

THE INVESTIGATION OF THE KINETICS
OF THE ELECTRODE REACTIONS
OF ORGANIC COMPOUNDS
BY POTENTIOSTATIC METHODS

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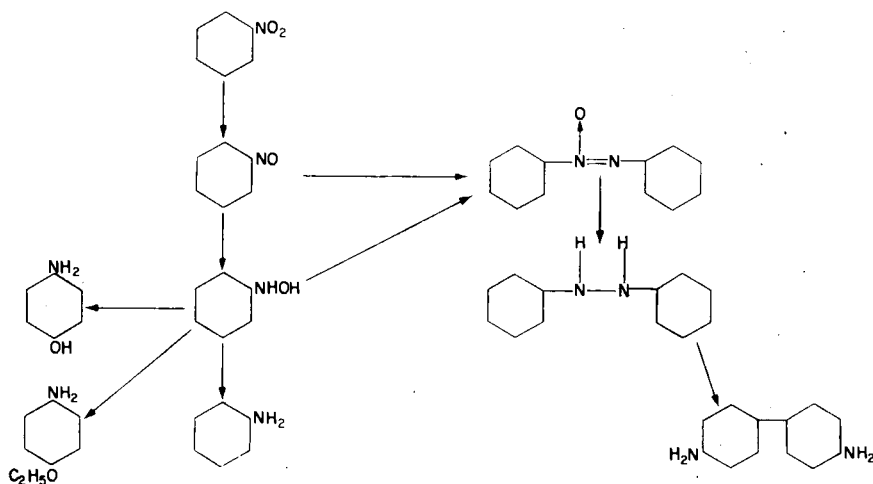
Abstract—In this paper results are presented on the reduction of nitrobenzene which was first investigated by Haber who pointed out the usefulness of working at constant potential. The oxidation and reduction of intermediates formed in the reaction have also been studied. The form of the relation between current and the potential of the working electrode is interpreted and the concentration and pH dependence of the reaction rates is examined in different regions. It is shown that simple kinetic laws govern the reduction processes under some conditions and the role of the solvent in affecting the reduction is emphasized. Quantitative reductions can be carried out in many cases and these results show that the reduction scheme proposed by Haber must be modified in some respects. The detailed kinetic scheme suggests that the products of electrolysis can be changed by pulsing the electrode between two different potentials for controlled lengths of time and this has been confirmed.

As an example of an oxidation reaction at an electrode the kinetics of the Kolbe reaction have been examined using controlled potential pulse electrolysis. It is shown that above a certain pulse length ethane is formed by a second order reaction while for shorter pulses there is a "relaxation", methanol being formed (and further oxidized) by a pseudo first-order process. The possibility of controlling reactions by pulse length as well as by potential height is discussed, as an example of controlling reactions by relaxation methods.

INTRODUCTION

THE earliest emphasis of the role of the potential of a working electrode in controlling the rates and nature of electrode processes is probably to be found in the work of Haber.¹ In 1898 he suggested that in view of the dependence of these processes on the potential rather than the current, organic electrode reactions should be carried out at fixed potentials and

that in this way some control over the nature of the reaction product might be exercised. The change in the products caused by changing the metal used as an "inert" electrode in the reduction of nitrobenzene was interpreted as being due largely to the change in electrode potential. By manual control of the potential of platinized platinum electrodes, used for the reduction of nitrobenzene in neutral, alkaline and acid solutions, Haber succeeded in showing that the products of electrolysis could be changed. In particular phenylhydroxylamine could be made at low and aniline at high electrode potentials. From the study of the minor products of reaction Haber suggested the following reaction scheme:



This scheme is accepted at the present time but it should be noted that it refers to the reaction on platinized platinum. Furthermore, the reaction scheme applies to the particular potentials at which the reduction was carried out.

Since these early experiments by Haber there have been numerous applications of controlled potential electrolysis in the field of polarography, including the polarography of nitro-compounds.² A.c. polarography³ of nitro-compounds has been used for purposes of identification of isomers⁴ and for the identification of reaction intermediates.⁵ Coulometric estimates⁶ of the compounds being reduced have also been used to confirm the electron number of the reduction steps,⁷ as determined polarographically, while in recent years there have been a number of controlled potential reductions using electro-mechanically operated potentiostats.⁸ It has been

shown that the yield and selectivity of the reductions can be frequently improved in this way.

There have not, however, apparently been any investigations of the kinetics of reduction and oxidation of organic compounds at controlled potential under conditions where the effects of diffusion can be neglected. The development of electronic potentiostats with a high output rating, a high accuracy in stabilization of the working electrode potential and a fast frequency response⁹ makes such measurements feasible on electrodes of intermediate area (*ca.* 1 cm²). In this paper we give some details of such an investigation of the kinetics of reduction of nitrobenzene and the reduction products or intermediates which have been found to be present.¹⁰ These experiments suggest some modifications to the reduction scheme proposed by Haber.

