It is clear that the polymerisation of 1,2-epoxides and investigation of the structure and properties of the polymers obtained are of great theoretical and practical interest. The synthesis of sterically regular polyether compounds from optically active monomers and racemic mixtures forms part of the extremely interesting and complex problem of directed stereosynthesis.

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Institute for Petrochemical Synthesis,
Academy of Sciences of the USSR

APPLICATION OF POLAROGRAPHY TO ORGANIC CHEMISTRY

Yu. P. Kitaev and G. K. Budnikov

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I. INTRODUCTION

The present review is dedicated to the centenary of Butlerov's theory of the structure of organic compounds and to the fortieth anniversary of the invention by J. Heyrovský of the polarographic method of analysis, which is being successfully employed at the present time for the investigation of the structure, properties, and reactions of organic compounds.

By 1959 the number of publications on the theory and practical applications of polarography exceeded 10 000, with a steady increase in the annual output[1]. The award in 1959 of a Nobel prize to Heyrovský testifies to world recognition of the scientific and practical value of polarography.

The polarographic method consists essentially in an examination of the relation between current and potential in the electrolysis of a dilute solution of the test material in the presence of an inert electrolyte. The electrolysis is carried out in a special cell at a polarised microelectrode (usually a dropping mercury electrode), the potential of which is measured relative to that of a macroelectrode, most often a saturated calomel half-cell.

The relation between current and potential is expressed graphically in the form of polarisation curves or polarograms. These make it possible to estimate the quantity of the test material from the magnitude of the limiting current i_d and to determine its nature from the half-wave potential.

The main parameters in polarography are the half-wave potential $\pi_{\frac{1}{2}}$ and the wave height i_d. The former is defined as the potential corresponding to the point on the polarogram whose ordinate is $\frac{1}{2}i_d$. Quantitative polarographic analysis is based on measurement of the limiting current (wave height), which in most cases is governed by diffusion of the substance towards the electrode, and is represented by the Ilkovič equation[2]

$$i_d = 60.7\, n D^{1/2} m^{2/3} t^{1/6} C,$$

where n is the number of electrons involved in the electrode reaction, D the diffusion coefficient of the test substance (in $cm^2\ sec^{-1}$), m the quantity of mercury flowing through the capillary (in $g\ sec^{-1}$), t the drop time (in sec), and C the concentration of the polarographically active substance (in moles $litre^{-1}$).

In deriving this equation, Ilkovič introduced the concept of the half-wave potential and elucidated its physical significance. Lingane and Loveridge[3], Stackelberg and Strehlow[4], and Koutecký[5] subsequently modified the Ilkovič equation to allow for the fact that diffusion takes place, not linearly, but towards a curved surface.

The theory of polarography has now been developed in considerable detail, and accounts of it can be found in several textbooks, monographs, and handbooks[6-15]. The main literature on polarography is listed in the monograph mentioned in Ref. 13.

Among the early polarographic investigations, quite a large number were concerned with the reduction of organic compounds. Nevertheless, during the first decades it was the polarography of inorganic compounds which was mainly developed, since the reactions of organic compounds at a mercury electrode proved to be too complex to be interpreted unambiguously at that time. With the development of the theory of polarography, the investigation of organic compounds, which had been spasmodic in character, began to play an important part in the experimental verification of theory.

The publication of several monographs on polarography in the early 1940's contributed to the further development and growth in popularity of the method. Until recently, however, it has evolved solely as a highly sensitive electrochemical method of analysis. By means of polarography, it became possible to analyse complicated systems, both inorganic and organic, without preliminary separation, isolation, or purification of the components.

The value of the method, however, is not exhausted merely by its analytical application. While remaining a very convenient method of analysis, polarography has also become an important means for solving various problems of theoretical chemistry, mainly organic; applied in combination with one or more physicochemical methods, and sometimes alone, it can give extremely valuable results.

Research workers have recently taken an increasing interest in the polarography of organic compounds, since it has proved possible to solve several quite complicated problems of the structure and reactions of organic compounds.

The surveys of the polarography of organic compounds published regularly by Wawzonek[16-21] normally cover all the work in which polarography has been used, and the still not very numerous theoretical investigations of organic compounds and their chemical reactions are lost among the hundreds of papers of an analytical character.

The present review represents an attempt to summarise the principal achievements of the application of the polarographic method to organic chemistry.

At the present time polarography is employed in organic chemistry in several ways: (1) in studying the structure of organic compounds; (2) in studying the nature and positions of substituents and their effect on reactivity; (3) in detecting hydrogen bonds and chelate rings; (4) in studying tautomeric changes; (5) in studying geometrical isomerism; (6) in solving problems of chemical kinetics; (7) in studying molecular rearrangements and reactions; (8) for identifying natural products[22]; and (9) in studying the physical properties of compounds (for example, diffusion coefficients, surface activity[23]).

A large amount of experimental results has been amassed since the invention of polarography, and this cannot be reported and discussed in detail in a single paper. The present review covers mainly work carried out during recent years, which, in the opinion of the reviewers, is of the greatest significance for organic chemistry.

II. INVESTIGATION OF STRUCTURE AND THE EFFECT OF SUBSTITUENTS ON THE REACTIVITY OF ORGANIC COMPOUNDS

The reactivity of a compound is determined by its structure. In polarography the electrochemical reaction taking place at the electrode has a numerical characteristic, the half-wave potential. Since an electrochemical reaction does not differ in principle from a chemical reaction, the half-wave potential to a certain extent characterises not only the "electrochemical" but also the "chemical" reactivity of a compound.

The half-wave potential of an organic compound is determined both by the nature and also by the position of the polarographically active group in the molecule, since, when more than one substituent is present, the value of $\pi_{\frac{1}{2}}$ is affected by their relative positions in the molecule. Thus the value of $\pi_{\frac{1}{2}}$ is directly related to the nature and the position of a substituent: *i.e.* both molecular structure and the effect of substituents on reactivity can be assessed from polarographic data.

During the early development of the polarographic method, Shikata and Tachi formulated their experimental "electronegativity rule of reduction potentials", according

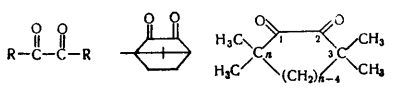
to which reduction of organic compounds is facilitated by the presence of electronegative groups in the molecule[24]. This rule enabled the influence of different substituents on the polarographic behaviour of organic compounds to be characterised qualitatively. Numerous investigations on this problem have confirmed the correctness of the Shikata–Tachi rule.

Thus it has been established that the introduction of electronegative groups into the α-position with respect to a carbon atom combined with a halogen atom facilitates the electrochemical reduction of the $-C-Hal$ bond, which is shown as a shift in $\pi_{\frac{1}{2}}$ to lower cathodic potentials. On passing from CH_3Br to CBr_4, the value of $\pi_{\frac{1}{2}}$ corresponding to reduction of the first carbon–bromine bond is displaced respectively from -1.60 V to -1.44, -0.60, and then to -0.26 V.[25] When oxygen-containing groups are introduced into the α-position with respect to the bromine in alkyl bromides, the shift in $\pi_{\frac{1}{2}}$ towards more positive potentials increases in the sequence CHOH < CHO < COOH.[26]

As Mairanovskii *et al.*[27] have shown, introduction of nitro-groups into the α-position also considerably facilitates reduction of a carbon–halogen bond, their effect increasing with increase in their number. In the series of bromides from bromonitromethane to bromotrinitromethane the half-wave potential shifts from +0.06 to +0.36, *i.e.* changes by 0.30 V. A similar effect is observed with the corresponding chlorides, the difference between the first and last members being still greater (0.76 V). Knowledge of the polarographic behaviour of various halogen derivatives enabled Postovskii and Beiles to establish the structure of the compounds obtained by the chlorination of naphthacene-5,11-quinone with sulphuryl chloride[28].

Polarographic investigation of several cyclic disulphides has shown that their ease of reduction is appreciably affected by the size of the ring[29]. It has been suggested on the basis of a polarographic study that α-lipoic acid is a six-membered cyclic disulphide[30].

Laitinen *et al.*[31] made a detailed study of the behaviour of the following 1,2-diketones:



and established in particular that the ease of reduction of cyclic diketones depends on the size of the ring and the extent of alkyl substitution at the α-carbon atom.

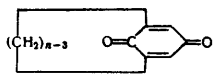
Krupička[32] investigated the effect of substituents in the 2-position on the ease of reduction of 4-hydroxy-3-methylcyclopent-2-en-1-one.

Several papers give values of $\pi_{\frac{1}{2}}$ obtained under comparable conditions for substituted nitrobenzenes[33,34], benzaldehydes[33,35,36], and iodobenzenes[33,37]. The results conform to the Shikata–Tachi rule, and explain the orienting effect of substituents in the benzene ring.

Coulson and Crowell[35] have established that an *ortho*-substituent has a weaker effect in benzaldehydes than in the corresponding acetophenones.

Valyashko and Rozum[38] showed, in a detailed investigation of the effect of substituents on the reduction of acetophenones, that, when one or two hydroxy- or methoxy-groups are introduced into the acetophenone molecule, reduction is most facilitated by a *para*-substituent.

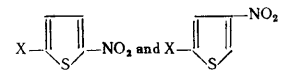
Prelog *et al.*[39] used a polarographic method to determine the effect of the size of the polymethylene ring in the 2,6-position on the reduction of a series of benzoquinones having the structure



where n was varied from 9 to 19. The values of $\pi_{\frac{1}{2}}$ obtained were close to those for 2,6-diethyl- and 2,6-dimethyl-benzoquinones. From this Prelog concluded that the polymethylene ring in these compounds is unstrained.

A polarographic study by Vladimirtsev and Postovskii[40] of some hydroxyazo-compounds showed that introduction of a hydroxy- or a methoxy-group *para* to the azo-group shifts the half-wave potential to more negative values owing to an increase in electron density on the azo-group. Introduction of a sulpho-group into the *para*-position, however, facilitates reduction, also in conformity with the electron-acceptor properties of this substituent.

The influence of substituents on the half-wave potentials of the following substituted nitrothiophens was studied by Tirouflet[41]:



where X = CH_3, I, $CH(OCOCH_3)_2$, CH=NOH, COOH, $COCH_3$, CN, $C(CH_3)$=NOH, CHO, $COOC_2H_5$. He also explained the mechanism of the nitration of substituted thiophens on the basis of the polarographic data.

The arrangement of the conjugated bonds involved in the reduction can be assessed from polarographic data, since reduction is known to take place more readily the longer the conjugated system and the larger the number of π-electrons participating in the conjugation.

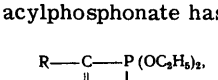
Fields and Blout[42] investigated the polarographic behaviour of a series of unsaturated aldehydes of general formula $CH_3[CH=CH]_xCHO$, where x = 1–5, and established that the half-wave potentials become more positive as double bonds accumulate in the molecule.

$CH_3CH=CHCHO$	1.20 V (relative to sat. calomel electrode)	
$CH_3(CH=CH)_2CHO$	0.98 V	ditto
$CH_3(CH=CH)_3CHO$	0.83 V	»
$CH_3(CH=CH)_4CHO$	0.72 V	»
$CH_3(CH=CH)_5CHO$	0.64 V	»

An analogous shift in half-wave potentials with accumulation of double bonds occurs also with ketones, indicating an increase in reactivity of the reducible multiple bond.

The existence of a double bond in the side-chain of 4-(4′-hydroxyphenoxy)-3,5-diiodocinnamic and 4-(4′-hydroxy-3′,5′-diiodophenoxy)-3,5-diiodocinnamic acids was demonstrated polarographically by Wawzonek *et al.*[43]

Ackerman *et al.*[44] showed on the basis of polarographic data that a diethyl acylphosphonate has the structure



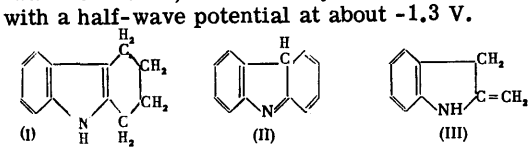
and not one containing tervalent phosphorus, for in the latter case there would be no conjugation of the oxo-group with the $P\rightarrow O$ bond, and such a molecule could not be reduced at least up to -2 V; these workers confirmed this structure spectroscopically.

