which show that there is association of methyl halides in benzene. As indicated above, the chemical shifts of methyl halides in 100 and 0% solutions of benzene can be calculated on the basis of bulk diamagnetic susceptibility, and comparison with the observed values indicates that the chemical shifts of the hydrogen atoms are influenced by benzene, probably by virtue of its magnetic anisotropy.

Influence of Substituents on the Chemical Shift of an Adjacent Methyl Group.—The chemical shifts of the hydrogen atoms in the methyl groups of twenty-one compounds (not including the methyl derivatives of the halogens) relative to water are recorded in Table II. The observed order is attributed mostly to changes both in electronegativity and in hybridization. In general, for a series of compounds in which the hybridization in the methyl-to-substituent bond remains approximately constant, trends are observed which can be correlated with properties associated with inductive effects. As examples, (a) the chemical shifts of the methyl groups bonded to oxygen are all in the range 19 to 62 cycles, and the chemical shifts of the methyl groups bonded to carbon are all in the range 79 to 154 cycles; (b) the greater chemical shift, indicating more electronic shielding, of dimethyl sulfite than of dimethyl sulfate parallels the lower acid strength of sulfurous acid in comparison with sulfuric acid; and (c) the chemical shifts of acetone and of acetoxime indicate that the electron-withdrawing powers of $>C=O$ and $>C=NOH$ are approximately equal. It is noted that the changes of hybridization and of the chemical shift of the methyl group in the series formed by toluene, methyl cyanide and tetramethylmethane are comparable with the changes of hybridization and of the chemical shifts (reported by Meyer, Saika and Gutowsky[10]) of the hydrogen atoms in the series formed by ethylene, acetylene and ethane.

Since the hybridization of orbitals forming the methyl–halogen bond varies considerably, in general, from that of the methyl-substituent (other than halogen) bond, the relation shown in Fig. 2 cannot accurately be used to assign effective electronegativity values to all substituent atoms or groups. However, for a series of compounds in which the hybridization of orbitals in the methyl-substituted bond is approximately constant, it may be concluded that the chemical shifts of the compounds in very dilute solutions of carbon tetrachloride should reflect the electronegativity of the substituent.

Meyer, Saika and Gutowsky[10] observed the hydrogen NMR spectra of many of the compounds reported in this section. Their data, obtained mostly for pure compounds, agree well with the corresponding data of this research. Dailey and Shoolery[11] reported the chemical shifts of hydrogen in the methyl and the ethyl derivatives of many of these substituents in 50% solutions of benzene. As mentioned above, they reported the chemical shifts of the ethyl derivatives as the difference of the resonance frequencies of the methyl and methylene groups, but their results show the same qualitative order as ours.

Acknowledgments.—A. L. A. wishes to thank the Natvar Corporation for a generous Fellowship. We are grateful to Dr. Aksel A. Bothner-By and to Dr. M. Kent Wilson for helpful discussions, and to the Esso Education Foundation and the Office of Naval Research for grants in aid.

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[CONTRIBUTION FROM SIR JOHN CASS COLLEGE, ALDGATE]

Localization of π-Electrons and the Mechanism of Free Radical Reactions

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RECEIVED MAY 8, 1957

Simple molecular orbital theory is used to show that a collision process between a conjugated molecule and an attacking reagent in which the C–H bond at the position of attack is displaced out of the plane of the molecule will tend to produce a free electron derived from the π-electron system at the position of attack. This process is suggested as forming part of the mechanism of free radical attack upon conjugated molecules.

It has generally been supposed in the interpretation of the reactions of conjugated molecules with free radicals that the conjugated molecule provides a free electron derived from the π-electron system for bond formation at the position of attack.[2-6] The extent to which this notion may be taken literally is perhaps a matter of opinion, though clearly the formation of a localized σ-type bond C–X in the conventional transition state configuration (Fig. 1) implies a large probability for a spin coupled pair in the region of the bond, one drawn from the π-electron system, the other from the free radical.

