

# Electrochemiluminescence of Aromatic Hydrocarbons

BY G. J. HOYTINK

Dept. of Chemistry, The University, Sheffield S3 7HF

*Received 25th January, 1968*

The thermodynamics and kinetics of the cation-anion annihilation involved in the electrochemiluminescence of aromatic hydrocarbons are discussed qualitatively. For various hydrocarbons the direct population of singlet excited states is competitive with the population of excited triplet states.

In recent years several successful attempts have been made to observe the emission of light from the annihilation of cations and anions of aromatic molecules.<sup>1-4</sup> The present paper deals with the electrochemiluminescence of aromatic hydrocarbons. This is a special case in which the cations and anions involved in the annihilation reaction originate from the same parent hydrocarbon. A brief discussion is given of the thermodynamics that lead to the expectation of the phenomenon and the kinetics of the main reactions involved are described qualitatively.

## THERMODYNAMICS OF CATION-ANION ANNIHILATION

Let us consider the reaction



The free enthalpy of this reaction can be expressed in terms of the oxidation and reduction potentials of the molecule M:

$$\Delta G^\circ = \{\varepsilon_{\text{red}}^\circ - \varepsilon_{\text{ox}}^\circ\}F \quad (2)$$

where  $F$  is Faraday's constant.

From (2) we can derive the enthalpy of reaction (1):

$$\begin{aligned} \Delta H^\circ &= \Delta G^\circ + T\Delta S^\circ = \Delta G^\circ - T\partial\Delta G^\circ/\partial T \\ &= \{\varepsilon_{\text{red}} - \varepsilon_{\text{ox}}\}F - T\partial\{\varepsilon_{\text{red}} - \varepsilon_{\text{ox}}\}F/\partial T. \end{aligned} \quad (3)$$

Information about the amount of energy liberated in reaction (1) can be obtained once we know the oxidation and reduction potentials of the molecule M and their temperature dependence.

## REDUCTION POTENTIALS OF AROMATIC HYDROCARBONS

Polarographic reduction of aromatic hydrocarbons have provided a large series of reduction potentials.<sup>5</sup> In solvents like 96 % dioxan + water, dimethyl formamide and acetonitrile in which the negative ions are fairly stable, the current-voltage curve shows two one-electron steps which can be attributed to the following reactions.<sup>6</sup>



The first reaction is reversible, i.e., the rate of electron transfer back and forth is fast in comparison with the rate of diffusion of  $M$  and  $M^-$  to and from the electrode surface layer. Under these conditions we may use the Nernst equation and the expression for the half-wave potential of the first reduction step becomes <sup>7</sup>

$$\varepsilon_{\frac{1}{2}} = \varepsilon_{\text{red}}^{\circ} + 0.059 \log_{10} (k_{M^-}/k_M), \quad (6)$$

where  $k_M$  and  $k_{M^-}$  are constants proportional to the square roots of the diffusion constants of  $M$  and  $M^-$ . Since these constants are practically the same for the molecule and its ion, the half-wave potential practically equals the standard reduction potential.

If we add some proton donor to the solution (e.g., (more) water) the height of the first reduction wave increases until, after sufficient addition, the height has become equal to that of a two-electron addition. The essential reactions taking place now are <sup>6</sup>



From theory the radical  $MH\cdot$  has a much higher electron affinity than the parent molecule  $M$ , so that reaction (8) and, consequently (7), become extremely irreversible. Consequently, the potential-determining step is still reaction (4) but the height of the current-voltage curve now corresponds to the overall addition of two electrons.

