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The Dissociative Breakdown of Negative Ions

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Most neutral molecules are able to accept low-energy electrons to become negative ions, but the cross-section for capture varies tremendously from one type of molecule to another. For example, Clemons and Altschuller have indicated a response for halogenated compounds which covers a range of $10^7$ in the appropriate units. This great difference in sensitivity makes it possible to use electron-capture methods for clinical purposes, for the analysis of pesticides, and as an adjunct to gas chromatography. The possible biological significance of the affinity of organic compounds for free electrons with thermal or near-thermal energy has been discussed by Lovelock. However, despite the importance of this whole process, there are many features about it which are not properly understood. We now draw attention to one such feature, involving halogenated organic molecules, where some of the experimental results can be explained.

Our interest in this process stems from an observation by one of us (D. D. C.) that there is a linear free energy relationship between the electron absorption coefficients of a series of phenolic acetates and the sigma values of Hammett. The large value of $\rho$ (ca. 5), the slope of this line, suggested to us that the electron absorption coefficient should be considered as a measure of a rate constant for a dissociative process rather than the equilibrium constant for a non-dissociative electron capture.

The capture of low-energy electrons by this type of molecule has been studied by various authors but the most complete account is given by Wentworth, Becker, and Tung. This capture may be either dissociative or non-dissociative, though most previous papers on this topic have failed to give a satisfactory explanation of the distinction between the two situations. However, a careful study of the nature of the potential energy curves for the possible states of the negative ion, and their symmetry, does enable us to make this distinction much clearer, and to show in what types of molecule we may expect a large cross-section for dissociation.

We illustrate our discussion by an account of one particular molecule, chlorobenzene. We then show that the argument may be easily extended to more general cases. Information about the capture process for chlorobenzene has been given by Stockdale and others. The capture of a slow electron leads initially to the ion $(\text{Ph}-\text{Cl})^-$. If dissociation follows, the reaction is:

$$ (\text{Ph}-\text{Cl})^- \rightarrow \text{Ph} + \text{Cl}^- \quad (1) $$

In order to understand these two steps we must consider three potential energy curves (see Figure). Curve I is the P.E. curve for neutral chlorobenzene, in which the abscissa is the C-Cl distance. Curve II is the P.E. curve for the ground state of the anion $(\text{Ph}-\text{Cl})^-$, and curve III is the curve describing the dissociation process (1).

In plotting the energy in terms only of the C-Cl distance, we are making an approximation. The energy depends on all the molecular parameters, and ideally we should deal with a potential energy surface rather than a curve. But relaxations in the rest of the molecule, which

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A discussion is given of the process whereby a substituted aromatic molecule captures a slow electron and dissociates. It is shown that the process often goes via two stages, and that the relative symmetries of the electron-capture state and the final dissociation state are very important. Both the sensitivity of the process to changes in the substituent and the existence of an activation energy are explained in the model.
would accompany a change in the C–Cl bond distance, will be very small. Their effect on the energy will not be large enough to affect the conclusions to be drawn from the Figure.

Curve I needs little comment. The equilibrium distance R(C–Cl) is given by the minimum F and the depth of this point below the asymptotic value G is the dissociation energy D(Ph–Cl). The only important feature of this curve is that there is dissociation into neutral Ph and Cl, corresponding to the breaking of the C–Cl σ bond. During this process the π-electron system of the benzene ring, which we shall write as πs, remains largely unaffected. This is because, in the ground state, there is relatively little conjugation between the π-electrons on Cl and the πs group on the ring. Thus the energy difference D(C–Cl) is essentially the energy of a normal C–Cl bond, and is therefore approximately 78 kcal.mole\(^{-1}\) (2·9 ev, but Wentworth \textit{et al.} suggest a slightly larger value of 87 kcal.mole\(^{-1}\)).

Curve II refers to the ground state of the negative ion. The only low-lying orbital into which the additional electron can go is the πs anti-bonding orbital of the benzene ring. Thus the ion could be written as Ph–\(^{-}\)–Cl. The electron affinity of chlorobenzene does not appear to be known accurately, but our argument shows that it must be fairly close to that of benzene, for which various values have been proposed. Kimura and Nagakura, from a study of charge-transfer spectra inside molecules of type PhX, concluded that the electron affinity of benzene is \(-1·1 \pm 0·3\) ev. This lies between the two theoretical values of \(-1·63\) ev of Hedges and Matsen and \(-0·54\) ev of Pople and Hush, and near to the value \(-1·1\) ev proposed by Dr. Scott (private communication, quoted by Kimura and Nagakura). We therefore take the value \(-1·0\) ev, which is unlikely to be in error by more than 0·2 ev. The difference in electron affinity between benzene and chlorobenzene is due to the electron-withdrawing effect of the chlorine, the magnitude of which is difficult to estimate. For bromobenzene Wentworth \textit{et al.} suggest a change of 0·2 ev but on the basis of dipole moments we should expect a rather larger change for chlorobenzene. Perhaps 0·3–0·4 ev is a reasonable value. If we adopt 0·3 ev, we estimate the electron affinity of PhCl to be a \(-0·7\) ev, but the value may be in error by 0·3 ev. The negative value implies that, in the Figure, the point B lies about 0·7 ev above F, and not below it (as would be the case in chloronaphthalene). Moreover, our value of \(-0·7\) ev agrees well with the value \(-0·76\) ev found by Stockdale and Hurst (by electron swarm measurements), for the maximum cross-section for electron capture, and with the value \(-0·86\) ev of Christophorou, Compton, Hurst, and Reinhardt.