Polarography has been used also to determine the structure of the bactericidal preparation Allicin[45], the results indicating that it contains the compound

$$CH_2{=}CH{-}CH{=}CH{-}S{-}S{-}CH{=}CH{-}CH{=}CH_2.$$
$$\underset{\|}{O}$$

Bezuglyi *et al.*[46] investigated dimethylamino- and acetamido-acetophenones under various conditions with the aim of linking the principal polarographic characteristics with the presence of different groups in the molecule and also with the state of the substance in solution. In acid media at pH < 2.2 all three isomeric *NN*-dimethylaminoacetophenones have similar reduction potentials, which in the opinion of these workers is due to the participation of the lone electron pair of the nitrogen in salt formation, *i.e.* to the elimination of its mobility. When salt formation does not take place, the lone pair of the nitrogen is involved in conjugation with the π electrons of the benzene ring, and affects the half-wave potential in accordance with the position of the dimethylamino-group. With the acetamido-acetophenones the tendency to salt formation is weaker, and their behaviour on reduction in acid medium is very different from that of the amino- and dimethylamino-acetophenones.

Ender *et al.*[47] employed polarography in studying the structure of alkaloids containing indole systems. It was found that, in neutral medium, indole and tetrahydrocarbazole (I) are not reduced at a dropping mercury electrode, whereas 3*H*-indole and 4a*H*-carbazole (II) give a polarographic wave at -1.7 V, and 2-methyleneindoline (III) gives a wave with a half-wave potential at about -1.3 V.



The difference in behaviour among these structures is caused by the different positions of the double bond with respect to the nitrogen and to the benzene ring. Thus in indole the double bond is conjugated with the double bonds in the ring and with the lone pair of electrons on the nitrogen, which confers an aromatic character on the compound: it is not reduced. The great ease of reduction of 2-methyleneindoline compared with 3*H*-indole is explained[47] by the different roles of the lone pair of electrons on the nitrogen atom in these compounds.

Ender suggested using polarography to determine the interaction energy of the bonds as a quantitative measure of reactivity[48], and employed it in the study of different conjugated systems.

The results obtained by Ender are well illustrated by Table 1, which gives the bond interaction energies E_C for several carbonyl compounds measured in neutral solution. He found by extrapolation the limiting half-wave potentials π_{lim} for aldehydes and ketones to be -1.77 and -1.99 V respectively, which are characteristic of compounds free from any effect of substituents. The difference between the limiting potential and the half-wave potential expresses quantitatively the extent to which reduction is facilitated by the substituent, which the author terms "conjugation", not always with sufficient justification. Thus a quantitative measure of the effect of different radicals on the carbonyl group can be obtained from polarography. Table 1 gives energy values calculated from polarographic data.

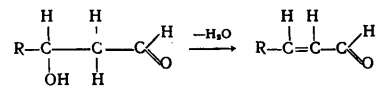
Whereas the calculation of heats of reaction previously in use, based on bond energies, often gave results which

TABLE 1.

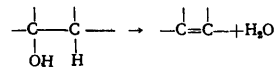
Compound	$-(\pi_{lim}-\pi_{1/2})$, V	E_c, kcal mole^{-1}
HCHO	0.22	5.1
CH_3CHO	0.00	0.0
CH_3CH_2CHO	0.00	0.0
$CH_3CH_2CH_2CHO$	—0.02	—0.5
$CH_3CH{=}CHCHO$	0.39	9.0
C_6H_5CHO	0.37	8.5
$C_6H_5COCH_3$	0.38	8.7
$CH_3C_6H_4COCH_3$	0.31	7.1
$C_6H_5COC_6H_5$	0.64	14.7
$C_6H_5CH(OH)COC_6H_5$	0.69	15.8
$C_6H_5COCOC_6H_5$	1.38	31.2

did not agree with the experimental data even in sign, the used polarographic values of the bond interaction energies in these calculations makes it possible to predict the occurrence of several reactions. When the energy balance of a reaction has been calculated, the probability of its occurrence can be determined from the sign and magnitude of the change in molar enthalpy.

As an example, Ender ascertains whether all β-hydroxycarbonyl compounds tend to split off water. From the equation to the reaction



he wrote out the bonds involved in the change:

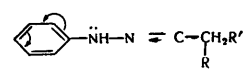


and computed their energy, bearing in mind that a double bond in the $\alpha\beta$-position with respect to the carbonyl contributes 9 kcal to the molecule energy as a result of conjugation.

Energy absorbed		Energy evolved	
C—H	87 kcal	C=C	110 kcal
C—O	70 kcal	O—H	100 kcal
C—C	58 kcal	E_c	9 kcal
	215 kcal		219 kcal

The heat of reaction ($-\Delta H$) is +4 kcal. The magnitude and sign of ΔH, which are not governed by the presence of any substituents, indicate that all β-hydroxycarbonyl compounds tend to eliminate water intramolecularly.

Kitaev[49] explained bond interaction in arylhydrazones and their polarographic behaviour on the basis of the general theory of conjugation. Hydrazone molecules contain a system in which the multiple bonds are conjugated *via* the 2*p* electrons of the nitrogen atom, *i.e.* they have a $\pi p\pi$-conjugated system, the direction of polarisation in which is determined by the nitrogen atom (since the C = N bond is polar), while the electrophilic aromatic ring intensifies the polarisation:



Arylhydrazones in the enehydrazine form contain two multiple bonds (one of which is aromatic) separated by two nitrogen atoms each having two 2*p* electrons, *i.e.* these compounds contain a $\pi pp\pi$-conjugated system, which is less polar than a $\pi p\pi$-conjugated system. It is therefore to be

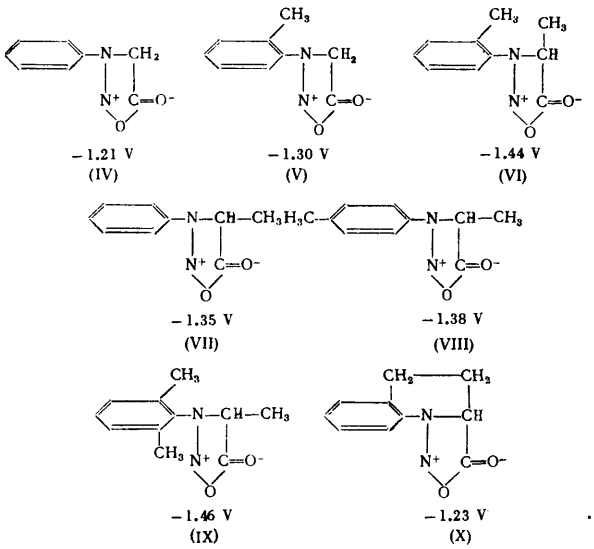
expected that hydrazones will be reduced at a dropping mercury electrode at more positive potentials than will enehydrazines, as was confirmed experimentally. The difference between the values of $\pi_{\frac{1}{2}}$ for these forms can serve as a quantitative measure of the bond interaction energy in these systems.

The reactivity and the properties of organic compounds are influenced by all the types of interaction between structural units in the molecule[50]. In most cases these interactions develop simultaneously, and it is by no means always possible to separate them. Since, however, polar effects and those due to conjugation often predominate over steric influences, they were assumed to be responsible for the polarographic behaviour of the compounds.

It has been shown recently that steric effects also can play a decisive part in the polarographic behaviour of some classes of organic compounds. The effect of spatial interaction on the polarographic behaviour of a molecule may hinder its reduction. Table 2 illustrates the influence of branching in the alkyl radical of an alkyl bromide on the reduction of a C – Br bond[51].

The more negative half-wave potentials observed with the *o*-alkylated compared with the *p*-alkylated nitrobenzenes, acetophenones, benzophenones, and azobenzenes[52,53] are also due to the steric effect of the *ortho*-substituent on the reduction of the polarographically active group (the so-called *ortho*-effect[50]).

Zuman[53] examined in detail various cases of a steric effect in the reduction of organic compounds at a dropping mercury electrode. Thus, for example, he detected the steric inhibition of coplanarity in alkylphenylsydnones[53,54] for which he found the following half-wave potentials:



Introduction of a methyl group into the *para*-position in the benzene ring causes a shift in $\pi_{\frac{1}{2}}$ of -0.025 V. The polar effect of an *ortho*-group should be of the same order. The negative shift in $\pi_{\frac{1}{2}}$ is considerably greater with the *o*-methylated than with the *para*-substituted 3-phenylsydnone and 4-methyl-3-phenylsydnone. Zuman explains this by the breakdown in coplanarity of the rings caused by an *ortho*-substituent. The relative positions of the rings should not be affected by a second *o*-methylation. The shift in the half-wave potential observed with di-*o*-methylated compared with the mono-*o*-methylated compounds is only that due to the polar effect of the methyl group.

TABLE 2.

Compound	$-\pi^*_{\frac{1}{2}}$, V
Ethyl bromide	2.13
Propyl bromide	2.20
Isobutyl bromide	2.32
Neopentyl bromide	2.37

* Relative to saturated calomel electrode. Supporting electrolyte — tetrabutylammonium iodide in dimethylformamide.

On ring closure between substituents (compound X), the benzene ring again becomes coplanar with the sydnone ring. Therefore the half-wave potential of X is more positive than that of 4-methyl-3-*o*-tolylsydnone.

With the polarographic behaviour of aldehydes of the holarrhiminic series as an example, Zuman showed that the spatial configuration of the molecule may affect the hydration of the functional group[53,55,56]. It was known that aldehydes are more difficult to reduce at a dropping mercury electrode than the corresponding aldimines. Aldehydes of the holarrhiminic series do not obey this rule: they are reduced at considerably more positive half-wave potentials than the steroid aldehydes, for example, which are similar in structure, and their aldimines are reduced at more negative potentials than the free aldehydes. Zuman explains such anomalous polarographic behaviour of these compounds by assuming that the aldehyde group is not hydrated owing to steric hindrance, whereas the carbonyl group of the steroid aldehydes is hydrated, which makes it more difficult to reduce than the carbonyl group in the holarrhiminic aldehydes. Therefore the possible hydration of the carbonyl compounds must be taken into account in assessing the intensity of reduction of such compounds and of their azomethine derivatives. In a review[53] Zuman quotes other examples of the application of polarography to the solution of stereochemical problems, which we shall discuss in greater detail below.

One of the most urgent problems of modern organic chemistry is to establish a quantitative relation between the structure of an organic compound and its reactivity. In the general case this problem still remains very complex, but partial regularities, represented by empirical and semiempirical equations, are readily available, and make it possible to express numerically the influence of structural units on the reactivity of a compound. This applies primarily to the well-known Hammett rule[57,58], which covers the rate constants and the equilibrium constants of nucleophilic substitution reactions of aromatic derivatives having substituents in the *meta*- and *para*-positions, and also the Taft rule[50], derived from the rate of hydrolysis of esters of aliphatic carboxylic acids. We shall discuss in greater detail the use of these semiempirical rules in organic polarography.

Most electrochemical reactions involving organic substances take place irreversibly; the value of $\pi_{\frac{1}{2}}$ is proportional to the logarithm of the rate constant of the irreversible process[59–61]:

$$\pi_{1/2} = \frac{RT}{\alpha n F} \ln 0.87 k_f \cdot \sqrt{\frac{t_1}{D}},$$

where α is the transport number, t_1 the drop time of the mercury electrode, D the diffusion coefficient, and k_f° the specific rate constant of the electrode process, the magnitude of which is determined by the free energy change for the compound.

In order to establish a quantitative relation between the value of $\pi_{\frac{1}{2}}$ and the effect of substituents on reactivity, it is necessary to investigate the electrochemical behaviour under identical conditions of a series of compounds containing the same polarographically active group and different substituents, and the mechanism of the electrochemical reaction undergone by the functional group must be identical within this series.

If $\pi_{\frac{1}{2}}^0$ and $\pi_{\frac{1}{2}}^*$ represent half-wave potentials of unsubstituted and substituted compounds respectively, the following relation is obtained for irreversible processes:

$$\pi_{1/2}^* - \pi_{1/2}^0 = \Delta\pi_{1/2} \simeq \Delta \ln k_f^\circ = \ln \frac{k_{f^\circ}^*}{k_{f^\circ}^0}.$$ [61]

This expression corresponds to Hammett's equation[57], which for an electrochemical reaction becomes

$$\Delta\pi_{1/2} = \rho'\sigma, \qquad (A)$$

where ρ' is a constant for a certain type of electrochemical reaction, and measures the susceptibility of the reactive centre (polarographically active group) to the influence of substituents; and σ is a constant measuring the effect of a given substituent in the benzene ring on the reducibility of the compound, its value depending on the position and the nature of the substituent.

