergoes a one-electron oxidation with a constant of  $4.81 \mu\text{a. mM}^{-1}$ . These measurements suggest that tropilidene undergoes a two-electron oxidation. There was no change in half-wave potential when 2.89 and 0.23 *mM* tropilidene solutions were made 0.065 and 0.040 *M* in perchloric acid, respectively.<sup>4</sup>

Chronopotentiometric measurements on tropilidene solutions over the concentration range 3.49 to 0.578 *mM* gave a transition time constant,  $i\tau_1^{1/2}/C$ , (where  $\tau_1$  is the transition time and  $i$  is the electrolysis current) of  $0.380 \pm 0.005$  amp. sec.<sup>1/2</sup> *M*<sup>-1</sup>. The value of  $E_{\tau/4}$  was  $+1.06 \pm 0.02$  v. *vs.* Ag, AgNO<sub>3</sub>.<sup>5</sup> Using the same platinum electrode the transition time constant for the hydroquinone oxidation was  $0.340$  amp. sec.<sup>1/2</sup> *M*<sup>-1</sup> and for triiodide ion,  $0.173$  amp. sec.<sup>1/2</sup> *M*<sup>-1</sup>. Since the transition time constant is directly proportional to the number of electrons involved in the electrode reaction, the preceding data also indicate that tropilidene undergoes a two-electron oxidation.

Final conclusive evidence that the electrode reaction is indeed



was obtained by carrying out controlled potential electrolyses with a macro platinum electrode and examining the electrolyzed solution. Table I

TABLE I  
CONTROLLED POTENTIAL ELECTROLYSIS OF TROPILIDENE<sup>a</sup>

Concn., <i>mM</i>	$\frac{n}{\text{faradays/mole}}$	(H <sup>+</sup> ) <sub>final</sub> , <i>mM</i>	$a_m^{274} \text{ m}\mu$ $\times 10^{-3}$	$a_m^{246} \text{ m}\mu$ $\times 10^{-2}$	$a_m^{217} \text{ m}\mu$ $\times 10^{-4}$
7.23	1.98	7.0	4.27	6.4	4.11
2.56	1.90	2.40	4.08	5.5	4.18
1.20	1.90	...	..	..	..
11.96	1.90	10.64	4.0	4.4	4.03
5.98	1.90	5.4	4.14	4.8	4.23

<sup>a</sup> Electrolysis of 20-ml. volumes at +1.5 v. *vs.* Ag, AgNO<sub>3</sub>; "91.4% Shell" tropilidene used throughout except for first entry where the purified material was employed.

summarizes coulometric, titrimetric and spectrophotometric data. The hydrogen ion liberated in the electrode reaction was titrated with diphenylguanidine using crystal violet as indicator.

The absorption spectrum of the electrolyzed solution had the same shape as the spectrum of

(4) Perchloric acid was added in the form of a 0.96 *M* solution in anhydrous glacial acetic acid.

(5) The quantity  $E_{\tau/4}$  has no theoretical significance for an irreversible wave, but it is a convenient potential to tabulate for comparison purposes.

(1) (a) W. E. Doering and L. H. Knox, *THIS JOURNAL*, **76**, 3203 (1954); (b) W. E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956); (c) W. E. Doering and L. H. Knox, *THIS JOURNAL*, **79**, 352 (1957); (d) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. I. Pearson, *ibid.*, **79**, 4557 (1957).

(2) D. H. Geske, *J. Phys. Chem.*, **63**, 1062 (1959).

(3) V. A. Pleskov, *Zhur. Fiz. Khim.*, **22**, 351 (1943).

tropylium perchlorate—maxima at 217 and 274  $m\mu$  and a minimum at 246  $m\mu$ . Data in Table I show the extent of agreement between the electrolyzed solution and known spectral data for tropylium perchlorate,  $a_m^{217\ m\mu} = 4.29 \times 10^4$ ,  $a_m^{274\ m\mu} = 4.42 \times 10^3$ ,  $a_m^{246\ m\mu} = 3.4 \times 10^2$ .

It is seen from data in Table I that where the "91.4% Shell" tropilidene was used the coulometric data were consistently 5% low. This probably is indicative of an impurity in the tropilidene that was not detected by vapor phase chromatographic analysis.

The chronopotentiogram (potential-time curve) in Fig. 1 was obtained by reversing the current at the transition time for tropilidene oxidation.