In such cases the rate constant  $k_{M^-}$  in (6) refers to the proton addition to the mononegative ion. Since the accuracy of the current measurements in polarography is about 1 %, the minimum conditions for the observation of a two-electron wave is that the rate of protonation of  $M^-$  is two orders higher than its rate of

TABLE 1.—COMPARISON OF ESTIMATED ENTHALPIES OF THE CATION-ANION ANNIHILATION WITH SINGLET AND TRIPLET ENERGIES

	$\varepsilon_{\frac{1}{2}, \text{ox}}$	$-\varepsilon_{\frac{1}{2}, \text{red}}$	$-\Delta G^{\circ}$	$-\Delta H^{\circ}$	$\Delta E_s$	$\Delta E_t$
benzene	2.26	(3.16)	5.6	5.4	4.7	3.6
naphthalene	1.57	2.60	4.4	4.2	3.9	2.6
phenanthrene	1.49	2.48	4.2	4.0	3.6	2.7
pyrene	1.14	2.10	3.4	3.2	3.3	2.1
anthracene	1.10	1.98	3.3	3.1	3.3	1.8
perylene	(0.77)	1.67	2.6	2.4	2.9	—
tetracene	0.80	1.58	2.6	2.4	2.6	1.3

All energy data are in eV. The oxidation and reduction potentials are in V (S.C.E.). Lund's oxidation potentials have been given with reference to the  $\text{Ag}/0.1 \text{ M Ag}^+$  electrode in acetonitrile. The potential of the reference electrode with respect to S.C.E. is +0.26 V.

diffusion out of the electrode layer.<sup>6</sup> Accordingly, if one observes a two-electron step, its half-wave potential will be shifted to less negative potentials by an amount of 0.12 V at least. If the proton addition to  $M^-$  becomes very fast, i.e., of comparable magnitude as the rate of electron transfer, reaction (4) itself becomes irreversible and the current-voltage curve will deviate substantially from the logarithmic Nernst curve. Since the electron transfer process is very rapid <sup>8</sup> this will occur only at very high rates of proton addition, probably four orders of magnitude higher than the rate of diffusion.

All the reduction potentials listed in table 1 (so far as measured experimentally) have been taken from current-voltage curves in which the first step corresponded to a one-electron wave, so that the foregoing exposition is irrelevant for them.

## OXIDATION POTENTIALS OF AROMATIC HYDROCARBONS

Lund<sup>9</sup> has measured the polarographic oxidation curves of a number of aromatic hydrocarbons using a rotating platinum electrode. As a solvent he used acetonitrile. His curves show only one wave, although the monopositive ion can exist in acetonitrile.<sup>10</sup> Its life time in this solvent, however, is fairly short. The results obtained by Lund can be understood in the light of what we have said about the reduction in the presence of proton donors. If the mono-positive ion reacts with the solvent or with water in the solvent (it is extremely difficult to remove water from acetonitrile below a concentration of 1 mM) and the rate of this reaction is higher than the rate of diffusion the following scheme holds:



We can expect, from theory, that the ionization potential of the radical  $MY\cdot$  is lower than that of the parent molecule  $M$ . Hence reaction (11) becomes extremely fast and makes (10) irreversible so that (9) is still the potential-determining step, but the overall height of the curve corresponds to two electrons per molecule. Because of this reaction of  $M^+$  with the solvent the half-wave potential is shifted to less positive potentials and a correction ought to be made in order to obtain the standard oxidation potential. It is difficult to find out how large this correction should be. The curves still show the logarithmic shape so that we can safely say that the shift of the half-wave potential with respect to the standard potential will be between  $-0.12$  and  $-0.24$  V. The rate of reaction (10) does not necessarily need to be the same for all hydrocarbons considered. In general, we may expect the rate to be faster the smaller the size of the ion. It is, however, difficult to make any allowance for this. In the following discussion we have assumed a rounded-off value of  $+0.2$  V for the half-wave oxidation potentials reported by Lund, which we think is a minimum. The values for  $\Delta G^\circ$  given in table I include this correction. Some of the values in this table are placed within brackets. In these cases either the oxidation or the reduction potential was unknown and have been estimated by the following procedure.