It is also possible to examine the current-time transients obtained on switching the potential directly and to correlate these transients with the kinetics of the electrode processes. A particular form of these experiments which is suitable for reactions in which several compounds are formed, is the measurement of the amount of a product as a function of the length of polarization, using repetitive pulses of potential. In this paper some results are presented for the Kolbe reaction¹¹ (the formation of ethane from acetate ions) which were obtained in this way but the current-time transients are not discussed. This technique is related to the well established method of the investigation of electrode processes by relaxation methods using a.c. currents of small amplitude¹² and to the general field of the measurement of reaction kinetics by perturbation methods.¹³ In this case, however, large amplitude square waves are used. It will be shown that in this way some measure of control over the products of reaction can be achieved, the products being selected according to the "relaxation time" for their formation. The method is also illustrated by the direct electro-synthesis of benzidine from nitrobenzene in acid solution.¹⁰

EXPERIMENTAL

The way in which the experiments at constant potential were carried out is illustrated by means of the block diagram, Fig. 1. The working electrode at which the reactions are to be examined is connected to earth potential while the reference electrode is connected to one of the inputs of the potentiostat. The signal which is to be applied to the working electrode is set with respect to earth potential at the second input of the potentiostat. For slow changes of the current with time an appropriate signal

is selected from one of two low-resistance potentiometers while for rapid changes the potential-time waveform is generated by an electronic pulse generator. This generator provides positive or negative going pulses either in "single shots" or repetitively and of known amplitude, length and repetition frequency. The output is produced from a network of low impedance so that a bias potential may be added by means of the potentiometers without introducing distortion of the pulse shapes due to parasitic capacities to ground.

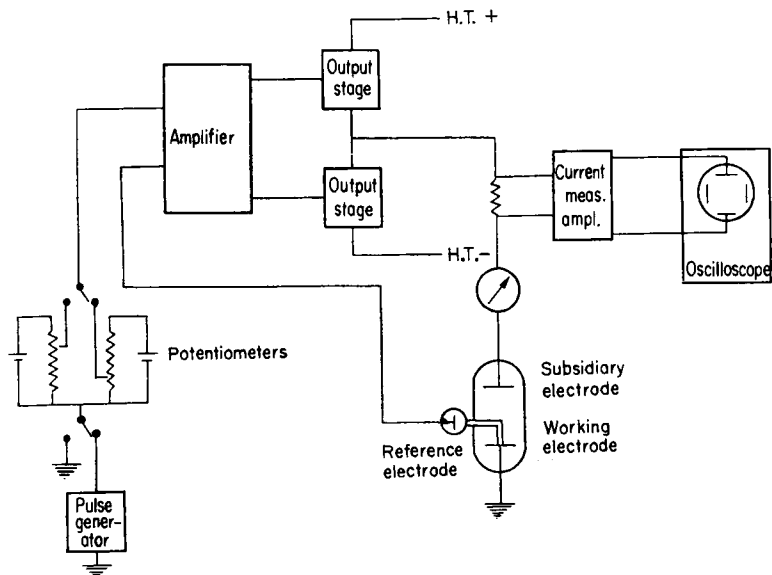


FIG. 1. Block diagram of potentiostatic equipment.

The potentiostats used in these investigations were of a standard design made in these laboratories⁹ which have the following specification: the push-pull discrimination at the two inputs is greater than $10^4 : 1$ so that the voltage between the working and reference electrodes could be subtracted from the set potential to an accuracy better than this figure; the gain of the amplifier without feedback is 10^4 so that a precision of stabilization of the working electrode of the order 1 mV can be achieved for currents in the range 0 – 100 mA; the gain frequency and phase frequency response curves are adjusted in such a manner that any transient oscillations in the potential of the working electrode on switching the potential die out within about 10μ so that current readings may be made after this interval of time; the output stage is designed with two valve systems one above

and one below earth potential, the impedance levels being matched so that, using the configuration of the cell shown in the diagram, anodic and cathodic reactions can be examined with equal precision and time resolution. Steady currents of up to 200 mA can be drawn from the instrument while the voltage swing is ± 100 V so that cells of comparatively

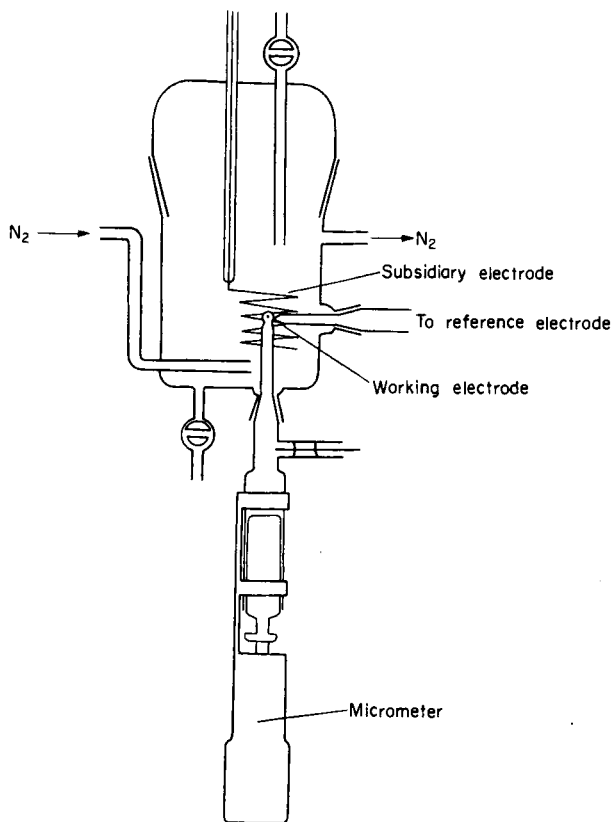


FIG. 2.

high resistance may be used. The pulse current can rise to 1 A so as to permit rapid charging of the double layer on switching the potential. In view of the high output, electrode reactions can be examined on comparatively large electrodes using repetitive pulses of potential and it is also possible to investigate the effect of pulse length on the electro-synthesis in this way. For greater time resolution instruments of different design and special pulse profiles have been used.

