ANIONIC FREE RADICALS

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Received February 24, 1964

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I. INTRODUCTION

Under suitable reducing conditions, many types of molecules can take up one or more electrons. For example, naphthalene in dioxane solution reacts with sodium in the following way

$$C_{10}H_8 + Na\cdot \rightarrow (C_{10}H_8)^- Na^+$$

the resulting, green-colored compound being sodium naphthalene (also referred to as sodium naphthalenide).

This reaction arises through the transfer of the valence electron of the sodium atom to the lowest energy molecular orbital which is available in the naphthalene molecule (60). Many such reactions involving aromatic molecules are known. In each case, a negative ion containing one unpaired electron is obtained: the name *anionic free radical(s)* (AFR) will be assigned to such species.[1] The parent molecule from which the AFR is formed will be referred to as the *generator* of the AFR.

The anionic free radicals formed in the above way should be carefully distinguished from the compounds formed by reactions such as

$$C_2H_5Br + 2Li \rightarrow C_2H_5Li + LiBr$$
$$C_6H_5Cl + 2Na \rightarrow C_6H_5Na + NaCl$$
$$R_2Hg + Na\ (\text{excess}) \rightarrow 2RNa + Na(Hg)_x$$

These organometallic compounds, which are *not* free radicals, may be regarded as derived by the replacement of a hydrogen atom of the parent hydrocarbon by the alkali metal. An excellent survey of these organometallic compounds is given by Coates (32a). Further reversible reduction of AFR is frequently possible. The resulting dinegative ions, although not free radicals, possess many properties in common with AFR.

The conditions under which stable AFR can be formed are discussed below. Here, it may be noted that, for a generator to be able to form an AFR, it must have, under the experimental conditions, a suitably large electron affinity. Hence generators of AFR are usually aromatic or unsaturated molecules (113, 145). In terms of the molecular orbital (MO) theory, this means that, associated with the generator, there must be an unoccupied MO of suitably low energy; in aromatic molecules, this is the lowest energy antibonding π-orbital (60), and the unpaired electron is delocalized over the whole aromatic system. From the point of view of valence-bond theory, the formation of AFR is of interest. The electron delocalization and stabilization of the ion occurs through resonance between somewhat unusual structures such as

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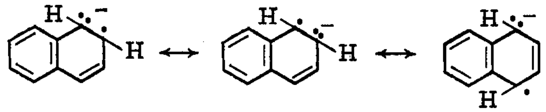
(1) Some nonaromatic AFR are known, which are formed in other ways: *e.g.*, CO_2^- (29). These are not considered in the present review.



The reducing agents most frequently used for AFR formation are the alkali metals in the presence of a polar solvent (113, 114) such as ether, dioxane, or ammonia. AFR have been formed by reduction in polar solvents by alkaline earth metals and their amalgams (10, 86) and by alkali metal alkyls (25) and aryls (148). AFR occur as intermediates in reductions by zinc and alkali, and by glucose in sodium ethoxide solution (9). Electrochemical reduction also yields small concentrations of AFR. In the latter case, the quantities of AFR formed are sufficient for electron spin resonance (e.s.r.) experiments to be carried out on them (41, 81, 82), and the combination of electrochemical and e.s.r. techniques has lately proved to be a powerful tool (*e.g.*, 111, 112). The formation of AFR in aqueous solutions of derivatives of aliphatic hydrocarbons has even been studied by this method (103).

Considerable study of AFR has been made in recent years. In part, this is because AFR are suitable systems for quantum mechanical calculations. Interpretations of the absorption spectra in the visible and ultraviolet regions, and of the e.s.r. spectra, have yielded valuable tests of current theories. In addition, because of the radical–ion nature of the species, e.s.r. investigations have yielded information about ion association which is complementary to that obtainable from conductivity measurements. The reactions which AFR can undergo are of interest. AFR and dinegative ions occur as intermediates in the reduction of organic molecules by alkali metals in liquid ammonia (22), and theoretical treatments have been given for predicting the products of the reduction (49, 118). Studies have been made on electron-transfer reactions with organic halides in solution which are analogous to the gaseous phase "sodium flame" reactions. Numerous polymerization reactions have been initiated by AFR. Finally, AFR occur as intermediates in the photolysis of aromatic compounds (106).

