U. D. C. 543.253 : 547.52/53

Polarography of Benzenoid Aromatic Hydrocarbons

S.I.Zhdanov

This review summarises the results of the study of the reduction and oxidation in protogenic, aprotic, and strongly acidic solutions of benzenoid polynuclear aromatic hydrocarbons whose molecules do not contain electrochemically active substituents. The characteristic features of the adsorption of aromatic hydrocarbons on mercury and various other metals are noted. The bibliography contains 167 references.

CONTENTS

I. Introduction	608
II. Mechanism of reduction	608
III. Reduction in strongly acidic medium	615
IV. Mechanism of oxidation	616
V. Correlation of the values of the half-wave potentials	617
VI. Characteristic features of the adsorption of benzenoid aromatic hydrocarbons	621

I. INTRODUCTION

The investigation of the problem of aromaticity[1,2], resulting to a considerable extent from the outstanding progress in the field of quantum chemistry, has led to the publication of a large number of papers on the study of the polarographic properties of aromatic compounds. This is due primarily to the fact that the polarographic method is an extremely convenient method for studying the mechanism of electrode processes and can be successfully used to verify theoretical conclusions by correlating polarographic half-wave reduction and oxidation potentials ($E_{1/2}$) with the energy parameters of the molecules, obtained by quantum-chemical calculations. It is now an appropriate time to systematise this extensive published material, which includes valuable information of interest to a wide circle of chemists. These papers have of course been examined in reviews devoted to the polarography of organic compounds, but the treatment has been incomplete[3-8]. The most successful review of these papers is that of Peover[9], but this is published in a source not readily available to Soviet readers, and a number of problems were not examined in it.

The present review to some extent fills this gap. It includes papers on the polarography of only those benzenoid aromatic hydrocarbons which do not contain electrochemically active substituents, and also on the polarography of unsaturated compounds, but only to the extent necessary for an understanding of the phenomena examined. A review of papers on the polarography of non-benzenoid aromatic hydrocarbons was published separately[10].

II. MECHANISM OF REDUCTION

The reduction of unsaturated and aromatic hydrocarbons at a dropping mercury electrode is generally studied in a supporting electrolyte of tetra-alkylammonium salts, most frequently $(C_4H_9)_4NI$, since in solutions of these salts the processes taking place at the most negative potentials can be studied. The second electrode is usually a layer of mercury in contact with the solution being studied; the potential of the second electrode is measured relative to an aqueous saturated calomel electrode. When the values of $E_{1/2}$ are compared, it is not necessary to allow for the inter-phase potential at the interface between the aqueous KCl solution and the non-aqueous $(C_4H_9)_4NI$ solution.

To establish the mechanism of the electrode processes and in particular to obtain the polarographic characteristics ($E_{1/2}$), which can be correlated with the energy parameters of the molecules, it is very important to carry out the studies in solvents with low proton activity ("availability"). It was in so-called aprotic solvents that the stages of reversible electron transfer with the formation of fairly stable hydrocarbon anion radicals, almost uncomplicated by subsequent irreversible reactions of protonation, dimerisation, or disproportionation, were revealed. This behaviour is in complete accordance with the general empirical rules formulated by Stackelberg[11,12] (see also Ref. 3) on the basis of extensive experimental material.

1. The stage of electron transfer is reversible if the geometric structures of the starting material and product do not differ significantly.

2. The stage is irreversible if it is accompanied by the formation of stable σ bonds, for example C–H (protonation) or C–C (dimerisation) bonds.

3. The stage is irreversible if it is accompanied by rupture of a stable σ bond, for example the bonds C–Hal in halogen derivatives, O–O in peroxides, and N–O in hydroxylamines.

4. The stage is irreversible if it is accompanied by the attachment of a proton to a heteroatom with the formation of N–H or O–H bonds, since these bonds are kinetically labile.

The study of aprotic solvents in the polarography of organic compounds was begun by Wawzonek and coworkers[13-18]. Wawzonek was the first to use a dioxan–water (3 : 1) mixed solvent[13-15], and subsequently acetonitrile, dimethylformamide[16,17], and tetramethylurea[18].

Many other authors used solvents which are not strictly aprotic: 75% dioxan[18-34], 85% dioxan[35,36], 96% dioxan[23,25-27,37], 75% ethanol[36,38], ethylene glycol monomethyl ether (cellosolve)[39-41], 50% isopropyl alcohol[42], a tetrahydrofuran–water mixture (3 : 1)[43], and ethylenediamine[44]. Other authors, like Wawzonek, used purely aprotic solvents: dimethylformamide (DMFA)[45-60], acetonitrile[61,62], and

tetrahydrofuran[63]. Purely dioxan solutions have not yet been used in polarography, because of the very low electrical conductivity. DMFA is most frequently used. Similar polarographic properties are shown by tetramethylurea, but this solvent has not found extensive application.

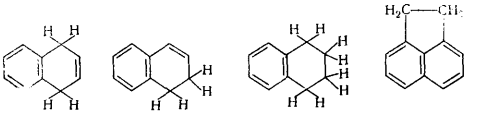
Simple unsaturated and aromatic compounds are reduced at a dropping mercury cathode in the range of high cathode potentials. Compounds whose molecules contain a single non-activated multiple bond[13] or benzene ring[14] are not reduced at all at a dropping mercury cathode in a range of potentials which can be measured. Aliphatic unsaturated compounds with conjugated bonds undergo two-electron reduction in 75% dioxan[20]. For allene ($CH_2=C=CH_2$), $E_{1/2}$ = −2.33 V, for butadiene ($CH_2=CH-CH=CH_2$), $E_{1/2}$ = −2.63 V, etc.

Vinylacetylene ($CH\equiv C-CH=CH_2$) gives two two-electron waves with $E_{1/2}$ = −2.44 V and −2.62 V. The first wave corresponds to the reduction of the triple bond to a double bond, and the second wave corresponds to the reduction of the butadiene produced. Thus the reduction of unsaturated compounds involves the hydrogenation of multiple bonds. Reduction is complete when the compound contains one or several non-conjugated and non-activated multiple bonds.

The reduction of compounds with multiple bonds activated by conjugation with phenyl rings takes place in exactly the same way[13,20]. In these compounds, the multiple bonds undergo electrochemical hydrogenation, whereas the phenyl rings are not attacked. Reduction is complete when the compound does not contain multiple bonds conjugated with other multiple bonds or with phenyl rings.

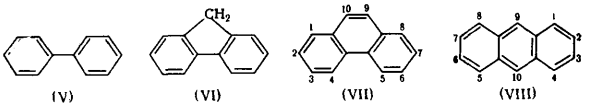
Increase in the conjugation facilitates reduction: $E_{1/2}$ becomes less negative in the series styrene ($Ph-CH=CH_2$), 1,1-diphenylethylene ($Ph_2=C=CH_2$), stilbene (Ph−CH=CH−Ph), triphenylethylene ($Ph_2=C=CH-Ph$), and tetraphenylethylene ($Ph_2=C=C=Ph_2$). The double bond is activated to a greater extent and is therefore more readily reduced when the two phenyl groups are arranged symmetrically with respect to the double bond (stilbene), than when they are arranged unsymmetrically (1,1-diphenylethylene). Styrene is more readily reduced than β-methylstyrene ($Ph-CH=CH-CH_3$), the effect of the methyl group being considerable ($\Delta E_{1/2} \simeq 200$ mV). 1,4-Diphenylbutadiene (Ph−CH=CH−CH=CH−Ph) gives only one wave corresponding to two-electron reduction. Thus this compound is attacked in the 1,4-position, and the molecule of the product contains one of the double bonds in the middle of the carbon chain, not conjugated with either of the two phenyl rings. Phenylacetylene ($Ph-C\equiv CH$) and diphenylacetylene ($Ph-C\equiv C-Ph$) have more negative $E_{1/2}$ values than styrene and stilbene, and they therefore undergo immediate four-electron reduction with the formation of ethylbenzene and bibenzyl respectively.

An analogous picture is observed in the reduction of aromatic hydrocarbons[14]. In the naphthalene molecule, only one double (more accurately aromatic) bond is hydrogenated. From this it follows that the reduction product is 1,5-dihydronaphthalene (I), in whose molecule the double bond is not conjugated with the phenyl ring. 1,2-Dihydronaphthalene (II) is reduced to tetralin (III), which does not exhibit electrochemical activity:



(I) (II) (III) (IV)

Acenaphthene (IV) is reduced in the same way as naphthalene: it gives only one two-electron wave. Biphenyl (V) and fluorene (VI) are hydrogenated in the 1,4-position.



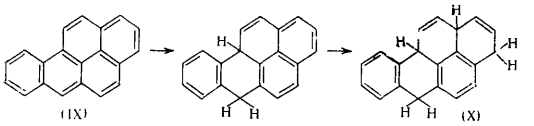
(V) (VI) (VII) (VIII)

The molecules of the products of the two-electron reduction contain only isolated double bonds and a phenyl ring.

Phenanthrene (VII) gives two two-electron waves, the value of $E_{1/2}$ for the second wave being close to the value of $E_{1/2}$ for 9,10-dihydrophenanthrene, and also biphenyl and fluorene. On this basis, the first wave for phenanthrene is attributed to the reduction of the double bond in the 9,10-position, and the second wave to reduction similar to the reduction of biphenyl and fluorene.

Anthracene (VIII) gives one two-electron wave, from which it follows that it is characterised by hydrogenation in positions 9 and 10 with isolation of the two phenyl rings.

Other polynuclear aromatic hydrocarbons studied by Wawzonek (chrysene, pyrene, 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, and 3,4-benzpyrene) give multi-wave polarograms with characteristic rapid breakdown of the molecule into isolated double bonds and phenyl rings. Thus of the ten aromatic bonds in 3,4-benzpyrene (IX)



(IX) (X)

only two are reduced, with the formation of compound (X), where the molecule contains two isolated phenyl rings and two isolated bonds.

The values of $E_{1/2}$ for the waves corresponding to the reduction of unsaturated and aromatic compounds are independent of pH (at pH > 7). The slope of the straight line obtained by plotting $\lg i/(i_d - i)$ against E is 0.06−0.07 V, that is it, as it were, corresponds to the theoretical slope (0.059 V) for a reversible potential-determining one-electron reaction. On this basis, Wawzonek[13] proposed the following mechanism of reduction:

$$R + e = R^{\cdot-} \text{ (reversible potential-determining state)} \quad (1)$$
$$R^{\cdot-} + e \rightarrow R^{2-} \text{ (irreversible stage)} \quad (2)$$
$$R^{2-} + 2H_2O \rightarrow RH_2 + 2OH^- \text{ (irreversible rapid stage)} \quad (3)$$

A second possible mechanism:

$$R + e = R^{\cdot-} \quad (1)$$
$$R^{\cdot-} + H_2O \rightarrow RH^{\cdot} + OH^- \quad (4)$$
$$RH^{\cdot} + e = RH^- \quad (5)$$
$$RH^- + H_2O \rightarrow RH_2 + OH^- \quad (6)$$

was also examined[13], but it was rejected, since for this mechanism $E_{1/2}$ should have been dependent on pH, and this is not observed experimentally. Subsequent studies showed, however, that most compounds are nevertheless reduced according to the second mechanism.

Considerable progress in the study of the mechanism of the reduction of aromatic and unsaturated compounds has been made by applying quantum-chemical calculations to polarographic data. The foundations for this work were laid in a short note published by Maccoll[64]. By developing Hückel's idea of the existence of a relationship between the

energy of the lowest vacant π electron molecular orbital, into which the molecule can accept one or two electrons, and the ease of attachment of alkali metals to aromatic compounds, Maccoll observed a relationship between the reduction potential of an aromatic compound and the energy of the lowest vacant molecular orbital (MO).

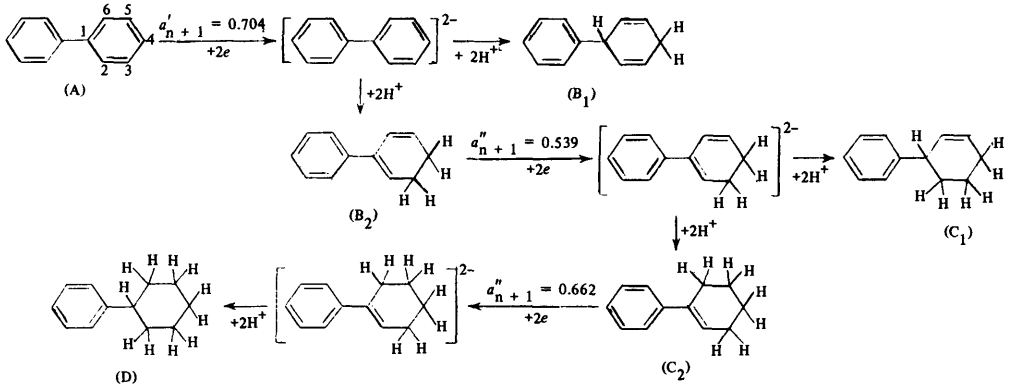
The best known subsequent papers are those of Hoijtink. In his first paper[22] he derived the relationship between $E_{1/2}$ and energy of the lowest MO:

$$E_{1/2} = a_{i+1}\beta - 1.05 \qquad (7)$$

(where a_{n+1} is a coefficient characterising the energy of the lowest vacant MO, β the exchange or resonance integral, and 1.05 the value of $E_{1/2}$ for the first wave of triphenylmethyl, taken as standard), and also put forward arguments which make it possible on the basis of these data to predict the direction of the process. Since $\beta < 0$ ($\beta \simeq -2.27 \pm 0.07$ eV [22]), the value of $E_{1/2}$ is more negative, the larger a_{n+1}.