In the experiments described in this paper the steady state currents were read by means of a suitably shunted microammeter and this was also used in conjunction with a stop watch for slow current-time transients. Rapid changes of the current with time, which are not discussed further here, were measured oscillographically in the manner shown.

Several different forms of cells were used in the experiments. Two, which were used with mercury electrodes, are illustrated in Figs. 2 and 3. For

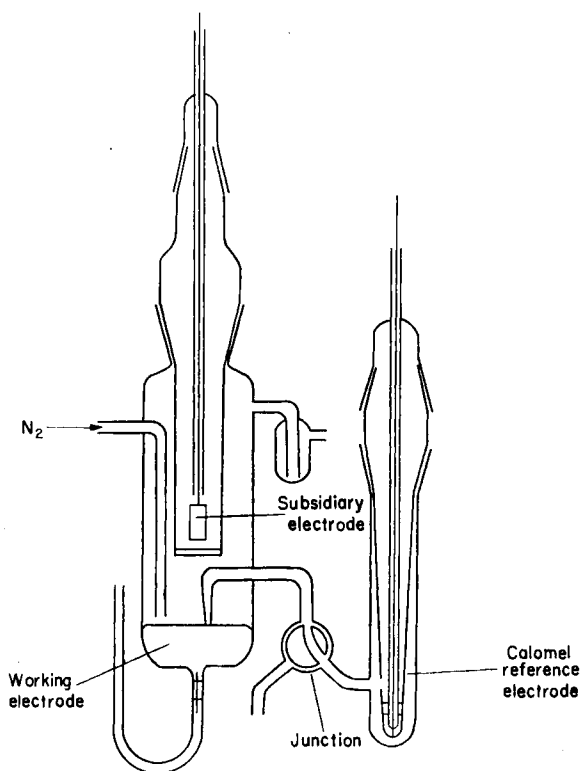


FIG. 3.

measurements of the steady state current potential relationship of nitrobenzene and its reduction products the cell shown in Fig. 2 was frequently found suitable. The working electrode was in the form of a segment of a sphere formed on the end of a capillary fed from a micrometer operated syringe. By using this arrangement the electrode could be rapidly changed, the size being set by viewing through a cathetometer, the appropriate potential applied and the current-time curve followed to the steady state.

The subsidiary electrode could frequently be made in the form of a platinum helix surrounding the working electrode, and this gave the optimum current distribution. For some experiments it was necessary, however, to separate the subsidiary from the working electrode by means of a sintered disc. The saturated calomel electrodes, made in aqueous solution, were connected to the working electrode by means of the Luggin capillary in the manner shown. The ends of this capillary and that of the working electrode were chamfered so as to reduce screening to a minimum.

For measurements at low current densities, for coulometric estimates of the products of reduction and for preparation of samples for spectroscopy, several cells of the type illustrated in Fig. 3 were used. The working electrode was in the form of a pool while the platinum subsidiary electrode was separated by means of a sintered disc, the reference electrode having the same form as in Fig. 2. After completion of the electrolysis at any one potential the solution could be withdrawn from the working electrode compartment and examined by u.v. spectroscopy. Both cells could be stirred with a stream of nitrogen.

Measurements on the Kolbe reaction were carried out in essentially similar cells except that the platinum wire or sheet working electrodes were placed over a Luggin capillary pointing upwards. In all these experiments the working electrode compartment was initially filled completely with solution, the gas evolved being collected in a narrow bore tube. After a suitable period of electrolysis the sample was transferred to a vacuum line, freed from water and acetic acid vapour and analysed mass-spectrometrically. Some results for the rate of ethane production only are reported here.

The behaviour of nitrobenzene and the following compounds was investigated using mercury electrodes: nitrosobenzene, phenylhydroxylamine, azoxybenzene, azobenzene, phenetidine and p-aminophenol. All these compounds have been suggested either as products or reaction intermediates in the reduction of nitrobenzene. In the potential range examined phenetidine and p-aminophenol could be neither oxidized nor reduced while phenylhydroxylamine was oxidized at high and reduced at low potentials. All the other compounds were only reduced. The electrode reactions were examined in sulphuric acid solutions made up in 75 per cent alcohol since a very wide range in potential can be covered in this medium (from 0.4 to -1.6 V with respect to the saturated calomel electrode the range being limited by the formation of mercurous sulphate and hydrogen evolution respectively). In every example examined the steady state current-potential plot was taken, the concentration dependence being measured

both as a function of acid concentration (in the range 0.1–4 N) at fixed concentration of the compound and as a function of the concentration of the compound (usually in the range 0.001 – 0.1 M) at fixed pH. In every case the quantity of electricity required for complete reduction was determined from current–time plots for one solution, and as a function of the potential. After reduction had been completed, and in some cases during reduction, the solutions were examined by u.v. spectroscopy, the spectra being compared with that of the known reduction products. In most cases, and over most of the potential range covered, the reduction was quantitative, a single product only being formed. From these coulometric estimates an assessment could be made as to the nature of the reduction process.