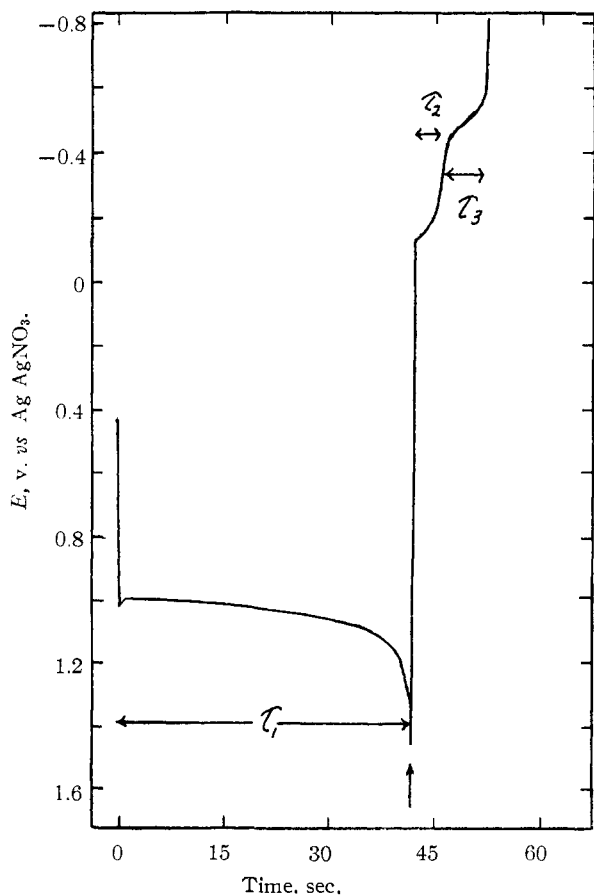
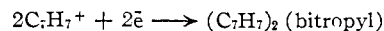


Fig. 1—Potential-time curve for a 2.89  $mM$  tropilidene solution, 0.1  $M$   $LiClO_4$ ; current, 181.4  $\mu A$ ; current reversed at 41.6 sec.; potential in volts vs.  $Ag, AgNO_3$  time in seconds.

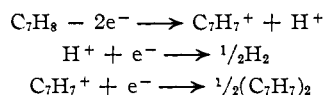
The point of reversal is marked with an arrow on Fig. 1. The two ions produced by the oxidation reaction undergo reduction reactions at potentials which are sufficiently separated that two distinct potential arrests are observed. The first re-reduction reaction ( $\tau_2$ ) corresponds to reduction of hydrogen ion to molecular hydrogen. Independent study of hydrogen ion reduction with the same electrode gave a transition time constant of 0.102 amp. sec.<sup>1/2</sup>  $M^{-1}$  and  $E_{\tau/4} = -0.15$  v. in reasonable agreement with a potential of  $-0.12$  v. observed in Fig. 1. The average value for  $\tau_1/\tau_2$  in the tropilidene study was 7.6 in comparison with a value of 8 predicted by an equation

derived by Berzins and Delahay<sup>6</sup> when the diffusion coefficients of the two species are assumed to be equal.

The electrode reaction corresponding to the second potential arrest ( $\tau_3$ ) on re-reduction is



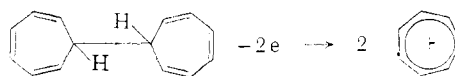
This statement is based on the fact that an independent study of reduction of tropylium ion gave  $E_{\tau/4} = -0.44$  v. and a transition time constant of 0.134 amp. sec.<sup>1/2</sup>  $M^{-1}$ . It is also known<sup>1c</sup> that reduction of tropylium ion by metallic zinc yields ditropyl.<sup>6</sup> Zhdanov and Frumkin<sup>7</sup> also report a one-electron reduction of tropylium ion on a dropping mercury electrode. The experimental value of the ratio  $\tau_3/\tau_2$  from seven experiments was 1.5. The calculated value of the ratio, assuming equal diffusion coefficients, is 2.60.<sup>8</sup> The entire reason for the discrepancy between calculated and experimental quantities is not yet apparent. The reaction scheme



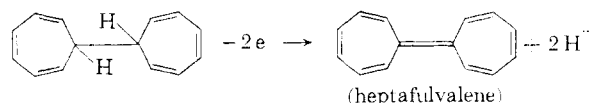
represents the ultimate definition of an over-all irreversible electrode reaction, *i.e.*, the back reaction follows an entirely different path than the forward reaction.

It was natural to extend the investigation to the electrooxidation of bitropyl (dihydrofulvalene). Bitropyl shows an oxidation wave at +1.03 v. vs.  $Ag, AgNO_3$  on a rotating platinum electrode in acetonitrile, the same potential region for electrooxidation of tropilidene. The current constant was 9.0  $\mu A \cdot mM^{-1}$ . A chronopotentiometric study showed a transition time constant of 0.310 amp. sec.<sup>1/2</sup>  $M^{-1}$ , and  $E_{\tau/4}$  varied from +0.95 v. to +1.05 v. When the polarizing current was reversed at the transition potential, a potential arrest was observed at  $-0.45$  v. as would be expected for reduction of tropylium ion. The ratio of the oxidation transition time to the reduction transition time was 2.8. The value calculated on basis of equal diffusion coefficients<sup>8</sup> is 3.

The anodic reaction was clearly established as



by use of controlled potential electrolysis. The apparent number of electrons per mole was 2.02 and the spectrum of the electrolyzed solution corresponded quantitatively to the spectrum of tropylium perchlorate in acetonitrile. Spectrophotometric data indicated that the reaction



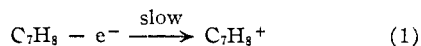
(6) T. Berzins and P. Delahay, *THIS JOURNAL*, **75**, 4205 (1953).

