

THE ELECTROREDUCTION OF HEPTAPHENYLTROPYLIUM ION TO THE FREE RADICAL IN ACETONITRILE

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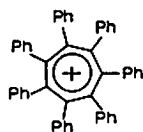
ABSTRACT

The reduction of heptaphenyltropylium ion (HPT⁺) in acetonitrile solutions containing 0.1 M tetra-n-butylammonium perchlorate at a platinum electrode was studied by cyclic voltammetry and controlled potential coulometry. A reversible wave for the production of the free radical at -1.20 V vs. SCE was observed. The radical was stable on the voltammetric time scale (\sim seconds) but decayed slowly. The production of a dimeric species involving coupling via the phenyl groups and reducible at about -1.9 V is proposed.

The electroreduction of tropylium cation (Tr⁺) has been the subject of a number of investigations [1–6]. The reduction occurs in aprotic media such as acetonitrile (ACN) at about -0.2 V vs. SCE in a one-electron step to produce the tropyli radical which rapidly couples to form bitropyli [3–6]. The rate of coupling is so rapid (a dimerization rate constant of 2×10^7 M⁻¹ s⁻¹ has been reported [7]) that no reverse wave for the electrogenerated radical oxidation in the cyclic voltammogram of Tr⁺ has been observed, even at very rapid scan rates. Attempts



Tr⁺



HPT⁺

to demonstrate the intermediacy of this radical in the reduction via spin trapping techniques, which were previously used in the detection of phenyl radical produced by electroreduction of phenyldiazonium cation [8], were also unsuccessful [9]. Battiste and Barton [10,11] have described the preparation and investigated the stability of phenyl-substituted tropylium ions. Their results suggested that addition of phenyl-substituents to the ring increases the stability of the ion. Moreover the rate of dimerization of the radical of the fully substituted ion, heptaphenyltropylium (HPT⁺), should be much slower than that of the unsubstituted Tr⁺ because of steric effects. We report here a brief study of the electrochemistry of the HPT⁺ system and demonstrate the existence of the radical HPT[•] and discuss its mode of coupling.

EXPERIMENTAL

The preparation and purification of heptaphenyltropylium bromide (HPTBr) has been described [10,11]. The supporting electrolyte, tetra-n-butylammonium

perchlorate (TBAP), polarographic grade (Southwestern Analytical Chemicals, Austin, Texas), was dried under vacuum at 100°C for 24 h and stored in a glove box. Acetonitrile (ACN) used as the solvent for all experiments, was purified as previously reported [12]. The electrochemical cell used for cyclic voltammetric and coulometric studies was a standard three compartment cell with a silver wire quasi-reference electrode isolated from the test solution by a fine porosity frit. The potential of this reference was determined following each series of experiments by adding 9,10-anthraquinone and observing the voltammetric behavior of this species, whose reversible potential in ACN is known with respect to an aqueous saturated calomel electrode (SCE). The working electrode was a platinum disk with an area of 0.039 cm². The components and design of a similar cell have been previously described [13].

All the solutions were prepared in a inert atmosphere glove-box (Vacuum Atmospheres Corporation, Hawthorne, Calif.) equipped with a Model MO-40-1 Dri Train. Cyclic voltammetry (c.v.) and coulometric experiments were carried out with a PAR Model 173 potentiostat with a Model 179 digital coulometer equipped with positive feedback for iR compensation and a Model 175 universal programmer (Princeton Applied Research Corporation, Princeton, N.J.). A Houston Model 2000 XY recorder (Houston Instruments, Austin, Texas) was used to record the current-potential curves for scan rates up to 500 mV s⁻¹. For higher scan rates a Nicolet Model 1090A digital oscilloscope (Nicolet Instrument Corporation, Madison, Wisc.) was employed.

RESULTS AND DISCUSSION

Cyclic voltammetry

The c.v. of a solution containing HPTBr and 0.1 M TBAP in ACN showed a reduction wave at -1.2 V vs. SCE with a second smaller wave near background

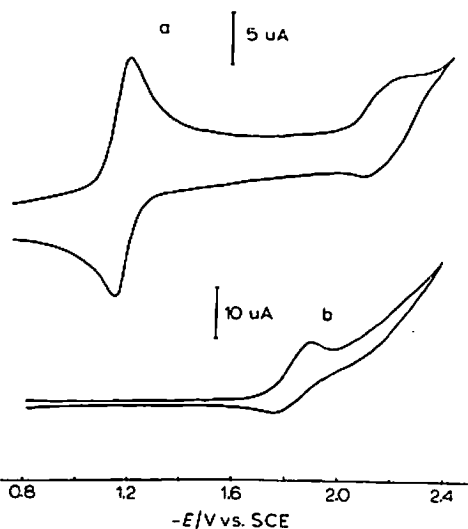


Fig. 1. (a) Cyclic voltammogram of 1.2 mM HPT⁺Br⁻ in 0.1 M TBAP/ACN solution; scan rate, 200 mV s⁻¹; (b) after coulometric reduction at -1.4 V.

TABLE 1

Cyclic voltammetric data for the reduction of heptaphenyltropylium ion ^a

<i>c</i> / mM	<i>v</i> / V s ⁻¹	<i>E</i> _{pc} /V (vs. SCE)	<i>E</i> _{pa} /V (vs. SCE)	ΔE / mV	<i>i</i> _{pc} / μ A	<i>i</i> _{pa} / μ A	<i>i</i> _{pa} / <i>i</i> _{pc}	$(i_{pc}/v^{1/2}c^b)/$ $(\mu A V^{-1/2}$ $s^{1/2} M^{-1})$
0.462	0.050	-1.19	-1.13	60	2.50	2.00	0.80	23
	0.100	-1.19	-1.13	60	3.50	3.01	0.86	
	0.200	-1.20	-1.12	80	5.00	4.45	0.89	
	0.500	-1.21	-1.13	80	6.95	6.00	0.86	
0.768	0.050	-1.18	-1.12	60	4.4	3.56	0.81	22
	0.100	-1.19	-1.12	70	5.7	3.9	0.79	
	0.200	-1.18	-1.10	80	7.0	5.9	0.84	
	0.500	-1.20	-1.12	80	11.5	9.0	0.78	
	1.000	-1.21	-1.15	60	15.0	13.8	0.92	
	2.000	-1.23	-1.14	90	27.0	23.0	0.85	
	5.000	-1.22	-1.14	80	38.0	36.0	0.95	
	10.00	-1.20	-1.12	80	50.0	41.0	0.84	
20.00	-1.24	-1.16	80	78.0	66.3	0.85		
1.15	0.050	-1.18	-1.12	60	6.15	5.10	0.83	23
	0.100	-1.19	-1.13	60	8.50	7.00	0.82	
	0.200	-1.18	-1.12	60	11.0	9.8	0.89	
	0.500	-1.22	-1.13	90	17.5	16.0	0.91	

^a Solution contained HPT⁺Br⁻ and 0.1 M TBAP in ACN; Pt working electrode, area = 0.039 cm², temperature 25°C.

^b These values lead to diffusion coefficient of 4.8×10^{-6} cm² s⁻¹ for HPT⁺ in this medium.

reduction at -2.2 V (Fig. 1a). The cathodic peak potential, *E*_{pc}, was almost independent of the scan rate, *v*. The current function, *i*_{pc}/*v*^{1/2}*c* (where *i*_{pc} is the cathodic peak current and *c* is the concentration of HPT⁺), was essentially constant in the range of concentrations and scan rates studied. On scan reversal following the first reduction wave an anodic peak with a peak current, *i*_{pa}, was observed; the current ratio, *i*_{pa}/*i*_{pc}, was near unity and independent of *v* and *c*. The voltammetric data are summarized in Table 1. The wave at -2.2 V was not investigated further, because its proximity to the reduction limit of the solvent made quantitative measurements difficult.

Coulometry

It was difficult to obtain accurate and reproducible coulometric data because of the low solubility of HPTBr in ACN. However, three controlled potential reductions at -1.4 V of 12.2 to 18.2 μ mol of HPT⁺ contained in 17 ml of 0.1 M TBAP/ACN at a platinum foil electrode yielded an average *n*_{app} value of 1.15 ± 0.12 (where *n*_{app} is the number of electrons per molecule). The bright orange solution of the parent compound changed to a purple color during reduction. The reduced product was apparently not stable on the coulometric time scale, since the purple color faded to a greenish-yellow tint within minutes after reduction. Four hours after the completion of electrolysis the color of the solution had changed to light yellow. After coulometry, a scan in the positive direc-

tion starting at -1.4 V showed no anodic waves; however, when the potential was scanned toward negative potentials, a new reduction wave at -1.9 V was observed. The size of this wave was about the same size as the original wave.

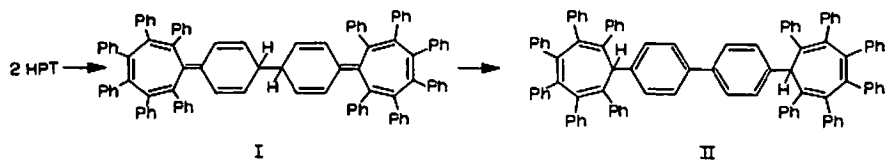
The results from the c.v. and controlled potential electrolysis show that the reduction of HPT^+ occurs via a reversible or a quasi-reversible one electron transfer to produce a product which is stable on the c.v. time scale (up to at least 20 s). This product is probably the free radical HPT^\cdot , so that the reduction reaction can be written



The coulometric results suggest that the radical is not stable on the time scale of bulk electrolysis experiments. Since n_{app} is near one in these experiments, dimerization probably occurs:



Dimerization through the carbons of the seven-membered ring, as occurs in the coupling of Tr^\cdot to form bitropyyl, is unlikely for HPT^\cdot because of the blocking action of the phenyl groups. A more reasonable possibility involves coupling via the phenyl groups:



The cross-conjugated compound, I, would probably convert to the more stable form, II, by a 1,5 hydrogen shift. The reduction of II produces the cathodic wave at -1.9 V following coulometry.

These results can be contrasted with those of Tr^+ obtained under identical conditions. Here c.v. shows an irreversible wave at -0.22 V and a second wave at -2.6 V (Fig. 2). We did not observe the small wave at -1.51 V vs. SCE reported by Breslow and Shu [5] and attributed to the reduction of Tr^\cdot . After coulometric reduction at -0.4 V which resulted in a $n_{\text{app}} = 0.92$, the wave at -2.6 V for the reduction of bitropyyl, remained.

The wave for Tr^+ reduction occurs at potentials about 1.0 V positive of those for HPT^+ . This can be ascribed to the fast irreversible dimerization following the

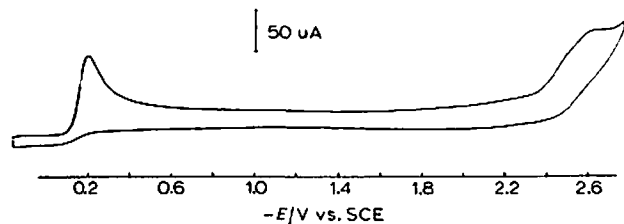


Fig. 2. Cyclic voltammogram of 3.25 mM tropylium tetrafluoroborate in 0.1 M TBAP/ACN solution; scan rate, 500 mV s⁻¹.

electron transfer step. At these scan rates this would cause a shift of about 45 mV from the reversible potential [14,15] assuming the previously quoted dimerization rate [7]. The remainder of the shift must be attributed to added stabilization of the tropylium ion upon addition of the phenyl groups, facilitating the oxidation of the radical.

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