Eqn. (7) is useful chiefly because it can be used to calculate $E_{1/2}$ for the starting material and the assumed products of the two-electron reduction. If the product has a more negative $E_{1/2}$ value than the starting material, the polarogram will show two two-electron waves; if it has a less negative $E_{1/2}$ value, one four-electron wave will be produced. Thus if the value of a_{n+1} for the starting material is greater than the value of a_{n+1} for the product, four-electron reduction ($n = 4$) should take place immediately.

The calculation also makes it possible to make predictions regarding the structure of the product. If we accept the mechanism of reduction proposed by Wawzonek[13] (reactions 1–3), the structure of the product (intermediate or final) will be determined by the distribution of the π electrons over all the carbon atoms of the framework of the molecular doubly-charged anion R^{2-} and the radical-anion $RH^{\cdot}$, since their protonation (reaction 3) will have the greatest probability at the carbon atom at which the negative charge is a maximum[64]. Hoijtink states[22] that consideration of the other mechanism (reactions 1, 4–6) leads to the same results. For example, for the reduction of biphenyl:



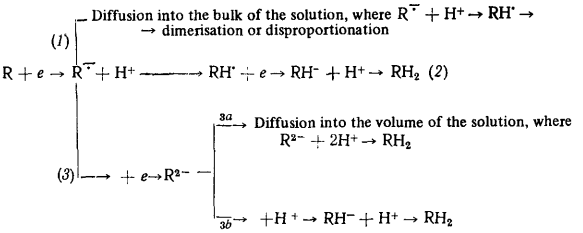
Calculations show that $a'_{n+1} > a''_{n+1}$ and $a'_{n+1} > a'''_{n+1}$. Thus all three substances, that is A, B_2, and C_2, should give a single reduction wave. Moreover, according to the calculation, in the AH^- anion obtained by the attachment of the first proton to the doubly-charged anion A^{2-}, the π electron density should be the same at the carbon atoms in positions 1, 3, and 5. Since positions 3 and 5 are identical, one third of the biphenyl (A) should be reduced to B_1, and two thirds to B_2. Of these two products, only B_2 can undergo further reduction, since B_1 contains only isolated double bonds. Thus the number of electrons in the second stage of the reduction, calculated on the biphenyl, is $n_2 = n_1 2/3 = 4/3$. For the same reasons, half of the intermediate product B_2 is reduced to the product C_1, which does not show polarographic activity, and half is reduced to C_2, which undergoes reduction to the polarographically inactive product D. The number of electrons in the third stage is $n_3 = n_2 1/3 = 2/3$, and the overall wave should correspond to the transfer of $n_{total} = n_1 + n_2 + n_3 = 2 + 4/3 + 2/3 = 4$ electrons. A mixture of products consisting of equal quantities of B_1, C_1, and D should be formed.

This examination was carried out for 12 aromatic hydrocarbons, and very good agreement was obtained between the values of $E_{1/2}$ and the experimental values[14] if allowance is made for the approximate nature of the method of calculating the values of a_{n+1} and the derivation of Eqn. (7).

An analogous approach was used in the examination of the reduction of diphenylpolyenes[37] with general formula $Ph-(CH=CH)_m-Ph$ ($m = 2-6$). For all the compounds studied, $a'_{n+1} < a''_{n+1} < a'''_{n+1}$ etc. Thus the diphenylpolyenes give separate waves for the reduction of individual double bonds.

Application of Wawzonek's mechanism led Chopard-dit-Jean and Heilbronner[65] to the conclusion that there is a difference in the mechanisms of reduction of alternant (for example naphthalene) and non-alternant (for example azulene) aromatic hydrocarbons. In their opinion, alternant hydrocarbons always give two-electron waves, whereas non-alternant hydrocarbons may give one-electron and two-electron waves. Hoijtink and coworkers[25] criticised this view and showed that in an aprotic medium both alternant and non-alternant hydrocarbons give a first one-electron wave. When even weak proton donors (e.g. water) are added, this wave in most instances becomes a two-electron wave. The first wave for azulene, however, even under these conditions, remains a one-electron wave, the reason for which will be examined below.

On the basis of these experimental results, the following general mechanism was proposed



In contrast to the mechanism of Laitinen and Wawzonek, it is assumed that $E_{1/2}$ for the attachment of the first electron is less negative than $E_{1/2}$ for the attachment of the second electron (path 3). On the other hand, $E_{1/2}$ for $RH^{\cdot}$ is always less negative than $E_{1/2}$, since a_{n+1} for this species is smaller than that for the original molecule R. Thus in the absence of proton donors, or when the protonation of the radical-anion $R^{\cdot-}$ is too slow (path 1), the attachment of only one electron takes place at the potentials of the first wave; the radical-anions formed diffuse into the bulk of the solution, where they are slowly protonated and either dimerise or disproportionate. At more negative potentials, the second electron is attached (path 3), and the doubly-charged anion is protonated. The second wave often corresponds to the transfer of more than one electron. This means that R^{2-} has a higher affinity for the proton and is able to undergo protonation in direct proximity to the electrode. If the new molecule RH_2 can undergo further reduction, this process also increases the second wave. The electron affinity of $R^{\cdot-}$ is less than that of RH_2 for, for example, perylene, coronene, fluoranthene, azulenes, and decacyclene.

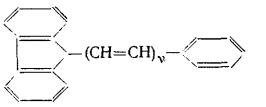
If the rate of protonation of the anion-radical $R^{\cdot-}$ is greater than the rate of diffusion of $R^{\cdot-}$, the $RH^{\cdot}$ radicals formed close to the electrode add on a second electron, the first wave is increased, and the wave for the reduction of $R^{\cdot-}$ at more negative potentials disappears. Path 3 can of course still be realised at these potentials, since in the final analysis increase in the cathode potential makes path 3 more rapid than path 2.

In experiments with the addition of weak proton donors, an intermediate case, where the rates of the diffusion and protonation of $R^{\cdot-}$ are commensurate, has been realised. As a result of simultaneous reduction by paths 1 and 2, the first wave acquires an intermediate height ($2 > n > 1$).

To obtain more information on the mechanism a detailed study has been made of the influence of the concentration of proton donors and the concentration of depolariser on the form of the waves and the magnitude of $E_{1/2}$.[25] An approximate method involving the use of the Nernst equation and the material balance equations was used to derive equations for the wave and $E_{1/2}$, which were compared with experiment. It is obvious that this derivation is inapplicable, if the transfer of both the first and the second electrons takes place reversibly. It has been shown[26] that the Nernst equation can be used if the rates of electron transfer in both directions are appreciably greater than the rates of the diffusion and attachment of protons to the anions.

Analysis of the properties of the waves for hydrocarbons in the presence of weak proton donors, again by an approximate method, made it possible to obtain relationships which correspond, qualitatively at least, to the experimental results. In this way, the new mechanism has to a large extent been confirmed.

In subsequent work, Hoijtink[26] extended the measurements to 1-phenyl-*p*-biphenylenepolyenes, 1-phenyl-*p*-(2,3-benzo)-biphenylenepolyenes, and dibiphenylenepolyenes in 75% and 96% dioxan. In 96% dioxan, the compounds studied gave polarograms with either two one-electron waves or one two-electron wave. It was shown that in the first instance the reduction takes place by Hoijtink's mechanism[25]. In the second instance, two mechanisms are possible: Hoijtink's mechanism (high proton affinity of $R^{\cdot-}$, leading to rapid protonation of $R^{\cdot-}$ and slow reduction of $RH^{\cdot}$) and the mechanism of Laitinen and Wawzonek (electron affinity of $R^{\cdot-}$ greater than that of R). Hoijtink was able to show that here the reduction (two-electron) takes place by the mechanism of Laitinen and Wawzonek. He observed the following relationship: the values of $E_{1/2}$ for both waves of 1-phenyl-*p*-biphenylenepolyenes (XI):



(XI)

become less negative with increase in the length of the polyene chain (with increase in ν), but in such a way that the difference in $E_{1/2}$ decreases. At $\nu = 6$, the values of $E_{1/2}$ for the two waves coincide. Analysis of the properties of the waves by means of a method similar to that just described showed that for substances which give two-electron waves in 96% dioxan, the reduction takes place by the mechanism of Laitinen and Wawzonek.

These results show that in the electrochemical reduction of hydrocarbons, direct transfer of electrons to the molecule being reduced takes place with the formation of radical and molecular carbanions. These anions are unstable towards protonation, but it might be expected that they would have appreciable stability in aprotic media. Various compounds, even in 96% dioxan, that is in a medium which is not strictly aprotic, give two one-electron waves on the polarograms. The radical-anions are evidently fairly stable even under these conditions. The direct observation of the formation of radical-anions and the study of their properties was of considerable interest. This problem was solved in two ways: by electrolysis in acetonitrile or DMFA[16] and by reaction with alkali metals in dimethoxyethane or tetrahydrofuran[66,67].

In acetonitrile and DMFA, a number of the compounds studied form one-wave polarograms ($n = 2$ for styrene, triphenylethylene, and tetraphenylethylene), whereas stilbene, anthracene, and 9-anisylidenefluorene give two waves of unequal height[16]: the first wave is appreciably higher than the second and on the addition of water or benzoic acid (in lower concentration) the first wave increases until it becomes the only wave.

Electrolysis of solutions in acetonitrile or DMFA on a large stationary mercury cathode in all instances produces an intense colour in the solution, characteristic of solutions of radical-anions. The products of the electrolysis of stilbene in DMFA were found to contain 1,2,3,4-tetraphenylbutane, which is evidently obtained by dimerisation of the radical-anions. Further proof of the existence of stable radical-anions was provided by the isolation of dicarboxylic acids from the products of the electrolysis of stilbene in the presence of carbon dioxide.

The reaction of metallic sodium with an aromatic hydrocarbon in dimethoxyethane or tetrahydrofuran gives a salt-like compound of sodium and the hydrocarbon, in which the hydrocarbon forms the anionic part. These compounds

are readily soluble in dimethoxyethane and in tetrahydrofuran and are completely or partly (for the disodium compound) dissociated.

Use has been made[66,67] of the fact that a solution of sodium biphenyl can be used to titrate solutions of other hydrocarbons which have a higher electron affinity than biphenyl. If the potential of the indicator electrode is measured, it is possible to determine the normal potentials of the hydrocarbons (relative to the potential of biphenyl). If the potential for the transfer of a second electron is sufficiently high, the titration may also give the radical-anion and the doubly-charged anion. Experiment showed that the values of the normal potentials obtained in this way are close to the values of the polarographic $E_{1/2}$, the difference in the values of $E_{1/2}$ for the first and second stages amounting to 0.4–0.6 V. The absorption spectra of the radical-anions of aromatic hydrocarbons have been measured[68] and it has been shown[69,70] that these spectra can be interpreted by the methods of quantum chemistry.

The spectra of the radical-anions on the one hand and of the doubly-charged anions on the other[71] have characteristic absorption bands, all the bands being displaced towards longer wavelengths with increase in the length of the conjugated system of double bonds (from stilbene to diphenyldodecahexaene). The reactions of radical-anions with aromatic hydrocarbons exhibiting a less negative half-wave potential have also been studied by EPR spectroscopy[60].

In their discussions, Hoijtink and coworkers suggested that the transfer of electrons to the hydrocarbon molecule and the hydrocarbon radical-anion takes place reversibly; the reversibility was proved by the methods of classical polarography (form of the wave). More rigorous proof can be obtained by alternating-current polarography, in which the reversible processes are characterised by the Faraday current peaks, which exhibit definite properties[72–74]. Hoijtink and coworkers studied the reduction of aromatic hydrocarbons and diphenylpolyenes in DMFA by alternating-current polarography and obtained the following results[47,48,51,57,75].

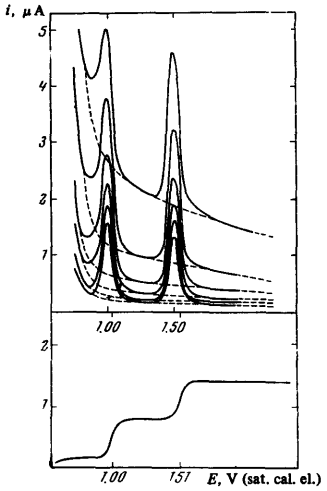


Figure 1. Alternating-current and classical polarograms for dibiphenyleneethylene in dimethylformamide. Frequency, Hz (from lower curve to upper): 32.1, 43.1, 62.5, 94.0, 174, and 392 (published data[47]).

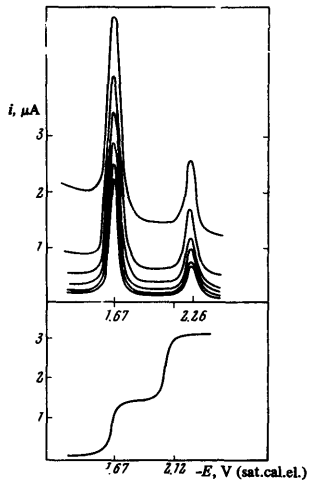


Figure 2. Analogous data for perylene in dimethylformamide.