(7) S. I. Zhdanov and A. N. Frumkin, *Doklady Akad. Nauk SSSR*, **122**, 412 (1958). Polarographic studies of the reduction of tropylium ion are also reported by M. E. Volpin, S. I. Zhdanov and D. N. Kursanov, *Doklady Akad. Nauk, SSSR*, **112**, 264 (1957); P. Zuman, J. Chodkowski, H. Potesilova and F. Santavy, *Nature*, **182**, 1535 (1958).

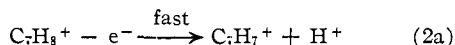
(8) D. H. Geske, unpublished.

did not occur. (Heptafulvalene has an intense peak at 362  $\mu\mu$ .)

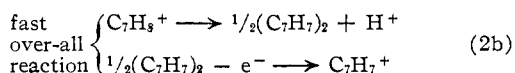
Some comments can be made on the mechanism of the electrode reaction for tropilidene oxidation. The fact that a change in bulk hydrogen ion concentration had no effect on the half-wave potential indicates that a proton is not produced in or before the rate-determining step (if it is assumed that electron transfer is the slow step). Thus the following reaction scheme is plausible.



followed by



or



A plot of  $E$  vs.  $\log [1 - (t/\tau_1)^{1/2}]$  for a typical chronopotentiogram of the oxidation of tropilidene gave a straight line with a slope of 137 mv., corresponding to a value of 0.43 for the term  $(1 - \alpha)n_a$ .<sup>9</sup> If we employ the usual assumption of a transfer coefficient  $\alpha$  of approximately 0.5,  $n_a$ , the number of electrons in the rate-determining step, is approximately one which is consistent with eq. 1. Available experimental data do not distinguish between reactions 2a and 2b. The fact that bitropyl is oxidized in the same potential region as tropilidene means that eq. 2b cannot be excluded.

One does expect reasonable limits to be imposed on electrode reactions. Thus it is perhaps not surprising that bicyclo[2.2.1]hepta-2,5-diene which undergoes pyrolytic isomerization to tropilidene,<sup>10</sup> is electrolytically inert. Another isomer of tropilidene, bicyclo[3.2.0]hepta-2,5-diene,<sup>10d</sup> would require a less acute structural rearrangement for electrooxidation to tropylium ion, but it is also electrolytically inert.

The electrooxidation of tropilidene as described here could be adapted to a preparative scale. How-

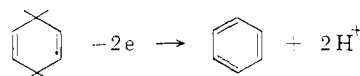
(9) See P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 187.

(10) (a) J. S. Chirtel and W. M. Halper, U. S. Patent 2,754,337 (1956); (b) Shell Chemical Corp., 50 West 50th St., New York 20, N. Y., Technical Information Bulletin, "Laboratory Preparation of Cycloheptatriene from Bicycloheptadiene," June, 1956; (c) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958); (d) this compound was kindly furnished by Dr. V. M. Evans.

ever the hydride exchange reaction<sup>1d</sup> for preparation of tropylium salts is conveniently simple. The analytical implications of the electrode reaction have been alluded to above. The only requirement for analytical purposes is that the impurities be electrolytically inert at the potential used for electrolysis.<sup>11</sup>

The peculiar genius of a non-aqueous electrooxidation is reinforced by the observation that there has been no homogeneous chemical oxidation of tropilidene to tropylium ion by means of the conventional chemical oxidants.<sup>12</sup> Doering and Knox<sup>13</sup> obtained only a small yield of tropolone (cycloheptatriene-2,4,6-ol-2-one-1) when tropilidene was oxidized with permanganate ion in basic ethanol solution at  $-5^\circ$ . Tropylium ion has, however, been obtained by chemical oxidation of cyclooctatetraene<sup>14</sup> and cyclohepta-2,4,6-trienecarboxylic acid.<sup>15</sup>

The successful preparation of tropylium ion by electrooxidation of tropilidene suggested that benzene, another aromatic system, could be obtained by electrooxidation of its "parent" hydrocarbon. A discrete oxidation wave,  $E_{1/2} = +1.6$  v. vs. SCE,  $I_1 = 9.7 \mu\text{a. mM}^{-1}$ , was observed for 1,4-cyclohexadiene. It is likely that the electrode reaction is

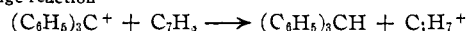


**Acknowledgment.**—The author is grateful to Robert Selim for translation of a Russian paper, to Dr. James Ross for stimulating discussion and to the Milton Fund for partial financial support.

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(11) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957), has shown that toluene, which was the major impurity in the Shell sample, is oxidized at a potential which is significantly more positive than tropilidene. Thus controlled potential coulometric analysis would be feasible in this case.

(12) We consider the triphenylcarbonium ion, as used in the hydride exchange reaction<sup>1d</sup>



to fall outside of the definition of a conventional chemical oxidant such as permanganate ion.

(13) W. E. Doering and L. H. Knox, *THIS JOURNAL*, **73**, 828 (1951).

(14) C. R. Ganellin and R. Pettit, *ibid.*, **79**, 1767 (1957).

(15) M. J. S. Dewar, C. R. Ganellin and R. Pettit, *J. Chem. Soc.*, 55 (1958).