

Summary

This study shows that C atoms react with H₂ to form CH, CH₂, and CH₃. The reactions of these intermediates with ethylene have been identified and the stable products resulting provide an indication of the yields of the primary processes. The latter are shown in Figure 5 as a function of the relative amounts of hydrogen and ethylene. A quantitative treatment of this system is quite complex but becomes possible by making certain simplifying assumptions. Good fits are obtained to the equations derived implying that the general kinetic framework has validity.

The more detailed conclusions of the work are summarized as follows. (1) Hot C atoms may react with H₂ to give CH₂ or CH but with an efficiency of only 0.05 that of hot C atom reaction with ethylene. The efficiency of this process for thermal carbon is even lower. The probable reason for the low yield is that in most cases the CH₂* complex immediately reverts to C + H₂.

(2) Some of the CH₂*, particularly that formed by hot carbon, does not revert to C + H₂, possibly because it has a linear H-C-H structure making the back-reaction sterically unlikely. Instead, it must be collisionally deactivated to CH₂ or decompose to CH + H. The rates for these processes appear comparable at ordinary pressures. This may be surprising in view of the sim-

ilarity of CH₂, which would indicate a very short lifetime with respect to decomposition, particularly if it contains the excitation corresponding to a 9-ev C atom. It becomes quantitatively reasonable, however, when it is realized that most of the energy of the hot atom appears as translational energy of the CH₂* and that the resulting high velocity shortens the time elapsed before CH₂* undergoes a deactivating collision.

(3) Reaction of C to abstract H from H₂ and thus directly form CH appears to be less rapid than its insertion to give CH₂* which then decomposes to CH.

(4) The CH radical adds to ethylene to give allyl radical. In these systems, this then reacts further to give pentene-1. CH will also react with H₂ to form CH₂. This reaction may proceed *via* insertion to give CH₃* which then decomposes to CH + H, or it may involve direct abstraction.

(5) Both CH₂ and CH, as formed in this work, have a somewhat higher reactivity toward ethylene than toward H₂. This difference in reactivity is less for methylene, which may be largely due to its reacting with a higher translational energy.

Acknowledgment. We wish to thank the directors and staffs of the Yale HILAC and electron accelerator for aid in performing the irradiations. This work was supported by the U. S. Atomic Energy Commission.

One-Electron Oxidation of Aromatic Hydrocarbons

L. S. Marcoux, J. M. Fritsch, and R. N. Adams

Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66044. Received October 17, 1966

Abstract: The electrochemical oxidation of aromatic hydrocarbons has been studied in nitrobenzene as a solvent. The hydrocarbons fall experimentally into two classes. The first class consists of compounds for which unequivocal electrochemical and electron paramagnetic resonance evidence shows a one-electron oxidation to the stable cation radical. The other class of compounds involves rapid follow-up chemical reaction after the initial electron transfer, and the total number of electrons involved varies with compound, solvent, etc.

The confirmed existence of the cation radicals of several aromatic hydrocarbons produced by chemical oxidation^{1,2} would seem to imply that an initial one-electron (1-e) step should be observed when these compounds are oxidized electrochemically. The first electrochemical investigation³ and several subsequent studies⁴⁻⁶ of the oxidation of these compounds indicated an initial two-electron (2-e) step. Hoijtink tacitly assumed a 1-e mechanism in correlating oxidation potentials and molecular orbital parameters.⁷

(1) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965), and references contained therein.

(2) F. A. Malachuk, L. S. Marcoux, and R. N. Adams, *J. Phys. Chem.*, **70**, 2064 (1966).

(3) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

(4) E. S. Pysch and W. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

(5) W. C. Neikam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, **111**, 1190 (1964).

(6) W. C. Neikam and M. M. Desmond, *J. Am. Chem. Soc.*, **86**, 4811 (1964).

(7) G. J. Hoijtink, *Rec. Trav. Chim.*, **77**, 555 (1958).