The aim of the present review is to give an account of a number of aspects of this work which are of current interest, some reference being made to the application of the MO theory to the interpretation of the properties of AFR. Since the e.s.r. work has lately been reviewed on several occasions (21, 26, 67, 93, 144), only incidental references will be made to this very important field.

II. FORMATION AND STABILITY OF ANIONIC FREE RADICALS

A. ELECTRONIC STRUCTURE

The Hückel MO approximation can be used to obtain a qualitative interpretation of the properties of AFR. In this treatment, the π-electrons are assigned orbitals ψ_i which are linear combinations of $2p_z$-type atomic orbitals φ_μ, centered on the ($2N$, say) atoms μ in the conjugated system

$$\psi_i = \sum_{\mu=1}^{2N} c_{i\mu}\varphi_\mu, \quad i = 1,2,\ldots 2N \qquad \text{(Eq. 1)}$$

The coefficients $c_{i\mu}$ are found by means of the variation principle. Associated with each ψ_i is an eigenvalue E_i, which is identified with the energy of an electron occupying the orbital ψ_i. The energies E_i calculated by the Hückel procedure take the form $E_i = \alpha + \chi_i\beta$, where α is the carbon coulomb integral, and β is the exchange integral between two adjacent carbon atoms. Both α and β are negative.

In the ground state of the generator, the lowest N orbitals on the energy scale are doubly occupied, in accordance with the Pauli principle. Hence, the total π-electron energy is

$$\sum_{i=1}^{N} 2E_i = 2N\alpha + 2\beta\sum_{i=1}^{N}\chi_i \qquad \text{(Eq. 2)}$$

When the generator takes up an additional electron to form the AFR, this must occupy the orbital ψ_{N+1}, with an energy $E_{N+1} = \alpha + \chi_{N+1}\beta$ (χ_{N+1} is usually negative.) The properties of the AFR greatly depend on the nature of ψ_{N+1} and the value of E_{N+1}.

B. ELECTRON AFFINITIES OF GENERATORS

1. Calculation of Electron Affinities

The electron affinity of the generator determines many of the properties of an AFR. If self-consistent field MO calculations are carried out for the generator, the electron affinity is, by the Koopmans theorem (63), approximately numerically equal to the energy of the lowest unoccupied (virtual) orbital, and of opposite sign to the latter. An approximate method, based on this, of calculating electron affinities of alternant hydrocarbons has been described (63). In the Hückel MO treatment, the electron affinity is also related to the energy of the lowest unoccupied orbital and has a value $-(\alpha + \chi_{N+1}\beta)$.

2. Experimental Data Related to Electron Affinities (108)

The polarographic reduction of aromatic and unsaturated hydrocarbons has been investigated extensively (39). In solvents with low proton activity, such as dimethylformamide or 96% dioxane–water mixture, the first reduction step involves the addition of one electron to the hydrocarbon molecule to form the AFR. At more negative potentials, a second electron is taken up (*e.g.*, 7, 54, 141).

$$X + e \rightleftharpoons X^-$$

$$X^- + e \rightleftharpoons X^{-2}$$

For a series of compounds X, the half-wave potential $\epsilon_{1/2}$ (volts) associated with the first step is related to the electron affinity A of gaseous X (53) if the solvation energy of the ions is assumed constant

$$\epsilon_{1/2} = A + C \qquad \text{(Eq. 3)}$$

where A is in electron volts and where C is a constant dependent on the solvent. C may be evaluated from the measured values of A and $\epsilon_{1/2}$ for triphenylmethyl (122), or from the values of the solvation energy of the ion and the work function of mercury (83). Putting

$$A = -\alpha - \chi_{N+1}\beta \qquad \text{(Eq. 4)}$$

one has (53, 80)

$$\epsilon_{1/2} = -\chi_{N+1}\beta + C' \qquad \text{(Eq. 5)}$$

The best fit with experimental data for hydrocarbons is found (48) when $C' = -0.85$ v. and $\beta = -2.54$ e.v.

Estimates (79) of solvation energy show that it cannot be constant, even in a related series of molecules. It was pointed out (53), however, that variations in solvation energy, dependent on the size of the anion, are compensated for by variations in the value of α in Eq. 4, and the agreement of Eq. 5 with experiment is to some extent due to this. The applicability of Eq. 5 has been discussed by several authors (47, 109).

