Anodic Oxidation of Methylbenzenes at Potentials in the First Voltammetric Wave

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The mechanism of the anodic oxidation of hexamethylbenzene, durene, and mesitylene in acetonitrile at the first anodic wave is discussed on the basis of data from product studies, specular reflectance spectroscopy, linear sweep voltammetry, controlled potential coulometry, and measurements at a rotating disc electrode. The oxidation waves are shown to involve the transfer of two electrons with the formation of the corresponding carbonium ions. In the case of mesitylene, the process is seen to follow an e.c.e. sequence in which the proton loss from the cation radical formed in the first electron transfer is sufficiently slow to be detectable on the time scale of the experiments.

THE anodic oxidation of hydrocarbons is a potentially simple and efficient route to a range of functionalised derivatives. The stabilities and the mechanism of formation of the various cationic intermediates participating in such oxidations are also of considerable interest. Studies of hydrocarbons requiring more extreme oxidative conditions [1] and which are of greater synthetic interest have been restricted by the limited range of solvents and electrolytes suitable for such reactions. In much of the earlier work, the reaction took place, at least in part, *via* the oxidation of the anion of the electrolyte.[2] More recent studies [3] using electrolytes with a greater anodic range have avoided this complication. Detailed mechanisms have been established for the oxidation of polynuclear aromatics but not for cases such as the methylbenzenes or for saturated hydrocarbons. One of the major questions is the mechanism

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[1] J. Bertram, J. P. Coleman, M. Fleischmann, and D. Pletcher, *J.C.S. Perkin II*, 1973, 374.

[2] S. D. Ross, M. Finklestein, and R. G. Peterson, *J. Amer. Chem. Soc.*, 1967, **89**, 4088; V. D. Parker and B. E. Burgert, *Tetrahedron Letters*, 1968, 2411; K. Nyberg, *Acta Chem. Scand.*, 1970, **24**, 473.

[3] M. Fleischmann and D. Pletcher, *Tetrahedron Letters*, 1968, 2655.

of generation of the carbonium ion which appears to be the dominant intermediate in the oxidative process. Is this formed in an e.e.c. process or *via* the cation radical in an e.c.e. process and, in the latter case, how does the stability of the cation radical depend upon its structure and the nature of the solvent? A further problem of importance to synthesis is that of the efficient capture of the carbonium ion by a suitable nucleophile to yield a product resistant to further oxidation. An interesting distinction between the range of products observed in the anodic oxidation of mesitylene and durene has already been observed.[4] In methylene chloride, the major product from the former is the biphenyl dimer whereas the latter yields the diphenylmethane. These results suggest the cation radical and carbonium ion respectively as the reactive intermediates in the coupling reactions.

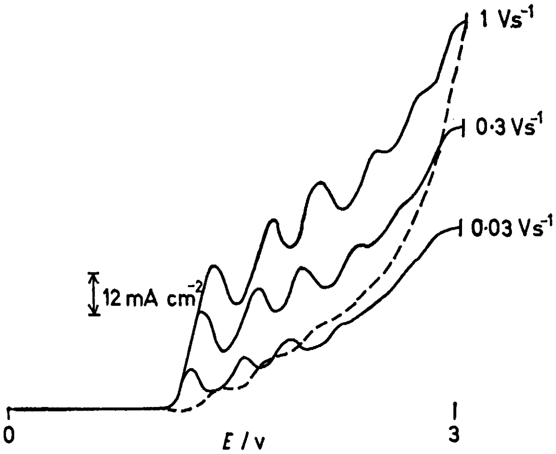

FIGURE 1 Linear sweep voltammetry of 0.02M-hexamethylbenzene. 0.1M-$Bu^n_4NBF_4$ in dry MeCN at a platinum anode (0.16 cm^2)

TABLE 1

Voltammetric data for the anodic waves of hexamethylbenzene, mesitylene, and durene. Sweep rate 0.3 V s^{-1}, solution 0.02M-substrate in 0.1M-$Bu^n_4NBF_4$–MeCN, reference electrode Ag–Ag$^+$ (0.01M)