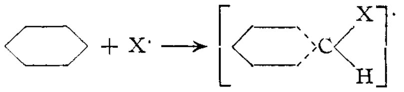

Fig. 1.

One of the difficulties of such an interpretation lies in the phenomenological explanation of the localization of the free electron which is derived from the π-electron system. The usual explanation supposes that the free electron is provided to satisfy the valence requirements of the attacking reagent. One objection to this explanation is that on the one

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k	1.00		0.7071		0.5		0.25		0	
ϵ_4	$+1.000$		$+ .765$		$+ .560$		$+ .286$		0	
ϵ_3	-1.000		$- .765$		$- .560$		$- .286$		0	
ψ_j	ψ_3	ψ_4	ψ_3	ψ_4	ψ_3	ψ_4	ψ_3	ψ_4	ψ_3	ψ_4
C_{1j}	$+2/\sqrt{12}$	$-2/\sqrt{12}$	$+0.65$	-0.65	$+0.68$	-0.68	$+0.70$	-0.70	$+1/\sqrt{2}$	$-1/\sqrt{2}$
C_{2j}	$+1/\sqrt{12}$	$+1/\sqrt{12}$	$+ .35$	$+ .35$	$+ .38$	$+ .38$	$+ .40$	$+ .40$	$+1/\sqrt{6}$	$+1/\sqrt{6}$
C_{3j}	$-1/\sqrt{12}$	$+1/\sqrt{12}$	$- .19$	$+ .19$	$- .13$	$+ .13$	$- .06$	$+ .06$	0	0
C_{4j}	$-2/\sqrt{12}$	$-2/\sqrt{12}$	$- .50$	$- .50$	$- .45$	$- .45$	$- .43$	$- .43$	$-1/\sqrt{6}$	$-1/\sqrt{6}$
C_{5j}	$-1/\sqrt{12}$	$+1/\sqrt{12}$	$- .19$	$+ .19$	$- .13$	$+ .13$	$- .06$	$+ .06$	0	0
C_{6j}	$+1/\sqrt{12}$	$+1/\sqrt{12}$	$+ .35$	$+ .35$	$+ .38$	$+ .38$	$+ .40$	$+ .40$	$+1/\sqrt{6}$	$+1/\sqrt{6}$

$1/\sqrt{2} = 0.707$; $1/\sqrt{6} = 0.408$; $1/\sqrt{12} = 0.289$. $\psi_j = \sum_{n=1}^{6} C_{nj}\phi_n$

hand the π-electron system often extends over comparatively large regions of space, whereas, on the other, valence forces which must surely be invoked in this kind of explanation are short range in character. Even if we allow the sufficiency of forces of this kind, it still remains difficult to visualize a mechanism by which the free electron is drawn to the position of attack, while the remaining π-electrons are removed from this region.

In this paper we give a simple phenomenological description of a process of localization leading to the conventional transition state configuration, which makes no greater demands upon the physical situation than that there should be a collision process between the highly reactive attacking free radical and the conjugated molecule in which the C–H bond at the position of attack is distorted out of the plane of the molecule. This collision process is not merely physically plausible, but almost certain to take place, in which case the localization at the position of attack of a free electron derived from the π-electron system will certainly tend to take place physically. It is perhaps opportune to point out in this context that the localization is strictly one of orbitals and not of electrons, and that the implicit exchange of electrons among orbitals preserves their indistinguishability.

The description is given in terms of simple molecular orbital theory, but the interpretation thus derived is not limited by the method which is simply a convenient vehicle for its description.