The polarographic reduction of heteroaromatic molecules has also been studied (39). For an initial, one-electron reduction found in aprotic solvents (42), one again expects Eq. 5 to hold, and this has been found for a series of quinones (102). For the reduction of a series of substituted nitrobenzenes (81), a linear relationship was found between $\epsilon_{1/2}$ and Q_N, the coupling constant for the nitrogen atom in the nitro group, as found from e.s.r. measurements. The explanation given (81) is that Q_N measures the unpaired-electron density at the nitrogen atom of the nitro group (70), and the presence of electrophilic substituents (which reduce this charge density) would increase the electron affinity of the molecule.

The energy of the ^{1}p (31) or ^1L_a (104) band in the spectrum of an alternant hydrocarbon arises (34) through the excitation of an electron from the Nth to the $(N + 1)$th π-orbital. According to the Hückel MO theory, the excitation energy is $2\chi_{N+1}\beta$. Hence, the frequency of this band is expected to be simply related to the electron affinity of the alternant hydrocarbon (87, 139). Such a relationship was found experimentally. It also holds approximately for nonalternant hydrocarbons (20).

The lowest energy n → π transitions (115) occurring in molecules containing nitrogen or oxygen atoms are also related to the electron affinities of the molecules (*e.g.*, 43). Mention may also be made of the relationship of electron affinities to the frequencies of charge-transfer bands in the spectra of molecular complexes (15) and to photoelectron emission in alkali metal–hydrocarbon addition compounds (120).

The reduction potentials of various aromatic hydrocarbons and their AFR have been found by potentiometric titration of the solutions with a solution of sodium biphenyl (51). The following reactions occur (B = biphenyl)

$$\mathrm{X + B^- \rightleftharpoons X^- + B}$$
$$\mathrm{X^- + B^- \rightleftharpoons X^{-2} + B}$$

The standard potential for the first reduction step (relative to the standard reduction potential of biphenyl) was thus shown to bear the expected linear relationship with χ_{N+1}.

Equilibrium constants for exchange reactions such as $\mathrm{X + Y^- \rightleftharpoons X^- + Y}$ have been determined spectrophotometrically (101). The results are not wholly consistent with those derived by potentiometric titration in the same solvent. For example, the equilibrium constants for the reactions of naphthalene + anthracene$^-$ and of tetracene + anthracene$^-$ are given as $\sim 10^{-4}$ and ~ 1, respectively, whereas the values calculated from the reduction potentials are $\sim 10^{-11}$ and $\sim 10^{5}$.

The results obtained by the calculations and experimental methods described above allow the generators to be placed in an ordered sequence of electron affinities. Typical members of this series, in order of increasing electron affinity, are: benzene < biphenyl < naphthalene < stilbene < anthracene < tetracene < benzophenone < fluorenone. Benzene, at the beginning of the series, does not yield stable solutions of AFR, whereas these are readily obtainable for fluorenone at the other end of the series.

3. *Reduction of Generators by Metals*

In dimethoxyethane solution, the reduction of biphenyl by sodium does not go to completion, and the concentrations of biphenyl and its AFR in equilibrium with sodium indicate (51) an equilibrium constant for the reduction of $K \approx 10^{-2}$. From the standard reduction potentials of generators with respect to the standard potential of biphenyl, the values of K for the reduction of other hydrocarbons can be determined. Thus, for anthracene in dimethoxyethane solution, $K = 10^{11}$, and hence $\Delta G^\circ = -15$ kcal. mole^{-1}.

Independent determinations (18, 19, 71) of ΔG° have been made from studies of (a) the e.m.f. values of the cells

$$\begin{array}{c|c|c} \text{Na} & \mathrm{Na^+\,X^-} & \text{X, Pt} \\ \text{amalgam} & \text{solution} & \end{array}$$

and (b) the distribution of sodium between mercury and a solution of X. Thus (19), for the reaction of sodium with anthracene in ether solution, $\Delta G^\circ = -12.4$ to -13 kcal. mole^{-1}.