The properties of the radical-anions of α,ω-diphenylpolyenes and tetraphenylcumulenes, that is compounds of the type $Ph_2=C=C=C=C=Ph_2$ (tetraphenylbutatriene) were studied in exactly the same way[71]. It was observed that the difference in the normal potentials of the first and second one-electron stages (and hence $\Delta E_{1/2}$) for these compounds is much smaller (~ 0.20 V) than that for aromatic hydrocarbons (0.4–0.6 V). The cumulenes are reduced much more readily than the polyenes, since the conjugation in the former is stronger. Polarographic study of tetraphenylbutatriene in DMFA and in aqueous dioxan solutions[53–55] confirmed these results. The intermediate products are tetraphenylbutadiene and tetraphenylbut-1-ene, in which the double bonds are conjugated with the phenyl groups and are reduced further. The final products are tetraphenylbut-2-ene (with an isolated double bond) and tetraphenylbutane.

The alternating-current polarograms for solutions of dibiphenyleneethylene (Fig. 1) and dibiphenylenebutadiene show two Faraday current peaks, corresponding to the two waves on the classical polarograms; on the alternating-current polarograms for aromatic hydrocarbons (tetracene, perylene, fluoranthene, anthracene, coronene, pyrene, 1,2-benzpyrene, and naphthalene) the second peak is always lower than the first peak (Fig. 2)[47]. Judging from the frequency dependence of i_f for both peaks of dibiphenyleneethylene and dibiphenylenebutadiene, both electrons are transferred reversibly. The second electron in the reduction of aromatic hydrocarbons is transferred irreversibly. It is suggested that the irreversibility of the transfer of the second electron for aromatic hydrocarbons is due to R^{2-} protonation, which, thanks to the high proton affinity of R^{2-}, takes place rapidly even in DMFA.

The first stage in the reduction of α,ω-diphenylpolyenes in DMFA is also reversible[48]. On the classical polarograms, however, the first wave is appreciably higher than the second (with the exception of stilbene, whose polarogram consists of two waves of equal height), and on going to higher α,ω-diphenylpolyenes, a tendency for the first wave to increase further at the expense of the second is observed. The second peaks on the alternating-current polarograms of all α,ω-diphenylpolyenes decrease with increase in the frequency of the applied alternating potential, indicating that the second stage of the reduction is irreversible (due to the protonation of R^{2-}). The increase in the first wave at the expense of the second is related to the protonation of the radical-anions $R^{\cdot-}$; the proton affinity of $R^{\cdot-}$ increases with increase in the number of double bonds in the α,ω-diphenylpolyenes. These experiments, however, do not give an unambiguous indication of the reason for the irreversibility of the second stage of the reduction, since it may also be due to slow transfer of the second electron to the radical-anion $R^{\cdot-}$. It has been pointed out[51] that the kinetics of this stage may be influenced by the structure of the electrical double layer.

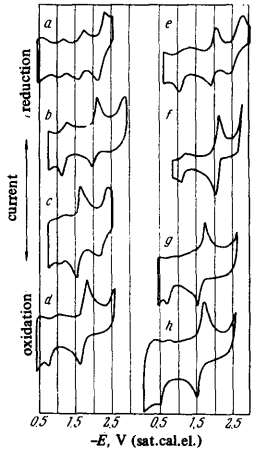


Figure 3. Cyclic polarograms in 0.1 M $(C_4H_9)_4NClO_4$ in dimethylformamide on a stationary platinum electrode for the two-electron reduction of: *a*) perylene; *b*) pyrene; *c*) tetracene; *d*) fluoranthene; *e*) 1,2-benzanthracene; *f*) coronene; *g*) acenaphthylene; *h*) acridine. 50 pulses per second (published data[76]).

It was later confirmed by cyclic volt-ammetry with a platinum electrode[76] or hanging mercury drop electrode[77] that the first stage in the reduction of polynuclear aromatic hydrocarbons (perylene, pyrene, tetracene, and various others) in an aprotic medium is reversible, whereas the second stage is partly or completely irreversible; the anodic branch of the cyclic volt-amperogram shows a clearly defined peak due to oxidation of the radical-anion, whereas the peak for the oxidation of the doubly-charged anion is either very small or completely absent (Fig. 3).

The question of whether it is possible in principle to achieve the electrochemical preparation of triply-charged radical-anions of aromatic hydrocarbons by the attachment of three electrons is of considerable interest. It has been reported[78] that the electrolysis of tetracene in acetonitrile at −2.5 V gives radical species whose EPR signal differs from that of the singly-charged tetracene radical-anion. Hoijtink[57] showed by alternating-current polarography that these experiments actually gave the singly-charged dihydrotetracene radical-anion. The alternating-current polarogram of tetracene shows two Faraday current peaks, corresponding to the first and third waves on the classical polarogram of tetracene. This means that the second stage of the reduction of tetracene is irreversible, because of the rapid protonation of R^{2-} with the formation of dihydrotetracene, whose molecule still contains the naphthalene aromatic system. The third wave on the classical polarogram and the second peak on the alternating-current polarogram thus correspond to the transfer of a single electron to the dihydrotetracene molecule with the formation of the radical-anion. This of course does not mean that the formation of triply-charged radical-anions is in general excluded, but the probability of their production is low, because of their extremely high proton affinity.

We see that the application of the methods of quantum chemistry makes it possible to predict the path for the reduction of complex aromatic and unsaturated compounds. In practice, however, the most probable route is not always realised. For example, according to theory, biphenyl should undergo four-electron reduction in one wave with the formation of a mixture of three substances[22], whereas the experimental results[14] show that it gives only one two-electron wave.

To explain these discrepancies, Hoijtink introduced the idea that the electrical field of the double layer on the electrode or of the counter-ions in solution (primarily protons) influences the electron density distribution in the doubly-charged hydrocarbon anions, determining the nature of the product in the first stage of the reduction[79,80]. In the Soviet literature, this view is held in particular by Bezuglyi[81-83]. Calculations showed[79] that up to a field strength of 1.5 V/Å the negative charge in the doubly-charged naphthalene anion remains greatest in the peri-positions (1,4 or 5,8), whereas in the doubly-charged anions of anthracene, phenanthrene, pyrene, and terphenyl, under the influence of the electric field, the negative charge may be greatest at positions which are not the positions at which it is a maximum in the absence of the field. The change in the reaction centre in the doubly-charged anion takes place at a field strength of about 0.6 V/Å for anthracene, at a strength of about 0.2 V/Å for phenanthrene, and at the even smaller strength of 0.12 V/Å for terphenyl. Thus if the aromatic hydrocarbon is reduced in a protonic solvent and its doubly-charged anion is protonated on the electrode surface, the electric field at the electrode can in principle influence the direction of the process. For example, for anthracene it has been shown theoretically that the primary product is 9,10-dihydroanthracene at field intensities below 7×10^7 V/cm, and 1,4-dihydroanthracene at higher field intensities. In the first instance the molecule has two isolated benzene rings, and under the conditions of polarography, 9,10-dihydroanthracene will be the final product. In the second instance, the molecule of the product still contains a naphthalene system and an isolated double bond. A second wave due to reduction of the naphthalene group should therefore be observed. Hoijtink pointed out the generality of the mechanism of the electrochemical, chemical, and catalytic hydrogenation of aromatic and arylethylenic hydrocarbons (with the primary attachment of one or two electrons to the molecule being reduced). On this basis, he introduced into the analysis of the experimental results data on not only the electrochemical reduction (primarily polarographic data), but also

on chemical reduction (by alkali and alkaline earth metals in inert and proton-active solvents) and on catalytic hydrogenation. These results for the most part agree with the conclusions of the theory. By comparing the compositions of the products obtained under different conditions with the theoretical schemes, it is possible to estimate the magnitude of the electric field gradient under the conditions of a given experiment. For example, the catalytic hydrogenation of anthracene in a solvent of low dielectric constant gives a mixture of 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene, whereas more severe hydrogenation conditions give a mixture of symmetrical and unsymmetrical octahydroanthracenes. This means that the intensity of the field acting on the doubly-charged anion under these conditions is $(6-7) \times 10^7$ V/cm.

From this interesting and important work it follows that the reduction of even fairly simple aromatic hydrocarbons is a complex process. Thus if an organic compound gives a polarogram with two two-electron waves, determination of the nature of the product in the first stage of the reduction is not sufficient to enable a definite conclusion to be reached regarding the nature of the product in the second stage of the reduction. In general, the second wave may be produced as a result of the change in the nature of the product from the first reduction stage with increase in the electric field strength close to the electrode. In principle, this change may also take place without visible transformation of the polarogram. Thus the study of the mechanism of the reduction of complex organic compounds should combine a study of the nature of the influence of many factors with an analysis of the products obtained (see for example Refs. 84 and 85).

A number of papers have been devoted to a more detailed study of the action of proton donors on the reduction of aromatic compounds in an aprotic medium. Schwabe and Schmidt[36] found that when water is added to a dioxan solution of anthracene, fluorene, and pyrene, the first one-electron wave increases at the expense of the second, so that when the concentration of ethanol is sufficiently high, the polarogram shows only one two-electron wave.

Given and Peover[4,49,50] made a detailed study of the influence of various proton donors on the polarography of aromatic hydrocarbons and found that the most convenient proton donor is phenol, which is a sufficiently powerful donor, but which does not give a hydrogen liberation wave. Benzoic acid and HI are inconvenient, because in their solutions the hydrogen liberation waves mask the waves due to the reduction of the aromatic hydrocarbons. Acetic acid is used as an even stronger proton donor. The proton-donating properties of water are too weak, so that its action is appreciable only at high concentrations.

By analysing the form of the first wave for a number of aromatic compounds in the presence of a proton donor at concentrations sufficiently high for the first wave to be a two-electron wave, Given and Peover established that in DMFA the protonation is brought about by undissociated molecules of the proton donor (MA) and not by solvated protons. This conclusion cannot be regarded as proved for all proton donors used, however.

The nature of the action of proton donors depends on the nature of both the proton donor and the depolariser. Given and Peover distinguish various possibilities.

1. If the addition of the proton donor leads to the protonation of the anion-radical $R^{\cdot-}$ produced by attachment of the first electron, the first wave increases at the expense of the second until the latter disappears completely, since the radical $RH^{\cdot}$ is reduced more readily than the original molecule. Most aromatic hydrocarbons behave in this way.

2. If only the doubly-charged ion R^{2-} produced after the attachment of the second electron is protonated fairly rapidly, the first wave remains unchanged on the addition of the proton donor (the anion-radical $R^{\cdot-}$ is too weak a base), but the second is displaced towards less negative potentials. This behaviour is characteristic of quinones.

3. If the original molecule R is protonated, a new wave corresponding to the reduction of the protonated complex is produced in the range of less negative potentials. This behaviour is observed for aromatic carbonyl compounds.

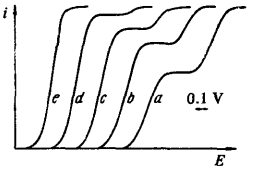


Figure 4. Influence of increase in the concentration of water on the polarogram for anthracene: *a*) 96% dioxan; *b*) 92% dioxan; *c*) 89% dioxan; *d*) 75% dioxan; *e*) 96% dioxan + 2×10^{-4} M HI (published data[25]).

4. The protonation of the doubly-charged anion makes more extensive (multi-electron) reduction possible. When the proton donor is added, the second wave is not only displaced towards less negative potentials but also undergoes an increase in height. Sometimes, additional waves appear. This behaviour is observed for pyrene, perylene, and phenanthrene.

5. If dimerisation of the radical-anions or radicals plays a significant part in the electrode process, a complex picture is observed on the introduction of proton donors. Sometimes, between the two original waves there appears a new wave, which increases with increase in the concentration of the proton donor at the expense of the second wave (benzaldehyde and xanthone in the presence of phenol).

This summary shows that experiments with the addition of proton donors in general do not contradict Hoijtink's scheme for the reduction of aromatic hydrocarbons. In fact, it may be considered that these experiments provide further important evidence in support of the scheme.

Grodza and Elving[56,86] tried to apply various criteria of classical polarography to the determination of the mechanism of the reduction of arylethylenes in ahydrous DMFA and in DMFA–water mixtures (80% or 90% DMFA). The experimental results for styrene, stilbene, 1,1-diphenylethylene, triphenylethylene, and tetraphenylethylene do not satisfy completely any of the postulated mechanisms. These authors consider, however, that the idea that the mechanism of the reduction changes along the polarographic wave corresponds most closely to the experimental results. At the foot of the wave, the reduction is preceded by protonation of the hydrocarbon molecule, whereas close to the limiting current plateau it is followed by protonation of the carbanions ($R^{\cdot-}$ or R^{2-}). Nevertheless, the mechanism involving preliminary protonation of the hydrocarbons in an aprotic medium can hardly be accepted. The authors themselves attribute their lack of success in attempts to

establish the mechanism reliably to the influence of the structure of the electrical double layer, for which it is difficult to allow.