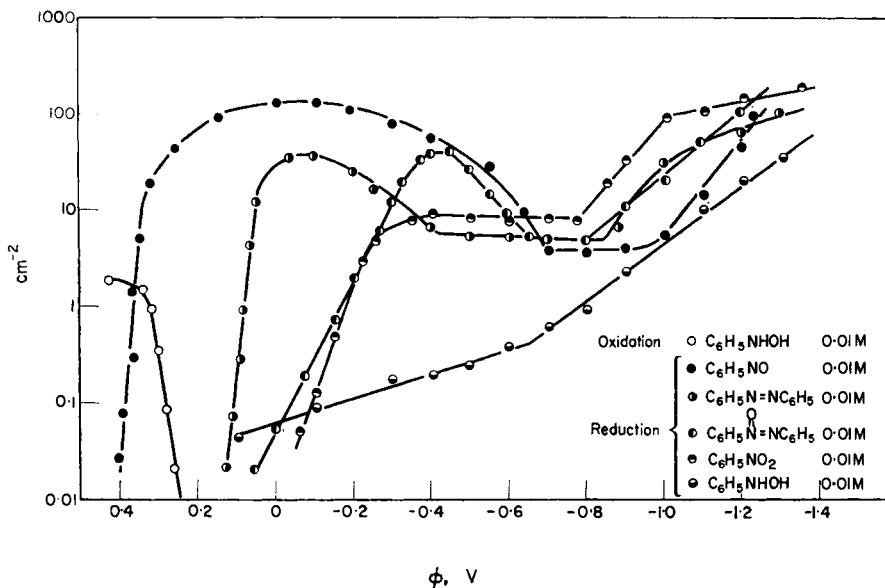
An examination of the complete reduction mechanism as a function of potential suggested that the products of electrolysis of nitrobenzene could be changed either by using a sequence of potentials or by repetitive pulse electrolysis, the mercury cathode being pulsed between two fixed potentials and for controlled lengths of time. This was confirmed using pulses with a duty ratio 1 : 1.

A further example of pulse electrolysis which has been examined is the formation of ethane from aqueous sodium acetate – acetic acid solutions. In the experiments reported here the electrodes were pulsed from a potential about 0.15 V positive to the reversible hydrogen potential in the appropriate solution, to a potential at which ethane formation takes place, the pulses having a duty ratio of 1 : 9. By changing the length of the shorter “on” pulse, during which ethane is formed, the length of the “off” pulse is simultaneously changed. Therefore, by collecting gas for a fixed length of time, the electrode is automatically maintained for the same time at the potential at which ethane is formed. By changing the length of the “on” pulse the effect of the length of polarization on the rate of formation could then be examined. The time range covered in these experiments was 0.001–10 sec.

RESULTS AND DISCUSSION

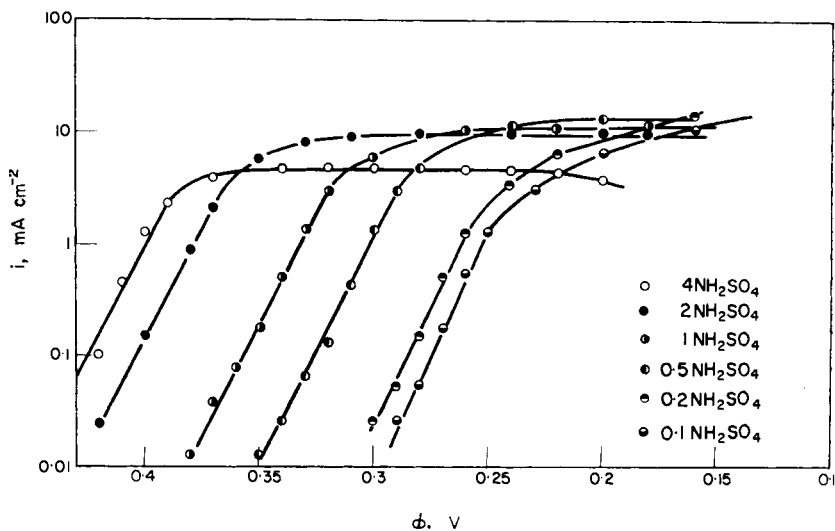
The steady state current potential curves for the reduction of nitrobenzene, nitrosobenzene, azoxybenzene and azobenzene and the oxidation and reduction curves for phenylhydroxylamine are illustrated by the data for one solution in each case in Fig. 4. These curves are representative of the behaviour which is observed although the extent of features such as the height and width of the maxima in the polarization plots varies with solution composition. In general the current initially increases expo-

nentially with the potential, that is a "Tafel" line is observed. The current then reaches a maximum whose definition depends on the concentration



ϕ , V

FIG. 4.