From the values of the standard electrode potentials of the metals in water, it might be expected that calcium, strontium, and barium would be even better reducing agents than sodium. This has not been found experimentally. The reason may be a consequence of the nature of the reduction process. The rate of the latter is probably related to the electron affinity of the generator and the photoelectric work function φ (45) of the metal. This would explain why sodium (φ = 2.3 e.v.) and potassium (φ = 2.2 e.v.) give rapid reduction, whereas, in order to obtain reduction by calcium (φ = 2.7 e.v.), the metal amalgam must be used (86). Barium (φ = 2.5 e.v.) and magnesium (φ = 3.7 e.v.) compounds of anthracene cannot be obtained (86), although they would have been expected on the basis of the electrode potentials. Lithium (φ = 2.3–2.4 e.v.) reduces more slowly than sodium (133).

The effectiveness of the metal as a reducing agent also depends on the presence of a suitable solvent (114). For example, naphthalene can be reduced to the dinegative ion by sodium when liquid ammonia is used as solvent (61) but only to the mononegative ion when the solvent is dimethoxyethane (51).

C. DISPROPORTIONATION

The difference Δ between the electron affinities of gaseous X and gaseous X^- (A and A', say) is approximately equal to the coulomb repulsion energy of two electrons in the $(N + 1)$th π-orbital of X (62)

$$\Delta = A - A' = \iint \bar{\psi}_{N+1}(1)\bar{\psi}_{N+1}(2)\frac{e^2}{r_{12}}\psi_{N+1}(1)\psi_{N+1}(2)\mathrm{d}\tau(1)\mathrm{d}\tau(2)$$

$$\approx \sum_{\mu,\nu} c_{N+1,\mu}{}^2 c_{N+1,\nu}{}^2 \gamma_{\mu\nu} \qquad \text{(Eq. 6)}$$

(where $\gamma_{\mu\nu}$ is the coulomb repulsion integral between 2p atomic orbitals φ_μ and φ_ν (105)), for an alternant hydrocarbon. The coefficients $c_{N+1,\mu}$ refer to the $(N + 1)$th orbital as found from a self-consistent field calculation for the neutral molecule, but, as an approximation, Hückel MO values can be used.

As the coulomb repulsion integral is a positive quantity, $A > A'$, and the disproportionation reaction

$$2X^- \rightarrow X + X^{-2} \qquad \text{(Eq. 7)}$$

would not occur in the gaseous phase.

In solution, disproportionation depends in addition on the change ΔG_{solv} in solvation free energy associated Eq. 7. Thus, the free energy of disproportionation in solution is

$$\Delta_{\text{sol}} = \Delta - \Delta G_{\text{solv}} \qquad \text{(Eq. 8)}$$

neglecting the (probably small) entropy of disproportionation in the gaseous phase. The term ΔG_{solv} is difficult to estimate, although attempts to do this have been made (47, 51). Some results are shown in Table I. The results in the third column indicate that variations in Δ are compensated for by variations in ΔG_{solv}, so as to keep Δ_{sol} approximately constant. This is to be expected, since both Δ and ΔG_{solv} are dependent on the size of the anion. This is the explanation for the almost constant (to within ~0.1 e.v.) difference between the first and second reduction potentials found for a series of alternant hydrocarbons (51) and 1,n-diphenylpolyenes (52). The calculated values of Δ_{sol} are, however, too large by about 3 e.v. An alternative method of calculating ΔG_{solv} (column 4) gives lower, but still unsatisfactory values of Δ_{sol}.

TABLE I[a]

Generator	Δ[b]	Δ_{sol}[b]	Δ_{sol}[c]	Δ_{sol} (exptl).
Benzene	7.03	3.5	3.0	...
Naphthalene	5.64	3.5	1.9	...
trans-Stilbene	5.51	3.8	2.4	0.23[d]
Phenanthrene	5.17	3.5	...	...
Anthracene	5.10	3.4	1.7	0.58[e]
Tetraphenylethylene	4.76	3.6	...	...

[a] All energies are in electron volts. [b] Calculated energies of disproportionation in the gaseous phase (Δ) and in solution (Δ_{sol}), taken from ref. 62. The solvation energy was calculated by assuming that the solvation of an AFR is essentially that of a set of point charges $ec_{N+1,\mu}{}^2$ centered on atoms μ, and applying the Born equation separately to each. [c] Values taken from ref. 79. The solvation energy was obtained by regarding the AFR as spherical, with an effective radius (used in the Born equation) derived from the molar volume. [d] Ref. 52. [e] Ref. 51.