Experiment indicates[87] that aprotic media show different efficiencies in increasing the difference in $E_{1/2}$ for the separate stages of the reduction (differentiating action). Thus for 9,10-anthraquinone and its derivatives in alkaline aqueous-alcoholic or aqueous-dioxan solutions, $\Delta E_{1/2} = 0.16-0.18$ V; in acetonitrile in a supporting electrolyte of $(C_2H_5)_4NClO_4$, $\Delta E_{1/2} \simeq 0.5$ V; and in DMFA in the same supporting electrolyte, $\Delta E_{1/2} \simeq 0.7$ V. The phenomenon must undoubtedly be attributed to the difference in the rates of protonation of the carbanions. The magnitude of $\Delta E_{1/2}$ is influenced not only by the solvent, however, but also by the dissolved electrolyte. For example, for the same derivatives of 9,10-anthraquinone in DMFA in a supporting electrolyte of LiCl, $\Delta E_{1/2} = 0.30$ V, and in a supporting electrolyte of $(C_2H_5)_4NClO_4$, $\Delta E_{1/2} = 0.70$ V. It has been suggested that the influence of the electrolyte is also manifested in a displacement of the acid-base equilibrium, but it is of course not excluded that it is due to some extent to the influence of the change in the structure of the electrical double layer. Moreover, as shown by Peover and Davis[88], the association of the carbanions with the counter-ions of the electrolyte may have a significant influence. Ion association is responsible for the displacement of the wave towards less negative potentials, and the effect may be considerable. Thus for R^- the change from Li^+ to $(C_4H_9)_4N^+$ gives an effect of about 40 mV, whereas for R^{2-} it amounts to 300–600 mV. An even greater effect is produced by positive cations. For example, Nd^{3+} cations at a concentration of 2×10^{-3} M displaces the first wave for quinone by 550 mV, and the second by as much as 950 mV. Thus $\Delta E_{1/2}$ for the change from Li^+ to $(C_4H_9)_4N^+$, according to the data of Peover and Davis[88], decreases, whereas according to the data of Kheifets and Bezuglyi[87] it increases. The reason for the discrepancy in these result is not known.

The radical states postulated for the reduction of aromatic hydrocarbons have been studied many times by EPR spectroscopy[46,58,60]. It has been shown that the electrolysis of solutions of anthracene, anthraquinone, and benzophenone in an aprotic medium at the potentials of the limiting current of the first wave gives solutions with a high concentration of radical-anions[46]. The final products, however, were the dihydro-derivatives. This means that the radical-anions do not undergo dimerisation, but are protonated and undergo further electrochemical reduction. The radical-anions (unlike the radicals, whose EPR spectra are not recorded) are fairly stable, and although it is not stated in the works cited, their stability is undoubtedly due to the presence of the charge, which provides significant hindrance to both disproportionation and dimerisation.

In an elegant piece of work, Umemoto[60] used the EPR method to investigate the fate of the radical-anions in the bulk of the solution. The radicals were generated in an electrochemical cell, from which the solution was circulated along a capillary passing through the resonant cavity of the EPR spectrometer. The kinetics of the disappearance of the radical-anions were studied in the stationary solution (after the flow of solution through the capillary had stopped). The concentration of water was varied over a wide range (0–40%). The radical-anions in the bulk of the solution are protonated $R^- + H_2O \rightarrow RH^{\cdot} + OH^-$ and either are reduced at the electrode (if the radicals reach it, for example, in the cell) or remove an electron from another R^- radical-anion: $RH^{\cdot} + R^- \rightarrow RH^- + R$ (disproportionation). This reaction is possible since the $RH^{\cdot}$ radical has a greater electron affinity than the R^- radical-anion. Kinetic study showed that the reaction of the RH radicals with the R^- radical-anions is the only route by which the radical-anions disappear in the bulk of the solution.

III. REDUCTION IN STRONGLY ACIDIC MEDIUM

A solution of perylene in concentrated sulphuric acid shows absorption in the EPR spectrum similar to the absorption of a solution of the R^- radical-anion. The ultraviolet spectra of solutions of perylene in concentrated sulphuric acid and of its radical-anion in tetrahydrofuran[89] are also very similar. The suggestion that the radical-anions are formed in the sulphuric acid solutions is rejected on the basis of the fact that the reduction of perylene in these solutions corresponds to a polarographic wave for which $E_{1/2}$ is less negative by 0.5 V than $E_{1/2}$ for the triphenylcarbonium ion. Moreover, $E_{1/2}$ for the radical-anion of perylene (second wave for perylene) is more negative by 0.7 V than $E_{1/2}$ for the triphenylmethyl radical. Thus in solutions of perylene in sulphuric acid, singly-charged cations or the products of the attachment of protons (proton complexes) are formed[89].

Subsequent studies[90] showed that the proton complexes of aromatic hydrocarbons RH^+ in the presence of oxidising agents (oxygen, sulphuric acid, etc.) may be converted into R^+ cations, for example according to the reaction:

$$RH^+ + O_2 \rightarrow R^+ + HO_2^{\cdot} . \qquad (8)$$

If oxygen is removed from the solution, the hydrocarbon cations are slowly converted into proton complexes. The polarograms for solutions of perylene, tetracene, anthracene, and 3,4-benzpyrene in a mixture of trifluoroacetic acid and boron trifluoride, free from oxygen, each show two waves (Fig. 5)[91]. The first wave, lying in the range of negative potentials, is assigned to the reduction of hydrocarbon cations

$$R^+ + e \rightarrow R \qquad (9)$$

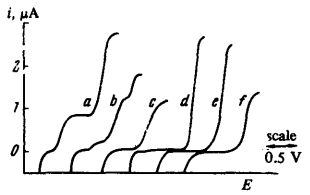


Figure 5. Polarograms for 10^{-3} M solutions of perylene (*a*), tetracene (*b*), anthracene (*c*), 3,4-benzpyrene (*d*), pyrene (*e*), and 1,2-benzanthracene (*f*) in $CF_3COOH + H_2O.BF_3$ (29 mole %) (published data[91]).

For the same concentrations of the hydrcarbons, the heights of the first waves differ considerably, due to the difference in the stabilities of the cations in the absence of oxygen. For this reason, the polarograms for pyrene and 1,2-benzanthracene do not show the first waves at all.

The second waves in most instances are twice as high as the first. This is observed particularly clearly in the polarograms for perylene, which is converted completely

into the cationic state. Thus the second wave is assigned to the two-electron reduction of the proton complexes RH^+:

$$R + H^+ \rightarrow RH^+ \quad (10)$$

$$RH^+ + e \rightarrow RH^{\cdot} \quad (11)$$

$$RH^{\cdot} + H^+ \rightarrow RH_2^{+\cdot} \quad (12)$$

$$RH_2^{+\cdot} + e \rightarrow RH_2 \quad (13)$$

From these studies it follows that the hydrocarbon cations are reduced more readily than the corresponding proton complexes. The proton complexes of hydrocarbons with linearly fused rings (anthracene, tetracene, and 1,2-benzanthracene) are reduced much more readily ($\Delta E_{1/2} \simeq 0.2$–$0.4$ V) than hydrocarbons with rings fused in angular fashion (pyrene, 3,4-benzpyrene, and perylene). It is suggested that the greater stability of the proton complexes of angular hydrocarbons to reduction is related to the more even distribution of the positive charge in the RH^+ cations of these hydrocarbons

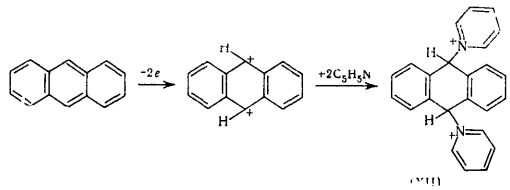
The electrolysis of a solution of perylene in trifluoroacetic acid containing a small quantity of H_2SO_4 (a relatively weakly oxidising medium) at the potentials of the limiting current of the first wave gave the original hydrocarbon—perylene[92]. This confirmed the suggestion that the first wave corresponds to the reduction of the R^+ cation.

IV. MECHANISM OF OXIDATION

The mechanism of the electrochemical oxidation of aromatic hydrocarbons has been studied by modern methods exclusively in an aprotic medium[62,77,93–105]. Either 0.1–2 M sodium perchlorate or 0.1 M tetraethylammonium perchlorate have been used as supporting electrolyte. Oxidation has been studied at vibrating[93,102], stationary[62,94,104], or rotating[77,95–97,99–101,103,105] platinum electrodes. Ag/Ag^+ or aqueous saturated calomel electrodes have been used as reference electrodes. With the latter, precautions were taken to prevent the entry of water into the solutions being studied.

Lund[93] found that a large number of aromatic hydrocarbons give normal or deformed oxidation waves, which he attributed to the removal of two electrons from the highest occupied molecular orbitals, the process involving only one benzene ring of the polynuclear hydrocarbon. Thus tetracene gives a second wave with approximately the same $E_{1/2}$ value as 5,12-dihydrotetracene, close to $E_{1/2}$ for a 2,3-dialkylnaphthalene. In lund's opinion, normal waves are given only by compounds for which the products of the two-electron oxidation are stable. For example, the product of the oxidation of indene, in Lund's opinion, is indane, that is a stable product, whereas the product of the oxidation of fluorene—presumably a derivative of dihydrofluorene—has a marked tendency to polymerise, so that the electrode is insulated from the solution by a layer of insoluble polymer. Other authors[77,96] also attribute the distortion of the waves to the adsorption of oxidation products on the electrode.

The removal of two electrons previously localised on one or two carbon atoms should lead to the formation of a doubly-charged carbonium cation. For example, for anthracene the charges are localised in positions 9 and 10. In the presence of electron donors such as pyridine, the doubly-charged cation is stabilised by the attachment of two molecules of the electron donor in the 9 and 10 positions:



(14)

(XII)

Preparative electrolysis of anthracene in acetonitrile in the presence of pyridine did in fact give 9,10-dihydroanthranyldipyridinium diperchlorate (XII). This compound contains only isolated benzene rings, so that it is not oxidised further (at the oxidation potential of anthracene). According to Lund's data, the $E_{1/2}$ values for the oxidation waves for aromatic alcohols[106] and the original aromatic hydrocarbons are very close, and on this basis he concluded that the first stage in the oxidation of the aromatic alcohols also involves the removal of two electrons from the aromatic rings.

The behaviour of aromatic hydrocarbons differs considerably for electrochemical reduction and oxidation. The attachment of a second electron takes place at a much more negative poential than that of the first, whereas in oxidation, two electrons are removed at the same potential. However, since the highest occupied and lowest vacant molecular orbitals in alternant hydrocarbons are positioned symmetrically with respect to the energy level of the atomic orbital (taken as zero), we should expect the aromatic hydrocarbons to show analogous behaviour during reduction and oxidation, that is successive removal or attachment of two electrons at significantly different potentials[77]. More distinct waves for the oxidation of aromatic hydrocarbons were obtained with a rotating indicator electrode[95,97] than with a vibrating electrode[93]. The electrolysis of anthracene in acetonitrile in the absence of pyridine gave the dimeric product bianthrone[98]. It has been possible to record the EPR spectra of the radical-cations produced in the oxidation of methoxybenzene[99] and 9-arylaminoanthracenes[105].

Study of the oxidation of aromatic hydrocarbons by cyclic volt-ammetry[62] showed that more positive $E_{1/2}$ values are obtained by using fast voltage sweeps than by using slow sweeps. The difference is attributed to the influence of conjugated chemical reactions of the radical-cations, which is felt when slow sweeps are used but not when fast sweeps are used. According to these results[62], the radical-cations are much less stable with respect to reaction with the solvent (their lifetime is of the order of several milliseconds) than the radical-anions produced during reduction.

According to the results[77] of the study of the oxidation of 60 hydrocarbons, the polarisation curves recorded by the classical polarograph give distinct first waves, whose slope (60–80 mV) corresponds to that for a reversible one-electron process. For *p*-phenylenediamine and its *N,N'*-tetramethyl derivative, alternating-current polarography showed a high degree of reversibility for both one-electron oxidations. Anilines give distinct one-electron waves, and also waves corresponding to further oxidation at more positive potentials. When pyridine is added, the first wave becomes a two-electron wave, probably as a result of an increase in the rate of the removal of a proton from the radical-cation. For dibenzanthracene, dibenzpyrene, 3,4-benzpyrene, and pyrene, the first waves are again one-electron waves. Other hydrocarbons give many-electron

waves; for example, the first wave for anthracene corresponds to the transfer of five electrons. In the work cited[77] various hydrocarbons were also studied by cyclic volt-ammetry with a stationary platinum electrode. The radical-cations of different hydrocarbons have different stabilities. Thus 9,10-dimethylanthracene at a rate of change of potential equal to 10–20 V min^{-1} shows a peak corresponding to the reduction of the radical-cation. The doubly-charged cation is even less stable. The radical-cation of anthracene is less stable than that of its 9,10-dimethyl derivative. The oxidation products of 1,2,5,6-dibenzanthracene are very unstable. Many-electron waves are observed when the product of the subsequent transformation of a very unstable radical-cation, which is produced by removal of the first electron, can undergo further oxidation at the potential of formation of the radical-cation. These results show that the removal of two electrons produces the same situation as the attachment of electrons: the successive removal of two electrons, sometimes complicated by chemical transformation of the radical-cation.

The radical-cations of aromatic hydrocarbons are more stable in methylene chloride than in acetonitrile[104]. For 9,10-diphenylanthracene, rubrene, and 1,3,6,8-tetraphenylpyrene, cyclic volt-ammetry with a stationary electrode has shown completely reversible one-electron processes, whereas for tetracene and anthracene, rapid chemical reactions take place under these conditions.