Using the principles of theoretical organic chemistry, Taft[50] divided the changes produced by substituents into polar, steric, and conjugation effects. As mentioned above, these effects are in most cases additive, *i.e.* the value of $\Delta\pi_{\frac{1}{2}}$ is governed by the sum of these three factors. When the polar effect predominates, Taft's equation becomes for an electrochemical process

$$\Delta\pi_{1/2} = \rho'\sigma^*; \qquad (B)$$

where σ^* is the polar constant of the substituent in an aliphatic compound. This σ^* is analogous to the Hammett constant, but is written with an asterisk to denote the difference in its nature and origin[61]. Values of σ and σ^* have been tabulated[50,57,58].

We considered above the effect of different substituents on the ease of reduction of different benzene derivatives. The conclusions reached on the basis of the experimental data were qualitative in character. Recently the validity of Eqn. (A) has been demonstrated for a large number of electrochemical reactions of benzene derivatives containing substituents in the *meta*- and *para*-positions[61-68], and the possibility of a quantitative assessment of the effect of substituents was shown. Each series of reactions studied is characterised by a definite value of ρ'.

Fig. 1 shows the dependence of $\pi_{\frac{1}{2}}$ on σ values given in Zuman's review[61]. Some substituents [NH_2, $(CH_3)_2N$, OH] can conjugate, when in the *para*-position, with the double bond of the reducible group. This explains frequent deviations in the values of $\Delta\pi_{\frac{1}{2}}$ found for these substituents from those required by a linear relation between $\pi_{\frac{1}{2}}$ and σ.

Some authors[62] ascribe the discrepancies in the values of $\pi_{\frac{1}{2}}$ with *p*-amino-compounds to the influence of the supporting electrolyte (participation of the amino-group in salt formation), which increases the σ value.

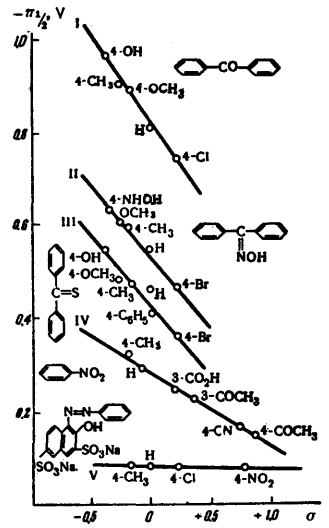


Fig. 1. Variation of half-wave potential with the σ value of substituent:
I) benzophenones (pH 0); II) oximes of benzophenones (pH 0); III) diphenyl sulphones (pH 0); IV) nitrobenzenes (pH 2.0); V) phenylazonaphthalenes (pH 2.6).

Where the values of $\pi_{\frac{1}{2}}$ for *para*-substituents deviate from a linear variation with the σ values, ρ' can be determined from the plot of $\pi_{\frac{1}{2}}$ against σ for the corresponding *meta*-substituents. This can then be used to calculate more exact σ values for the *para*-substituents from the half-wave potentials of the compounds. In this way polarographic results can be used to calculate σ values from the known value of ρ' and these can be used for the quantitative characterisation of homogeneous organic reactions.

If the half-wave potential shifts to more positive potentials with increase in the positive σ value of the substituent (*i.e.* with increase in its electrophilic character), the sign of ρ' will be positive, in conformity with the kinetics of homogeneous reactions. This is the case with the vast majority of electrochemical reactions undergone by organic compounds at a dropping mercury electrode. The mechanism of the potential-determining stage was found to be the same for these reactions — nucleophilic addition of an electron.

When the benzene ring contains more than one substituent in the *meta*- and *para*-positions or the compound contains two substituted benzene rings combined with the polarographically active group, the effects due to the substituents have been shown to be additive[61,63-67]:

$$\Delta\pi_{1/2} = \rho\Sigma\sigma.$$

With *ortho*-substituted benzene derivatives, in which, as mentioned above, steric interaction occurs, Zuman[61] suggests using the Hammett equation in the following form:

$$\Delta\pi_{1/2} = \rho'\sigma_0 - \delta E_0. \qquad (C)$$

where E_0 is a steric coefficient, values of which are given in Tables[50], and δ is a steric constant of the electrochemical reaction, which is found in a similar manner to ρ'.

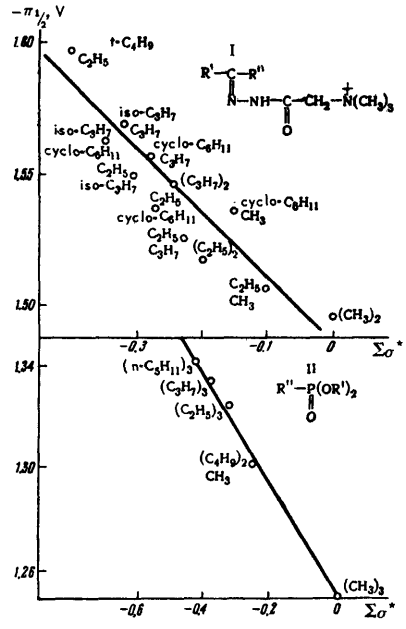


Fig. 2. Dependence of half-wave potentials on the $\Sigma\sigma$ values of substituents:
I) β-ene hydrazones; II) phosphonic esters.

Thus by means of Eqn. (C) it is possible to give a numerical value to the steric effect of an *ortho*-substituent on the reduction of a particular group in an aromatic compound. Elving *et al.*[69] were the first to point out the possibility of using the Taft equation (B) in the polarography of aliphatic compounds. Subsequently Zuman[61] confirmed the validity of Eqn. (B) for sixty series of electrochemical reactions undergone by various aliphatic derivatives. When more than one substituent is present in a compound, Eqn. (D) can be used with some approximation:

$$\Delta\pi_{1/2} = \rho'\Sigma\sigma^*. \qquad (D)$$

Here, too, the relation between $\pi_{\frac{1}{2}}$ and $\Sigma\sigma^*$ is satisfactorily represented by a straight line (see Fig. 2). With many electrochemical reactions of aliphatic compounds, it was found that ρ' could have a negative value, and steric effects as well as those due to conjugation are encountered far more often than in the aromatic series. The relation between $\pi_{\frac{1}{2}}$ and $\Sigma\sigma^*$ can, by analogy with the benzene series, be used to form the basis of a quantitative measure of these effects.

Kabachnik and his collaborators[70] have been carrying out a great deal of work on the quantitative assessment of the reactivity of several organophosphorus compounds using the Hammett equation. Although the polarographic study of such compounds has been far from adequate, and it is as yet difficult to say anything about the mechanism of their electrode reactions, we have used published data[71] to plot $\pi_{\frac{1}{2}}$ against $\Sigma\sigma^*$ for phosphonic esters (see Fig. 2), for which the values of $\pi_{\frac{1}{2}}$ lie satisfactorily on a straight line.

The value of ρ' may depend on the pH of the solution, the solvent, etc. It is better to compare half-wave potentials of substituted compounds under conditions such that $\pi_{\frac{1}{2}}$ is independent of pH, or else in a pH range where $d\pi_{\frac{1}{2}}/d\text{pH}$ has approximately the same value for compounds of the given series.

More detailed accounts of the problem of assessing quantitatively the effect of substituents on the reactivity of organic compounds, as well as various cases of the use of Eqns. (A)–(D) for predicting half-wave potentials and establishing the mechanism of an electrode process, can be found in papers by Zuman[61] and Nürnberg[65].

III. DETECTION OF HYDROGEN BONDS AND CHELATE RINGS

A hydrogen bond represents a special type of intermolecular or intramolecular interaction between a hydrogen atom which tends to ionise and an atom which has a lone pair of electrons and is located close to the hydrogen atom in space.

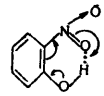
Although the hydrogen bond has attracted the attention of many investigators during the past two decades, its nature has still not been finally elucidated. Whether a hydrogen atom forming such a bond remains in a fixed position or whether it oscillates between two equilibrium positions remains an unsolved problem.

The presence of hydrogen bonds in compounds produces changes in several of their physical properties, such as solubility, boiling and melting points, optical properties, etc. A hydrogen bond also has a certain effect on the chemical behaviour of compounds. Hydrogen bonds are studied mainly by infra-red spectroscopy (the occurrence of shifts in the characteristic frequencies of functional groups).[72] If, however, hydrogen bonding involves a polarographically active group, it can be successfully detected by a polarographic method, which is considerably simpler and more convenient than infra-red spectroscopy.

The present section will be confined to a consideration of intramolecular hydrogen bonds. Intermolecular bonds, which result in the association or hydration of molecules, and determine the state of a substance in solution, will be discussed in the section on the kinetics of chemical reactions.

The earlier work, referred to in Terent'ev and Yanovskaya's monograph[14], was concerned with hydrogen bond formation in various aliphatic and aromatic hydroxy-nitro-compounds and flavanols. A hydrogen bond, for example, facilitates the reduction of *o*-nitrophenol, whereas the esterification of this compound, by destroying the hydrogen bond, increases the value of $-\pi_{\frac{1}{2}}$. The half-wave potential of *o*-nitrophenol is also displaced towards negative values at pH ~11, which indicates that the hydrogen bond has disappeared owing to formation of the phenoxide, in which hydrogen bonding is impossible.

The formation of a hydrogen bond usually facilitates the electrochemical reduction of an active group; for example, several *ortho*-substituted benzaldehydes and nitrobenzenes are reduced at a more positive potential than the *para*-isomers (by about 0.05–0.07 V). This is probably due to a strengthening of conjugation by intramolecular hydrogen bonds, which complete a ring of conjugated multiple bonds in these compounds.

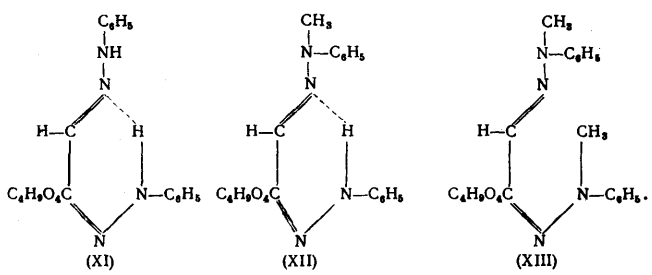


Cases are known, however, in which hydrogen bonding hinders reduction. The hydrogen bond weakens the conjugation, lowering the activity of the reducible group, as in the flavanols, for example.

Rabinowitz and Wagner[73] showed by a polarographic method that a hydrogen bond is formed between the nitro- and the imino-groups in 4-nitrobenzoimidazole. This method has also enabled the presence of a chelate ring to be demonstrated in *o*-nitroaniline[74], *o*-nitroacetanilide, and *N*-*o*-nitrophenyl-*N'*-phenylacetamidine[75], and also the presence of a hydrogen bond in 2-cyclohexyl-4,6-dinitrophenol and 4-cyclohexyl-2,6-dinitrophenol[76].

Wiles[77] also detected the presence of hydrogen bonds in several hydroxyanthraquinones, and Miller and Wagner found them in nitrobenzotriazole[78]. Holleck *et al.*[79] have published a quite detailed survey of work on the effect of a hydrogen bond on the half-wave potentials of various nitrobenzenes, -benzaldehydes, and -naphthols, so that there is no need to give here a list of all the cases of the polarographic detection of hydrogen bonds.

Study of the behaviour of glucosazones at a dropping mercury electrode has shown that compounds (XI) and (XII) have a chelate structure, since they are reduced at the same potential, whereas osazone (XIII), in which a hydrogen bond cannot be formed, is reduced at a potential which is 200 mV more positive[80].



(XI) (XII) (XIII)

Haas and Lynch[81] investigated the hydrazones of aldopentoses, and found that the observed currents were kinetic in character, since they were independent of the height of the mercury reservoir. The kinetic nature of the reduction process was indicated also by the high temperature coefficient (6.86% deg^{-1}). They concluded that these hydrazones have a cyclic structure. The rate of the kinetic process

hydrazone (cyclic form) → hydrazone (acyclic form)

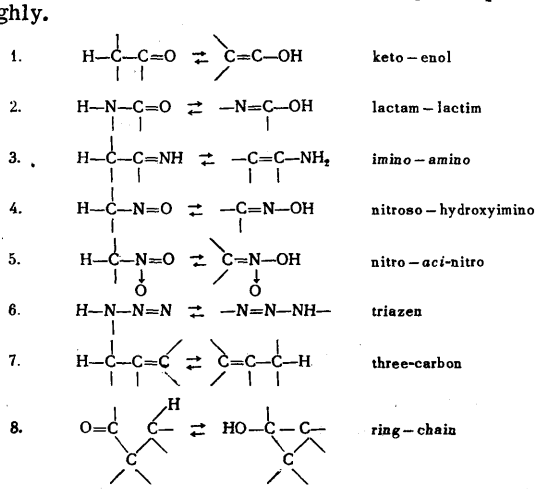
governs the height of the polarographic wave.