	First wave			Second wave			Third wave			Other waves		
Hydrocarbon	E_p	$E_{p/2}$	$E_{(p-p/2)}$	E_p	$E_{p/2}$	$E_{(p-p/2)}$	E_p	$E_{p/2}$	$E_{(p-p/2)}$	E_p	E_p	E_p
Hexamethylbenzene	1.26	1.19	0.07	1.63	1.55	0.08	1.94	1.85	0.09	2.34	2.60	2.93
Mesitylene	1.72	1.67	0.05									
Durene	1.43	1.37	0.06	1.80	1.72	0.08						
2,2′,4,4′,6,6′-Hexamethoxydiphenylmethylamine	0.200	0.145	0.055									
2,3,4,5,6-Pentamethylbenzylacetamide	1.22 (not present on second sweep)			1.42			1.74			2.08		

Although extreme conditions utilising strongly acidic media appear to be required for the anodic oxidation of the less reactive saturated hydrocarbons,[1] moderate yields of amides have been reported from the oxidation of some saturated hydrocarbons in acetonitrile.[5] The potentialities of the less extreme conditions have not been fully explored.

The work described in this paper was aimed at the problem areas outlined. It was expected that the combination of mechanistic studies using conventional electrochemical techniques together with the powerful new tool of *in situ* reflectance spectroscopy would allow the direct detection and identification of the transient intermediates formed in the oxidation of methylbenzenes. The present discussion is limited to the anodic behaviour of the hydrocarbons at potentials in the region of the first voltammetric wave; the data for oxidation at higher potentials will be presented elsewhere.[6]

RESULTS

Voltammetry.—The linear sweep voltammograms for the three hydrocarbons in dry acetonitrile showed several anodic waves. Figure 1 illustrates typical voltammograms obtained for hexamethylbenzene using a platinum anode; similar results were obtained at vitreous carbon. The characteristic data for the various anodic waves of the three hydrocarbons are collected in Table 1. For hexamethylbenzene and durene, the first two waves are well defined, simple, irreversible, two-electron waves over the range of sweep speeds employed. Figure 2 illustrates this in a plot of peak current density *versus* the square root of sweep speed for the data from durene. Hexamethoxydiphenylamine was used to give a standard reversible one electron oxidation to establish the *n* values. In the case of mesitylene the data are less clear cut, the wave being rather too sharp and giving rather higher *n* values although the (sweep speed)$^{\frac{1}{2}}$ plot is linear and passes through the origin. In wet solution, the major products of controlled potential electrolysis of durene and hexamethylbenzene were 2,4,5-trimethylbenzyl- and pentamethylbenzyl-acetamide, respectively. The voltammetry of these two amides was investigated. The first gave two anodic waves and the second five. None of the waves corresponded to the second anodic wave of the parent hydrocarbon. In each case the first oxidation wave of the amide was at almost the same potential as the first wave of the parent hydrocarbon showing that the unprotected amide product is susceptible to further oxidation. At sweep speeds in excess of 0.1 V s^{-1}, however, the first oxidation wave of the amide was seen only on the first sweep and it was absent from subsequent sweeps; a delay of a few seconds between successive potential sweeps was sufficient to ensure its appearance on each sweep. This behaviour can be readily accounted for if the amide adjacent to the electrode

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[4] K. Nyberg, *Acta Chem. Scand.*, 1970, **24**, 1609.

[5] D. Clark, M. Fleischmann, and D. Pletcher, *J.C.S. Perkin II*, 1973, 1578.

[6] A. Bewick, G. J. Edwards, and J. M. Mellor, *Annalen*, in the press.

picks up protons generated in the chemical reactions following the anodic reaction. The protonated, electroinactive amide is then replaced by free amide from the bulk by diffusive mixing. Experiments carried out in the presence of added acid confirmed this conclusion.

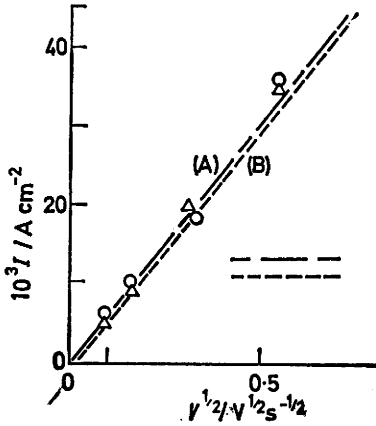

FIGURE 2 Plots of peak current density *versus* (sweep speed)$^{\frac{1}{2}}$ for durene: (A) first wave; (B) second wave. Solution as Table 1