In the preceding section of this review it was shown that in strongly acidic media (concentrated sulphuric acid or a mixture of trifluoroacetic acid and boron trifluoride) the radical-cations of various hydrocarbons are fairly stable. The stability is apparently due to the difficulty of removing a proton from the radical-cation in strongly acidic media. From this it may be concluded that in aprotic solvents the low stability of the radical-cations is probably due to the possibility of proton removal

$$M^{\cdot+} \rightarrow R^{\cdot} + H^{+} \qquad (15)$$

The radicals formed may undergo subsequent reactions (dimerisation, disproportionation, oxidation). The study of the stages involved in the oxidation of aromatic hydrocarbons may apparently be more successful in strongly acidic than in aprotic media. If the reaction

$$R^{\cdot+} + e \rightarrow R \qquad (9)$$

studied in strongly acidic media, and

$$R \rightarrow R^{\cdot+} + e \qquad (16)$$

studied in aprotic media, are completely reversible, the $E_{1/2}$ values of the corresponding waves should be the same. Unfortunately, the $E_{1/2}$ values can be compared only very roughly, since the $E_{1/2}$ values for reaction (9) in strongly acidic media were measured either relative to the mercury bottom[92] or relative to the potential of the start of the dissolution of mercury[91], whereas the $E_{1/2}$ values for reaction (16) in aprotic media were measured either relative to an Ag/Ag^{+} reference electrode (with fast potential pulses)[62] or relative to an aqueous saturated calomel electrode (with slow potential pulses)[77]. The errors become even greater due to neglect of the interphase potentials. The difference in the $E_{1/2}$ values is greater than the maximum possible errors, however. Thus for perylene, according to a rough estimate, $E_{1/2}$ (sat. cal. el.) is +0.1V for reaction (9) and +1.04 V for reaction (16). This discrepancy is possibly due to the fact that the processes taking place are actually more complex than at present assumed.

From the foregoing it follows that for an exact comparison of the $E_{1/2}$ values of oxidation with other molecular parameters it is necessary to determine $E_{1/2}$ by cyclic volt-ammetry with fast potential pulses, as in Ref. 62.

V. CORRELATION OF THE VALUES OF THE HALF-WAVE POTENTIALS

At the present time, in the polarography of aromatic and unsaturated hydrocarbons, extensive use is made of correlations between the values of the half-wave potentials and various molecular constants. The most important of these is undoubtedly the correlation of the half-wave potentials with the energies of molecular orbitals. This has made possible a fairly rigorous verification of the conclusions reached by applying quantum-chemical calculations to the molecules of aromatic and unsaturated hydrocarbons. It has been correctly noted[107] that the application of correlation relations makes it possible to predict $E_{1/2}$ values for compounds which have not been studied, and also to find molecular parameters which are not readily obtainable by other methods, such as ionisation potentials and electron affinities. Thus the study of correlation relations is stimulating further experimental and theoretical studies in this field.

Correlations are most successful when the mechanism of reduction or oxidation is the same for the series of compounds being considered and particularly when these processes are reversible. This last feature is necessary for the application of the relationships for thermodynamically reversible processes.

The idea forming the basis of the correlation of $E_{1/2}$ with the energies of molecular orbitals was formulated by Maccoll[64], who extended to the electrochemical reduction of aromatic hydrocarbons Hückel's concept of the relationship between the energy of the lowest vacant molecular orbital and the ease of attachment of alkali metals to aromatic hydrocarbons. In both instances, one or two electrons (from the alkali metal or the electrode) are transferred to the lowest vacant antibonding molecular orbital. The reversible reduction potential is related to the changes in enthalpy (ΔH) and entropy (ΔS) by the familiar relationship

$$nFE_0 \quad \Delta H - T\Delta S \,. \qquad (17)$$

It is subsequently pointed out that ΔH depends on the energy required for the transfer of one or two electrons to the lowest vacant orbital, that is it is related to the coefficient a_{n+1} in the expression for the energy of the lowest vacant orbital. Comparison of the $E_{1/2}$ values found by Wawzonek and Laitinen[13,14] with the coefficients a_{n+1} calculated by the simple Hückel molecular orbital method (Fig. 6) showed a fairly good linear relationship between these quantities.

This idea was used by Lyons[108] to predict the influence of substituents on the value of $E_{1/2}$ by calculating the change in the energy of the lowest vacant molecular orbital on introduction of the substituent. If the energy of the lowest vacant molecular orbital is increased, reduction is made more difficult, and vice versa. For example, for the introduction of a methyl group into the pyridine ring, theory predicts a displacement of $E_{1/2}$ by 30 mV towards more negative potentials.

Pullman and coworkers[109] verified the correlation of $E_{1/2}$ with a_{n+1} for a large number of compounds (alternant aromatic hydrocarbons and unsaturated compounds). It was found that the plot of $E_{1/2}$ against a_{n+1} cannot be represented by a single straight line for all groups of com-

pound. The linear relationship is observed most rigorously for condensed benzenoid hydrocarbons. Linear condensation of the benzene rings leads to a decrease in a_{n+1} and to an increase in the ease of reduction. The easier reduction of anthracene compared with phenanthrene indicates that the energy of the lowest vacant orbital is greater in phenanthrene. This correlation predicts that for benzene the half-wave potential should be about -3.6 V, This explains why benzene cannot be reduced by direct transfer, whereas reduction by the most active alkali metal—lithium—takes place when it is produced electrochemically[44,110]. The data of phenylethylenes and phenylacetylenes do not fall within the $E_{1/2}$–a_{n+1} correlation for benzenoid hydrocarbons[109]. They lie on an independent straight line, with the exception of the results for tetraphenylethylene. The deviation of this group of compounds from the general straight line is related[109] to the limited accuracy of the calculation of a_{n+1}.

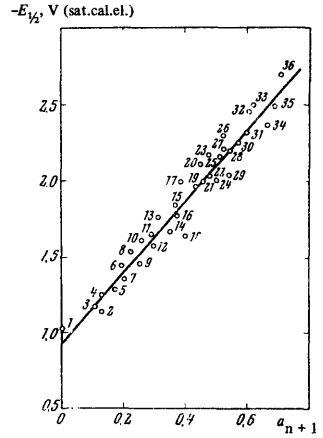


Figure 6. Dependence of the half-wave potentials (in aqueous dioxan) on the coefficient a_{n+1}:
1) triphenylmethyl; *2*) 1,4-dibiphenylenebutadiene; *3*) 1,6-dibiphenylenehexatriene; *4*) 1-phenyl-12-biphenylenedodecahexaene; *5*) 1-phenyl-8-biphenyleneoctatetraene; *6*) 1,12-diphenyldodecahexaene; *7*) 1-phenyl-6-biphenylenehexatriene; *8*) 1,10-diphenyldecapentaene; *9*) 1-phenyl-4-biphenylenebutadiene; *10*) 1,8-diphenyloctatetraene; *11*) acenaphthylene; *12*) anthanthrene; *13*) 1,6-diphenylhexatriene; *14*) perylene; *15*) 1,2-benzpyrene; *16*) fluoranthene; *17*) 1,4-diphenylbutadiene; *18*) azulene; *19*) anthracene; *20*) pyrene; *21*) 1,2-benzanthracene; *22*) 1,2,5,6-dibenzanthracene; *23*) 1-phenylbutadiene; *24*) 4,5-benzpyrene; *25*) stilbene; *26*) chrysene; *27*) 2,2′-binaphthyl; *28*) quaterphenyl; *29*) coronene: *30*) 1,1-diphenylethylene; *31*) terphenyl; *32*) phenanthrene; *33*) naphthalene; *34*) styrene; *35*) triphenylene; *36*) biphenyl (published data[2]).

The fact that tetraphenylethylene does not fall within the correlation for the unsaturated compounds is tentatively attributed to the non-coplanarity of this compound, as a result of which the conjugation is is weakened, the lowest vacant orbital is raised, and the reduction is made more difficult. Other authors[27,31,82,111,112] have also drawn attention to the part played by coplanarity. Thus according to Hoijtink's data[27], the molecules of such aromatic hydrocarbons as 9,9′-bianthryl, rubrene, and 1,1′-binaphthyl are also non-coplanar, their structure being much closer to one in which the separate parts of the molecule joined by simple C–C bonds are mutually perpendicular, since the $E_{1/2}$ values almost coincide with those for anthracene, tetracene, and naphthalene. The effect of departure from coplanarity in the arylethylene series has been studied in more detail. Pointeau and de Villepin[111] calculated the dependence of the energy of the lowest vacant orbital for biphenyl derivatives on the angle between the planes of the two rings and compared the results with experimental measurements. In the calculations it was assumed that the energy of the orbital is a sinusoidal function of the angle between the rings. The calculation showed that even fairly marked departure from coplanarity gives a scarcely perceptible effect. Thus for rotation of the rings through 20° we should expect a change in $E_{1/2}$ by only 40 mV. The departure from coplanarity was brought about by the introduction of substituents into the ortho-position. The expected effect could not be detected, however, since it was masked by the effects of the substituents.

The effect of the departure from coplanarity is also revealed[82] by comparing the $E_{1/2}$ values for two aromatic compounds with the same number of benzene rings, of which one is condensed, so that the molecule must be planar, whereas the molecule of the other contains a simple C–C bond, about which rotation of sections of the molecule can take place. It is true that the molecules of these compounds also differ in the number of π electrons, so that the effect of coplanarity cannot be established in pure form. Nevertheless, this comparison is useful. Thus $E_{1/2}$ for naphthalene is less negative by 95 mV than $E_{1/2}$ for biphenyl; for anthracene and terphenyl, $\Delta E_{1/2} = 445$ mV, and for tetracene and quaterphenyl, $\Delta E_{1/2} = 630$ mV. The values of $E_{1/2}$ were taken from Bergman's papers[39,40].

Phenylacetylenes are less readily reduced than phenylethylenes[109]. This phenomenon is due to the greater localisation of electrons on the triple bond and the consequent raising of the lowest vacant orbital.

A detailed derivation of the relationship between $E_{1/2}$ and a_{n+1} was first tiven by Hoijtink and van Schooten[22].

For the change in free energy for the attachment of an electron to a conjugated molecule R, which is related to the reduction potential by Eqn. (17), we can write

$$\Delta G^0 = [\mu^0_R]_{aq} + [\mu^0_{el}]_{Hg} - [\mu^0_{R^-}]_{aq} \qquad (18)$$

where $[\mu^0_R]_{aq}$ and $[\mu^0_{R^-}]_{aq}$ are the chemical potentials of the molecule R and the radical-anion R^- in solution, and $[\mu^0_{el}]_{Hg}$ the chemical potential of the electron in mercury. Eqn. (18) transforms into

$$\Delta G^0 = [\mu^0_R]_g + [\mu^0_{el}]_{Hg} - [\mu^0_{R^-}]_g + [\Delta G^0]_{solv} \qquad (19)$$

where the subscript "g" denotes the gaseous state, and $[\Delta G^0]_{solv}$ is the change in ΔG^0 resulting from the solvation of R and R^-. $[\mu^0_R]_g - [\mu^0_{R^-}]_g$ is equal to the electron affinity of the molecule R in the gaseous state (A). Thus

$$\Delta G^0 = A + [\mu^0_{el}]_{Hg} + [\Delta G^0]_{solv} \qquad (20)$$

But,

$$E = E_0 + \frac{RT}{F} \ln \frac{C_R}{C_{R^-}} = E_{1/2} + \frac{RT}{F} \ln \frac{(i_d - i)}{i} \qquad (21)$$

$$E_0 = \frac{\Delta G^0}{F} = E_{1/2} + \frac{RT}{F} \ln \frac{D_R^{1/2}}{D_{R^-}^{1/2}} \qquad (22)$$

From Eqns. (20) and (22) we have

$$A = FE_{1/2} + RT \ln \frac{D_R^{1/2}}{D_{R^-}^{1/2}} - [\mu_{el}^0]_{Hg} - [\Delta G^0]_{solv} . \quad (23)$$

To the first approximation it may be assumed that $\lg (D_R/D_{R^-})^{1/2}$ and $[\Delta G^0]_{solv}$ are the same for the compounds being considered. We then have

$$A = FE_{1/2} + C . \quad (24)$$

The electron affinity is equal to the negative value of the energy of the lowest vacant orbital $(n + 1)$:

$$\varepsilon = \alpha - a_{i+1}\beta \quad (25)$$

where α is the energy of a π electron localised on an individual carbon atom, β the exchange integral for two neighbouring carbon atoms, and a_{n+1} the numerical coefficient obtained by solving the secular equation in the method of molecular orbitals. Thus

$$-\alpha + a_{n+1}\beta = FE_{1/2} + C . \quad (26)$$

The constants α and C are eliminated by writing the difference for the two compounds:

$$\begin{gathered} -\alpha + a_{i-1}\beta = FE_{1/2} + C \\ -\alpha + a'_{i+1}\beta = FE'_{1/2} + C \\ \hline (a_{n+1} - a'_{n+1})\beta = (E_{1/2} - E'_{1/2})F \end{gathered}$$

or in electron-volts

$$(a_{n+1} - a'_{n+1})\beta = E_{1/2} - E'_{1/2} \quad (27)$$

As standard, it is convenient to take the triphenylmethyl radical, for which $\varepsilon = \alpha$ $(a_{n+1} = 0)$ and $E'_{1/2} = -1.05$ V. By substituting these values in Eqn. (27) we obtain the final expression

$$E_{1/2} = a_{n+1}\beta - 1.05 \quad (7)$$

previously given in the first section.

It can be seen from the discussion that Eqn. (7) is approximate, since assumptions known to be inaccurate were made in its derivation. The change in $\ln (D_R/D_{R^-})^{1/2}$ and $[\Delta G^0]_{solv}$ on going from one compound to another with similar structure, however, is also apparently monotonic, so that $E_{1/2}$ still remains an approximately linear function of a_{n+1}.