According to Pople's SCF approach for alternant hydrocarbons the sum of ionization potential and electron affinity should be constant<sup>11</sup>:

$$I + A = \text{constant.} \quad (12)$$

For large ions, as in the present case, it is reasonable to assume that the solvation energies of the positive and negative ions of the same molecule are practically equal. Under that condition, eqn. (12) may be rewritten as

$$\varepsilon_{\text{ox}}^\circ + \varepsilon_{\text{red}}^\circ = \text{constant.} \quad (13)$$

A plot of Lund's oxidation potentials against reduction potentials indeed shows a linear dependence.<sup>12</sup> The slope is somewhat smaller than the expected  $45^\circ$  which could just account for the deviations of Lund's potentials from the standard potential. From the experimental potentials we derived the equation:

$$\varepsilon_{\frac{1}{2},\text{ox}} + \varepsilon_{\frac{1}{2},\text{red}} = -0.90(\pm 0.08). \quad (14)$$

The value within the brackets is twice the standard deviation from the mean.

## TEMPERATURE DEPENDENCE OF OXIDATION AND REDUCTION POTENTIALS

No thorough investigation has yet been made on the temperature dependence of oxidation and reduction potentials. A decade ago, however, the polarographic reduction of various aromatic hydrocarbons has been carried out at 25 and 75°C<sup>5, 13</sup>; one finds that there is little change in the reduction potential. The average change found for a large number of potentials hardly exceeds the uncertainty in the individual experimental values ( $\pm 0.01$  V), although there is a trend to more negative values at higher temperatures, as is expected. We, therefore, take as an upper limit a change of  $-0.02$  V over 50°C.

Because of the close analogy between oxidation and reduction it is reasonable to assume that for the oxidation potentials the change will be the same in the opposite direction. Hence

$$\partial(\varepsilon_{\text{red}}^{\circ} - \varepsilon_{\text{ox}}^{\circ})/\partial T = -0.008 \text{ V deg.}^{-1} \quad (15)$$

so that

$$\Delta H^{\circ} = \Delta G^{\circ} + 0.2 \text{ eV.} \quad (16)$$

Values of  $\Delta H^{\circ}$  for reactions (1) are given in table 1. We see that the entropy corrections are very small. In table 1 we have also given the energies of the lower excited states of the molecules. In many cases the enthalpy of reaction (1) is sufficiently negative to leave one of the molecules in the lowest singlet excited state. In all cases the enthalpy suffices to populate the lowest triplet state. Which of the two states will be more favoured depends on the rates of the two reactions.

## KINETICS OF CATION-ANION ANNIHILATION

Since our study deals with ions in solution we may expect solvation to play an important role in the kinetics of the annihilation reactions. If we leave out of consideration whether or not in the final state one of the molecules will be in a singlet or a triplet excited state we may write the reaction equation:



In the initial state there are two ions, whereas in the final state both molecules are neutral. Reactions of this kind have been studied theoretically by Marcus.<sup>14</sup> On passing from the initial to the final state we must reach a crossing point on the free enthalpy surface at which both states have the same nuclear conformation. For large molecules like the ones considered here, there will be little difference in nuclear conformation between the ions and the ground-state and excited-state molecules. Far the greatest change is due to solvent re-orientation. We, therefore, leave the nuclear rearrangement out of consideration.

As shown later, the minimum distance between the ions required for a maximum probability of crossing from the initial to the final state is that in which the two ions are separated by two solvent layers (*ca.* 10 Å). At such a distance the electrostatic attraction between the ions in solvents like acetonitrile is still small (or the order of  $kT$  at room temperature) and will, therefore, be neglected.