Localization of a Single π-Electron.—Let us suppose that an attacking free radical collides with the position of attack and knocks the C_r–H bond at this position out of the plane of the molecule. Then the ϕ_r ($2p_z$) orbital associated with the carbon atom C_r will be distorted away from its alignment with the $2p_z$ orbitals of the remaining carbon atoms of the conjugated molecule. In conventional molecular orbital theory we may say that its overlap and resonance integrals with these remaining carbon atoms will be reduced. If we express this process in the simplest molecular orbital theory in which the overlap integral is neglected and the resonance integrals between nearest neighbors only are retained and set equal to β, then the distortion can be represented by a reduction of the resonance integrals β_{rs} between the atom C_r and its nearest neighbors C_s. We therefore write $\beta_{rs} = k\beta$ where β is the usual carbon–carbon resonance integral and k is to be reduced from the value unity which describes the unperturbed molecule. It is convenient but not necessary for k to be the same for all (usually two in number) conjugated bonds adjacent to C_r.[7]

It is convenient to describe the changes taking place in the π-electron system as k is reduced from the value unity in the unperturbed molecule, by reference to the energy level schemes for the unperturbed molecule (Fig. 2a) and for the residual molecule[6] (Fig. 2b) which is defined as the conjugated system exclusive of the position C_r of attack, and clearly applies to the transition state configuration.

The zero of energy in this scheme is, as usual, taken to be α_0, the coulomb integral for a carbon atom. In an even alternant hydrocarbon the levels lower than this zero are doubly occupied in the ground state, and the remaining levels are unoccupied. We now consider the effect upon the unperturbed ground state (Fig. 2a) of reducing k from the value unity. As k decreases the $n/2$ lowest energy levels ϵ_j ($j = 1,2,\ldots n/2$) are raised toward the $n/2$ lowest levels ϵ_h ($h = 1,2 \ldots n/2$) of the residual molecule as suggested by the broken lines in Fig. 2, while the $n/2$ highest levels ϵ_j ($j = n/2 + 1, \ldots n$) are lowered toward the $n/2$ highest levels ϵ_h ($h = n/2, \ldots n - 1$) of the residual molecule. The levels of the residual molecule always lie one between each pair of levels of the unperturbed molecule, the actual positioning within these limits depending upon the position of attack. There appears to be no general proof of this fact. It is clear that the levels $j = n/2 + 1$ and $n/2$ of the unperturbed molecule are changed toward the same level of the residual molecule, namely, $h = n/2 = \alpha_0$, and tend therefore toward the formation of a doubly degenerate level. The wave functions ψ_j ($j = 1,2 \ldots n/2 - 1, n/2 + 2, \ldots n$) which describe the corresponding levels ϵ_j change systematically toward the ψ_h ($h = 1,2, \ldots n/2 - 1, n/2 + 1, \ldots n - 1$), describing the levels of the residual molecule. A given wave function is associated with the same energy level throughout these processes, and no crossing of levels occurs.

We shall consider the changes in the two remaining orbitals ψ_j ($j = n/2$ and $n/2 + 1$) separately. For this purpose we shall give numerical results for the case of benzene with $r = 1$ which illustrate the nature of the changes taking place.

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[7] The author is glad to record the suggestion of a member of the Editorial Board acting as a referee, that variation of the resonance integral $\gamma = \beta - ES$ inclusive of overlap S would be more nearly correct, since ultimately reduction of β is attributed to the reduced overlap of the $2p_z$ orbital at the atom C_r with its neighbors. The essential features of the localization process described here in terms of variation of β alone are preserved in the more nearly correct treatment.

These results indicate that the molecular orbitals ψ_3 and ψ_4 which corresond to ψ_j ($j = n/2$ and $n/2 + 1$) in the general problem, and describe in both cases the highest occupied and lowest unoccupied levels, embrace the whole benzene structure throughout the perturbation process. This means that the π-electron pair occupying ψ_3 (ψ_4 is unoccupied) is, thus far, in no way localized. For the condition $k = 0$ or $\beta_{rs} = 0$ the two wave functions describe the corresponding doubly degenerate level $\epsilon_3 = \epsilon_4 = 0$. An equally valid description is therefore given by taking the two orthogonal combinations