Subsequently, attempts were made to analyse the experimental data on the basis of more accurate relationships [113,114]. This gave nothing fundamentally new, however. Moreover, the simple relationship (7) has proved satisfactory. It has been verified many times [22,23,27,29,30,37,52,67,115-121]. Without giving details of these papers, we would point out that a satisfactory correlation is also obtained under experimental conditions in which the reduction is not completely reversible (75% dioxan), apparently because the irreversibility resulting from protonation of the radical-anions has little influence on the value of $E_{1/2}$. When comparing $E_{1/2}$ values it is best to use experimental data obtained under identical experimental conditions, since even apparently insignificant changes in the conditions of the experiment may have a significant influence on the $E_{1/2}$ values, through change in the potential of the reference electrode or diffusion potentials, or through the radical-anions forming ion pairs [88,114] with the counter-ion of the supporting electrolyte.

The correlation given by Eqn. (7) covers not only alternant aromatic hydrocarbons, but also the non-alternant azulene. Azulene, however, shows appreciable departure from this correlation. Thus according to the calculation, $E_{1/2} = -1.87$ V [65] whereas experiment gives $E_{1/2} = -1.64$ V [65]. Various suggestions have been put forward to explain this anomaly. In Hoijtink's opinion [27], this phenomenon cannot be due to the fact that in the approximate calculation by the molecular orbital method used, all the bond lengths in the azulene molecule were taken as equal, since a more rigorous treatment making allowance for the difference in the bond lengths leads to an even greater discrepancy. Hoijtink suggested that the increased ease of reduction of azulene is due to decreased strain of the rings in the azulene molecule when it loses an electron.

In Streitwieser's opinion [2], the correlation can be improved by using a higher value of β for the 9,10 bond (common to both rings).

An even more striking difference between the $E_{1/2}$ values predicted on the basis of correlation (7) and the experimental values is observed for charged non-alternant hydrocarbons—the tropylium and azulenium cations. For these compounds the discrepancy in the $E_{1/2}$ values reached 1.4–1.5 V.

It has been suggested [122] that this anomaly is due to the polarity of the molecules of non-alternant hydrocarbons, leading to a change in the solvation energies of the reacting species and in the electron affinities. For example, on going from the reduction of benzene to the reduction of the tropylium cation these quantities change as follows. Preferential solvation of the product (the R^- radical-anion) is replaced by preferential solvation of the starting material (the tropylium cation). The difference in the solvation energies for these two reactions is about 4 eV, the reduction of the tropylium cation becoming more difficult as a result of the change in the solvation of the components. This effect is masked, however, by the effect of the increased electron affinity of the tropylium cation (by more than 6 eV compared with benzene).

The correlation (7) can be extended to non-alternant hydrocarbons by the introduction of a term allowing for the polarity of the molecule

$$E_{1/2} = a_{n+1}\beta - E^0_{1/2} + kq_r \quad (28)$$

where q_r is the maximal positive charge on a carbon atom of the molecule.

The rule formulated by Hoijtink, according to which the radical RH· of an aromatic hydrocarbon is always reduced more readily than the original hydrocarbon R, may not apply for a non-alternant hydrocarbon, because of the effect of the polarity of the molecule. For this reason, apparently, azulene is reduced more readily than the RH· radical of azulene.

The problem of a possible correlation of the $E_{1/2}$ values of aromatic hydrocarbons with the para-localisation energies has been widely discussed [123-130]. The discussion was initiated by Basu and Bhattacharya [123], who, on the basis of the data of Wawzonek and Laitinen [14] obtained with solutions in 75% dioxan, indicated for the first time the possibility of a correlation between $E_{1/2}$ and the energy of localisation of two electrons in the para-position of the hydrocarbon. A basis for this conclusion was provided by the fact that in 75% dioxan the first wave corresponds to the transfer of two electrons, and reduction generally takes place in the para-position. In fact, they found a satisfactory linear relationship between the $E_{1/2}$ values and the para-localisation energies. Serious objections were raised to this work, however. Pullman and Pullman [124] corrected various para-localisation energy values, and the correlation with $E_{1/2}$ was thereby destroyed. They also pointed out that reduction does not always involve the para-position, and the absence of a linear relationship was demonstrated for a large number of examples. For example, the energy of

para-localisation in polyphenyls remains approximately constant with increase in the number of benzene rings, whereas $E_{1/2}$ becomes less negative. Pullman and Pullman point out that the parallelism sometimes observed between $E_{1/2}$ and the para-localisation energy is possibly due to the fact that the localisation (polarisation) energy is often revealed in the energy of the first vacant orbital. Given's objections[127] reduce to the fact that since in the reduction of aromatic hydrocarbons, two electrons are in fact transferred in stages, the energy of para-localisation is not related to the least negative $E_{1/2}$. It is more correct to expect a correlation of $E_{1/2}$ with the energy of localisation of an electron in an individual position, and this correlation is in fact satisfactory[127]. At present, the correlation of the $E_{1/2}$ values with the para-localisation energies has not been accepted.

By analogy with the correlation of $E_{1/2}$ for the waves for the reduction of aromatic hydrocarbons with the root a_{n+1} of the Hückel secular equation for the first vacant molecular orbital, a correlation was found between $E_{1/2}$ for the oxidation waves and the root a_n for the highest filled bonding orbital[131]. The experimental values of $E_{1/2}$ for oxidation were taken from Lund's paper[93]. A satisfactory correlation was observed (Fig. 7), despite the fact that the waves corresponded to a two-electron oxidation, and, as shown later[62], this oxidation takes place irreversibly because of subsequent rapid transformation of the radical-cations.



Figure 7. Plot of $(E_{1/2})_{ox}$ against a_n for alternant hydrocarbons (circles) and fluoranthene (triangle) (published data[131]).

Since for alternant hydrocarbons the vacant and occupied orbitals are positioned symmetrically with respect to the atomic orbital, that is $a_n = -a_{n+1}$, there is a linear relationship between $E_{1/2}$ for the oxidation and $E_{1/2}$ for the reduction of alternant hydrocarbons[131]. This correlation is important, because it makes it possible to investigate the characteristic features of the behaviour of non-alternant hydrocarbons, which depart even further from this correlation (Fig. 8) than from the linear relationship between $E_{1/2}$ for the reduction or oxidation and a_{n+1} or a_n.

The values of $E_{1/2}$ for the reduction waves have been used to find the electron affinities of the molecules of aromatic hydrocarbons, which are identified with the energies of the first vacant orbital. This possibility was first examined by Lyons[132]. We shall take the derivation of the relationship between $E_{1/2}$ and the electron affinity (A) from Matsen's paper[133].

The electrode processes in the measurement of $E_{1/2}$ for reduction, relative to a saturated calomel electrode, are arbitrarily broken down into the following stages:

$$R_g + e_g \rightarrow R_g^- + A \quad (29)$$

$$R_{soln} + R_g^- \rightarrow R_g + R_{soln}^- + \Delta G^0_{solv} \quad (30)$$

$$e\,(Hg) \rightarrow e_g - 4.54\ eV\ (work\ function) \quad (31)$$

$$Hg_{liq} + Cl^-\ (sat.aq.) \rightarrow (HgCl)_{solid} + e\,(Hg) - 0.56\ eV \quad (32)$$

$$Cl^-\ (sat.aq.) \rightarrow Cl^-\ (sat.aq) + 0.03\ eV \quad (33)$$

$$R_{soln} + Hg_{liq} + Cl^-\ (sat.aq) \rightarrow R^-_{soln.} + HgCl_{solid} \quad (34)$$

$$E_{1/2} = A + \Delta G^0_{solv} - 5.07 \equiv A' - 5.07\ (eV) \quad (35)$$

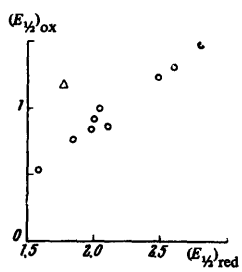


Figure 8. Plot of $(E_{1/2})_{ox}$ against $(E_{1/2})_{red}$ (published data[131]).

The difference in the free energy of solvation ΔG^0_{solv} is determined chiefly by the free energy of solvation of the ion, and can be calculated by means of the Born equation

$$\Delta G^0_{solv} \simeq 27.2\left(1 - \frac{1}{D}\right)\frac{a_0}{\bar{r}}\ (eV), \quad (36)$$

where $\bar{r}$ is the mean radius of the ion, a_0 the Bohr radius, and D the dielectric constant. In a first approximation, $\bar{r}$ is proportional to the cube root of the number of benzene rings in the molecule (p). Thus as $p \rightarrow \infty$ (graphite), $\Delta G^0_{solv} \rightarrow 0$ and $A' \rightarrow A$.

Since a linear relationship exists between $E_{1/2}$ and a_{n+1}, a linear relationship should exist between A' and a_{n+1}. This linear relationship is in fact observed (Fig. 9). Extrapolation of the straight line obtained by plotting A' against a_{n+1} to $a_{n+1} = 0$ (graphite) gave A for graphite (3.8 eV). From this it follows that for graphite $E_{1/2} = -1.27$ V. This value is obviously too negative. Other methods give for graphite $A = 4.39$ eV ($E_{1/2} = -0.68$ V). Finally, from the correlation between the values of A and the spectroscopic characteristics, we have for graphite $A = 4.8$ eV ($E_{1/2} = -0.27$ V). Direct measurements of the reduction potentials of graphite have not been made, but in this connection it may be mentioned that the low current efficiencies in the reduction of benzene by metallic lithium generated electrolytically on graphite were attributed to the partial utilisation of electricity for the hydrogenation of graphite[44]. This suggestion is confirmed by the marked erosion of the graphite cathode, in contrast to the behaviour of a carbon cathode[134].

If the values of A are calculated, it is possible, by comparing them with the $E_{1/2}$ values, to estimate the solvation energy ΔG^0_{solv}.[135] It was established in this way that ΔG^0_{solv} generally decreases with increase in the number of

benzene rings in the molecule of an aromatic compound. For the estimation of the solvation energies, the measurement of the electron affinities of the molecules in the gaseous phase is of considerable importance. Wentworth and Becker[136] suggested a method based on the measurement of the equilibrium constants for the capture of thermal electrons by the gaseous molecules in a gas-chromatographic detector, and observed a good correspondence between the values of A and $E_{1/2}$.

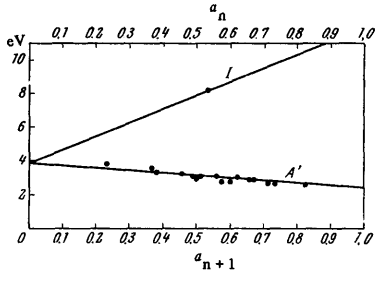


Figure 9. Dependence of the ionisation potential (I) on the energy of the highest filled orbital (the coefficient a_n) and of the apparent electron affinity (A') on the energy of the lowest vacant orbital (the coefficient a_{n+1}) for a number of hydrocarbons with condensed rings (published data[133]).

10)[137]. It has been the subject of a large number of studies[33,39,40,84,93,96,97,99,100,102,109,112,119,138-140]. The slope of the straight line obtained by plotting $E_{1/2}$ against E_ν should be equal to two. A bathochromic shift of the long-wave absorption band (that is towards longer wavelengths) corresponds to a decrease in the difference between the energies of the two orbitals, and a hypsochromic shift corresponds to an increase.

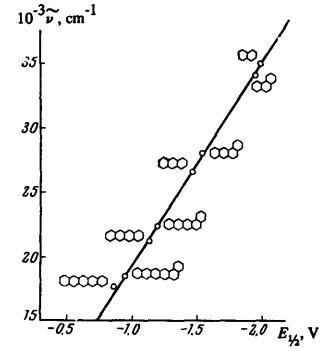


Figure 10. Plot of $\tilde{\nu}$, cm^{-1} against $E_{1/2}$ for the reduction of cata-condensed aromatic hydrocarbons in cellosolve ($\tilde{\nu}$ is the wave number of the p-band in the absorption spectrum) (published data[39]).

The $E_{1/2}$ values for the anodic oxidation waves are used[133] to determine ionisation potentials (I), that is the energies required to remove the least firmly bound electron (to remove an electron from the highest occupied orbital), so that the ionisation potential is equal to the energy of a π electron in this orbital and is an important characteristic of molecules. For graphite, $a_n = a_{n+1} = 0$ and $\Delta G^0_{solv} = 0$ and $A = 1$. Theory predicts that for alternant hydrocarbons the ionisation potential and electron affinity should be symmetric with respect to the work function of graphite (A).

We have seen that the $E_{1/2}$ values for reduction and oxidation contain information on the energy levels of molecules with generalised π electron systems. The same information is carried in the absorption spectra, so that a relationship should exist between the $E_{1/2}$ values and the spectroscopic characteristics of aromatic hydrocarbons. Watson and Matsen[137] were the first to draw attention to this relationship. On absorption of light energy the molecule is excited, and this is reflected in the transfer of an electron from one of the occupied orbitals to a higher vacant orbital. The lowest-energy transfer in the ground state of a molecule takes place from the first occupied orbital to the lowest vacant orbital. For alternant hydrocarbons, $a_n = -a_{n+1}$ and for the energies of the orbitals being considered we can write $\alpha + a_n\beta$ and $\alpha - a_{n+1}\beta$. The difference between the energies of these two orbitals, equal to the excitation energy $h\nu$, is

$$h\nu = -(a_n + a_{n+1})\beta = -2a\beta \quad . \qquad (37)$$

Since there is a linear relationship between a_{n+1} and $E_{1/2}$, there should be a linear relationship between $E_{1/2}$ and the frequency of the absorption band with longest wavelength. This correlation has in fact been observed (Fig.