On passing from the initial to the final state we have to change the solvent orientation. Suppose at some intermediate stage the electron stays for a fraction of time  $m$  on the positive ion. The contribution to the solvation energy due to electronic polarization is still the same as in the initial state, since this polarization follows the motion of the electron instantaneously. The orientation of the solvent dipoles,

## 18 ELECTROCHEMILUMINESCENCE OF AROMATIC HYDROCARBONS

however, is determined by the average electron distribution. The difference in free enthalpy due to the difference in solvent orientation in this intermediate state and the initial state has been derived by Marcus,<sup>15</sup> using the dielectric theory :

$$G_{\text{pol}} = Nm^2e^2\left(\frac{1}{2r_+} + \frac{1}{2r_-} - \frac{1}{R}\right)\left(\frac{1}{D_o} - \frac{1}{D_s}\right), \quad (18)$$

where  $r_+$  and  $r_-$  represent the radii of the positive and negative ion,  $R$  is the inter ionic distance,  $D_o$  and  $D_s$  are the optical and static dielectric constants and  $e$  represents the electronic charge. This formula depends strongly on the validity of the dielectric theory. It is, therefore, more straightforward to follow a procedure proposed by Marcus,<sup>14</sup> viz., to assume that the free enthalpy change is proportional to the square of the "fraction" of charge being transferred :

$$G_{\text{pol}} = m^2 \lambda. \quad (19)$$

Szwarc<sup>10</sup> shows that solvation energies of aromatic ions vary very little. This implies that it is reasonable to assume that  $\lambda$  is a constant for different hydrocarbons. Marcus made an estimate of  $\lambda$  from the experimental rate of electron transfer between tetramethylphenylenediamine (T.M.P.D.) and its positive ion<sup>14</sup> :

$$\lambda = 16 \text{ kcal mole}^{-1} \simeq 0.64 \text{ eV}. \quad (20)$$

Formulae (18) and (19) show that  $m$  is a suitable parameter for the re-orientation of the solvent. On plotting  $G_{\text{pol}}$  as a function of  $m$  we obtain two parabolae, one for the initial and one for the final state. At the crossing point, the initial and final states have assumed the same solvent orientation. The condition for this transition state is<sup>14</sup>

$$(2m+1)\lambda = \Delta G^\circ. \quad (21)$$

In fig. 1-4, the energy surfaces have been plotted for some aromatic hydrocarbons. In these plots we have included all relevant known excited states.

Before discussing these diagrams we consider the probability of crossing from the initial to the final state in the transition state of the "complex". In acetonitrile at room temperature the collision number is about two orders lower than in the gas phase. Consequently, the velocity of the ions in solution is about two orders lower than in the gas phase. Hence we calculate that the ions in solution travel in  $10^{-10}$  sec over a distance of  $10 \text{ \AA}$ . When the two ions have approached each other at this distance, the question whether or not they have to move closer in order that the annihilation reaction takes place depends on what time is required for the crossing in the transition state. According to the uncertainty principle, within a time of  $10^{-10}$  sec an interaction with an energy of  $10^{-5}$  eV can manifest itself. The interaction between the initial state and the final state that gives rise to electron transfer is first order in intermolecular overlap. Undoubtedly this interaction energy will exceed  $10^{-5}$  eV, particularly in solutions, where, because of the dielectric medium the "molecular orbitals are more extended into space than in the vacuum". We can, therefore, state that the crossing takes place with unit probability. The only factor to be considered is the statistical factor due to the electron spin. Since the two ions are both in a doublet ground state the encounter may lead to a singlet or a triplet transition state, depending on the orientation of the electron spins before the encounter. Hence we have to account for a statistical factor of  $\frac{1}{4}$  or  $\frac{3}{4}$  for singlet or triplet encounters respectively.