The anodic waves were also studied at a platinum rotating disc electrode at a number of rotation rates and a sweep speed of 0.03 V s^{-1}. Figure 3 is a plot of the rotating disc current function (r.f. = $I/\omega^{\frac{1}{2}}cA$ cm^{-2} rad$^{-\frac{1}{2}}$ s$^{\frac{1}{2}}$ mol^{-1} l) *versus* rotation speed for the current pleateau of the first wave. Hexamethylbenzene gave a constant r.f. value of 0.27 independent of rotation rate and durene showed a small drift to a value of 0.30 at lower rotation speeds. Mesitylene, on the other hand, showed a distinct transition from a value of 0.13 at high rotation rates to a value near 0.4 at lower rotation rates. 9,10-Diphenylanthracene and hexamethoxydiphenylamine were used as standard compounds to determine *n* values and these gave r.f. values of 0.095 and 0.11, respectively, indicating simple two-electron behaviour for durene and hexamethylbenzene assuming a 30% difference between the diffusion coefficients of the methylbenzenes and the standards. The data for mesitylene would be accommodated by an e.c.e. mechanism with a relatively slow chemical step, although the *n* value exceeds two at low sweep speeds (this may be due to further oxidation of oligomeric material, see Discussion section).

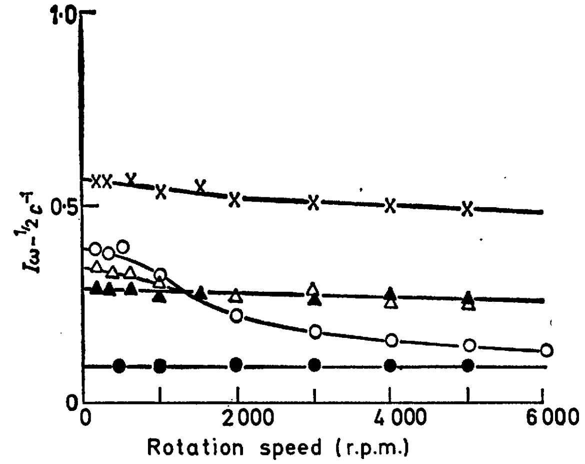

FIGURE 3 Plot of $I\omega^{-1/2}c^{-1}$ *versus* rotation speed at a rotating disc electrode for the first wave of: ▲ hexamethylbenzene; △ durene; ○ mesitylene; ● hexamethoxydiphenylmethylamine; and for the second wave of hexamethylbenzene ×

Reflectance Spectroscopy.—The u.v.-visible absorption spectra of the intermediate species formed at potentials in the region of the first anodic wave were obtained using the very sensitive, *in situ* technique of modulated specular reflectance (m.s.r.) spectroscopy.[7] Figures 4—6 give examples of these spectra in the range 250—1 150 nm for the three hydrocarbons and Figure 7 shows the absorbance *versus* potential plot for hexamethylbenzene at the wavelengths of the maxima. The latter plot shows clearly the production of an absorbing species as the potential reaches the region of the anodic wave, the increasing amount of

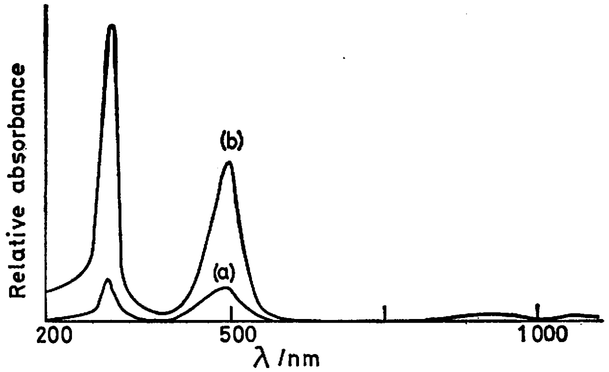

FIGURE 4 Spectra obtained by m.s.r. for a solution of 0.02M-hexamethylbenzene and 0.1M-Bu$^n{}_4$NBF$_4$ in dry MeCN. Square wave modulation at 12 Hz from +0.8 V to (a) +1.1 and (b) +1.2 V

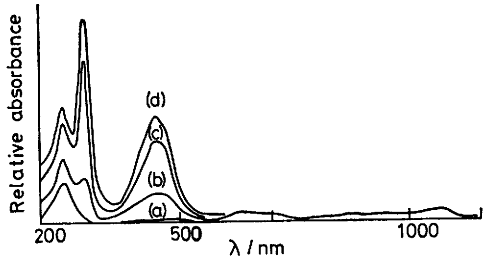

FIGURE 5 Spectra obtained by m.s.r. for a solution of 0.083M-durene and 0.1M-Bu$^n{}_4$NBF$_4$ in dry MeCN. Square wave modulation at 100 Hz from +0.8 V to (a) +1.2, (b) +1.3, (c) +1.4, and (d) +1.5 V