$$\bar{\psi}_3 = \psi_3 + \psi_4$$
$$\bar{\psi}_4 = \psi_3 - \psi_4$$

When suitably normalized $\bar{\psi}_4$ is identical with the atomic orbital ϕ_1, and $\bar{\psi}_3$ describes the level $\epsilon_h = 0 = \alpha_0$ of the residual molecule. The two electrons which originally occupied ψ_3 can now be allocated one to $\bar{\psi}_4$ and the other to $\bar{\psi}_3$. By this means the localization of a single electron at the position of attack is achieved, and for that matter the conventional transition state configuration for radical attack. The result obtained for benzene is quite typical of those obtained for alternant hydrocarbons. The energy levels change with reduction of the resonance integrals adjacent to the position of attack according to the pattern of Fig. 2, with the formation of the degeneracy at $\epsilon_h = \alpha_0$, formed by the highest occupied and lowest unoccupied levels. The wave functions describing these levels may then be combined as in the case of benzene illustrated above, to form two new orthogonal wave functions, the one being the remaining non-bonding orbital of the residual molecule, and the other the atomic orbital of the atom under attack. One electron in each, derived from the highest occupied orbital, gives an electron localized at the position of attack, and leads to the conventional transition state configuration.

A few points remain for discussion. Firstly by placing one electron in each of the two degenerate orbitals rather than both in one, we imply that in a better approximation the former configuration gives the lower energy. This assumption is plausible since the interelectron repulsive energy is reduced in the former configuration by comparison with the latter, largely owing to the spatial separation of the two orbitals. The interelectron repulsion, which is neglected in the simple approach therefore removes the degeneracy giving a lower energy for the configuration in which one electron occupies each of the two degenerate orbitals. It also might be added that this configuration gives a net density distribution equivalent to one π-electron per conjugated atom, and that this situation is preserved throughout the whole of the localization process described above. The alternative configuration with both electrons in the one orbital would give net charges at various carbon atoms, and would be inconsistent with the process giving rise to the proposed configuration, and with the non-ionic or largely non-ionic character of free radical reactions in general.

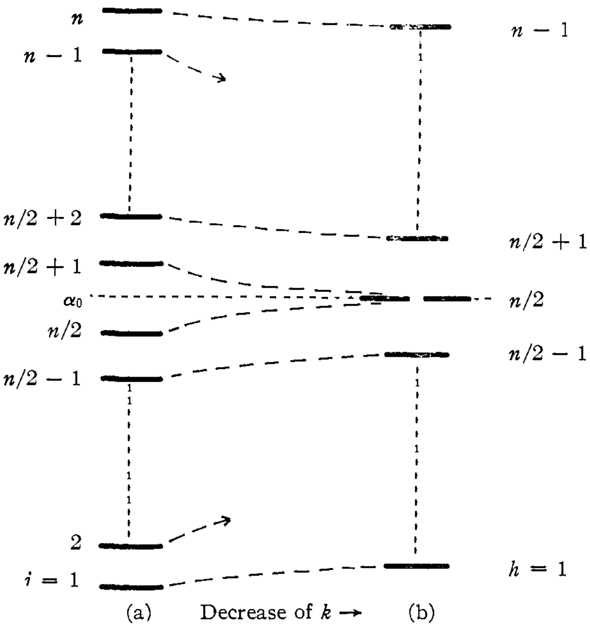

Fig. 2.—Schematic representation of π-electron energy levels for: (a) the unperturbed molecule and (b) the residual molecule.

Secondly, it is unnecessary to assume the formation of an exact degeneracy as a prerequisite for a degree of localization of a single electron which is physically adequate for bond formation with the attacking reagent. The given electron (or, in more accurate terms, orbital) will be less localized at the position of attack, and shared to an increasing extent by the remaining atoms of the conjugated system, the less exact the degeneracy.

Finally, because the localization can be explained in terms of a simple collision process without reference to valence forces, it does not follow that throughout the complete process these forces are negligible. Valence forces may be expected to become important when the given electron (or orbital) is largely localized at the position of attack as a result of the collision process, and when bond formation with the attacking reagent begins. Under these conditions the orbitals involved in bonding have large amplitudes at small (*i.e.*, short range or valence) distances of separation.

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