In a polarographic study of the complexes formed by 2,3-dimercaptopropanol with heavy metals, Zuman and Zumanova[82] found that Au^{III}, Hg^{II}, $C_6H_5Hg^{I}$, and Cu^{II} form mainly chelate compounds. They determined the composition of the complexes from the anodic wave.

Polarography has been used also to study the stability of some internal complexes (chelate compounds)[14]. The half-wave potential of the metal ion in the complex is shifted towards negative values on formation of a chelate compound. The magnitude of this shift is a measure of the stability of the resulting complex. Several amino-acids, which are polarographically inactive but give chelate compounds in solution, can be determined polarographically by utilising the internal complexes they form[12], most often with copper ions.

IV. STUDY OF TAUTOMERIC CHANGES

The phenomenon of tautomerism, or dynamic isomerism, first correctly explained by A. M. Butlerov, constitutes one of the main branches of theoretical organic chemistry. The most important tasks in studying the tautomerism of organic compounds are to define the tautomeric forms, study their interconversion, and determine the position of tautomeric equilibrium as a function of the medium and the structure of the compounds. The following are the principal tautomeric systems which have now been investigated quite thoroughly.



1. keto – enol
2. lactam – lactim
3. imino – amino
4. nitroso – hydroxyimino
5. nitro – *aci*-nitro
6. triazen
7. three-carbon
8. ring – chain

The phenomenon of dynamic isomerism occurs also in more complicated systems.

The problem of determining the position of equilibrium and the influence of the medium and of various substituents in displacing this equilibrium is often difficult to solve or even altogether insoluble by chemical methods. Various physical methods (spectroscopy, determination of magnetic susceptibility, refractive index, etc.) are therefore most often used in the study of tautomerism. However, these methods frequently prove to be ineffective, and therefore here too the application of polarography seems to be very promising.

The difference in structure between tautomeric forms results in a difference in energy, and hence in polarographic behaviour. It is possible by means of polarography to study the kinetics of tautomeric conversion, determine the equilibrium constant, investigate the effect of solvent and of structural changes on the position of equilibrium, etc. The brief electrolysis at a mercury electrode which is involved has no effect on the tautomeric system. However, many difficulties are still encountered in realising these possibilities. By obtaining polarograms in different solvents and at different pH values, it is easy to establish the presence of tautomerism and to ascertain the conditions for the existence and interconversion of the tautomers. But in the interpretation of a polarogram the presence of tautomeric forms may be assumed erroneously if it is not borne in mind that the presence of more than one wave may be due also to a stepwise reduction, the dissociation or hydration of the compound, a change in the mechanism of reduction with change in the pH of the solution, etc.

In order to avoid errors in deducing the structure of tautomers, it is necessary to apply where possible other physicochemical methods as well, and it is also essential to study the mechanism of the reduction of the compounds at the electrode, the effect of the pH of the medium, the

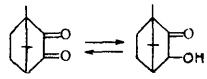
concentration of depolariser, and other factors on their polarographic behaviour. A chemical proof of tautomerism is also undoubtedly important.

A paper by Muller and Baumberger[83] provides an example of an incorrect conclusion that keto–enol tautomerism is present in pyruvic acid. Brdička[84] showed, on the model of the polarographic behaviour of phenylglyoxylic acid, in which enolisation is impossible, that the reason for the appearance of two waves with change in pH in Muller and Baumberger's experiments was not enolisation, but the existence of undissociated and dissociated forms of these acids in solution.

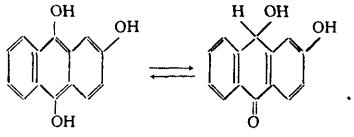
The polarographic method was used by Shikata and Tachi for studying keto–enol tautomerism as early as 1931,[85] and it has been subsequently employed many times for the same purpose. A large proportion of the earlier work, much of which is now only of historical interest, has already been discussed more than once (see for example Refs. 14 and 86).

Strange as it may seem, the classic example of keto–enol tautomerism, the acetoacetic ester, has not yet been subjected to polarographic investigation. It is mainly more complicated systems which have been studied. Thus a polarographic study of *l*-α-hydroxybenzyl methyl ketone and of 1-hydroxyethyl phenyl ketone in aqueous–alcoholic solutions showed that these compounds are in tautomeric equilibrium, and exhibit on the polarograms two waves in the pH range 4.5–7. The tautomeric equilibrium constants were found to be 0.6 and 1.8 in alkaline and hydrochloric acid solutions respectively[87].

Modiano[88] applied polarography to the study of the keto–enol tautomerism of camphorquinone. At pH ~12 its reduction uses up one electron, which Modiano explained by enolisation of the quinone:

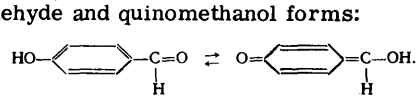


Gill and Stonehill[89] investigated the tautomerism of 2-hydroxy- and 2,6-dihydroxyanthraquinols. They found that within a certain pH range each compound gives an oxidation wave, the height of which diminishes with time. A new cathodic wave develops simultaneously, this being caused by reversible tautomeric conversion of the compounds to the corresponding oxanthranols:



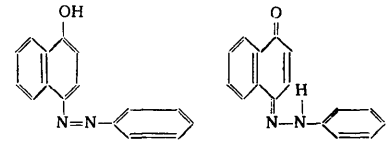
The position of tautomeric equilibrium varies with pH, maximum conversion to the oxanthranol occurring at pH 8.85–9.52.

The two waves of *p*-hydroxybenzaldehyde at pH 5.4–7.2 were ascribed by Kemula *et al.*[90] to tautomeric equilibrium between aldehyde and quinomethanol forms:



A study of methods for purifying and crystallising streptomycin revealed that it exists in two tautomeric forms, as was subsequently confirmed by a polarographic investigation of its solutions. Henser *et al.*[91] observed that fresh solutions of crystalline and amorphous streptomycin each give one wave, and then a second wave develops. A solution of the double salt of calcium chloride and streptomycin trihydrochloride gave two waves at once. These tautomeric changes were ascribed to changes in the aldehyde group of the streptomycin molecule, since they do not occur with salts of dihydrostreptomycin.

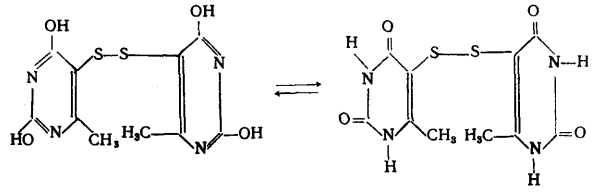
Phenylazo-1-naphthol showed no tautomerism under the polarographic conditions (aqueous–alcoholic acetate buffer solution)[40]:



(XIV) (XV)

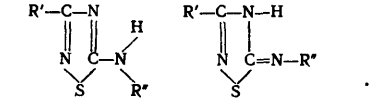
No wave was observed at the potential at which the fixed form of (XV) (the hydrogen atom on the N atom replaced by methyl) is reduced, which indicates the overwhelming predominance of structure (XIV) in the system.

A "lactam–lactim" type of tautomeric change was observed in a polarographic study of bis-2,4-dihydroxy-6--methylpyrimidin-5-yl disulphide, which in alkalis undergoes tautomeric conversion to a polarographically inactive lactim form, the polarogram showing a decrease in wave height with time:



It also proved possible to confirm the presence of a disulphide group in this compound[92].

Interpretation of polarograms obtained in the investigation of tautomerism usually requires that polarograms should also be obtained for solutions of model substances of rigorously fixed structure. This approach was employed, for example, by Sturm and Hans[93] in studying the imino–amino tautomerism of thiadiazoles:

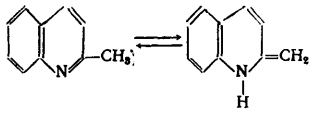


(XVI) thiadiazole (XVII) thiadiazoline

Compounds having a fixed thiadiazole ring, which is aromatic in character, are reduced at negative potentials (around 2.1–2.2 V). Thiadiazoline derivatives are reduced at half-wave potentials of about -1.6 V (relative to the saturated calomel electrode). The thiadiazoles (XVI) studied by Sturm and Hans gave no wave with $\pi_{\frac{1}{2}} \simeq -1.6$ V. These workers concluded that the compounds have the enamine type of structure, but this cannot serve as a rigorous proof that the imino-form is completely absent, since the concentration of the latter might be below that which can be detected polarographically (10^{-5} M). These workers also demonstrated the absence of tautomerism in 2-aminobenzothiazole, in agreement with the spectroscopic data.

Stromberg[94] investigated the mechanism of the electrochemical reduction of quinoline, isoquinoline, and quinaldine in buffered solutions, and observed two waves on the

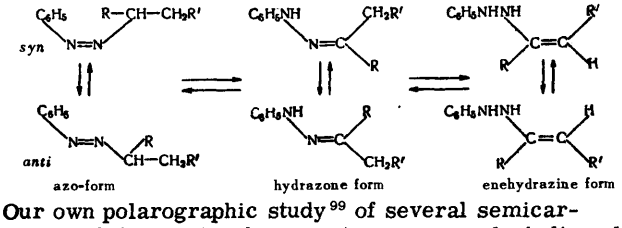
polarogram of quinaldine in the pH range 6.2–9.9, which were ascribed to its two tautomeric forms:



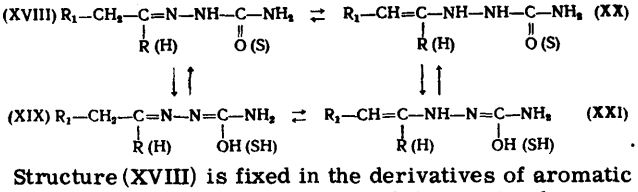
Korshunov and Shchennikova[95] consider, however, that both hydrogen ions and water molecules can take part in the reduction of the compounds, which then takes place at different potentials. In their opinion reduction involving hydrogen ions should take place in acid solutions, reduction involving water molecules in alkaline solutions, and both mechanisms should be possible in neutral solutions. But if this explanation is accepted as correct, it is still not clear, as Stromberg remarks, why two waves are absent from the polarograms of quinoline and isoquinoline at pH ~7.4.

Kitaev and Arbuzov[96-98] investigated the changes undergone by several arylhydrazones in methanol. By recording polarograms during the storage of alcoholic solutions of the phenylhydrazones of aldehydes and ketones, they obtained a set of curves for each compound. In order to interpret these curves, polarograms were also obtained for methanolic solutions of azobenzene and phenylazomethane as models of the azo-form, acetone *N*-ethyl-*N*-phenylhydrazone as a compound incapable of forming an azo-modification but able to form an enehydrazine, and benzaldehyde phenylhydrazone as a compound for which an enehydrazine form is impossible. Inspection of the polarograms established that phenylhydrazones of aliphatic and alicyclic ketones have the enehydrazine structure in freshly prepared solution. When solutions of these compounds are stored in the dark, the latter are converted *via* the hydrazone forms to mixed azo--compounds, and rearrangement of labile *syn*-isomers into stable *anti*-isomers also occurs. These workers found that potentials between -1.4 and -1.55 V correspond to waves due to enehydrazines; stereoisomers of mixed azo-compounds are reduced at potentials between -0.6 and -0.9 V, and those of hydrazones between -1.05 and -1.30 V.