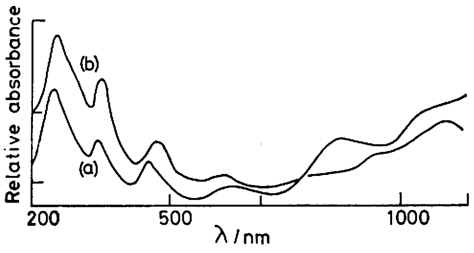

FIGURE 6 Spectra obtained by m.s.r. for a solution of 0.008M-mesitylene and 0.1M-Bu$^n{}_4$NBF$_4$ in dry MeCN. Square wave modulation at 30 Hz from +0.8 V to (a) +1.65 and (b) +1.7 V

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[7] A. W. B. Aylmer-Kelly, A. Bewick, P. R. Cantrill, and A. M. Tuxford, *Faraday Discuss. Chem. Soc.*, 1973, 96.

this species as the potential is made more positive, and finally a steady state amount being reached when the potential exceeds the peak potential of the wave. This is the expected behaviour for an unstable intermediate. At wavelengths shorter than 600 nm the spectra are similar for all three substrates and they correlate well with the spectra attributed by Hanazaki and Nagakura [8] to the benzyl carbonium ions (3,5-dimethyl-, 2,4,6-trimethyl-, and 2,3,4,5,6-pentamethyl-benzyl carbonium ion) formed from the corresponding benzyl chlorides in H_2SO_4 or in $AlCl_3$–CH_2Cl_2. An almost identical spectrum was obtained for oxidation of hexamethylbenzene in CH_2Cl–0.1M-Bu_4NBF_4 containing 5% trifluoroacetic acid and 1% trifluoroacetic anhydride; in this medium the voltammetry was also essentially the same as in acetonitrile. Further confirmation that the m.s.r. spectrum was that of the carbonium ion and not the nitrilium ion was given by the spectroscopic investigation of the purple solution obtained after controlled potential electrolysis of hexamethylbenzene in dry acetonitrile. The u.v.–visible absorption spectrum with maxima at 335 and 534 nm was different from that seen by m.s.r. and the extinction coefficients appeared to be low. Both of these peaks disappeared on addition of water. The nitrilium ion was also prepared by an independent route, the reaction of the corresponding azide with $NO^+BF_4^-$ according to the method of Doyle.[9]

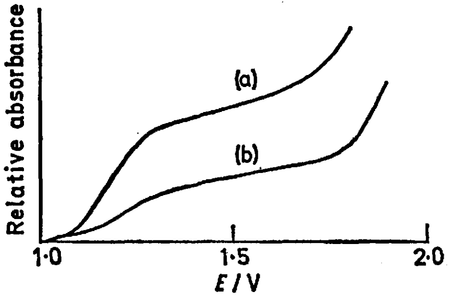
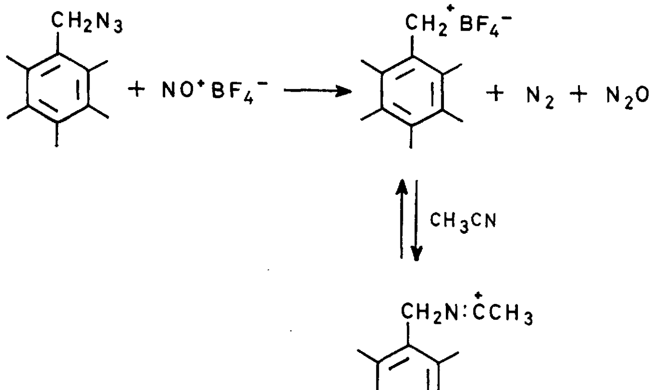


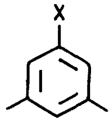
FIGURE 7 Plot of absorbance *versus* potential for hexamethylbenzene oxidation at the absorbance maxima: (a) 300; (b) 480 nm



The 100 MHz ^1H n.m.r. spectrum of the resultant solution showed a singlet at δ 5.34 that disappeared on the addition of small amounts of water, and the u.v. absorption spectrum of the solution had a maximum at 335 nm. The ^1H n.m.r. spectrum of the electrolysis reaction mixture had a line in exactly the same position. This resonance can be assigned to the methylene protons of the nitrilium ion (*cf.* the value δ 5.37 obtained by Doyle [9] for the benzyl nitrilium ion). No sign of the n.m.r. spectrum of the free carbonium ion was observed and it must be concluded that the equilibrium with the nitrilium ion is greatly in favour of the latter as might be expected.