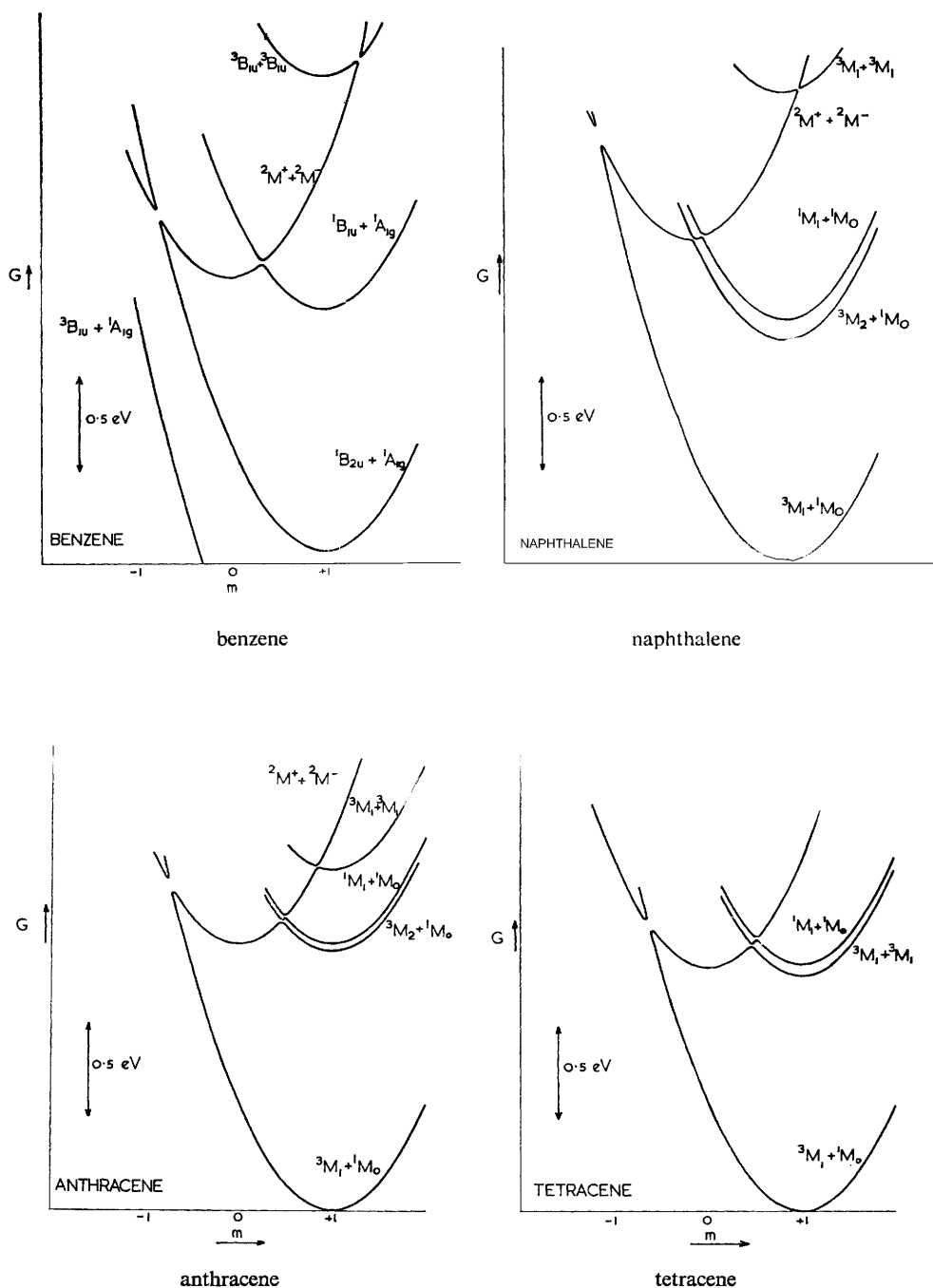


FIG. 1-4.—Schematic illustration of the free enthalpy for the cation-anion annihilation as a function of solvent orientation  $m$ .



## 20 ELECTROCHEMILUMINESCENCE OF AROMATIC HYDROCARBONS

The rate constants for the cation-anion annihilation thus become

$$k_s = \frac{1}{4}k_d \exp(-\Delta G_s^*/RT), \quad (22)$$

$$k_t = \frac{3}{4}k_d \exp(-\Delta G_t^*/RT), \quad (23)$$

where  $k_d$  is the diffusion-controlled rate constant.