Attempts have been made to correlate the $E_{1/2}$ values with various other properties of molecules. Thus a correlation has been noted between $E_{1/2}$ and the relative adsorbability of conjugated hydrocarbons on alumina[141]. It has been suggested that the $E_{1/2}$ values for the reduction of vinyl monomers change in the same sense as the ability of the monomer to undergo anionic polymerisation[29,30]. A parallelism has been noted between $E_{1/2}$ for the reduction of aromatic hydrocarbons and their thermal stability[142]. The $E_{1/2}$ values also show a correlation with the values of the g-factor in the EPR spectra of the radical-ions of alternant hydrocarbons[143,144]. The $E_{1/2}$ values have been compared with the carcinogenic activity of aromatic hydrocarbons[118,145]. In the last instance the regularity is not clear. Most carcinogenic substances exhibit both electron-donating and electron-accepting properties, but these functions are less marked for non-carcinogenic compounds[145].

VI. CHARACTERISTIC FEATURES OF THE ADSORPTION OF BENZENOID AROMATIC HYDROCARBONS

The specific electronic structure is also reflected in the adsorption characteristics of aromatic hydrocarbons[146]. Even in early papers it was noted that aromatic compounds are adsorbed much more readily at the mercury–solution boundary than at the free surface of the solution, the electrocapillary maximum being displaced in the cathodic direction[147,148]. The studies dealt chiefly with the hydroxy- and amino-derivatives, so that these experimental facts were interpreted as the result of an intensification of the interaction of the oxygen and nitrogen atoms of the hydroxy- and amino-groups with mercury, because of the flatter orientation of the benzene rings in the adsorbed layer on

mercury. Detailed measurements of the electrocapillary curves in solutions of unsubstituted condensed aromatic hydrocarbons by Gerovich[149-153] show, however, that unsubstituted non-polar aromatic hydrocarbons also displace the maximum of the electrocapillary curve towards more negative values and are preferentially adsorbed on the positively charged surface of the mercury electrode. This suggested that the observed anomalies are related to the adsorption characteristics of the aromatic rings themselves, and not of the polar substituents. In fact, the adsorbability of aromatic hydrocarbons on a positively charged surface increases in the order: benzene, naphthalene, phenanthrene, that is with increase in the number of benzene rings. On the other hand, hydrogenated benzene and naphthalene (cyclohexane and decalin) are adsorbed preferentially on a negatively charged mercury surface and displace the maximum of the electrocapillary curve in the anodic direction, which is characteristic of the adsorption of aromatic compounds[151].

It has been suggested that in the adsorption of aromatic hydrocarbons on a positively charged mercury surface an important part is played by the interaction of the system of π electrons of the hydrocarbon molecule with the positive charges of the mercury surface, with partial transfer of positive charge to the aromatic ring. This interaction is possible only with planar orientation of the molecules of the aromatic hydrocarbons in the adsorbed state. Calculation of the limiting adsorption (Γ_∞) for benzene, naphthalene, and phenanthrene on mercury from electrocapillary measurements showed that with increase in the number of benzene rings, Γ_∞ decreases, so that the area corresponding to one molecule of adsorbate increases[152]. This also confirmed the assumption regarding the flat orientation of the molecules of the adsorbed aromatic hydrocarbons.

Proof of the specific behaviour of aromatic hydrocarbons during adsorption on mercury is also found in work by Blomgren and coworkers[154], in which the dependence of the adsorbability of organic compounds on the solvation energy (solubility) was studied for a large number of substances. Aromatic compounds fall outside the established relationship, and this is again interpreted as due to the influence of the π electronic interaction of the molecules of these compounds with the mercury surface.

This interaction is so marked that it is not eliminated completely when a positive charge is introduced into the molecule of an aromatic hydrocarbon. For example, on going from aniline (neutral medium) to the anilinium cation (acid medium) the adsorption for positive charges on the surface is weakened considerably as a result of electrostatic repulsion but is not eliminated completely[155,156], and the quantity absorbed is almost independent of the potential of the electrode over a fairly wide range (~ 1 V).[157]

Gerovich[151] suggested that the formation of an adsorption layer of aromatic hydrocarbon molecules orientated parallel to the mercury surface should not be accompanied by marked changes in capacity. This suggestion was supported by the fact that the slope of the ascending branches of the experimental electrocapillary curves for solutions of aromatic hydrocarbons are almost the same as those for the solutions of the indifferent electrolyte (Fig. 11).

Direct measurements of the differential capacity showed that for the most positive charges on the surface the differential capacity in solutions of the indifferent electrolyte and the aromatic hydrocarbon coincide[158]. Moreover, in acidic solutions of aniline, from which adsorption of the anilinium cation takes place, the curves obtained by plotting C against E coincide throughout the entire range of potentials[159]. The calculated C–E curves do not coincide with the experimental curves in the range of positive charges on the surface, because of neglect of the π electronic interaction[160,161]. If the hydrogen atoms in the molecules of the aromatic compounds are replaced by fluorine atoms with high electron affinity, the π electron interaction is weakened to such an extent that it is not a decisive factor in the adsorption on mercury[162,163].

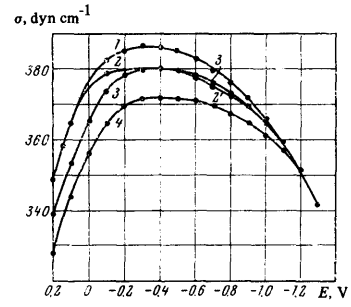


Figure 11. Electrocapillary curves for an aromatic hydrocarbon (naphthalene) in ethanol: *1*) ethanol + 0.1 M NH_4NO_3; *2*) 0.3 M decalin; *3*) 0.05 M naphthalene; *4*) 0.3 M naphthalene (published data[151]).

Under certain conditions the C–E curves for aromatic hydrocarbons, for positive charges on the surface, show peaks, which, however, do not correspond to the adsorption–desorption process (unlike the cathodic peaks). The production of these peaks is related to the re-orientation of the molecules of the aromatic hydrocarbon, that is to the change from a flat orientation for positive charges on the surface to an orientation close to vertical for negative charges on the surface[158,160]. This phenomenon was not detected by a less sensitive method for measuring electrocapillary curves.

The ideas put forward here have been used in an examination of the adsorption of aromatic hydrocarbons on other metals: cadmium[164], gold[165], iron, nickel, copper, and platinum[166]. The study of the characteristic features of the adsorption of organic compounds on metals may be useful in the detection of aromatic properties[167].

In conclusion is should be noted that work on the polarography of aromatic hydrocarbons has had a marked influence on the entire field of the polarography of organic compounds. At the present time, in the study of the mechanism of the reduction of organic compounds, extensive use is made of aprotic media for breaking down multistage processes into individual stages and for revealing the reversible elementary stages; the effect of the addition of proton donors to aprotic media is used to determine the basic nature of the original molecules, radicals, and radical-anions; alternating-current polarography makes it possible to verify more rigorously the reversibility of the electron-transfer stages and to measure the rate constants of these processes; the combination of polarography and EPR spectroscopy is finding application in the electrochemical preparation and study of the properties of radical species. In the study of the mechanism of the oxidation of organic compounds, use is made of experience gained in the study of the oxidation of aromatic hydrocarbons (the

use of acetonitrile as solvent, the rotating platinum microelectrode, and fast potential pulses). The determination of the correlational dependence of polarographic characteristics on molecular constants calculated by quantum-chemical methods has been widely applied.

A review of the published information on the polarography of aromatic hydrocarbons reveals various problems which have been insufficiently studied, and work on these problems should give most promising results.

1. Systematic studies of the path of the electrochemical reduction of various aromatic hydrocarbons and the role of the nature of the solvent and the indifferent electrolyte (the formation of ion pairs and complexes).

2. Deeper study of the mechanism of oxidation of aromatic hydrocarbons.

3. Study of the mechanism of the reduction of aromatic hydrocarbons in strongly acidic media.

4. Study of the correlational relationships, particularly the anomalous relationships (non-alternant hydrocarbons, compounds whose molecules are non-coplanar, etc.) on the basis of more accurate quantum-chemical calculations

5. The development of a theory of the adsorption of aromatic hydrocarbons on metals.

REFERENCES

1. M. E. Vol'pin, Uspekhi Khim., 29, 298 (1960) [Russ. Chem. Rev., No. 3 (1960)].
2. A. Streitwieser, "Molecular Orbital Theory for Organic Chemists" (Translated into Russian), Izd. Mir, Moscow, 1965.
3. Z. R. Grabowski, "Proceedings of the Conference on Polarography", PWN, Warsaw, 1957, p. 91.
4. P. H. Given and M. E. Peover, "Advances in Polarography" Vol. 3, Pergamon Press, 1960, p. 948.
5. G. J. Hoijtink, Ric. sci., 30, Suppl. 5 (contributi teor. sper. polarography), 217 (1960).
6. G. Le Guillanton, Bull. Soc. chim. France, 2359 (1963).
7. S. Wawzonek, Talanta, 12, 1229 (1965).
8. Ya. P. Stradyn' and E. S. Levin, in collected papers "Uspekhi Elektrokhimii Organicheskikh Soedinenii" (Collected Papers on Progress in the Electrochemistry of Organic Compounds), Izd. Nauka, Moscow, 1966, p. 82.
9. M. E. Peover, Electroanal. Chem., 2, 1 (1967).
10. S. I. Zhdanov, see Ref. 8, p. 144.
11. M. von Stackelberg and P. Weber, Ztschr. Elektrochem., 56, 806 (1952).
12. M. von Stackelberg, in: E. Müller, Methoden der Organischen Chemie, Band III; "Physikalische Forschungsmethoden", Teil 2, Stuttgart, 1955, p. 255.
13. H. A. Laitinen and S. Wawzonek, J. Amer. Chem. Soc., 64, 1765 (1942).
14. S. Wawzonek and H. A. Laitinen, J. Amer. Chem. Soc., 64, 2365 (1942).
15. S. Wawzonek and J. Wang Fan, J. Amer. Chem. Soc., 68, 2541 (1946).
16. S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, J. Electrochem. Soc., 102, 235 (1955).
17. S. Wawzonek and D. Wearring, J. Amer. Chem. Soc., 81, 2067 (1959).
18. S. Wawzonek and R. C. Duty, Rev. Polarogr. Japan, 11, 1 (1963).
19. F. Goulden and F. L. Warren, Biochem. J., 42, 420 (1948).
20. M. von Stackelberg and W. Stracke, Ztschr. Elektrochem., 53, 118 (1949).
21. A. G. Pozdeeva and A. G. Volkov, Zhur. Prikl. Khim., 25, 1058 (1952).
22. G. J. Hoijtink and J. van Schooten, Rec. trav. chim., 71, 1089 (1952).
23. G. J. Hoijtink and J. van Schooten, Rec. trav. chim. 72, 903 (1953).
24. T. I. Gornykh and A. G. Pozdeeva, Zhur. Prikl. Khim., 27, 118 (1954).
25. G. J. Hoijtink, J. van Schooten, E. de Boer, and W. J. Aalbersberg, Rec. trav. chim., 73, 355 (1954).
26. G. J. Hoijtink, Rec. trav. chim., 73, 895 (1954).
27. G. J. Hoijtink, Rec. trav. chim., 74, 1525 (1955).
28. A. A. Petrov and V. P. Petrov, Zhur. Obshch. Khim., 29, 3987 (1959).
29. T. Fueno, K. Asada, K. Morokuma, and J. Furukawa, J. Polymer Sci., 40, 511 (1959).
30. T. Fueno, K. Asada, K. Morokuma, and J. Furukawa, Bull. Chem. Soc., Japan, 32, 1003 (1959).
31. L. H. Klemm, C. D. Lind, and J. T. Spence, J. Org. Chem., 25, 611 (1960).
32. A. G. Pozdeeva, Zhur. Prikl. Khim., 34, 1842 (1961).
33. L. H. Klemm, A. J. Kohlik, and K. B. Desai, J. Org. Chem., 28, 625 (1963).
34. L. H. Klemm and A. J. Kohlik, J. Org. Chem., 28, 2044 (1963).
35. R. E. Burdett and B. E. Gordon, Analyt. Chem., 19, 843 (1947).
36. K. Schwabe and E. Schmidt, Ztschr. phys. Chem., Sonderheft, 278 (1958).
37. G. J. Hoijtink and J. van Schooten, Rec. trav. chim., 72, 691 (1953).
38. A. G. Stromberg and A. G. Pozdeeva, Zhur. Obshch. Khim., 20, 54 (1950).
39. I. Bergman, Trans. Faraday Soc., 50, 829 (1954).
40. I. Bergman, Trans. Faraday Soc., 52, 690 (1956).
41. I. Bergman, Experientia, 18, 46 (1962).
42. R. J. Crawford, S. Levine, R. M. Elofson, and R. B. Sandin, J. Amer. Chem. Soc., 79, 3153 (1957).
43. L. Silverman, W. G. Bradshaw, and M. E. Shideler, Analyt. Chem., 31, 1669 (1959).
44. H. W. Sternberg, R. Markby, and I. Wender, J. Electrochem. Soc., 110, 425 (1963).
45. P. H. Given, J. Chem. Soc., 2684 (1958).
46. D. E. G. Austen, P. H. Given, D. J. E. Ingram, and M. E. Peover, Nature, 182, 1784 (1958).
47. A. C. Aten, C. Büthker, and G. J. Hoijtink, Trans. Faraday Soc., 55, 324 (1956).
48. A. C. Aten and G. J. Hoijtink, Ztschr. phys. Chem., N. F., 21, 192 (1959).
49. P. H. Given and M. E. Peover, J. Chem. Soc., 385 (1960).
50. P. H. Given and M. E. Peover, Coll. Czech. Chem. Comm., 25, 3195 (1960).
51. A. C. Aten and G. J. Hoijtink, Advances in Polarography, Pergamon Press, 2, 777 (1960).
52. A. Streitwieser, Jnr. and I. Schwager, J. Phys. Chem., 66, 2316 (1962).
53. W. Kemula and J. Kornacki, Roczniki Chem., 36, 1835 (1962).
54. W. Kemula and J. Kornacki, Roczniki Chem., 36, 1849 (1962).
55. W. Kemula and J. Kornacki, Roczniki Chem., 36, 1857 (1962).
56. P. G. Grodzka and P. J. Elving, J. Electrochem. Soc., 110, 231 (1963).
57. G. J. Hoijtink, Ztschr. phys. Chem., N. F., 45, 248 (1965).