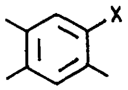
At wavelengths longer than 600 nm, the m.s.r. spectra for durene and hexamethylbenzene show no absorption whereas the spectrum for mesitylene has absorption peaks near 850 and 1 100 nm. It appears, therefore, that a further intermediate species is present in detectable amounts in addition to the carbonium ion.

Preparative Electrolyses and Coulometry.—Table 2 gives details of controlled potential preparative electrolyses for the three hydrocarbons in dry acetonitrile and also with added water. The substrate concentrations were kept in the same range as those used in the m.s.r. measurements and the voltammetry experiments in order to assist mechanistic



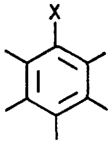
(1)

a; X = $CH_2NHCOMe$
b; X = CHO
c; X = $C_6H_2Me_3$



(2)

a; X = $CH_2NHCOMe$
b; X = $CH_2C_6HMe_4$



(3)

a; X = $CH_2NHCOMe$
b; X = CH_2OH
c; X = Me

TABLE 2

Electrochemical oxidation of methylbenzenes in acetonitrile–0.1-$Bu^n{}_4$-NBF_4

Compound (concentration)	Water concentration	Potential (V)	Charge consumed (F mol^{-1})	Products (coulombic yields %)
Mesitylene (20 mM)	Dry	1.80	1	Polymer
Mesitylene (20 mM)	0.1M	1.90	2	(1a) (20), (1b) (1), (1c) (4)
Durene (80 mM)	Dry	1.40	1.4	(2a) (1), (2b) (5), Polymer
Durene (83 mM)	0.39M	1.40	2	(2a) (70), (2b) (5)
Hexamethylbenzene (20 mM)	Dry	1.25	1.5	(3a) (100)
Hexamethylbenzene (20 mM)	0.1M	1.40	1.5	(3a) (28), (3b) (<1), (3c) (<1)

[8] I. Hanazaki and S. Nagakura, *Tetrahedron*, 1965, **21**, 2441.
[9] M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, 1972, **94**, 3896.

interpretation rather than to maximise the yields of particular products. There is a clear distinction between the simple result for hexamethylbenzene, quantitative yield of monoamide from dry solution, and the results for durene and mesitylene, the latter giving no volatile products in dry solution. The presence of water leads to appreciable yields of monoamide in these two cases but a substantial drop in the yield for hexamethylbenzene. The results also confirm the observation of other workers [4] that the dimer product from mesitylene is the biphenyl whereas durene gives the diphenylmethane.

Coulometry was performed at controlled potential to measure the number of Faradays consumed during the course of the electrolysis in dry solution. The current density can be used as a measure of the concentration of substrate and thus the slope of the plot allows the value of charge consumption in Faradays per mole of reactant to be determined as the reaction proceeds. The data for hexamethylbenzene (Figure 8) lie on a good straight line corresponding to the consumption of 1.9 F mol^{-1} throughout the electrolysis. The plot for durene (Figure 9) is also quite linear with a slope of *ca.* 1.7 F mol^{-1}. On the other hand, the data for mesitylene follow a smooth curve the slope of which approaches 1 F mol^{-1} at the start of the electrolysis and 2 F mol^{-1} towards the end.

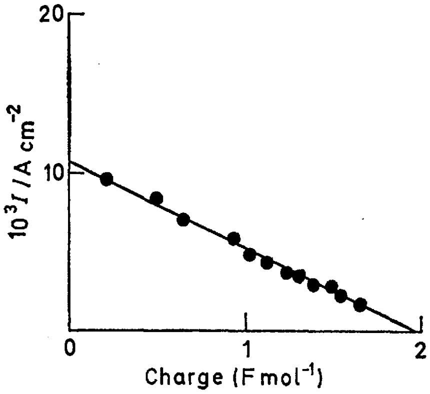


FIGURE 8 Coulometry for oxidation at +1.25 V of 0.02M-hexamethylbenzene and 0.1M-Bu$^n_4$NBF$_4$ in dry MeCN