Recently 1-e oxidations have been demonstrated for certain hydrocarbons of interest in electrochemiluminescence,⁸ and well-resolved epr spectra have been obtained for a few electrochemically generated cation radicals.^{2,9} Friend and Ohnesorge¹⁰ on the basis of product isolation have advocated a 1-e process for anthracene. Most recently Peover and co-workers have shown by cyclic voltammetry that in acetonitrile these compounds first undergo a 1-e oxidation which in many cases is followed by rapid irreversible chemical reactions.¹¹⁻¹³ Bard and co-workers¹⁴ have also drawn

(8) R. E. Visco and E. A. Chandross, *J. Am. Chem. Soc.*, **86**, 5350 (1964).

(9) R. E. Sioda and W. S. Koski, *ibid.*, **87**, 5573 (1965).

(10) K. E. Friend and W. E. Ohnesorge, *J. Org. Chem.*, **28**, 2435 (1963).

(11) T. A. Gough and M. E. Peover, "Polarography 1964," Proceedings of the 3rd International Polarography Congress, The Macmillan Co., London, 1965, p 1017.

(12) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967).

similar conclusions from a study which employed methylene chloride as the solvent.

Notwithstanding these studies, uncertainty continues to exist concerning this electrode process. This is especially true in the area of electrolytic preparation of organic compounds and among workers interested in correlating polarographic half-wave potentials with ionization potentials and molecular orbital calculations.⁴⁻⁶ Ebersson and Nyberg have reviewed much of the preparative organic electrochemical literature and indicated the arguments for the 2-e process.¹⁵

The 1-e *vs.* 2-e initial oxidation question is of considerable consequence especially in the two broad areas of study mentioned above. It is the purpose of this work to present unequivocal evidence for the 1-e oxidation of several polycyclic aromatic hydrocarbons. Further, the experimental evidence, together with the work of Peover¹¹⁻¹³ and Bard,¹⁴ strongly suggests that the removal of one electron is the initial stage in the electrochemical oxidation of most aromatic hydrocarbons. Rapid chemical reactions following this electron transfer (which sometimes cannot be separated in time sequence from the initial process even with rapid electrochemical techniques) cause the electrooxidations of many hydrocarbons to appear to involve two or more electrons. Since these chemical follow-up reactions are predominantly with the solvent or trace impurities (or additives therein), experimental proof of the 1-e process depends strongly on the solvent system. The common aprotic solvents are not necessarily chemically inert enough to show the 1-e behavior for many hydrocarbon oxidations. In this connection nitrobenzene can be shown to be a particularly advantageous solvent which has not been used extensively for anodic oxidations. We also wish to emphasize the utility of the rotated disk electrode (rde) for the study of hydrocarbon oxidations.

Experimental Section

Apparatus. The potentiostat and triangular wave generator for cyclic voltammetry have been described.¹⁶ The platinum rotated disk electrode had a geometric area of 0.045 cm² and was constructed by force-fitting a platinum wire into a Teflon shield mounted on a brass shaft and then polished with fine abrasives. The assembly for controlled rotation has been described.¹⁷ The stationary platinum electrode was a Beckman platinum button (No. 39272), and the aqueous sce was isolated in a porous glass bridge. A Varian V-4500 epr spectrometer equipped with 100-kc field modulation and a Fieldial attachment was used.

Reagents. Nitrobenzene was first passed through an alumina column and then vacuum distilled. All hydrocarbons with the exception of 9,9'-bianthryl were obtained from commercial sources and purified by column chromatography. The 9,9'-bianthryl was prepared by reduction of anthraquinone.¹⁸ *Anal.* Calcd for C₂₈H₁₈: C, 94.86; H, 5.14. Found: C, 94.38; H, 5.30. The compound 5,10-dihydro-5,10-dimethylphenazine used as a model system was that previously described.¹⁹

Procedures. All experimental procedures were conventional, and all potentials are reported *vs.* the aqueous sce. Solutions in nitrobenzene contained 0.1 M tetra-*n*-propylammonium perchlorate.