Curve II is likely to lie almost vertically above curve I, since the R-value at its minimum B is not expected to differ by more than a few thousandths of an Ångström from the R-value at F. This is because the added π electron is almost confined to the benzene ring, and even there its contribution to the average C–C bond order is only 1/12th. This would correspond to ca. 0·014 Å increase in C–C bond length. The increase in C–Cl would be much smaller.

If the negative ion remains coplanar then at B we have a situation represented by πs. The important feature of a π orbital for our present purposes is that it is antisymmetrical with respect to the molecular plane. All other orbitals in the molecule are symmetrical. If there are an even number of π molecular orbitals the resulting wave function is even with respect to the molecular plane; otherwise it will be odd. Furthermore this overall symmetry will remain unchanged if the chlorine atom is withdrawn along the nuclear plane. This is the easiest direction for the chlorine atom to follow on dissociation. The πs situation at B implies that the complete wave-function for the molecule must be antisymmetric with respect to the plane of the molecule. As the P.E. curve moves away from the point B we must preserve this symmetry. The ion therefore cannot dissociate into a chloride ion Cl– and a ground-state phenyl radical, since this latter system is πs, with a symmetrical wave-function. Thus the asymptotic point H will correspond to a situation Ph–(πs) + Cl, in which the extra electron remains in the ring. The height of H above B, which is the dissociation energy in the process (Ph–Cl)\(-\)\(\rightarrow\) Ph– + Cl, will be very similar to that of B above F. So curve II will lie closely parallel to curve I, at a height varying between about 0·7 and 1·0 ev above it.

When dissociation occurs according to process (1), we have a chloride ion Cl–, with rare-gas structure, and a neutral phenyl radical with electron configuration πs. Curve III, which describes this process, corresponds to a wave-function symmetrical with respect to the molecular plane. Its general shape is most easily discussed by considering the reverse process, in which we start with Ph+ and Cl and bring them together. Since there is no way in which a normal electron-pair bond can be formed, this curve is almost certain to be repulsive at all values of R. By the time that the chloride ion is at a typical bond distance away from the phenyl radical, these are three σ-electrons in the C–Cl region. This is unlikely to lead to a stable system. We have therefore drawn curve III so that it has no minimum other than at infinity. The point J corresponds to Ph + Cl and will therefore lie a distance E\(_A\)(Cl) below G, where E\(_A\)(Cl) is the electron affinity of chlorine (3·7 ev). Thus J lies 3·7 – 2·9 = 0·8 ev below F, indicating that the overall process Ph+ + e \(\rightarrow\) Ph + Cl is exothermic, as pointed out by Wentworth, Becker, and Tung.

Now since the molecular symmetries of the species whose potential energies are described by curves II and

\[ 14 \text{ J. A. Pople and N. S. Hush, } \textit{Trans. Faraday Soc.}, 1955, \textbf{51}, 600. \]

III are different, there is nothing to prevent the curves crossing, as at A in the Figure. The precise position of A relative to B is not easy to estimate with certainty, and will depend chiefly on the depth of J below H. We shall return to this point later in this discussion.

We can now discuss the complete phenomenon of electron capture. The original neutral Ph-Cl is represented by the point F of curve I. A low-energy electron, whose energy must be at least 0.7 ev, is captured, so that there is a jump to the point B. (Strictly, the Franck-Condon principle requires a move to a point on curve II vertically above F. But we have already given reasons to believe that this will be very close to B.) The resulting anion is quite stable against dissociation into Ph + Cl$. In order that it may so dissociate an electron switch from $\pi^*$-type symmetry to $\pi^2$-type is required. On the one hand this needs energy, represented by the height of A above B; and on the other hand it requires some mechanism, such as a collision, to alter the symmetry, and permit a transfer from curve II to curve III. The first of these requirements explains why there is a temperature dependence and an activation energy, pointed out by Wentworth et al.,$^{31}$ since an increase of temperature will lead to more vibrational energy in the potential well around B, and thus facilitate the transition to the cross-over point A. The second requirement suggests a possible pressure dependence.