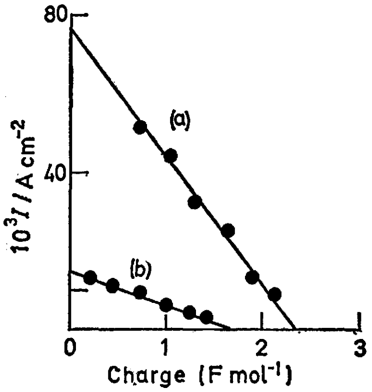


FIGURE 9 Coulometry for oxidation at (a) +1.8 and (b) +1.4 V of 0.13M-durene and 0.1M-Bu$^n_4$NBF$_4$ in dry MeCN

DISCUSSION

The results presented show clearly that all three aromatic hydrocarbons are oxidised in the first anodic wave to form the corresponding benzyl carbonium ion. The total evidence for this intermediate from the reflectance spectroscopy, from the voltammetry and coulometry showing the number of electrons transferred to each substrate molecule reaching the surface and from the nature of the products is overwhelming. Other workers have reached the same conclusion on the basis of much more limited evidence.[10–13] Hexamethylbenzene can be regarded as the model compound because the fully substituted ring reduces the number of possible reactions of the carbonium ion. The Scheme shows the simplest decay route for this species in acetonitrile; it involves nucleophilic attack by the solvent to form the nitrilium ion and finally the amide by hydrolysis. In dry acetonitrile, the nitrilium ion is the stable product and its spectrum can be obtained by conventional u.v.–visible spectroscopy of the coloured solution after electrolysis. In wet solution, some carbonium ion can be intercepted directly by water and this is the probable route for the formation of the small amounts of alcohol and aldehyde.

The amount of carbonium ion present in the very thin reaction layer adjacent to the electrode can be estimated from the m.s.r. results if a value is assumed for the extinction coefficient. Assuming a value of 10^4 (based on the data of refs. 8 and 14), this gives *ca.* 10^{-11} mol cm^{-2} of carbonium ion as the steady state amount during oxidation of a 10^{-2}M solution under diffusion controlled reactions. This is consistent with efficient nucleophilic scavenging by acetonitrile (approximate lifetime of carbonium ion 10^{-5}—10^{-4} s) leaving an amount of intermediate too small to be detected by conventional linear sweep voltammetry.

Durene and mesitylene show more complex behaviour. These substrates are susceptible to nucleophilic attack by the carbonium ion at the free ring positions, and therefore dimer, trimer, and polymer products with diphenylmethane linkages are obtained. These reactions complicate the coulometry and they make the voltammetry less clear cut and also time dependent due to further oxidative processes and the blocking of the electrode by polymeric material. In addition, mesitylene shows a consistent set of unique features in m.s.r., rotating disc voltammetry and product distribution. This substrate alone gives a biphenyl type dimer (bimesityl) which under appropriate conditions can be the dominant product.[15] The inference that this product arises from the cation radical [2] is confirmed by other data. The rotating disc voltammetry shows that the normal two electron oxidation at lower rotation speeds becomes a one electron oxidation at higher speeds as would be expected if formation of the carbonium ion is by an e.c.e.

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[10] L. Eberson and K. Nyberg, *Tetrahedron Letters*, 1966, 2389.

[11] L. Eberson and K. Nyberg, *J. Amer. Chem. Soc.*, 1966, **88**, 1686.