(13) M. E. Peover in "Electroanalytical Chemistry," A. J. Bard, Ed., in press.

(14) J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Am. Chem. Soc.*, **89**, 1752 (1967).

(15) L. Ebersson and K. Nyberg, *ibid.*, **88**, 1686 (1966).

(16) J. R. Alden, J. Q. Chambers, and R. N. Adams, *J. Electroanal. Chem.*, **5**, 152 (1963).

(17) K. B. Prater and R. N. Adams, *Anal. Chem.*, **38**, 153 (1966).

(18) F. Bell and D. H. Waring, *J. Chem. Soc.*, 267 (1949).

(19) R. F. Nelson, D. W. Leedy, E. T. Seo, and R. N. Adams, *Z. Anal. Chem.*, **224**, 184 (1967).

Because all of the compounds studied tended to film the electrode, it was wiped with tissue before each measurement.

The oxidation of 5,10-dihydro-5,10-dimethylphenazine (5,10-DMPZ) has been established as a model electrochemical system. It undergoes two successive, 1-e stages of oxidation. Both stages adhere *strictly* to criteria of reversibility when examined by single sweep and cyclic voltammetry, as well as chronopotentiometry in certain solvents.¹⁹ Because the structure, and hence diffusion coefficient, of 5,10-DMPZ resembles many of the compounds in this study, it served ideally as a basis of comparison for peak currents, etc. Only the first oxidation stage of 5,10-DMPZ was used in these comparisons. The measurement of ratios of cathodic to anodic peak currents was as previously described.

The epr techniques were conventional and have been described.²⁰

Results and Discussion

The hydrocarbons studied fall into two classes of compounds according to their experimental behavior. The class A compounds exhibit clear 1-e, quasi-reversible oxidations leading to stable cation radicals, although follow-up reactions are indicated in several cases. With the class B compounds, the follow-up reactions are so rapid and extensive that the net observable process appears to involve two or more electrons leading, in general, to unidentified products.

Typical cyclic polarograms (in acetonitrile and methylene chloride) have been shown recently by Peover, *et al.*,¹² and Bard and co-workers¹⁴ and need not be repeated here. A second oxidation peak is also observed but this is discussed later. (Unless otherwise noted, all current ratios, potentials, etc., refer to the primary (first) oxidation peak of the hydrocarbons.) The peak current ratios ($i_{p,c}/i_{p,a}$) for the model 5,10-DMPZ and the six class A hydrocarbons are listed in Table I. The results obtained by cyclic voltammetry may be interpreted using theoretical treatments.²¹⁻²⁵ Because of the proximity of the second wave, the ratio of cathodic to anodic peak currents serves only as a qualitative indication of the stability of the cation radical. It can be seen from Table I that even at the relatively slow scan rate of 5.05 v/min the value of this ratio of 9,10-DPA, perylene, and rubrene is unity in agreement with theory. The radicals formed by 9,10-DMA, 9-PA, and TPP are less stable.

Table I

Compound	$i_{p,c}/i_{p,a}^a$
5,10-DMPZ	1.02
9,10-DPA	1.01
Perylene	1.02
Rubrene	1.00
TPP	0.89
9,10-DMA	0.84
9-PA	0.45

^a These measurements were made at 5.05 v/min.

A valuable diagnostic test for follow-up chemical reactions is the variation of $i_p/V^{1/2}C$ with $V^{1/2}$. If follow-up reactions are present, $i_p/V^{1/2}C$ will decrease with increasing sweep rate. If not, the plot will be a horizontal straight line. Figure 1 illustrates the behavior of the hydrocarbons. Rapid follow-up reac-

(20) R. N. Adams, *J. Electroanal. Chem.*, **8**, 151 (1964).