In freshly prepared solutions the phenylhydrazones of aldehydes and of alkyl–aryl ketones have the hydrazone structure, and they are also gradually converted to the azo--compounds. On the basis of the polarographic data the following scheme was suggested for the tautomeric and stereoisomeric changes undergone by arylhydrazones:



Our own polarographic study[99] of several semicarbazones and thiosemicarbazones in aqueous–alcoholic solution showed that these compounds can in general exist in the following four forms:

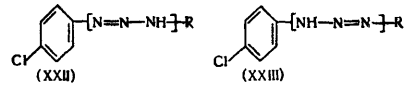


Structure (XVIII) is fixed in the derivatives of aromatic aldehydes. The semicarbazones and thiosemicarbazones of aliphatic aldehydes and ketones and of alicyclic ketones have structure (XX). These compounds probably have the same structure in the crystalline state as well, since it appears unlikely that, at the instant of dissolution, the multiple bond of the azomethine group would be almost entirely converted to a carbonyl group at a rate which cannot be measured. In alkaline solution form (XX) passes into the tautomer having structure (XXI). Structure (XIX) is fixed in benzaldehyde *S*-methylthiosemicarbazone. We have observed the equilibrium between forms (XVIII) and (XX) in the thiosemicarbazone of acetophenone. Solutions of cyclohexanone *S*-methylthiosemicarbazone yielded two waves corresponding to the two possible tautomers (XIX) and (XXI), which are in equilibrium. In the course of time, changes occur in alcoholic solution of the thiosemicarbazones of acetone and cyclohexanone, the enethiosemicarbazide form passing into a tautomer having a carbonyl structure. This information is the result of a preliminary study of these compounds.

The above technique for investigating tautomeric reactions, by recording the changes taking place in solution with time, appears to us to be most convenient for slow reactions. However, several conditions must be observed: the solvent should not vaporise on storage, the substance must not be subjected to the action of light, which might cause secondary processes, and it should not undergo oxidation, since the resulting products would give their own polarographic waves, which could be wrongly ascribed to tautomers[100]. Therefore before any conclusions are drawn it is first necessary to ascertain carefully the reasons for changes in the polarographic behaviour of solutions.

The only polarographic investigation of nitroso-hydroxyimino tautomerism which will be mentioned is the work of Tyutyulkov[101], who observed two waves with the *syn*-isomers of the oximes of aromatic aldehydes, which he ascribed to tautomers.

In a study of the structure and properties of some aromatic diazoamino-derivatives of guanidine it was found that compounds containing a triazen –N=N–NH– group can exist as two tautomeric forms:



[where R = CN or C(=NH)–C(CH$_3$)$_2$], which on polarographic reduction yield waves having different half-wave potentials. The compound having structure (XXII), like azobenzene, is reduced at -0.4 V (relative to the saturated calomel electrode), whereas the compound with structure (XXIII) is reduced at -0.21 V.[102] Polarographic data for the diazoamino-tautomeric equilibrium have enabled the differences in the behaviour of these compounds towards mineral acids to be explained.

The above work shows conclusively that polarography can be used to establish the presence of tautomerism and to determine the conditions for the existence and the interconversion of the tautomers. Furthermore, by enabling the concentrations of tautomers in solution to be followed separately, the polarographic method may provide great help in calculating the tautomeric equilibrium constants, *i.e.* in the quantitative characterisation of equilibrium isomerism. However, very few papers have been published on the quantitative study of the tautomerism of organic compounds.

Quite recently papers have appeared on the nitro–*aci*-nitro tautomerism of nitrocyclohexane [103] and of phenylnitromethane [104,105]. The nitro-form of the first compound gives a distinct wave over a wide pH range; the *aci*-form is stated [103] not to be reduced at a dropping mercury electrode. The investigation showed that at pH > 9.5 the nitro-form of nitrocyclohexane is completely converted to the *aci*-form (N → A), whereas at pH 4.5–7 the *aci*-form can be completely converted to the nitro-form (A → N). At pH 7.0–9.5 an equilibrium is established, which can be reached from both sides. The kinetics of the tautomeric conversion of nitrocyclohexane are represented by the equations

$$K_0\, a_{OH^-} = K_N = \frac{2.3}{t}\log\frac{C_0}{C_N}\ (N \rightarrow A),$$

$$\frac{K_0'\, a_{H^+}}{1+\frac{a_{H^+}}{K_1}+\frac{a_{H^+}^2}{K_1 K_2}} = K_A = \frac{2.3}{t}\frac{C_\infty}{C_0}\log\frac{C_\infty}{C_\infty - C_N}\ (A \rightarrow N),$$

where C_N is the concentration of the nitro-form at time t, K_N the experimental rate constant for the reaction N → A at constant pH, K_A the corresponding rate constant for the reaction A → N, K_0, K_0', K_1, and K_2 are constant at a given ionic strength, and a_{H^+} and a_{OH^-} represent the activities of the proton and of the hydroxide ion.

The following mechanism has been suggested for these reactions, based on the idea of an acid–base catalysis of the nitro–*aci*-nitro tautomeric conversion:

$$[C_6H_{10}=NO_2H]\,H^+ \overset{H^+}{\underset{K_2}{\rightleftarrows}} C_6H_{10}=NO_2H \overset{H^+}{\underset{K_1}{\rightleftarrows}} C_6H_{10}=NO_2^- \overset{\text{slow stage}}{\underset{\text{slow stage}}{\overset{H^+,K_0'}{\underset{OH^-,K_0}{\rightleftarrows}}}} C_6H_{11}NO_2\ ,$$

where K_0 and K_0' are the corresponding rate constants, $K_1 = [C_6H_{10}=NO_2^-][H^+]/[C_6H_{10}=NO_2H]$, and K_2 is the corresponding constant for the protonated complex $[C_6H_{10}=NO_2H]H^+$. The results obtained enabled the equilibrium constant of the process N → A to be calculated, as well as the activation energies of the processes N → A (18.4 kcal × × mole^{-1}) and A → N (16.0 kcal mole^{-1}).

Mairanovskii *et al.* [104,105] made a detailed polarographic investigation of the mechanism of the tautomeric changes undergone by phenylnitromethane. In conformity with the general principles of protolytic equilibria, they adopted a scheme of tautomeric conversions involving a single anion, similar to that given above for nitrocyclohexane. However, comparison with published data showed the inadequacy of such a scheme.

Using an original technique of investigation, these workers first established the polarographic activity of the *aci*-form of phenylnitromethane. When a solution of a salt of phenylnitromethane is acidified, the *aci*-form is formed practically instantaneously, and then changes gradually into the nitro-form at a rate depending on the acidity of the medium. Since the wave for the nitro-form is lower than that for the *aci*-form of phenylnitromethane, the isomerisation is accompanied by a gradual decrease in the limiting current of the polarographic wave due to the *aci*-form, which enabled the kinetics of its isomerisation to be studied. It was found that at pH < 2 the rate of isomerisation is independent of the hydrogen ion concentration, and represents the rate of interaction of the *aci*-form with water according to the equation

$$C_6H_5CH{=}NOOH + H_2O \rightarrow C_6H_5CH{=}NOO^- + H_3O^+.$$

With increase in pH the rate of isomerisation begins to rise, the pH at the start of the rise depending on the concentration of bases in the buffering system. With decrease in the concentration of the latter the inflection on the curve relating the rate of isomerisation and pH shifts to higher pH values. It was concluded from these results that the rate of isomerisation is governed by the rate of dissociation of the *aci*-form:

$$C_6H_5CH{=}NOOH + B \rightarrow C_6H_5CH{=}NOO^- + BH^+.$$

Mairanovskii *et al.* also studied the kinetics of the dissociation of phenylnitromethane when it reacts with various bases (B) and the kinetics of its recombination.

Brønsted's equation was applied to the reactions of *aci*-phenylnitromethane and phenylnitromethane with various bases and acids.

Kinetic analysis of the tautomeric changes undergone by this compound showed the existence of two types of anions, the *aci*- and the nitro-forms. As a result, the tautomerism of phenylnitromethane in aqueous solution, for the particular case in which water alone acts as base and H_3O^+ as acid, was represented by the following scheme:

$$\begin{array}{ccc} C_6H_5CH_2NO_2 + H_2O & \overset{K_{ND}}{\underset{K_{NR}}{\rightleftarrows}} & C_6H_5C^-HNO_2 + H_3O^+\ , \\ K_1\downarrow\uparrow K_2 & & \\ C_6H_5CH{=}NOOH + H_2O & \overset{K_{AD}}{\underset{K_{AR}}{\rightleftarrows}} & C_6H_5CH\ NOO^- + H_3O^+\ , \end{array}$$

where the subscripts attached to the rate constants K have the following significance: A and N the *aci*- and nitro-forms, and D and R dissociation and recombination, respectively.

This scheme is probably valid for other nitro-compounds as well. Thus the potentialities of the polarographic method are not confined to the qualitative identification of the reactions undergone by organic compounds, but also enable these reactions to be elucidated and evaluated quantitatively.

Until recently it was considered that tautomerism causes compounds to have dual reactivity. Nesmeyanov and Kabachnik [106] clearly showed the error of such a view. They concluded that dual reactivity is often due to the migration of a reactive centre along a conjugated chain. Polarography will probably be used in the near future to study the dual reactivity of organic compounds, of which, according to present-day ideas, tautomerism forms a particular case.

V. STUDY OF THE STEREOISOMERISM OF ORGANIC COMPOUNDS

The polarographic method for studying geometrical isomerism can be employed in all cases where the isomerism is due to different positions of substituents relative to an electrochemically active double bond, since the structure of organic compounds is known to have a definite effect on their polarographic behaviour. The different behaviour of isomers is caused by steric factors either hindering or facilitating the approach of the electrochemically active group to the electrode surface.

The investigations have shown that it is usually more difficult to reduce the *trans*-forms than the *cis*-forms, but cases are also known in which the opposite relation between the structure of isomers and their ease of reduction holds. In addition, the difference in adsorption and solvation properties between isomers also affects their electrochemical behaviour, and in some cases even the mechanism of cathodic reduction can change with structure. However,

the difference in the behaviour of stereoisomers at a dropping mercury electrode depends in most cases on the pH of the solution, and within a certain pH range the stereoisomers may give identical waves. This often complicates the polarographic study of stereoisomerism, and sometimes even makes it impossible.

Elving *et al.*[107] made a detailed study of the polarographic behaviour of maleic and fumaric acids, and found that, between certain pH values, the difference in half-wave potential is so great that the acids can be determined when present together.

Fig. 3 shows the relation between $\pi_{\frac{1}{2}}$ and solution pH for maleic and fumaric acids plotted from published data[107]. The difference in the relative reducibility of the C=C bond in these molecules is evidently determined by the difference between their dissociation constants. This is further confirmed by the fact that the ethyl esters of these acids, which contain no free carboxyl group, show essentially the same type of variation of $\pi_{\frac{1}{2}}$ with pH (Fig. 3), the difference in half-wave potential being almost independent of pH. The polarographic behaviour of *cis-cis-* and *trans-trans-*muconic acids proved to be identical, *i.e.* the polarographic method is unsuitable for their determination[108].

Ryvolova[109] investigated the conversion of *trans*-dibenzoylethylene to the *cis*-isomer on exposure of its solution to ultra-violet radiation. It was found that in acid medium the *cis*-isomer is reduced at a more negative range of potentials than the *trans*-isomer.

Mairanovskii and Bergel'son[110] made a polarographic study of the *cis-* and *trans*-isomers of some 1,2-dibromoethylenes having a hydroxyl group in the allyl position. They found the *trans*-isomers to be more readily reduced than the *cis*-isomers (see Table 3), which in their view is associated with the easier *trans*-elimination of two neighbouring bromine atoms.

Among the various derivatives of aldehydes and ketones which are used in analysis, considerable attention has been paid to the polarography of oximes[101,111-113] but no systematic study of their stereoisomerism has yet been made. Tyutyulkov[101,113] derived an empirical rule, according to which isomers which give two polarographic waves have the *syn*-configuration; if, however, only one wave is obtained on the polarogram of a solution of an isomer, this isomer has the *anti*-configuration. This rule was derived

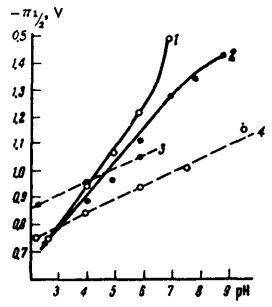
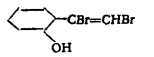
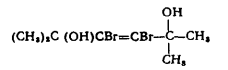


Fig. 3. Variation of half-wave potential with pH for maleic and fumaric acids and their diethyl esters:
1) fumaric acid; 2) maleic acid; 3) diethyl maleate; 4) diethyl fumarate.

TABLE 3.

Compound	$\pi_{\frac{1}{2}}$, V (relative to sat. calomel electrode)	
	trans-form	*cis*-form
	—1.15	—1.80
$(CH_3)_2C(OH)CBr{=}CHBr$	—1.42	merges with supporting electrolyte [LiBr + $(C_2H_5)_4NBr$ in 60% methanol]
	—0.72	—1.19

from the behaviour of the oximes of benzaldehyde and four of its derivatives in unbuffered solutions, but it can probably be applied to the stereoisomeric pair of other oximes.