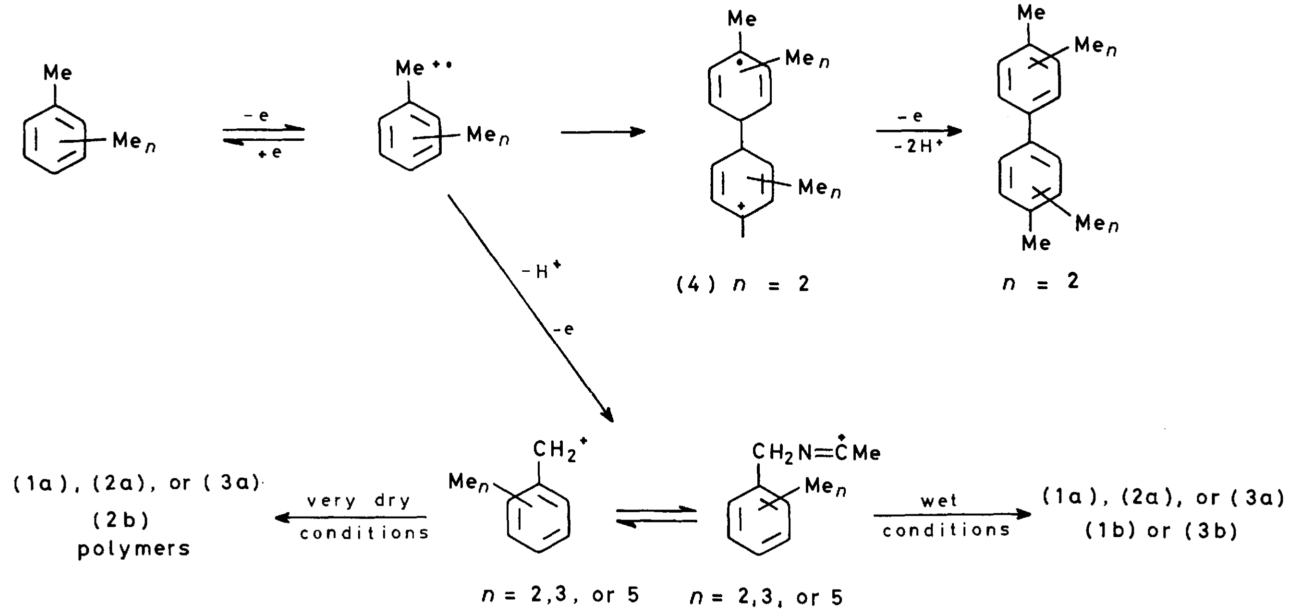
[12] L. Eberson, *J. Amer. Chem. Soc.*, 1967, **89**, 4669.

[13] E. A. Mayeda and L. L. Miller, *Tetrahedron*, 1972, **28**, 3375.

[14] H. M. Buck, M. J. Sluys, H. Dekkers, H. Brongersma, and L. Oosterhoff, *Tetrahedron Letters*, 1964, 2987.

[15] K. Nyberg, *Chemica Scripta*, 1971, **1**, 57.

process and the proton loss by the cation radical is not too fast. The m.s.r. results for mesitylene show absorbances at 800 and 1 100 nm as well as at 375 and 470 nm suggesting the appearance of new species in addition to the carbonium ion in this case. Comparison with the data of Badger and Brocklehurst [16] for the spectra of cation radicals produced by γ-radiolysis suggests that the most likely origin of these bands is cation radical species including the dimer cation radical (4) which is the precursor of the bimesityl product. The simple behaviour of durene in rotating disc and m.s.r. studies supports this view that the kinetics of the e.c.e. process are responsible for the more complex results for mesitylene rather than further oxidation of oligomer material.



In the case of durene it is concluded that proton loss from the cation radical is faster than in the case of mesitylene. Nyberg [17] has shown an interesting correlation between the extent of biphenyl formation for a series of methylbenzenes and the unpaired electron density at the free ring position of the cation radical. These data predict a smaller rate constant for dimerisation in the case of durene and that the durene cation radical will be a stronger acid than the mesitylene cation radical. Our data accord with this analysis, and indicate that both in the case of mesitylene and durene formation of the benzyl carbonium ion is by an e.c.e. process, but only with mesitylene is evidence of the intermediate cation radical clearly obtained.

The range of products obtained by controlled potential electrolysis and their relative yields (Table 2), are in accord with the data of Nyberg [18] and of Eberson and Olofsson.[19] The dependences on water content of the electrolyte and on substrate concentration are as expected on the basis of the mechanism shown in the Scheme. In very dry solution, both durene and mesitylene gave mainly polymeric material whereas in wet solution appreciable yields of amide and detectable amount of the dimer, diphenylmethane, and biphenyl, respectively, were obtained. It is clear that a major consequence of low water content is that the nitrilium ion is not quenched and thus the carbonium ion with which it is in equilibrium is available in solution to promote the formation of oligomeric and polymeric species. (I.r. spectroscopy on the polymer from durene showed the absence of acetamide groups and a molecular weight in the region of 450 was indicated by ebullioscopic measurements.) In agreement with this, electrolysis of hexamethylbenzene in dry solution yields a stable solution of the nitrilium ion which can be quenched to give a quantitative yield of amide. Although higher water concentration permits the formation of amide in the case of durene and mesitylene, very high yields cannot be obtained because the amide is itself oxidised at the potential of the electrolysis. This is seen clearly in the decreasing yield of amide with increasing water content in the case of hexamethylbenzene.