ϕ , V

FIG. 5.

of the solutions and on the compound studied. After a level section the current decreases to a second plateau and finally again increases.

The concentration dependence in the first three regions has been found to be different. The results are most easily interpreted in the first region where the current increases with increasing negative potential. The extreme patterns of behaviour are illustrated by the reduction of nitrosobenzene Fig. 5 and of azoxybenzene, Fig. 6. The slope of the "Tafel" plots in Fig. 5 is $(30 \text{ mV})^{-1}$ while coulometric analysis and the spectra of the products show that phenylhydroxylamine is formed, which in part couples

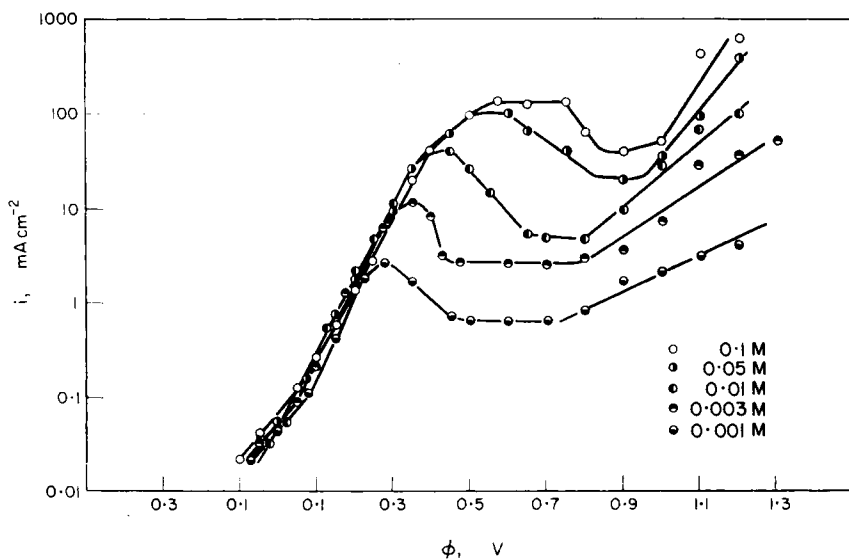


FIG. 6.

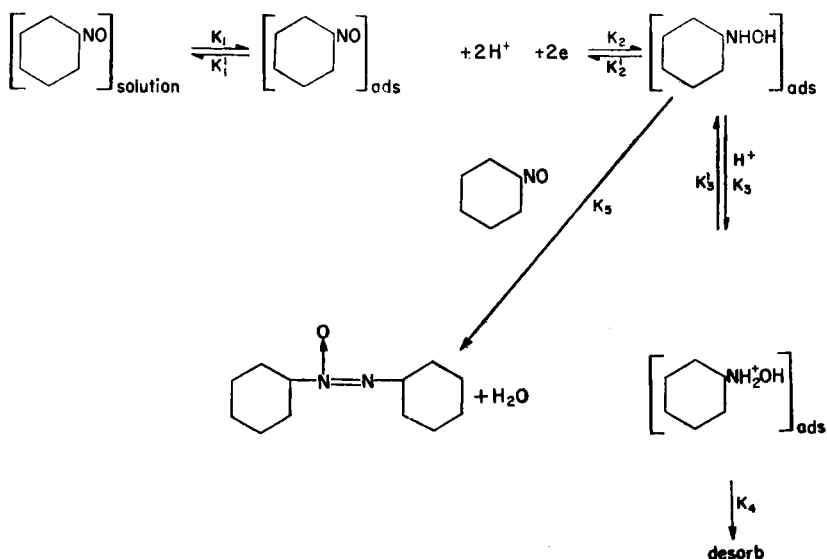
with excess nitrosobenzene to form azoxybenzene. The overall reaction therefore consists of a two-electron transfer so that the kinetics of the process may be represented by

$$i = 2Fk \left[\text{C}_6\text{H}_5\text{NO} \right]^{\nu_1} \left[\text{H}^+ \right]^{\nu_2} \exp - \frac{2\varphi F}{RT}$$

where k is the overall rate constant of the reaction, φ is the potential of the cathode and ν_1 and ν_2 are the orders of reaction with respect to nitrosobenzene and hydrogen ion concentration. These orders are most easily determined by the shift in potential with concentration at constant current, also keeping the other concentrations in the solution constant. It can be seen from Fig. 5 that the order with respect to H^+ is three. Similar measurements with respect to the nitrosobenzene concentration give an order

one. The potential dependence itself is most easily explained by assuming a rate determining chemical step succeeding the electron transfer reaction (since the α in the exponent is unity). A rate determining desorption, 4, of a protonated adsorbed phenylhydroxylamine molecule is consistent with the data according to the steps 1, 2, 3, 4 in the reaction scheme 2.

Reaction scheme 2



The rate of the reaction is therefore given by

$$i = \frac{2Fk_1k_2k_3k_4}{k_1'k_2'k_3'} \left[\text{Cyclohexane-NO} \right] \left[\text{H}^+ \right]^3 \exp - \frac{2\varphi F}{RT}$$

at low coverage of the adsorbed species.