From fig. 1-4 we see that some very low lying excited states give rise to a crossing on the left hand side of the diagram. In such a case the solvent orientation in the transition state corresponds to even higher than unit charges on both ions. If the free enthalpy at such a crossing is of the order of a few vibrational quanta we may expect that the actual crossing will take place at a lower free enthalpy whereby the initial state makes a smooth crossing into a vibrationally excited electronic excited state. If this vibrational energy is not too high our assumption that the nuclear conformations are approximately the same on both ends of the reaction will still hold.

When the first excited triplet is located at a relatively low energy, the second excited triplet may take over its role (see, e.g., naphthalene). Since internal conversion and the dissipation of excess vibrational energy take place within  $10^{-12}$  sec the excited molecule will be already in its lowest triplet before the two molecules separate.

For molecules, with a very low-lying first excited triplet state, like e.g., tetracene and pentacene, the cation-anion annihilation may lead to the formation of two triplet excited molecules. In general, this is not a favourable case for chemiluminescence, since it usually means that the triplet is so low that triplet-triplet annihilation cannot reach the lowest singlet excited state, so that for light emission one depends entirely on the direct formation of singlet excited states. Tetracene is a boundary case, since here the combination of two triplets is only a few hundredth of a volt below the lowest singlet.

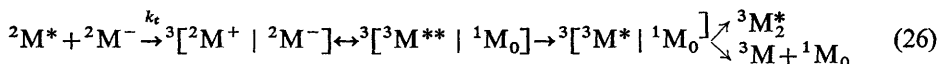
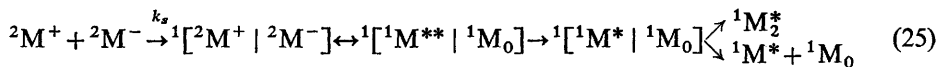
An interesting aspect, especially for photochemistry, is that the reverse reaction



can proceed with very little activation, so that in certain cases it may well compete with the production of singlet excited molecules. Jarnagin *et al.*<sup>16</sup> have found experimental evidence for this reaction.

The most interesting conclusion we may draw from the figures and from table 1 is that cation-anion annihilation of aromatic hydrocarbons in principle does not lead exclusively to the population of the triplet excited state. In various cases the population of the singlet excited state may well be competitive.

Summarizing, we may write the following schemes for the two reactions:

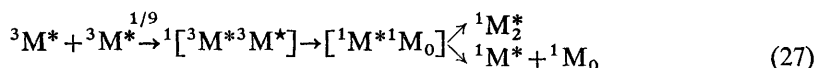


The extra asterisk accounts for the possibility that the crossing takes place to a vibrationally excited electronic state or to a higher excited electronic state. At the nearest distance of approach for the cation-anion annihilation the interaction between the excited molecule and the ground state molecule in the final state is still much smaller than  $kT$  at room temperature. Only a fraction of the encounters will, therefore, lead to the formation of excimers. Triplet excimers are, in general, less stable than singlet excimers, but there is strong evidence for their existence in solutions.<sup>18</sup>

With the production of excited molecules by means of electrochemistry, photochemistry has to take over. In the following a brief summary of the essential reactions following the cation-anion annihilation will be given.

Emission due to the decay of the lowest triplet state to the ground state in solution is very weak and will not give a substantial contribution to the electrochemiluminescence. Induced emission due to exchange interaction of the triplet with a positive or negative ion (or with another triplet)<sup>19</sup> may increase this contribution to some extent but the efficiency will still be very low compared with other reactions.

The main contribution of the excited triplets to the chemiluminescence is through triplet-triplet annihilation:



Here the statistical factor for the electron spin is 1/9.

The ratio between excimer and excited monomer need not necessarily be the same in (27) and in (25). Parker and Short<sup>20</sup> used this to show that the chemiluminescence was not due to triplet-triplet annihilation only. They compared the ratio of the intensities of monomer and excimer emission of 9,10-dimethylantracene obtained from chemiluminescence with that known for triplet-triplet annihilation and found a fairly large difference.