In buffered solutions at pH ~4 the stereoisomeric oximes of benzaldehyde are indistinguishable polarographically, and it is only at higher pH values that distinct waves can be obtained for the *syn-* and *anti*-isomers[112]. With the oximes of cinnamaldehyde no separation of the waves was observed over the pH range 1.05–7.4.

Thus the half-wave potentials of stereoisomers depend on the pH of the solution, the form of the variation in $\pi_{\frac{1}{2}}$ with pH being different for each stereoisomer, so that the difference $\Delta\pi_{\frac{1}{2}}$, which is to some extent a measure of the energy of the stereoisomeric conversion, also depends on the acidity of the medium. This makes it difficult to use polarographic data to calculate this energy, since it is evidently not always possible to create standard conditions under which the values of $\pi_{\frac{1}{2}}$ for the stereoisomers would be governed solely by the free energy of the molecule.

A polarographic study of arylhydrazones by Kitaev and Arbuzov[96-98] showed that in general two geometrical isomers are possible for each tautomer. Thus the polarograms of benzaldehyde phenylhydrazone contained two pairs of waves, the first corresponding to the two stereoisomers of the azo-form ($\pi_{\frac{1}{2}}$ = -0.56 and -0.89 V), while the second pair (-1.08 and -1.20 V) were due to the *syn-* and *anti*-isomers of the hydrazones. Three pairs of waves could be traced on the polarograms of the phenylhydrazone of ethyl methyl ketone: in this case all three tautomers exhibited stereoisomerism.

Brockman and Pearson[62] investigated the polarographic reduction of stereoisomeric pairs of semicarbazones in a series of benzophenones. They found that in this case the difference in half-wave potential between the stereoisomers was quite insignificant (see Table 4).

Semicarbazones and thiosemicarbazones of aromatic aldehydes and aryl alkyl ketones can exist in two stereoisomeric forms, as our own polarographic study has shown[114]. On exposure of solutions of these compounds to ultra-violet radiation, a new wave appears on the polarograms, with a more positive half-wave potential. The height of this wave increases with increasing duration of irradiation. The appearance of a second wave on the polarogram is due to the formation of a labile species.

Much work has been done on the behaviour of *cis-* and *trans*-azobenzenes at a dropping mercury electrode, and this has been quite thoroughly discussed in monographs[12,14]. At pH ~8.5 both stereoisomers give waves at the same

TABLE 4.

Compound	$-\pi^*_{1/2}$, V
Benzophenone semicarbazone	1.104
4-Methoxybenzophenone α-semicarbazone	1.114
4-Methoxybenzophenone β-semicarbazone	1.117
4-Bromobenzophenone α-semicarbazone	1.048
4-Bromobenzophenone β-semicarbazone	1.050

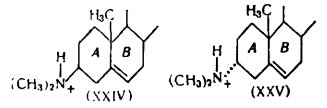
* At pH ~5.1, relative to 3.5M calomel electrode.

potential, and it is only in a faintly alkaline medium that they can be distinguished polarographically when they are present together. These results were subsequently confirmed by Castor and Saylor [115].

Freeman [116] found that *anti*-diazosulphonates are reduced polarographically at more negative potentials than the corresponding *syn*-isomers. Exposure of an aqueous solution of the stable isomer of a diazosulphonate to ultra-violet radiation or to sunlight, results in the appearance of a second wave on the polarogram, owing to formation of the labile species.

The polarographic behaviour of compounds is affected not only by geometrical isomerism but also by molecular conformation. The effect of the latter on the polarographic reduction of organic compounds was discovered with halogenated cyclohexanes [53,117].

Recently a study has been made of the effect of the geometrical configuration of organic molecules on their adsorption, which produces various capacitive phenomena [53,55]



A comparison was made of the behaviour of compounds (XXIV) and (XXV), which differ only in the location in space of the tertiary amino-group in position 3 of the steroid skeleton. The α-isomer (XXIV)† showed an increase in the capacitive current in a 0.1 M solution of LiOH in 50% ethanol. No such phenomenon was observed with the β-isomer. The isomers also differ in the suppression of polarographic maxima. Thus the α-isomer suppresses the oxygen maximum more strongly than does the β-isomer. The concentration of the latter required to halve the maximum is six times as great as that of the α-isomer. These results indicate that the α-isomer is more readily adsorbed on the dropping mercury electrode than is the β-isomer.

Differences in half-wave potentials cannot be expected with optical enantiomorphs, since such isomers do not differ in energy, and therefore polarography cannot be used to study this phenomenon. Diastereoisomers, in contrast, should differ in polarographic behaviour. Study of the cathodic reduction of the epimers of αα′-dibromotartaric acid [58,118,119] showed that the *erythro*-acid is reduced at a more positive potential than the *threo*-form, and by a different mechanism. The *threo*-dibromotartrate anion, however, is more readily reduced than the *erythro*-anion. With the dibromotartaric esters the difference in half-wave potential between the two epimers is insignificant.

† In I.U.P.A.C. nomenclature XXIV is the β-form.(Ed.of Translation).

The diastereoisomers of phenylcysteine have different catalytic effects on hydration evolution [120]. In ammoniacal Co^{2+} solution the *erythro*-form gives a higher catalytic wave than the *threo*-form of phenylcysteine. This difference is due to different values of the dissociation constants of the acids and also to a difference in the instability constants of the complexes formed by Co^{2+} with phenylcysteine.

VI. STUDY OF THE KINETICS OF CHEMICAL REACTIONS

The polarographic method has proved extremely convenient for observing the course of reactions, studying their kinetics and mechanism, and determining the structure of the final reaction products [121]. This field of application of the method has recently acquired very great importance both for organic and for physical chemistry. Opportunities for and ways of polarographic study of the course of a particular reaction depend on its velocity.

If the half-period of the reaction exceeds 0.5 min but is less than an hour, it is convenient to employ continuous recording of the change in concentration of one or more reactants. For this purpose a potential in the region of the limiting current of the corresponding reaction component is applied, the second reactant is introduced, and the magnitude of the limiting current, which is proportional to the concentration, is continuously recorded.

When the reaction is very slow (taking several hours or even longer), continuous recording is replaced by the usual method of obtaining polarographic waves from readings at definite time intervals, from which the concentrations of the reactants are found. Further, it is then no longer difficult to calculate the rate constants or the equilibrium constants of the processes by means of the well-known equations of reaction kinetics. From the temperature dependence of the resulting constant, the activation energy is obtained by means of the Arrhenius equation, and the entropy of activation by using the transition state theory. The following examples may be cited of the large amount of work on reaction kinetics based on such measurements.

Kastening *et al.* [122] studied the kinetics of the hydrolysis of benzylideneaniline and of the condensation of benzaldehyde with aniline. They found that hydrolysis of the anil was of first order, that its velocity depended on the acidity of the medium, and that it could be followed polarographically within the pH range 6–13.3, for hydrolysis is very rapid in a more acid medium. The effect of temperature on the hydrolysis was also investigated.

Fig. 4 shows plots of $\log K$ against solution pH, where K is the rate constant of the hydrolysis, whose value was calculated by means of the formula $K/2.3 = t^{-1} \log C_0/C_t$, C_0 being the initial concentration of anil in the solution and C_t the variable concentration determined polarographically. This investigation confirmed the hypothesis that hydrolysis takes place in two stages, the first involving addition of water at the azomethine double bond to form an amino-alcohol, which decomposes in the second stage.

The polarographic study showed that the condensation of benzaldehyde with excess aniline takes place by a mechanism similar to the hydrolysis but at a somewhat greater rate. Fig. 5 gives graphs for the dependence of the logarithm of the rate constant of condensation ($\log K$) on the pH of the solution. The values of K at different temperatures were used to calculate the thermodynamic properties of the reaction.

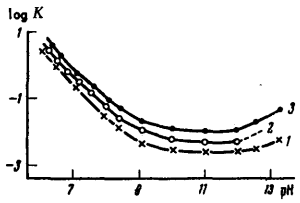


Fig.4. Variation with pH of the logarithm of the rate constant for the hydrolysis of benzylideneaniline:
1) 20.2°; 2) 30.4°; 3) 41.0°.

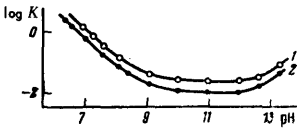


Fig.5. Variation of the logarithm of the rate constant with pH:
1) condensation of aniline with benzaldehyde;
2) hydrolysis of benzylideneaniline.

Crowe and Lynch [123,124] made a polarographic study of the kinetics of the condensation of formaldehyde with urea, acetamide, and benzamide. The reactions were followed by the change in height of the formaldehyde wave. These workers showed that the reaction of urea with formaldehyde to form monohydroxymethylurea is reversible. The activation energy of this reaction calculated from the polarographic data is 15.9 kcal mole^{-1} at pH 12.7, while that for the condensation of formaldehyde with acetamide is 13.85 kcal mole^{-1}, of the same order as in the condensation of formaldehyde with benzamide. The polarographic method showed that the increase in the rate of condensation with increase in pH is more rapid with benzamide than with urea or acetamide, owing to the influence of the phenyl radical on the reactivity of the carbamoyl group. Change in temperature has a considerably smaller effect than change in acidity of the medium on the rate of condensation. In view of the above facts, Crowe and Lynch suggested the following mechanism for the reaction of formaldehyde with amides:

$$H^+ + R{-}\overset{\overset{O}{\|}}{C}{-}NH^- + HCHO \rightleftarrows R{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_2O^- + H^+ \rightleftarrows R{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_2OH.$$

The rate of hydrolysis of nitrosamines in acid medium has been studied, the velocity constant being correlated both with the wavelength of maximum absorption and with the half-wave potential [125].

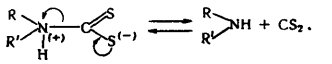
The results of a polarographic investigation of the course of hydrolysis of the sodium salt of *N*-*p*-chlorophenyldiazothiourea were used to study the stability of the preparation Muritan during storage and application [126].

The alkaline hydrolysis of some substituted isothioureas was measured by the growth of the anodic wave due to the thiol formed in this reaction [127].

Kofod [128] studied polarographically the kinetics of the isomerisation, in buffered solutions of pH 9.2–13.3, of the low melting hydroxyurea isomer. He found that, when the temperature is raised at pH ~12, the isomerisation is accompanied by partial decomposition of the hydroxyurea into hydroxylamine and a cyanate.

Zahradnik [129] studied the rate of reaction of some amino-acids with carbon disulphide in aqueous medium and in aqueous acetone in the presence of a buffer. From polarographic, spectroscopic, and chromatographic results, he suggested a reaction mechanism for the decomposition of dithiocarboxy-aminocarboxylic acids in acid medium.

Somewhat later Zahradnik and Zuman [130] investigated the kinetics of the decomposition of nine monoalkyl- and nine dialkyl-dithiocarbamic acids as a function of pH. They found that decomposition yields an amine and carbon disulphide, the rate-determining process being breakdown of the zwitterion, the concentration of which is governed by the dissociation equilibrium



Zuman *et al.* [131] investigated the rate of periodate oxidation of nine epimeric pairs of acyclic 1,2-diols of general formula RCH(OH)CH(OH)R'; they found the reaction to be of second order and catalysed by acids and alkalis. Zuman suggested that the rate-determining process in this reaction is proton transfer following interaction between the diol and the periodate. He also studied the effect of substituents (phenyl, alkyl) on the rate of oxidation of these diols. With hydrogen peroxide at pH > 6, dimercaptopropanol is readily oxidised, by a second-order reaction, to a disulphide [132–134]. Polarographic measurements showed that, when 2,3-dimercaptopropanol reacts with cystine, formation of a disulphide is accompanied by that of a monothiol by a second-order reaction [132–134].

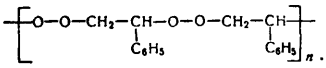
The same workers found that the anodic wave of dimercaptopropanol gradually disappears on reaction with benzoquinone, 1,4-addition taking place with two moles of the quinone. Both SH groups take part in the reaction, which occurs rapidly at pH 4–7.

A polarographic method has also been used to study the decomposition of adrenochrome during storage [135], and the photochemical decomposition of riboflavin, which was found to yield a mixture of glycolaldehyde, glyceraldehyde, and lumichrome [136].