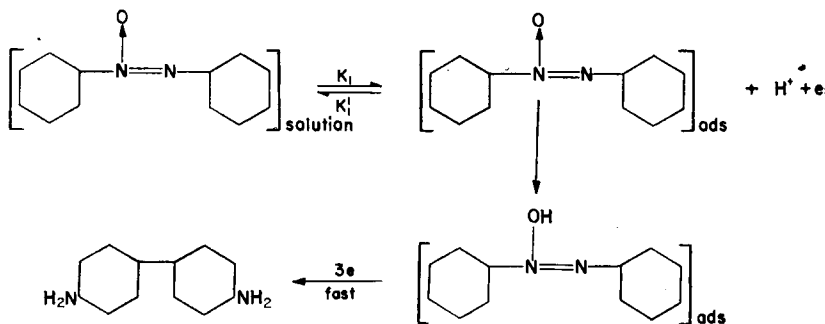
In the second region of potential in which the current is independent of potential the order of reaction is best measured from the change of current with concentration at constant potential. It can be seen from Fig. 5 that this order is zero for hydrogen. On the other hand the order is found to be greater than one with respect to nitrosobenzene at low nitrosobenzene concentrations and one at high concentrations. This behaviour is best explained by a limitation of the rate by the adsorption step 1 at high rates, a rate determining reaction 5 to form azoxybenzene also being of importance.

The opposite extreme pattern of behaviour is shown by the reduction of azoxybenzene. In the low-potential region the reduction to benzidine is quantitative and therefore requires four electrons per molecule. It can be seen from Fig.6 that the "Tafel" slopes are of the order $(100 \text{ mV})^{-1}$ while the reaction is of zero order with respect to the azoxybenzene. Similar measurements show that the reaction is of first order with respect to hydrogen ions. The rate-determining step is therefore the irreversible one-electron transfer to an azoxybenzene molecule which is present in a saturated monomolecular layer (step 2), that is according to the rate expression:

$$i = 4Fk_2 \left[\text{H}^+ \right] \exp - \left(\frac{\alpha \varphi F}{RT} \right)$$

The transfer of the remaining three electrons is fast. It is known that the final product, hydrazobenzene, must rearrange rapidly to benzidine under the conditions of the experiment. In the region in which the current is independent of potential the reaction is found to be of first order with respect to azoxybenzene so that the limiting rate determining step is again the adsorption process (step 1) in scheme 3.

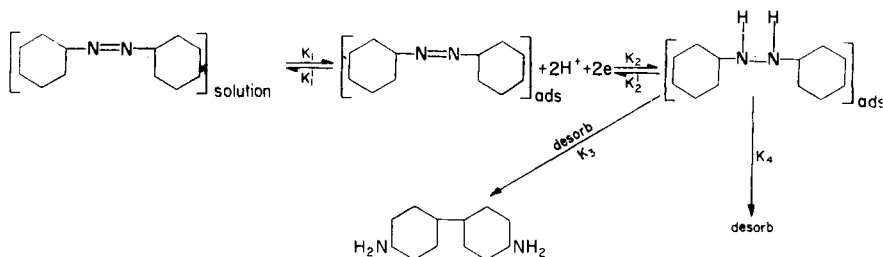
Reaction scheme 3



The electrode reactions of the remaining compounds lie between these two types of behaviour. The reduction of azobenzene has a "Tafel" slope of $(30 \text{ mV})^{-1}$ at low electrode potentials, the reaction being of second order with respect to hydrogen ions and first order with respect to azobenzene. In the region of the plateau the order is zero with respect to hydrogen and one with respect to azobenzene. It follows that the rate-determining step is either the desorption of hydrazobenzene (step 4) or the rearrangement to benzidine (step 3) at low electrode potentials and

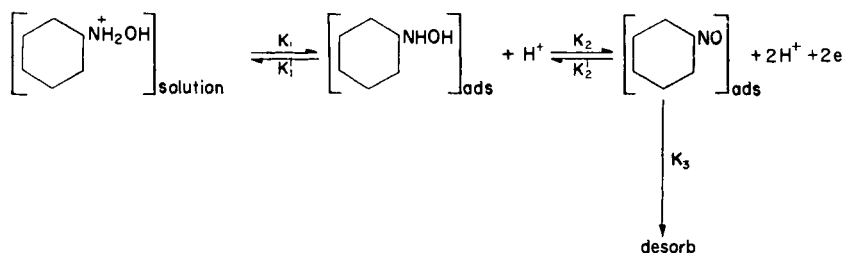
the adsorption of azobenzene (step 1) in the region of the plateau (scheme 4)

Reaction scheme 4



The oxidation of phenylhydroxylamine takes place essentially by the inverse of the reduction of nitrosobenzene. The two compounds would in fact form a reversible system but for the coupling reaction to azoxybenzene, which is the main product of reaction. At low positive electrode potentials the "Tafel" slope is $(30 \text{ mV})^{-1}$ and the reaction orders are one with respect to phenylhydroxylamine and three with respect to OH^- that is three with respect to $1/\text{H}^+$. In the region of the plateau the respective orders are one and zero so that the rate determining steps are the desorption of nitrosobenzene at low electrode potentials (step 3) and the adsorption of phenylhydroxylamine (step 1) at high electrode potentials.