(21) N. Matsuda and Y. Ayabe, *Z. Elektrochem.*, **59**, 494 (1955).

(22) J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327 (1948).

(23) A. Sevcik, *Collection Czech. Chem. Commun.*, **13**, 349 (1948).

(24) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(25) R. S. Nicholson and I. Shain, *ibid.*, **37**, 178 (1965).

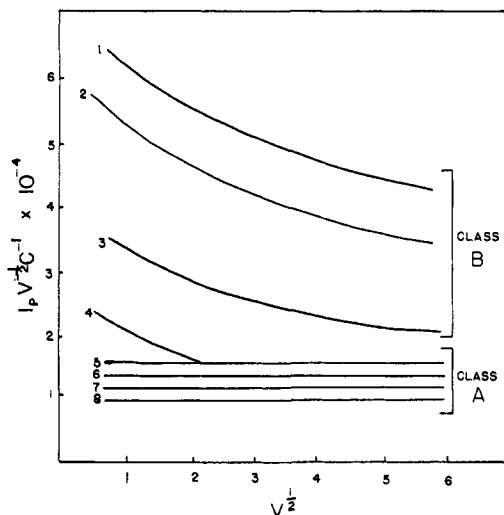


Figure 1. Peak current-scan rate dependence for anthracene (1), 9-MA (2), naphthacene (3), 9-PA (4), 5,10-DMPZ and 9,10-DMA (5), perylene and 9,10-DPA (6), TPP (7), and rubrene (8).

tions are confirmed for the class B compounds anthracene, 9-MA, and naphthacene (the $i_p/V^{1/2}C$ quotient for the other class B hydrocarbons studied has little meaning because of the complication in measuring i_p due to the close second peak).

The quotient $i_p/V^{1/2}C$ remains constant for 9,10-DPA, 9,10-DMA, perylene, rubrene, and TPP (class A). The value of this quotient is comparable to that obtained for the proven 1-e oxidation of 5,10-DMPZ. The differences observed in the values of these constants are in agreement with those one would expect due to differences in diffusion coefficients. This may be taken as evidence for a 1-e transfer uncomplicated by chemical reactions. The decrease of this quotient to the one-electron limit in the case of 9-PA indicates a 1-e transfer complicated by chemical reaction (probably an ece²⁵ process).

The results obtained at the rde are consistent with those presented above and a recent treatment of ece processes at the rde.²⁶ Qualitatively, the rde can be used to great advantage to detect ece mechanisms in the following manner. In the ece scheme, the initial electron transfer (n_1 electrons) is followed by a fast chemical reaction whose product undergoes further oxidations (reduction) at the same or lesser applied potentials and consumes an n_2 electron. It follows that, if the rde is rotated fast enough, mass transfer of the first product away from the electrode surface may be rapid enough that the ensuing chemical reaction and further electron transfers may not be possible. Hence, a plot of limiting current (i_L) vs. increasing rotation rate will decrease. Probably the best method to present such data is a plot of $i_L/\omega^{1/2}C$ vs. $\omega^{1/2}$, where ω is the rotation rate and C the bulk concentration of electroactive species. If there is no ece process, $i_L/\omega^{1/2}C$ vs. $\omega^{1/2}$ will, of course, be a horizontal straight line. If the rate of the chemical reaction can be "outrun" by rotation rate, $i_L/\omega^{1/2}C$ will limit at high rotation rates to a value consistent with an n_1 electron process. If not, it will show a continuous decrease with increasing rotation rate but not limiting at the initial n_1 process.

(26) P. A. Malachsky, L. S. Marcoux, and R. N. Adams, *J. Phys. Chem.*, **70**, 4068 (1966).