Several comments may be made on this description. (i) The process is exothermic because of the high electron-affinity of chlorine. If Cl is replaced by a group of lower electron-affinity the process would be endothermic. (ii) B lies above F because the electron-affinity of a phenyl group is negative. Now if the $\pi$-electron system is enlarged, e.g. in going from benzene to naphthalene or some bigger aromatic system, the electron-affinity may change sign and become positive.$^{13,14,16-19}$ In naphthalene, for example, the electron affinity is small, but positive, with a value 0.15 ev. Wentworth et al.$^{31}$ appear to be in error here when they suggest that the electron affinity of the naphthyl radical would be nearly the same as that of the phenyl radical. Their $\sigma$-affinities would indeed be about equal, but their $\pi$-affinities would not. Simple Hückel theory predicts a difference $(\alpha - \beta) - (\alpha - 0.618\beta) = -0.38\beta$. This increases the height of A relative to B, and leads to an increase in the activation energy for the jump from curve II to curve III. (iii) Theoretically the neutral molecule should be able to capture an electron and move directly to curve III, without the intermediate of curve II. This would be represented by going from F to C in the Figure. However, unless the relative positions of the three curves are very different from those in the Figure, the energy needed would be distinctly higher than in going from F to B. At this internuclear distance curve III will almost cer-
c
tainly not represent the lowest state of the anion, so that in order to reach it electrons of greater energy need to be captured. For this reason we believe that direct dissociation will not normally occur with low-energy electrons in systems of this kind. (iv) Since the crucial feature of our discussion lies in the difference of symmetry in curves II and III, it is essential that the ground state of the negative ion should not be able to dissociate directly into Cl$^-$ and a neutral radical. In this respect $\pi$-electron molecules, such as the one we have chosen, provide the simplest and most obvious example. Other types of symmetry would need separate consideration. Thus, in a tetrahedral molecule, e.g. CCl$_4$, if the lowest state of the negative ion is of symmetry $A$, i.e. the same as that of CCl$_4$, there need be no change of curve such as from II to III in our example, and therefore probably no activation energy. If that were the case, there would be a direct transition from the analogue of curve I to curve III. But if the ground state of the negative ion is of symmetry $E$, a situation similar to that shown in the Figure would apply. Each molecule will need to be considered on its own. In the case of CCl$_4$ we could perhaps reverse our argument and claim that the absence of an activation energy, as described by Wentworth et al.$^{31}$ could be regarded as evidence that the lowest state of the anion is of $A$-type symmetry. Unfortunately little is known about the symmetry characterization of negative species, other than diatomics, so that general conclusions are not yet possible. But the distinction between those molecules which can dissociate directly after electron capture and those that need an activation energy is important. It lies at the root of the classification proposed by Wentworth, Becker, and Tung.$^{31}$ This distinction is well-illustrated by a comparison of Ph-X and Ph-CH$_2$-X. In the case of the benzyl compound, the first step is the insertion of the extra electron into the anti-bonding $\pi^*$ orbital of the ring, leading as before to a $\pi^2$ grouping. Dissociation occurs and the neutral benzyl radical which remains is believed to be planar and of type $\pi^7$. There is thus no change in symmetry of the wave-functions, which leads to the conclusion that provided that the electron-affinity of X exceeds the bond dissociation energy $D$ (C-X), dissociation should occur easily. This situation, which is different from that with Ph-X, has been verified experimentally by Gallivan and Hamill.$^{20}$ (v) Finally, our prediction that there may be a pressure dependence, even if correct, will not be easy to verify, because of the low concentration of dissociating molecules (ca. 1 in 10$^8$ for Ph-Cl, according to our rough calculations). Certainly no pressure dependence was found for Ph-Cl by Bouby, Fiquet-Fayard, and Abgrall.$^{31}$

In conclusion, we point out the relationship between

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our work and that of Wentworth et al. Our description corresponds most closely to the situation represented by their Figure 3C (reproduced again in their Figure 4). We agree with them in suggesting that the first step, i.e. electron capture, does not lead to a state which dissociates at once into Ph and Cl⁻, so that a temperature effect, and an activation energy, are to be expected. But we differ in that our curve II for Ph⁻–Cl is quite differently located with respect to the curve I for Ph–Cl. We have given reasons for believing that these are almost parallel, and that their two minima occur at approximately the same value of R. Wentworth et al. invert their order at large R and appear to suggest a much more significant difference at the two minima; the result of this is that their versions of curves I and II intersect. We believe that this is not correct, and that the discrepancy stems from confusion of a σ-electron affinity of +51 kcal. mole⁻¹ with a π-electron affinity of about −16 kcal. mole⁻¹. But we do give complete support to the overall picture that they have proposed. However we believe that we have added a very important additional factor, the symmetry of the states represented by curves II and III. Thus the transition from curve II to curve III is not merely a temperature effect, as suggested by Wentworth et al., but a symmetry effect which requires a third body for its realisation. This has enabled us to show that characteristic experimental differences would be expected between chlorobenzene on the one hand, and CCl₄ and PhCH₂X on the other. Apart from the very considerable difficulty in making exact calculations it is now fair to say that the general principles of this dissociation process seem to be fairly well established.

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