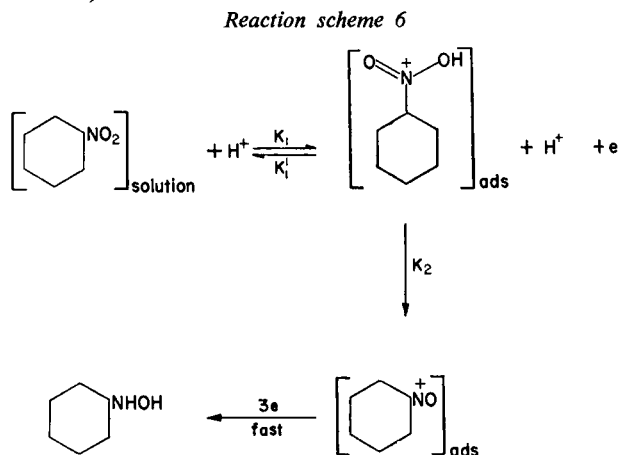
Reaction scheme 5



The fact that the rates of the adsorption steps are the limiting factors is also shown in the case of phenylhydroxylamine and nitrosobenzene by the overlap of the plateau regions. The usual explanation of such a plateau in terms of the formation of a saturated monolayer is clearly not consistent with the simultaneous saturation by the oxidized and reduced species.

The reduction of phenylhydroxylamine goes to aniline by way of an initial irreversible one-electron transfer step. This is also the case for the reduction of nitrobenzene which at low negative potentials goes quantitatively to phenylhydroxylamine and at high negative potentials to aniline.

Since the reaction is of the first order with respect to nitrobenzene and of second order with respect to hydrogen ions the most likely mechanism is the irreversible reduction of an adsorbed protonated species by the step 2 (scheme 6).



This scheme is also consistent with the observation that at high nitrobenzene concentrations the rate of reduction varies inversely with this concentration, because of competition by the adsorption of a non-protonated species.

Some general observations can be made about the reduction processes observed after the current peak and before the rise in current at the most negative potentials. In this region the reductions are independent of pH and potential and are first order with respect to the species being reduced. The height and width of the maxima (when these are observed) increase with the concentration of the appropriate compound while the "low current" plateau straddles the position of the electrocapillary maximum in aqueous solutions. The electrocapillary curve in sulphuric acid ethanol-water mixtures, as measured by a drop weight method, is truncated in the same region, and implies strong adsorption of the alcohol. All these observations are consistent with competitive adsorption of the alcohol and compound being reduced on the mercury surface. In the absence of adsorption the compounds can only be reduced at a low, potential-independent rate presumably by a tunnel mechanism through the adsorbed alcohol layer. The reduction curves have a formal similarity to the "dynatron characteristic" found in the passivation of metals although we are here dealing with cathodic processes. Although this characteristic is probably due to the formation of solid deposits in the case of passivation of metals,¹⁴

there can be little doubt that the explanation advanced in terms of inhibition by adsorption¹⁵ (by analogy with the similar inhibition of the hydrogen ionization reaction on platinum¹⁶) is correct in this case. The effects of this inhibition show that it may be possible to control the overall effects of organic electrochemical reactions by changing the solvent or by changing the solvent and electrode material. It is also somewhat doubtful whether a mechanism postulated for one medium and electrode material will have any general validity.

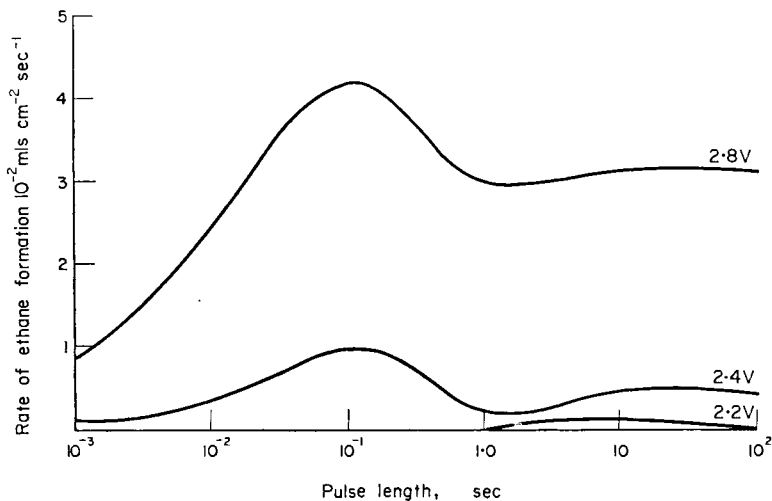
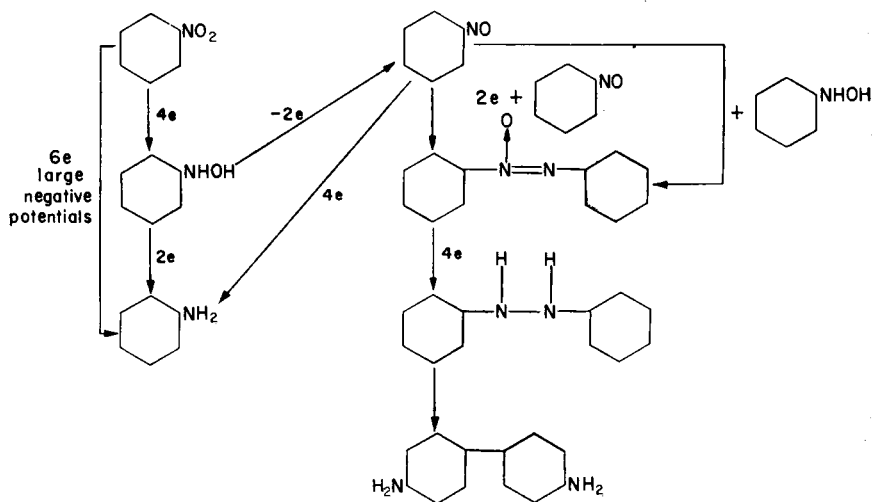