The other fast reactions taking place all involve the de-activation of excited molecules. In principle the excited molecules and excimers may be de-activated by collisions with triplet molecules and positive and negative ions. Apart from the statistical factor for the electron spin these quenching reactions probably will be diffusion controlled. In chemiluminescent experiments, however, the rate-determining step will be the diffusion transport of the ions to the "reaction zone". This process is slow compared with the fast reactions involved in the process itself so that the concentration of ions and triplets in the "reaction zone" will be very low. The quenching of excited molecules and excimers, therefore, will have little influence on the quantum yield of the process. In practice, the quantum yield is influenced strongly by the short life-time of the ions, particularly the positive ion in solvents like acetonitrile and dimethyl formamide. In this respect the use of a.c. methods is an improvement,<sup>1-3</sup> although still not ideal. There is a real need for a solvent in which both positive and negative ions could be stable for a reasonable time. This would simplify the experiments considerably.

Finally, the above consideration holds just as well for the chemiluminescent experiments recently carried out by Weller and Zachariasse.<sup>4</sup> They observed luminescence from the reaction between Wurster's blue cation and aromatic hydrocarbon negative ions. The free enthalpy values for these reactions are ideal for a very fast formation of the lowest excited triplet of the hydrocarbon molecule.

<sup>1</sup> D. M. Hercules, R. C. Lansbury and D. K. Roe, *J. Amer. Chem. Soc.*, 1966, **88**, 4578 and previous papers cited therein.

<sup>2</sup> E. A. Chandross, R. E. Visco and J. W. Longworth, *J. Amer. Chem. Soc.*, 1965, **87**, 3259, and related papers.

<sup>3</sup> A. Zweig, D. L. Maricle, J. S. Brinen and A. H. Maurer, *J. Amer. Chem. Soc.*, 1967, **89**, 473, and papers cited therein.

<sup>4</sup> A. H. Weller and K. Zachariasse, *J. Chem. Physics*, 1967, **46**, 4984.

<sup>5</sup> G. J. Hoytink, *Rec. Trav. Chim.*, 1955, **74**, 1525.

<sup>6</sup> G. J. Hoytink, J. van Schooten, E. de Boer and W. Y. Aalbersberg, *Rec. Trav. Chim.*, 1954, **73**, 355. G. J. Hoytink, *Ind. Chim. Belge*, 1963, **12**, 1371.

<sup>7</sup> I. M. Kolthoff and J. J. Lingane, *Polarography*, (Interscience Publishers, New York, N.Y.).



- <sup>8</sup> A. C. Aten, C. Büthker and G. J. Hoytink, *Trans. Faraday Soc.*, 1958, **55**, 324.  
<sup>9</sup> H. Lund, *Acta Chem. Scand.*, 1957, **11**, 1323.  
<sup>10</sup> unpublished work.  
<sup>11</sup> N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, 1955, **51**, 600.  
<sup>12</sup> G. J. Hoytink, *Rec. Trav. Chim.*, 1958, **77**, 555.  
<sup>13</sup> G. J. Hoytink, *Rec. Trav. Chim.*, 1954, **73**, 895.  
<sup>14</sup> R. A. Marcus, *J. Chem. Physics*, 1965, **43**, 2654 and references cited therein.  
<sup>15</sup> R. A. Marcus, *J. Chem. Physics*, 1965, **43**, 679.  
<sup>16</sup> R. Jarnagin, private communication.  
<sup>17</sup> J. Chandheiri, J. Jagur-Grodzinski and M. Szwarc, *J. Physic. Chem.*, 1967, **71**, 3063.  
<sup>18</sup> J. Langelaar, R. P. H. Rettschnick, A. M. F. Lambooy and G. J. Hoytink, in course of publication.  
<sup>19</sup> G. J. Hoytink, *Mol. Physics*, 1960, **3**, 67. J. N. Murrell, *Mol. Physics*, 1960, **3**, 319.  
<sup>20</sup> C. A. Parker and G. D. Short, *Trans. Faraday Soc.*, 1967, **36**, 2618.