58. J. M. Fritsch, Th. P. Layoff, and R. N. Adams, J. Amer. Chem. Soc., 87, 1724 (1965).
59. J. M. Bonnier, A. Braquet, and M. Gelus, Compt. rend., 260, 2501 (1965).
60. K. Umemoto, Bull. Chem. Soc. Japan, 40, 1058 (1967).
61. A. C. Allison, M. E. Peover, and T. A. Gough, Nature, 197, 764 (1963).
62. B. Case, N. C. Hush, R. Parsons, and M. E. Peover, J. Electroanalyt. Chem., 10, 360 (1965).
63. J. Perichon and R. Buvet, Electrochim. Acta, 9, 587 (1964).
64. A. Maccoll, Nature, 163, 178 (1949).
65. L. H. Chopard-dit-Jean and E. Heilbronner, Helv. chim. acta, 36, 144 (1953).
66. G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, Rec. trav. chim., 74, 277 (1955).
67. G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, Rec. trav. chim., 75, 487 (1956).
68. P. Balk, G. J. Hoijtink, and J. W. H. Schreurs, Rec. trav. chim., 76, 813 (1957).
69. P. Balk, S. de Bruin, and G. J. Hoijtink, Rec. trav. chim., 76, 860 (1957).
70. P. Balk, S. de Bruin, and G. J. Hoijtink, Molekular Phys., 1, 151 (1958).
71. G. J. Hoijtink and P. H. Vander Meij, Ztschr. physik. Chem., N. F., 20, 1 (1959).
72. J. E. B. Randles, Disc. Faraday Soc., No. 1, 11 (1947).
73. B. V. Ershler, Disc. Faraday Soc., No. 1, 269 (1947).
74. P. Delahay, "New Instrumental Methods in Electrochemistry" (Translated into Russian), Inostr. Lit., Moscow, 1957, p. 179.
75. A. C. Aten, J. Dieleman, and G. J. Hoijtink, Disc. Faraday Soc., No. 29, 182 (1960).
76. R. Dietz and M. E. Peover, Trans. Faraday Soc., 62, 3535 (1966).
77. T. A. Gough and M. E. Peover, "Polarography 1964", MacMillan, 1966, T. 2, p. 1017.
78. K. Möbius and M. Plato, Naturforsch., 19a, 1240 (1964), Vol. 2, p. 1017.
79. G. J. Hoijtink, Rec. trav. chim., 76, 869 (1957).
80. G. J. Hoijtink, Rec. trav. chim., 76, 885 (1957).
81. V. D. Bezuglyi, "Teoriya i Praktika Polyarograficheskogo Analiza" (The Theory and Practice of Polarographic Analysis), Izd. Shtiintsa, Kishinev, 1962, p. 12.
82. V. D. Bezuglyi, in "Metody Analiza Khimicheskikh Reaktivov i Preparatov" (Methods for Analysing Chemical Reagents and Products), No. 3, Moscow, 1962, p. 7.
83. V. D. Bezuglyi, "Polyarografiya v Khimii i Tekhnologii Polimerov" (Polarography in the Chemistry and Technology of Polymers), Izd. Khar'kov, Univ., 1964, p. 8.
84. I. Bergman, Experientia, 18, 46 (1962).
85. I. Bergman, see Ref. 77, p. 925.
86. P. G. Grodzka and P. J. Elving, J. Electrochem. Soc., 110, 225 (1963).
87. L. Ya. Kheifets and V. D. Bezuglyi, "Tezisy Soobshchenii na Pyatom Soveschanii po Elektrokhimii Organicheskikh Soedinenii" (Summaries of Papers Presented at the Fifth Conference on the Electrochemistry of Organic Compounds), Moscow, 1964, p. 35.
88. M. E. Peover and J. D. Davis, see Ref. 77, p. 1003.
89. G. J. Hoijtink and W. P. Weijland, Rec. trav. chim., 76, 836 (1957).
90. W. Ij. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, J. Chem. Soc., 3049 (1959).
91. W. Ij. Aalbersberg and E. L. Mackor, Trans. Faraday Soc., 56, 1351 (1960).
92. T. Takamura and K. Takamura, Ztschr. physik. Chem., N. F., 35, 146 (1962).
93. H. Lund, Acta Chem. Scand., 11, 1323 (1957).
94. J. D. Voorhies and N. H. Furman, Analyt. Chem., 31, 381 (1959).
95. J. W. Loveland and G. R. Dimeler, Analyt. Chem., 33, 1196 (1961).
96. A. Stanienda, Ztschr. phys. Chem., N. F., 33, 170 (1962).
97. E. S. Pysh and N. C. Yang, J. Amer. Chem. Soc., 85, 2124 (1963).
98. K. E. Friend and W. E. Ohnesorge, J. Org. Chem., 28, 2435 (1963).
99. A. Zweig, W. G. Hodgson, and W. H. Jura, J. Amer. Chem. Soc., 86, 4124 (1964).
100. A. Zweig, J. E. Lancaster, M. T. Neglia, and W. H. Jura, J. Amer. Chem. Soc., 86, 4130 (1964).
101. W. C. Neikam and M. M. Desmond, J. Amer. Chem. Soc., 86, 4811 (1964).
102. C. Parkanyi and R. Zahradnik, Coll. Czech. Chem. Comm., 30, 4287 (1965).
103. L. Eberson and K. Nyberg, J. Amer. Chem. Soc., 88, 1686 (1966).
104. J. Phelps, K. S. V. Santhanam, and A. J. Bard, J. Amer. Chem. Soc., 89, 1752 (1967).
105. J. P. Billon, G. Cauquis, J. Raison, and I. Tribaut, Bull. Soc. chim. France, 199 (1967).
106. H. Lund, Acta Chem. Scand., 11, 491 (1957).
107. R. Zahradnik and C. Parkanyi, Talanta, 12, 1289 (1965).
108. L. E. Lyons, Research (London), 2, 587 (1949).
109. A. Pullman, B. Pullman, and G. Berthier, Bull. soc. chim. France, 591 (1950).
110. H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, J. Electrochem. Soc., 113, 1060 (1966).
111. R. Pointeau and J. de Villepin, Compt. rend., 245, 1725 (1957).
112. L. H. Klem, W. C. Solomon, and A. J. Kohlik, J. Org. Chem., 27, 2777 (1962).
113. O. Chalvet and I. Jano, Compt. rend., 259, 1867 (1964).
114. I. Jano, Cahiers de Physique, 20, 1 (1966).
115. R. Bhattacharya and S. Basu, Naturwiss, 45, 208 (1958).
116. T. Fueno, K. Morokuma, and J. Furukawa, Bull. Inst. Chem. Research, Kyoto Univ., 36, 87 (1958).
117. F. T. Wallenberger, Experientia, 16, 83 (1960).
118. R. Pointeau, Ann. Chim., 7, 669 (1962).
119. R. Zahradnik, J. Michl, and J. Koutecký, J. Chem. Soc., 4998 (1963).
120. C. Parkanyi and R. Zahradnik, Abhandl. Deut. Akad. Wiss. Berlin, kl. Chem., Geol. Biol, No. 1, 368 (1964).
121. J. M. Bonnier, A. Braquet, and M. Gelus, Compt. rend., 260, 2501 (1965).
122. S. I. Zhdanov, Zhur. Obshch. Khim., 39, 1685 (1969).
123. S. Basu and R. Bhattacharya, J. Chem. Phys., 25, 596 (1956).
124. A. Pullman and B. Pullman, Compt. rend., 243, 1632 (1956).
125. J. I. Fernandez-Alonso and R. Domingo, Nature, 179, 829 (1957).
126. S. Basu and R. Bhattacharya, Nature, 180, 143 (1957).

127. P. H. Given, Nature, 181, 1001 (1958).
128. R. Bhattacharya and S. Basu, Naturwiss., 45, 208 (1958).
129. R. Bhattacharya and S. Basu, Naturwiss., 45, 361 (1958).
130. H. J. Gardner, Nature, 183, 320 (1959).
131. G. J. Hoijtink, Rec. trav. chim., 77, 555 (1958).
132. L. E. Lyons, Nature, 166, 193 (1950).
133. F. A. Matsen, J. Chem. Phys., 24, 602 (1956).
134. P. H. Given and M. E. Peover, Fuel, 39, 463 (1960).
135. R. M. Hedges and F. A. Matsen, J. Chem. Phys., 28, 950 (1958).
136. W. E. Wentworth and R. S. Becker, J. Amer. Chem. Soc., 84, 4263 (1962).
137. A. T. Watson and F. A. Matsen, J. Chem. Phys., 18, 1305 (1950).
138. S. V. Gorbachev and S. F. Belevskii, Zhur. Fiz. Khim., 31, 1656 (1957).
139. Z. R. Grabowski, Zhur. Fiz. Khim., 33, 728 (1958).
140. I. C. Lewis, H. Leibecki, and S. L. Bushong, U. S. Dept. Com., Office Tech. Serv. AD 426 666 (1963); Chem. Abs., 61, 6758b (1964).
141. L. H. Klemm and D. Reed, Am. Chem. Soc., Div. Petrol. Chem., Preprints, 3, 143 (1958); Chem. Abs., 54, 21 931b (1960).
142. H. F. Martin and B. J. Gudzinowicz, Nature, 200, 69 (1963).
143. K. Moebius, Naturforsch., 20a, 1093 (1965).
144. K. Moebius, Naturforsch., 20a, 1102 (1965).
145. A. C. Allison, M. E. Peover, and T. A. Gough, Nature, 197, 764 (1963).
146. A. N. Frumkin and B. B. Damaskin, "Sovremennye Aspekty Elektrokhimii" (Modern Aspects of Electrochemistry), Izd. Mir, Moscow, p. 170.
147. A. Frumkin, Ergebnisse der Exakten Naturwissenschaften, 7, 235 (1928).
148. A. N. Frumkin and D. U. Williams, Proc. Nat. Acad. Sci., 15, 400 (1929).
149. M. A. Gerovich, Dokl. Akad. Nauk SSSR, 96, 543 (1954).
150. M. A. Gerovich, and O. G. Ol'man, Zhur. Fiz. Khim., 28, 19 (1954).
151. M. A. Gerovich, Dokl. Akad. Nauk SSSR, 105, 1278 (1955).
152. M. A. Gerovich and G. F. Rybal'chenko, Zhur. Fiz. Khim., 32, 109 (1958).
153. M. A. Gerovich, "Trudy Chetvertogo Soveschaniya po Elektrokhimii" (Proceedings of the Fourth Conference on Electrochemistry), Izd. Akad. Nauk SSSR, Moscow, 1959, p. 139.
154. E. Blomgren, J. O'M. Bockris, and C. Jesch, J. Phys. Chem., 65, 2000 (1961).
155. M. A. Gerovich and N. S. Polyanovskaya, Nauch. Dokl. Vys. Shkoly, Khim. i Khim. Tekhnol., No. 4, 651 (1958).
156. A. N. Frumkin, R. I. Kaganovich, and E. S. Bit-Popova, Dokl. Akad. Nauk SSSR, 141, 670 (1961).
157. E. Blomgren, and J. O'M. Bockris, J. Phys. Chem., 63, 1475 (1959).
158. B. B. Damaskin, I. P. Mishutushkina, V. M. Gerovich, and R. I. Kaganovich, Zhur. Fiz. Khim., 38, 1797 (1964) [Russ. J. Phys. Chem., No. 7 (1964)].
159. S. L. Dyatkina and B. B. Damaskin, Elektrokhimiya, 2, 1340 (1966).
160. L. D. Klyukina and B. B. Damaskin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1022 (1963).
161. B. B. Damaskin, V. M. Gerovich, I. P. Gladkikh, and R. I. Kaganovich, Zhur. Fiz. Khim., 38, 2495 (1964) [Russ. J. Phys. Chem., No. 10 (1964)].
162. V. A. Kuznetsov and B. B. Damaskin, Elecktrokhimiya, 1, 1153 (1965).
163. B. B. Damaskin, M. M. Andrusev, V. M. Gerovich, and R. I. Kaganovich, Elektrokhimiya, 3, 667 (1967).
164. A. V. Pamfilov and V. S. Kuzub, Ukrain. Khim. Zhur., 28, 528 (1962).
165. H. Dahms and M. Green, J. Electrochem. Soc., 110, 1075 (1963).
166. J. O'M. Bockris, M. Green, and D. A. Swinkels, J. Electrochem. Soc., 111, 743 (1964).
167. V. Sh. Tsveniashvili, S. I. Zhdanov, and Z. V. Todres, Elektrokhimiya (in the press).

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow