

THE OXIDATION OF AROMATIC HYDROCARBONS IN METHYLENE CHLORIDE AT -70°C

L. Byrd, L. L. Miller

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521

and D. Pletcher

Department of Chemistry, The University, Southampton, SO9 5NH, England

(Received in USA 22 March 1972; received in UK for publication 5 May 1972)

Although temperature is a variable which affects an electrode process in several ways,¹⁻⁴ a dominant change expected when an electrode reaction is carried out at low temperatures is the retardation of chemical reactions preceding or following the electron transfer step. Therefore, the study of electrode processes at low temperatures should allow the positive identification of species which are postulated as intermediates in the reaction at room temperature but which are too short-lived to be observed directly. Conversely, the applications of electrochemical techniques at low temperatures should extend the range of transient intermediates whose chemistry may be studied.

Earlier work has shown that methylene chloride is an excellent solvent for the study of cation radicals.^{5,6} Furthermore, in contrast to a recent paper,² this work shows that this solvent is convenient for electrochemical studies at -70°C and, indeed, it is possible to carry out cyclic voltammetry at 10 V/sec without significant "ir drop" problems. Hence, it is possible to observe intermediates with lifetimes down to 1 msec at -70°C . Although the first step in the oxidation of all aromatic hydrocarbons is widely believed to be the reversible formation of a cation radical, at room temperature it is generally only possible to observe electrochemically those cation radicals formed from very large or highly substituted hydrocarbons.^{7,8,9} In this paper we report the study of the oxidation at -70°C of hydrocarbons which yield less stable cation radicals.

All electrochemical measurements were carried out with a PAR model 170 Electrochemistry System and rapid scan *i*-*E* curves were recorded on a Tektronix memory oscilloscope. An enclosed

three compartment cell was used; the Pt wire working electrode was separated from the Pt auxiliary electrode by a glass frit and from a Ag/sat. AgNO₃ reference electrode by a Luggin capillary and glass frit. The cell was immersed in an acetone/dry ice bath at -70°C and the whole experiment was carried out in a dry box. Fisher reagent grade methylene chloride was distilled from calcium hydride and the tetrabutylammonium tetrafluoroborate was prepared in water from the corresponding hydroxide and sodium tetrafluoroborate and dried in a vacuum oven at 80°C after multiple recrystallization.

The anodic oxidation of a series of aromatic hydrocarbons in methylene chloride containing 0.2 M tetrabutylammonium tetrafluoroborate at -70°C was studied by cyclic voltammetry and the data obtained for the hydrocarbon/cation radical couples are reported in Table I. The half lives for the cation radicals have been estimated using the calibration curves of Nicholson and Shain¹⁰ and assuming that the cation radical decomposes by a reaction which is first order in the cation radical.

TABLE I. Cyclic Voltammetry Data from Methylene Chloride Solutions at -70°C

Aromatic Hydrocarbon	$E_p^{ox \ a}$ (V)	ΔE_p^b (mV)	$t_{1/2}$
Rubrene	0.17	40	<u>c</u>
Tetracene	0.35	45	<u>c</u>
Thianthrene	0.64	90	<u>c</u>
1,4-Dimethoxybenzene	0.70	50	100 sec
Anthracene	0.73	42	0.5 sec
Hexamethylbenzene	1.05	45	25 msec
Phenanthrene	1.13	<u>d</u>	< 1 msec

^a Potentials are quoted versus the Ag/AgNO₃ reference electrode in CH₂Cl₂/0.2 M Bu₄NBF₄. The concentrations of substrate are $\sim 5 \times 10^{-3}$ M. $\frac{b}{F} \frac{2.3 RT}{F} = 41$ mV at -70°C. ^c The half lives of these cation radicals are too long to observe any decay on the timescale of slow sweep cyclic voltammetry, i.e., $t_{1/2}$ is at least several minutes. ^d No reverse peaks observed.

It is immediately clear that the behavior observed at -70°C is much simpler than that at room temperature; typical is the case of anthracene. At room temperature and even at fast

potential sweep rates, $v = 100$ V/sec, a single irreversible peak is observed and this has been ascribed to a complex process involving multielectron transfers coupled to chemical reactions. At -70°C and at potential sweep rates above 1 V/sec the curves for anthracene become identical to those observed for diphenylanthracene at room temperature.^{5,9} In other words, two oxidation processes may now be observed; the first process at $+0.73$ V fulfills all the criteria for a one electron, reversible process (i.e., $E_p^{\text{ox}} - E_p^{\text{ox}} = 41$ mV, $i_p^{\text{ox}} - v^{1/2}$ is linear, $\frac{i_p^{\text{C}}}{i_p^{\text{A}}} = 1$, and $\Delta E_p = 42$ mV)¹⁰ while the second process at $+1.55$ V is irreversible. At slower sweep rates, the first process begins to become irreversible, $\frac{i_p^{\text{C}}}{i_p^{\text{A}}} < 1$, showing that a chemical reaction is removing the cation radical.

The behavior observed for 1,4-dimethoxybenzene and hexamethylbenzene is entirely similar to that for anthracene while the cation radicals from thianthrene, rubrene, and tetracene are so stable that there is no evidence of decay on the timescale of slow sweep cyclic voltammetry, i.e., $t_{1/2} \gg \text{min}$. Conversely, the cation radical from phenanthrene remains too unstable for detection even at -70°C . The difference in stability between the cation radicals of anthracene and phenanthrene would be expected from M.O. calculations.

The cyclic voltammograms for rubrene at -70°C show a further interesting feature; a second reversible, one electron process occurs at $+0.72$ V ($\Delta E_p = 45$ mV) and this corresponds to the further oxidation of the cation radical to a doubly charged species which may be a dication or a dication diradical. It is, however, also a stable species on the timescale of these experiments, i.e., $t_{1/2} \gg \text{min}$. At room temperature the doubly charged species may be observed on a cyclic voltammogram¹¹ but it is a relatively short-lived intermediate, $t_{1/2} \approx 0.15$ sec.

It is not possible to draw quantitative conclusions concerning the differences in the potentials for the oxidation of the hydrocarbons at room temperature and at -70°C because the effect of the temperature change on the reference electrode potential is unknown. Such a comparison does, however, show an approximately constant difference. Moreover it should be noted that the peak potentials for the first oxidation processes for rubrene, tetracene, anthracene, 1,4-dimethoxybenzene and hexamethylbenzene are simply related to the reversible potentials for the hydrocarbon/cation radical couples. The data for rubrene represents the first example where thermodynamic data is available for both the hydrocarbon/cation radical and the cation radical/dication couples.

Finally it is apparent that the cation radicals and the rubrene dication have a greatly

enhanced lifetime due to the 100° reduction in temperature. Indeed, the half lives have been extended by factors in the range 10²-10⁴. This should prove a useful method for elucidating the details of follow-up reactions in electrooxidations. The reactions of nucleophiles with relatively unstable cation radicals or dications could, for example, be studied kinetically.

Acknowledgement: This study was supported by a NATO research grant.

References

1. M. Fleischmann and D. Fletcher, "Advances in Physical Organic Chemistry," V. Gold, Ed., in press.
2. R. P. Van Duyne and C. N. Reilley, Anal. Chem., 44, 142 (1972).
3. R. P. Van Duyne and C. N. Reilley, ibid., 44, 153 (1972).
4. R. P. Van Duyne and C. N. Reilley, ibid., 44, 158 (1972).
5. J. Phelps, K. S. V. Santhana, and A. J. Bard, J. Amer. Chem. Soc., 89, 1752 (1967).
6. J. Phelps and A. J. Bard, Abstracts, Electrochemical Society Meeting, Boston, Mass., May 1968, No. 204.
7. C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970.
8. M. E. Peover, "Electroanalytical Chemistry," Vol. II, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1967, p. 1.
9. M. E. Peover and B. S. White, J. Electroanal. Chem., 13, 93 (1967).
10. R. S. Nicholson and I. Shain, Anal. Chem., 36, 706 (1964).
11. J. Chang, D. M. Hercules, and D. K. Roe, Electrochim. Acta, 13, 1197 (1968).