Kreyči [137] investigated the variation with time, temperature, and solution pH of the concentration of the polarographically active intermediate formed in the decomposition of penicillin in acid medium. Comparison of the polarographic data with the ultra-violet absorption of penicillin solutions showed the intermediate to be very probably penicillic acid. He discussed in detail the reaction scheme suggested earlier, and calculated the rate constant at 25°.

Bricker and Vail [138] showed polarographically that the alkaline decomposition of streptomycin is of first order. Comparison of its velocity with that of the rearrangment of 2-hydroxy-2-methylpropionaldehyde into 3-hydroxybutan-2-one showed that both reactions were of first order, had the same activation energy, and exhibited the same dependence on pH. It was concluded from these observations that the rate-determining stage in the decomposition of streptomycin is rearrangement of the streptose residue to form a six-membered ring.

Barnes *et al.*[139] showed polarographically that, during the induction period in the emulsion polymerisation of styrene, oxygen plays an active part in the polymerisation, by forming with the styrene a polymeric peroxide:



The polarographic method has also been used to investigate the reaction mixture in the polymerisation of acrylonitrile and butyl methacrylate[140].

Sartori and Furlani[141] studied the kinetics of the following disproportionation reaction:

$$2C_6H_5IO \rightarrow C_6H_5IO_2+C_6H_5I,$$

all the components in which are electrochemically reducible.

Many interesting cases of the application of polarography to the study of the kinetics of organic reactions are discussed in Schwabe's booklet[142]. References to the original literature can also be found in the reviews by Wawzonek[16-21] and by Nürnberg[65].

Use of the polarographic method for studying kinetics is not confined to reactions in which polarographically active substances are obtained from inactive substances or in which the reactants show up polarographically at different potentials. Theoretically the method can also be employed in cases in which the reaction product is reduced at the same potentials as the starting materials but has a different diffusion coefficient[143], the reaction being followed in this case by the change in height of the wave.

The study of rapid reactions requires a sensitive method for recording the currents due to electrochemical reactions. When the half-periods of the reactions lie between 3 and 15 sec, continuous recording of i_d-t curves at individual drops of the mercury electrode at constant potential can be employed[144]. The effect of depletion of the solution in the vicinity of the electrode can be eliminated by means of a special bend in the capillary or by obtaining a calibration curve[145]. In this way the rates of change of the products formed in the electrochemical reduction of quinonoid dyes of the safranine type with hydrogen on palladium can be measured, and hence the hydrogenating activity and mode of action of different palladium catalysts can be determined[65].

With still more rapid reactions (having a half-period less than 3 sec) recourse is had to oscillographic polarography, with which the time required to obtain a polarogram can be reduced to fractions of a second. Examples are provided by the coupling of diazotised sulphanilic acid with sulphonated pyrazolone[146] and the reaction of pyruvic acid with ammonia[65].

During recent years the so-called "rapid" and "very rapid" reactions, the rate constants of which lie within the range 10^3-10^{11} sec^{-1}, have attracted particular interest. They include protolytic reactions, rapid hydrolyses, rearrangements, etc.

After Wiesner's early fundamental work[147] on the catalytic role of the leuco-form of some quinonoid dyes in the oxidation of hydrogen on palladium, polarographic kinetic currents came to be used, together with other modern methods (the relaxation method, measurements using nuclear magnetic resonance, etc.), to calculate the rate constants of rapid reactions.

For a complete theory of kinetic currents we are indebted primarily to the Prague school of polarography; a substantial contribution has been made also by our own Soviet and by foreign scientists. Much work has been done on the problem of kinetic currents in polarography. In the present paper we shall consider only a few cases of the application of kinetic currents in the polarography of organic compounds and their reactions. More detailed accounts of the main achievements of research on kinetic currents and references to the original literature can be found in the papers by Koutecký[148] and by Nürnberg[65].

Kinetic currents are not only governed by the diffusion of depolariser to the electrode but also depend on the relative rates of diffusion and of the chemical reaction preceding the electrochemical process. A condition for the occurrence of kinetic waves is that the depolariser should be present in the solution in at least two forms differing in their depolarising properties[149].

In order to distinguish a diffusion current from a kinetic current, the dependence of the height of the polarographic wave on the height of the mercury reservoir is determined. It follows from the Ilkovič equation that i_d varies linearly with the square root of the reduced height h of the mercury reservoir (*i.e.* the height of the reservoir less the back pressure determined by the geometry of the capillary).

For a kinetic process i_k should be independent of the pressure on the dripping mercury. However, some effect of h on i_k is often observed, and is determined by the relative rates of diffusion and of the chemical reaction. The temperature dependence of a kinetic current is usually much greater than that of a diffusion current, for which the temperature coefficient lies within the range 1–2% deg^{-1}.

A simplified scheme for the formation of a depolariser B from an electrochemically inactive substance A can be written as follows:

$$A \underset{K_2}{\overset{K_1}{\rightleftarrows}} B \xrightarrow{e} R.$$

The dissociation of weak acids (I) or the recombination of protons with the anion of an acid (II) belongs to this type of reaction:

$$\text{(I)}\quad RCOOH \underset{K_2}{\overset{K_1}{\rightleftarrows}} H^+ + RCOO^-,\ H^+ + e \rightarrow {}^1/_2H_2,$$

$$\text{(II)}\quad H_3C{-}CO{-}COO^- + H^+ \underset{K_1}{\overset{K_2}{\rightleftarrows}} H_3C{-}CO{-}COOH,$$

$$H_3C{-}CO{-}COOH \xrightarrow{2e+2H^+} H_3C{-}CHOHCOOH.$$

In the case of acid dissociation an equilibrium (I), which governs the concentration of protons, is established in the solution. Owing to the occurrence of the electrochemical process, however, this equilibrium is continually disturbed near the electrode, being displaced towards dissociation of the acid by an amount depending on the rate of such dissociation. At the same time molecules of acid are brought by diffusion from the bulk of the solution to the electrode, these compensating for the amount of acid used up in the dissociation. No doubt some of the protons recombine with the anions. The nearer to the electrode that dissociation takes place, the greater is the probability that the protons formed by dissociation will diffuse to the electrode surface and be discharged there.

Thus the kinetic limiting current depends on the rate of dissociation of the acid (K_1), the rate of diffusion of molecules of acid from the bulk of the solution to the layer adjacent to the electrode (D_{HA}), and the rate of diffusion of protons from the bulk of the solution. This last factor can

be neglected when pH ≥ 5 owing to the low proton concentrations. In the case of acid dissociation the equation for the kinetic current is

$$i_k = i_d \frac{0.87\sqrt{\frac{D_{H^+}}{D_{HR}}}\sqrt{\frac{K_1K_Dt}{[A^-]}}}{1+0.87\sqrt{\frac{D_{H^+}}{D_{HD}}}\sqrt{\frac{K_1K_Dt}{[A^-]}}},$$

which shows that the kinetic current differs from the diffusion current by a kinetic factor. If this factor exceeds 0.95, the current has a pseudo-diffusion character when K_1 is large, *i.e.* the limiting current behaves as a diffusion current, although a chemical reaction precedes the electrochemical stage. Only acids having dissociation constants (K_D) below 5×10^{-6} give a marked kinetic limiting current.

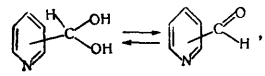
In the case of the recombination of the anion with a proton (II), when both the acid molecule and its anion contain reducible groups, the value of K_2 can be calculated directly from the kinetic limiting current, and hence K_1 can be determined, for $K_1/K_2 = K_D$. With pyruvic acid, for example, two waves are obtained, since the carbonyl group is reduced at a more positive potential in the acid molecule than in the anion. The limiting current of the first wave is governed by the rate of recombination, whereas the second wave should have a limiting current depending on the rate of diffusion of the anion. In an adequately buffered medium recombination may be pseudounimolecular, and the value of i_k can be found from the above formula for acid dissociation. Over seventy weak acids have been studied up to the present [150].

A definite relation exists between the rate constants of protolytic reactions and the dissociation constants of the acids and bases involved. Mairanovskii and Lishcheta [151] studied the variation of the limiting kinetic current, determined by the rate of reaction of the doubly charged maleate anion with proton donors, with the concentration of the acid components (in Brønsted's sense) of buffer systems at constant solution pH. They showed that, with all the buffer systems which they studied, the height of the kinetic polarographic wave increases with increase in the concentration of the proton donor, and that the rate constants for recombination of the maleate ion with proton donors satisfy the Brønsted equation.

In the study of polarographic currents limited by the rate of a chemical reaction preceding electron transfer the effect of adsorption of the substances on the dropping mercury electrode must be taken into account. Mairanovskii has recently shown [149,152] that when an electrochemically inactive form of the depolariser is adsorbed (which almost always occurs with organic depolarisers), the chemical reaction not only takes place in solution near the electrode surface but also involves the adsorbed material. The observed current then represents the sum of two quantities, the kinetic current limited by the occurrence of the chemical reaction in space (in the "reaction" layer), *i.e.* the "bulk" current, and a "surface" current, controlled by the occurrence of the same reaction but involving adsorbed reactant [152].

Mairanovskii found that even slight coverage of the electrode surface (of the order of 0.1%) increases the concentration of the substance in the reaction layer to such an extent that the observed current can be considerably increased, and the rate constant of the chemical reaction calculated from it exceeds the true value by several powers of ten.

Polarography can conveniently be used to study not only the above protolytic reactions but also the kinetics of other rapid reactions, such as the dehydration of formaldehyde hydrate [153] and also those of other aldehydes where only the dehydrated form acts as a depolariser. The formation of additional free aldehyde from its hydrate is catalysed by acids and bases [150]. Similar phenomena have been observed with a group of pyridine aldehydes [154,155]. It was found that these compounds exist in solution in equilibrium with the hydrated form:



and the rate of dehydration governs the magnitude of the limiting current.

In exactly the same way acids and bases catalyse the conversion of α- and β-pyranoses and of α- and β-furanoses to their polarographically active forms containing free carbonyl groups [156].

Los *et al.* [157] made a polarographic study of the kinetics of the mutarotation of α-glucose using Delahay's results on the reduction of aldoses.

Since we cannot consider further the various cases of the occurrence and use of kinetic currents in polarography, we shall just mention one further type of reaction undergone by organic compounds at a dropping mercury electrode:

$$A + e \rightarrow B,\ B + C \xrightarrow{K} A.$$

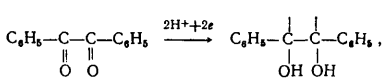
Here the gradually regenerated depolariser A acts as a catalyst for the polarographic reduction of the inactive substance [65,150]. The product of the reduction of haemin, for example, reacts with hydrogen peroxide to form a compound which is reduced at a more positive potential than is hydrogen peroxide. The ferric complexes of catechol, pyrogallol, ascorbic acid, peroxidase, and haemoglobin act similarly. These reactions, too, are utilised in studying the kinetics of chemical reactions [65].

VII. STUDY OF MOLECULAR REARRANGEMENTS AND REACTIONS

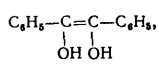
The polarographic method can be used to study molecular rearrangements and changes in polarographically active compounds. However, the number of papers on this application of polarography is small.

Ried and Wilk [158] used this method to follow the conversion of *o*-nitrobenzaldehyde to *o*-nitrobenzoic acid under the influence of light. The velocity of the Smiles rearrangement of 2-hydroxyphenyl 2-nitrophenyl sulphones into 2-*o*-nitrophenoxybenzenesulphonic acids has been studied in a similar way [159]. In the latter work the dependence of $\pi_{\frac{1}{2}}$ on solution pH was determined for each pair of sulphone and sulphonic acid. The pH range was then selected in which the reduction potentials of the nitro-groups of the sulphone and the sulphonic acid showed the greatest difference. The rate of the rearrangement as a function of temperature, nature of the compound, and position of substituents in the benzene ring was then studied within this pH range.

In a study of the reduction of benzoin and benzil it was found that the intermediate in the reduction



isomerising into an enediol [160]



is partly converted, at the electrode surface, to benzoin, which is detected polarographically [161].

Polarographic studies have also been made of the isomerisation of formazans [162] and of the mechanism of the Cannizzaro intramolecular rearrangement of mandelic acid to phenylglyoxal [163].