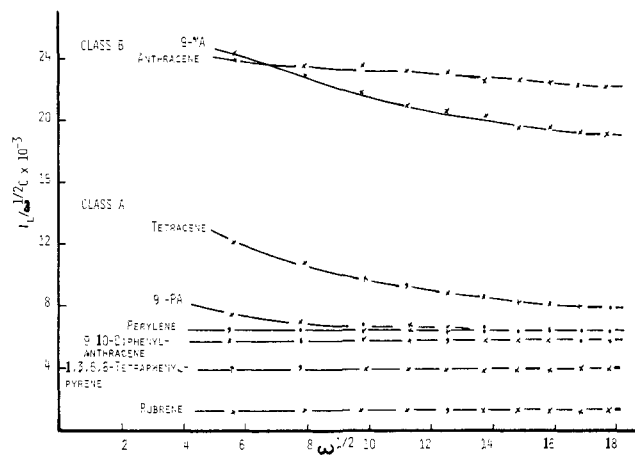


Figure 2. Limiting current-rotation rate dependence for class A and B hydrocarbons.

This is exactly the picture obtained for the hydrocarbon oxidations. As seen in Figure 2, the class A compounds show $i_L/\omega^{1/2}C$ to be constant in the region $\omega = 30\text{--}500$ radians/sec (5–60 rps) and comparable to that of 5,10-DMPZ, once again indicating a 1-e process. The class B compounds have an $i_L/\omega^{1/2}C$ value considerably higher than this and continuously decreasing as rotation rate increases which is consistent with fast follow-up (ece) processes.

Finally, well-resolved epr spectra can be obtained by standard *in situ* electrochemical techniques with 9,10-DPA, 9,10-DMA, and perylene as previously reported.² Epr signals were also obtained from the other class A hydrocarbons (9-PA, TPP, and rubrene) using similar techniques. The latter spectra could not be fully resolved and hence cannot be claimed unequivocally to be the parent cation radical. No attempts were made to obtain epr spectra by oxidation of the class B compounds since they obviously would be secondary radical ion species.

An attempt was made to identify the follow-up process involved in the oxidation (first peak) of anthracene. A possible reaction product is 9,9'-bianthryl. Anthracene and bianthryl give irreversible oxidations at +1.35 and 1.36 v, respectively. However, bianthryl exhibited two distinct peaks due to follow-up reaction products. These peaks, at +0.6 and +0.8 v, showed some signs of reversible character at scan rates >18 v/min. Nothing of this sort was evident in the cyclic voltammetry of anthracene itself, and it must be concluded that the 9,9'-bianthryl cannot be a final product of anthracene oxidation. We were also unable to identify the cyclic voltammetry of bianthronyl as "belonging" to anthracene oxidation in the nitrobenzene solvent system. A process consistent with the general picture of anthracene and the other class B hydrocarbons would be the formation of polymeric products as a result of successive ece processes.

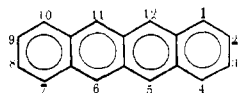
While it might seem foolish to use nitrobenzene as a solvent system, it is highly inert in the present context and deserves further consideration as a solvent for electrochemical oxidations. Exactly why nitrobenzene is more inert in the present instance than, say, acetonitrile cannot be answered until more is known of the nature of the chemical reactions of the hydrocarbon radical cations. However, its utility in this sense is

amply illustrated by the data of Figure 3. This shows a $i_p/V^{1/2}C$ vs. $V^{1/2}$ plot for 9-PA, which is a "borderline" compound; *i.e.*, it limits to a 1-e process but nevertheless its cation radical is moderately unstable. In nitrobenzene, at practically all sweep rates, the oxidation is a simple 1-e process. In acetonitrile, the cation radical is much more reactive, and the electrochemical results never limit to a 1-e process within the same sweep range. The effect of the chemical follow-up reactions is especially pronounced at the slow sweep rates. This is consistent with the data of Gough and Peover for acetonitrile.¹¹ The distinct advantage of the nitrobenzene is that it allows observation of more clearly defined 1-e processes.