The coulometric measurements made under the conditions of the preparative electrolyses confirm these conclusions. In dry solution, hexamethylbenzene gives a good plot corresponding to a simple two-electron process (Figure 8). Durene (Figure 9) and mesitylene give data which show the effects of dimer, trimer, and polymer formation. These coupling processes consume fewer than two electrons for each substrate unit used although the value approaches two as the chain length increases.

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[16] B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, 1969, **65**, 2582.

[17] K. Nyberg, *Acta Chem. Scand.*, 1971, **25**, 2499.

[18] K. Nyberg, *Acta Chem. Scand.*, 1971, **25**, 534.

[19] L. Eberson and B. Olofsson, *Acta Chem. Scand.*, 1969, **23**, 2355.

Our mechanistic analysis explains the high yields which may be achieved either by capture of the benzyl carbonium ion (as with hexamethylbenzene) or of bimesityl at high concentrations of mesitylene. The products obtained by efficient capture of the benzyl carbonium ion are electroinactive. We have analysed other syntheses where anodic oxidation of hydrocarbons leads to high product yields. The requirements of efficient carbonium ion capture and electroinactivity are satisfactorily met by hexamethylbenzene but with durene capture of the carbonium ion is less efficient. With mesitylene at high concentrations proton loss from the cation radical fails to compete with that process leading to bimesityl.

EXPERIMENTAL

General experimental details have been reported in previous papers [6,20] and the electrochemical techniques are described in ref. 21.

Electrolysis of Hexamethylbenzene in Dry Acetonitrile at 1.25 V versus Ag–Ag$^+$ (0.01M).—Hexamethylbenzene (39 mg) was oxidised until 1.5 F mol^{-1} of charge had been consumed. Water (0.2 ml) was added to the anolyte and a g.l.c. analysis showed a quantitative coulombic yield of pentamethylbenzylacetamide. The anolyte was dried, extracted with ether, and these extracts were recrystallised twice from acetone–light petroleum (b.p. 40—60°). Crystals of pentamethylbenzylacetamide (47 mg) were obtained, m.p. 238° (lit. 230—230.5°), δ (CDCl$_3$), 1.95 (3 H, s), 2.24 (9 H, s), 2.28 (6 H, s), 4.49 (2 H, d), and 5.30br (1 H); *m/e* 219 (18%, M^+), 162 (19), 161 (16), 160 (100, $M - \mathrm{NH_2COCH_3}$), and 145 (17); $\nu_{max.}$ (KBr) 3 303, 2 915, 1 639, 1 525, 1 370, 1 265, 1 060, 700 and 590 cm^{-1}.

Electrolysis of Durene in Dry Acetonitrile at 1.40 V.—Durene (530 mg) was oxidised until 1.4 F mol^{-1} of charge had been consumed. Water (0.2 ml) was added to the anolyte and a g.l.c. analysis showed a small yield of 2,2′,4,5,5′,6-heptamethyldiphenylmethane. In addition, there was a large amount of non-volatile polymeric material. The ether extract from the dried anolyte was distilled under reduced pressure at 20 °C to remove unchanged durene, the temperature was then raised to 90 °C, and the diphenylmethane collected (30 mg). After recrystallization from acetone–methanol (2 : 1) the product had m.p. 160° (lit. 160—162°), δ (CCl$_4$) 2.05 (21 H, m), 3.62 (2 H, s), 5.97 (1 H, s), and 6.67 (2 H, d); *m/e* 266 (39%, M^+), 251 (30, $M - 15$), 147 (15), 146 (100, $M - \mathrm{C_9H_{12}}$), 133 (16), 132 (38, $M - \mathrm{C_{11}H_{14}}$), and 131 (12); $\nu_{max.}$ (KBr) 3 006, 2 965, 2 923, 2 865, 1 500, 1 460, 1 020, 1 000, 863, 690 and 443 cm^{-1}.

The electrolysis of mesitylene in dry acetonitrile was carried out similarly and only polymeric material was isolated. The electrolyses of mesitylene and durene in wet acetonitrile gave appreciable yields of the amides which were isolated and identified as described for hexamethylbenzene. The other trace products were identified by g.l.c.–mass spectrometry.

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[20] S. R. Jones and J. M. Mellor, *J.C.S. Perkin I*, 1976, 2576.

[21] ' Physical Methods of Chemistry. Part IIa, Electrochemical Methods,' eds. E. Weissberger and B. W. Rossiter, Interscience, New York, 1971.