VIII. RELATION BETWEEN POLAROGRAPHIC DATA AND THOSE OF OTHER METHODS OF INVESTIGATION

The employment of different physical and physicochemical methods for investigating organic compounds has enriched and developed the Butlerov concept of chemical structure. The theory of chemical structure is based on an immense amount of experimental information. Recently many new facts have been established, most of which relate to the problem, posed long ago by A. M. Butlerov, of the mutual influence of atoms in a molecule. This problem is now one of the most important and general problems of chemistry. In this connection great interest attaches to the study of the structure of organic compounds, which determines the behaviour of the molecule in chemical reactions. The extensive use of dipole moments, optical spectroscopy, refractometry, radiospectroscopy, etc. has enabled investigators to reach a number of important conclusions on the molecular structure of several classes of organic compounds, and hence to obtain definite information on their reactivity.

Polarography occupies a leading position among the various methods which to a greater or lesser extent enable the problem of the mutual influence of structural units in organic molecules to be elucidated, the information obtained in this way about the structure of a substance in solution agreeing with the results of other methods of investigation.

It has been found that the general factors governing the ability of molecules to undergo an electrochemical reaction at a dropping mercury electrode are the presence in the molecule of certain polar bonds which possess electrophilic properties, the polarisability of atoms or bonds under the influence of the electric field of the electrode, and also the spatial arrangement of structural units in organic molecules.

Thus the value of $\pi_{\frac{1}{2}}$ depends on the polar and steric factors which govern the state of the molecule at the electrode surface, and bears a definite relation to the distribution of bonds in the molecule, the presence and state of certain groups of atoms, and their electrophilic character [164].

One method which makes it possible to characterise the distribution of electron density in molecules from chemical shifts is nuclear magnetic resonance. In essence, all types of polarographically active compounds can be investigated by this method [165,166]. Bennett and Elving [166] found that the $\pi_{\frac{1}{2}}$ values vary linearly with the values of the chemical shifts for aliphatic aldehydes and *meta*- and *para*-substituted benzaldehydes, iodobenzenes, and nitrobenzenes. With brominated aliphatic compounds and chloroacetic esters, and also with *ortho*-substituted benzene derivatives, however, this linear relation is not maintained. In these cases the value of $\pi_{\frac{1}{2}}$ is probably determined not only by the distribution of electron density in the molecule but also by adsorption on the electrode and by steric effects.

Several papers have been concerned with the relation between the value of $\pi_{\frac{1}{2}}$ and the energetic properties of the π electrons of reducible organic compounds. Such a relation has been found in hydrocarbons having conjugated bonds [167-170] and in several nitro-compounds [171].

Calculation of electron density based on molecular orbital theory was used by Fernandez-Alonso and Domingo [172] to compare values of $\pi_{\frac{1}{2}}$ with the reactivity and structure of polycyclic hydrocarbons. Values of $\pi_{\frac{1}{2}}$ for these hydrocarbons show good agreement with potentiometric data [169]. On the assumption that in the reduction of polycyclic hydrocarbons at a dropping mercury electrode protons add on at the same position as hydrogen atoms in reduction reactions, the localisation energy has been found [168] to be proportional to $\pi_{\frac{1}{2}}$. Table 5 lists values of $\pi_{\frac{1}{2}}$ and localisation energies (E).

The accumulated information in the literature has enabled Voitkevich [173] to link the ease of reduction of organic compounds with their polarity. He states that reduction at a dropping mercury electrode takes place by the transfer of electrons from the cathode surface to a positively charged part of the molecule with simultaneous or subsequent addition of protons at points of high electron density; the role of the polarity of the molecules then becomes quite obvious: electrons are most readily captured by molecules which have the greatest effective positive charge oriented towards the cathode, *i.e.* by molecules whose reducible groups posess the greatest dipole moment. Comparison of the depolarising ability displayed by different organic compounds on reduction at a mercury cathode shows that substances whose molecules possess large dipole moments are liable to be reduced. Table 6 compares the dipole moments and the reducibility of several compounds.

These data confirm the direct relation between ease of reduction and the polarity of molecules. With molecules containing more than one polar functional group, however, this simple relation between ease of reduction and dipole moment is somewhat complicated by the fact that the dipole moments of groups can partly offset one another, so that the net dipole moment is diminished.

TABLE 5.

Compound	Positions	$-\pi^*_{\frac{1}{2}}$, V	E, kcal mole^{-1}
Naphthalene	1:4	2.5	4.00
Anthracene	9:10	1.94	3.31
Phenanthrene	1:4	2.46	3.77
1,2-Benzanthracene	5:10	2.03	3.41
Biphenyl	1:4	2.70	4.38

* Relative to saturated calomel electrode.

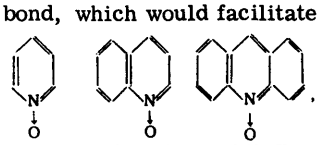
TABLE 6.

Compound	Dipole moment, 10^{18} e.s.u.	Ease of reduction
Unsymmetrical hydrocarbons containing one double bond Aliphatic carboxylic acids Aliphatic alcohols	0.3—0.5 0.8—1.6 1.6—1.7	not reduced
Aliphatic aldehydes and ketones	2.3—2.9	moderate reduction
Unsaturated aldehydes	3.5—3.6	readily reduced
Nitrobenzene Aromatic mono- and di-nitro--compounds containing a single substituent	4.2 3.1—4.8	very readily reduced

In the polarography of molecules containing more than one polar group the most important quantity is not the dipole moment of the whole molecule but only that of the reducible group, or in effect the magnitude of the effective positive charge which is oriented towards the cathode. Of course, a correction must be introduced each time for the mutual inductive effect of other functional groups.

A study of heterocyclic *N*-oxides by Pushkarëva and Varyukhina[174,175] showed that the dipole moment of the N→O bond decreases, and at the same time its ease of electrochemical reduction at a dropping mercury electrode increases, on passing from the *N*-oxide of the simplest six-membered *N*-heterocycle, pyridine, to those with fused ring systems, and also on passing from the *N*-oxides of monoheterocycles to the corresponding *N*-oxides of the pyrazine system. This fact is inconsistent with the generalisation established by Voitkevich. An attempt at an explanation was made by assuming that in this case reduction takes place as a heterogeneous process involving adsorbed molecules of the reducible organic substance. The greatest adsorption will apparently occur when the dipole moment of the N→O bond is least, since the geometry of the molecule is such that the negative end of the dipole will repel the molecule from the cathode surface, and hence will prevent adsorption of the compound on the surface. It seems to us that such an interpretation of the results is not altogether correct, and that the observed regularities can be explained on the basis of the general theory of conjugation[106].

The increase in ease of reduction on passing from *N*-oxides of pyridine to those of quinoline and acridine is obviously explained by a strengthening of conjugation between the N→O bond and the C=C double bonds of the fused benzene rings, not by increased adsorption. In this series of compounds such intensified conjugation should actually result in a decrease in electron density of the reducible N→O bond, which would facilitate the reduction



−1.364 V −1.164 V −−0.854 V

although the dipole moment decreases in this series. This again indicates that, in the investigation of complicated systems, the mutual inductive effect of all groups or heteroatoms in the molecule must be taken into account, and that the overall dipole moments of complicated molecules cannot give any indication of their polarographic behaviour.

Work aimed at establishing a relation between the electrochemical and the spectroscopic characteristics of compounds is of great interest. Indeed, the chemical action of an electric current resembles in many respects the action of light on a substance, the elementary act of change in the substance consisting in both cases in the transfer of electrons and in a change in the electronic state of the reactant molecules.

Gorbachev and Belevskii[176] attempted to link the absorption spectra of a series of nitro-derivatives of benzene with their reduction potentials on solid electrodes. They were able to establish a linear relation between the reduction potentials and the energy of the long-wave edge of the band of continuous absorption in the ultra-violet. It was found that the reduction potential falls as this energy increases. This was explained in terms of the donor–acceptor theory of A. N. Terenin.

It is obvious that, the larger the quantum which the molecule absorbs, the deeper is the electron which is expelled and the greater is the electron affinity of this molecule. In electrochemical reduction the electron affinity is measured by the reduction potential. Consequently, the higher the reduction potential of a molecule, the lower is the energy of the quantum which it absorbs. This relation is interesting, for, if it is observed with different classes of compounds, it will become possible to predict spectroscopic characteristics from electrochemical data, and to assess the electrochemical behaviour of compounds from their absorption spectra.

Holleck and Schindler[177] also established a definite relation between ease of reduction and position of the long-wave edge of the absorption bands of some substituted nitrobenzenes, expressing it by the empirical formula

$$E_{eV\,(energ)} = \alpha\pi_{1/2} + C,$$

where C depends on the energy state of the molecule, and α is a constant depending on the nature of the substance.

Komenda[178] studied the polarographic behaviour and ultra-violet spectra of 2-amino-4-hydroxy-6-methylpteridine, and found that the anion formed in alkaline medium is reduced at a more negative potential than is the neutral molecule. This worker also investigated the changes in the spectra of such compounds caused by dissociation and tautomerism.

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Polarography now occupies a leading position among physicochemical methods for the investigation of organic compounds. About 10% of organic compounds, which represents over 300 000, can be reduced or oxidised at microelectrodes, but only ~2000 compounds have yet been studied. There is no doubt that the polarographic method will play a leading part in further improvement of organic structural theory.

In the present survey an attempt has been made to report the main results of the polarographic study of organic compounds during the last decade, without considering the application of several new methods, such as oscillographic, derivative, and differential polarography, etc., which have developed only during the past few years.

Classical polarography is certainly no universal method of investigation, since it is unable to determine concentrations below 10^{-5} or above 10^{-2} M, and its resolving power is not very high. The production of oscillographic and other instruments of high sensitivity and resolving power has considerably broadened the possibilities of the method. By means of oscillographic polarography, it became possible to study complicated systems, the components of which are reduced at very similar potentials (see, for example, the papers by Volke [179-187]). Oscillographic polarography enables the kinetics of electrochemical reactions of organic compounds to be studied, and permits a more profound understanding of the relation between the behaviour of a substance at the electrode and its reactivity [188-192].

Only qualitative measurements have been made in by far the greatest proportion of the work in which polarography has been applied to organic chemistry. Quantitative calculations in organic chemistry based on polarographic data encounter a number of difficulties arising from the irreversibility of electrode reactions.

Knowledge of polarographic half-wave potentials provides great opportunities for energy calculations, since all the relations necessary for the transition from electrical characteristics to units of heat energy are known. Calculations are usually based on differences in $\pi_{\frac{1}{2}}$ for a standard and the unknown compound or between two forms of one compound. Since the charge on an equivalent of a substance is 94 600 C, while the electrical work associated with a charge of 1 C at a potential of 1 V is equivalent to 0.239 cal, it is easy to calculate that the work involved in the conversion of 1 mole of polarographically active substance at $\Delta\pi_{\frac{1}{2}} = 1$ V is $23.06n$ kcal, where n is the number of electrons taking part in the electrode reaction. This work corresponds to the difference in free energy between the molecules which are being compared.

Polarographic data can be used to calculate bond interaction energies (see, for example, Ref. 48), energies of interconversion of tautomers and geometrical isomers [97,98], etc. However, the irreversibility of a large proportion of electrode reactions undergone by organic compounds during polarography hinders such calculations, since the value of $\pi_{\frac{1}{2}}$ in such cases often varies in a complex fashion with the concentration of the substance, the pH of the medium, the composition of the electrolyte, and other factors. But even these obstacles can undoubtedly be overcome, and it is to be hoped that during the next few years the polarographic method will find still more extensive and fruitful application in organic chemistry as a quantitative instrumental method for investigating the structure and reactions of many classes of compounds.

Great progress has been made during recent years in the instrumental development of the method. The increase in sensitivity and resolving power of the apparatus has considerably extended the limits to the application of polarography. Much can be expected also from the application of oscillographic polarography to organic chemistry. The great development of polarography is due to its experimental simplicity and the properties of the dropping mercury electrode as an ideally polarisable electrode. Nowadays solid electrodes are being more and more widely used, and in some cases are indispensable. However, research workers are not inclined to forget the "mercury drop": "... it will still be many years before all its advantages have been investigated and exploited" (J. Heyrovský).

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Arbuzov Chemical Institute of the Kazan
Branch of the USSR Academy of Sciences

HIGH-TEMPERATURE GAS-LIQUID CHROMATOGRAPHY

N.A.Malafeev, I.P.Yudina, and N.M.Zhavoronkov

Two trends have arisen in the gas chromatography of high-boiling substances. The first is based on the use of