Summary

The initial step in the anodic oxidations of some aromatic hydrocarbons in nitrobenzene is clearly established to be a 1-e transfer. In many cases this electron transfer is followed by one or a series of rapid chemical reactions and further electrooxidations. The division of the hydrocarbons studied herein into classes A and B was purely arbitrary and based on experimental behavior. However, one can, in fact, predict such a qualitative subdivision based on general reactivity and simple molecular orbital considerations. Thus, as pointed out by Gough and Peover,¹¹ blocking the highly reactive 9,10 positions in anthracene, as in 9,10-DMA and 9,10-DPA, should give rise to stable cation radicals from the 1-e oxidation (*i.e.*, follow-up chemical reactions are minimal). Obviously there are other factors which play a role since the 9,10-DPA cation seems far more stable than 9,10-DMA. Here over-all charge delocalization in the cation radical undoubtedly exerts an influence. Furthermore, 9-PA, with one reactive site still open, exhibits considerable cation radical stability whereas 9-MA is totally irreversible.

Nevertheless, this reactive site argument can be extended to other class A *vs.* class B compounds. Thus, in tetracene, the reactive sites are the 5, 6, 11, and 12 positions. As a measure of the site reactivity one can take the simple HMO correlation with the squares of the atomic orbital coefficients in the highest filled molecular orbital. For tetracene, using the common numbering system, the squares of the coefficients are²⁷



Positions	C^2
1	0.053
2	0.032
12 (5,6,11)	0.145

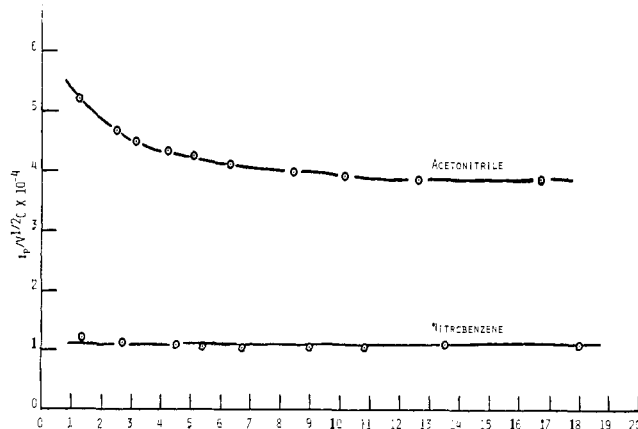


Figure 3. Peak current-scan rate dependence for 9-PA oxidation in acetonitrile and nitrobenzene solvent systems.

and it is clearly seen that the 5, 6, 11, and 12 positions are the points of highest reactivity. A more sophisticated molecular orbital parameter to represent reactivity seems neither necessary nor useful for these qualitative arguments. Thus, one expects rubrene (5,6,11,12-tetraphenyltetracene) to show class A behavior while the unsubstituted parent tetracene should be subject to extensive follow-up chemical reactions in accord with experiment.

Again, in pyrene the 1, 3, 6, and 8 positions are reactive although the 4, 5, 9, and 10 positions have moderate reactivity (the C^2 values are 0.14 and 0.08, respectively) and blocking in the 1,3,6,8-tetraphenylpyrene is expected to give the stable cation radical whereas the parent undergoes irreversible oxidation. Hence, it would seem that an examination of simple HMO reactivity parameters would allow one to predict the general electrochemical oxidation behavior of the hydrocarbons.

Acknowledgments. This work was supported in part by National Aeronautics and Space Administration Research Grant NsG-298 to the University of Kansas and by the National Science Foundation through Grant GP-5079X. This support is gratefully acknowledged. We wish to thank Dr. A. J. Bard for valuable discussions and R. F. Nelson and P. Malachuk for aid in the experimental work.

(27) Data from "Dictionary of π Electron Calculations," C. A. Coulson and A. Streitwieser, Jr., Ed., W. A. Freeman and Co., San Francisco, Calif., 1965.