FIG. 7.

The results and discussion given above refer to the slow steps for each compound. Some further general conclusions can, however, be drawn from the products of the reaction. We have found that azoxybenzene and azobenzene are always reduced to benzidine, only a small amount of aniline being formed at the most negative potentials. Nitrosobenzene, on the other hand, is reduced to phenylhydroxylamine, which couples with excess nitrosobenzene to form azoxybenzene, the main product at low negative potentials. At intermediate potentials, benzidine is formed by further reduction, but at the most negative potentials aniline is produced. We note that this aniline can be formed only by a second direct reduction mechanism of nitrosobenzene, since azoxybenzene forms benzidine under the same conditions. Nitrosobenzene has always occupied a key position in the postulated reduction mechanism for nitrobenzene. It has been assumed that it is the first reduction product, but as the reduction is "easier"

than that of nitrobenzene, it does not accumulate but is further reduced to phenylhydroxylamine. Examination of Fig. 4 however shows that this view is incorrect, at least for mercury in acid solution. Over an appreciable potential range the reduction of nitrosobenzene is slower than that of nitrobenzene, so that nitrosobenzene and its reduction derivatives azoxybenzene and benzidine should accumulate. Under these conditions, however, nitrobenzene gives only phenylhydroxylamine, so that nitrosobenzene cannot be a direct intermediate in the reduction of nitrobenzene. The complicated reduction products which have always been found to be present are more likely to have been formed from nitrosobenzene, itself formed by the reoxidation of phenylhydroxylamine. This would be favoured by the low potentials at which the reaction goes on on platinized platinum. We therefore postulate the following overall reduction mechanism, scheme 7:

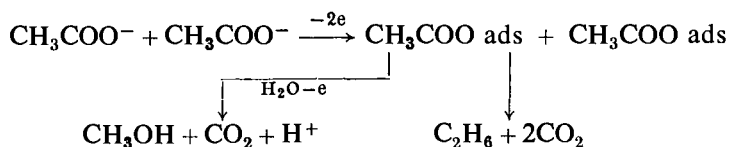
Reaction scheme 7



It should be noted that the use of potentiostatic methods, by permitting the exploration of the "dynatron" range, allows a more detailed formulation of the mechanism. This detailed characterization of the polarization curves, Fig. 4, shows that it should be possible to make azoxybenzene in high yield by successively reducing nitrobenzene at a low potential and then reoxidizing at a more positive potential, and we have confirmed this. Furthermore, by pulsing the electrode between two potentials at which on the one hand nitrobenzene is reduced to phenylhydroxylamine and azoxybenzene to benzidine and on the other hand phenylhydroxyl-

amine is oxidized and coupled to azoxybenzene, it should be possible to make benzidine in one process. We have confirmed that a quantitative reduction can be carried out in this way by using pulses of intermediate frequency.

A more direct demonstration of the potentialities in controlling electrode processes by pulse length as well as by the potential height is given by the formation of ethane from acetate ions. For pulse lengths in excess of 3×10^{-3} s ethane is formed by a second order reaction between acetate radicals discharged onto the platinum surface:



At pulse lengths less than this figure there is a "relaxation" of this second order process. The radicals can however react with water by a pseudo-first order reaction and this will almost inevitably have a shorter relaxation time. For these short pulse lengths methyl alcohol is in fact formed, although it is largely further oxidized to formaldehyde and carbon dioxide under the conditions of the experiment. The further features of the curves of ethane yield against pulse length can also be interpreted.

There can be little doubt that it should be possible in general to devise experimental techniques so as to single out reaction products in complicated simultaneous or succeeding reaction sequences according to the relaxation times for their formation. Electrochemical methods, by permitting rapid and large perturbations of the rate constants, offer a particularly simple method of carrying this out. We may note in conclusion that the time resolution of the most rapidly acting potentiostats⁹ ($1 - 10 \mu\text{s}$) should be sufficiently high to permit pulsing of electrodes below the range of relaxation times for all second order reactions in dilute solutions.

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