The calculated and experimental values of Δ_{sol} so far obtained indicate that the AFR do not disproportionate in solution. With a few generators (113), of which tetraphenylethylene is the best known example, it seems, however, that reduction in solution always proceeds directly to the dinegative ion, the mononegative ion not being formed. Thus, sodium tetraphenylethylene solutions are diamagnetic even in the presence of excess generator (99). The electrical conductivity of sodium tetraphenylethylene solutions can only be interpreted on the assumption that they contain dinegative ions (72). In the polarographic reduction of tetraphenylethylene, an initial two-electron wave is found, which corresponds to the formation of the dinegative ion as the initial reduction step (140).

The reason for this behavior is not completely clear. The value of Δ for tetraphenylethylene in Table I is smaller than the other values of Δ, but this is offset by a smaller value of ΔG_{solv} in this case. Furthermore, calculations show that perylene, which gives a stable mononegative ion, has an even lower value of Δ = 4.3 e.v. It is possible that the exceptional stability of the tetraphenylethylene dinegative ion is due in part to its ability to undergo distortions from planarity (33, 44).

D. DIMERIZATION

The ability of a reaction to proceed depends on the decrease in free energy, $-\Delta G^\circ$, for the reaction. In discussing a series of related reactions involving aromatic compounds, it is often assumed that ΔG° is governed by the change in π-electron energy $\Delta\zeta_\pi$, *i.e.*

$$\Delta G^\circ = \Delta\zeta_\pi + C \qquad \text{(Eq. 9)}$$

where C is a constant for the series (110).

In the dimerization of AFR, two negatively charged, aromatic fragments are formed, which are separated by a single bond, and are not, therefore, in conjugation with each other.

$$2X^- \rightarrow {}^-X\text{—}X^- \qquad \text{(Eq. 10)}$$

It is easily shown that, for symmetrical dimerization

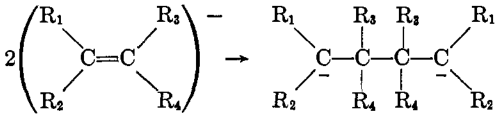
$$\Delta\zeta_\pi = 2L - 2\chi_{N+1}\beta \qquad \text{(Eq. 11)}$$

where L, the localization energy for the position at which dimerization occurs, is for this purpose defined to be

$$L = 2\beta\sum_{i=1}^{N}\chi_i' - 2\beta\sum_{i=1}^{N}\chi_i - \alpha \qquad \text{(Eq. 12)}$$

the first summation measuring the sum of the energies of the π-electrons in the aromatic fragments of the dimer.

From Eq. 11 and 12, it is possible to predict whether or not a stable, monomeric free radical can be formed. This has been applied to the behavior toward dimerization of the substituted ethylenes.



(Eq. 13)

In Table II are given $\Delta\zeta_\pi$, values for the formation of the most stable dimers in various cases, and they exhibit a trend which is consistent with the observed behavior.

TABLE II

Generator	$\Delta\zeta_\pi(\beta) + 2\alpha$	Log K	Behavior
Fulvene	−0.738	57	Dimer
Styrene	−2.084	−0.7	Dimer[a]
1,1-Diphenylethylene	−1.900	(7)[c]	Dimer
Stilbene	−3.308	−53	Monomer
Triphenylethylene	−3.118	−45	Monomer
Tetraphenylethylene	−4.102	−87	Monomer[b]

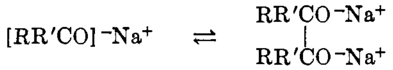
[a] Forms a polymer in the presence of excess styrene. [b] Forms a dinegative ion. [c] Experimental value, see text.

Within the scope of Eq. 9, the equilibrium constant K for the dimerization is given by

$$\log K = -\frac{\Delta\zeta_\pi + 2\alpha}{2.303RT} + D \qquad \text{(Eq. 14)}$$

The constant D may be evaluated from the measured (69, 117) value of K for the dimerization of 1,1-diphenylethylene ($K = 1.1 \times 10^7$ l. mole^{-1} at 28°). Using the value of $\beta = -2.54$ e.v. obtained from polarographic data (section IIB), one finds $D = 87.9$. The values of log K given in Table II have been derived from this. The numerical values probably have only a qualitative significance, because steric effects, which are neglected in the present treatment, will be important in some of the molecules.

It has been reported on several occasions that ketone AFR (the alkali metal ketyls) are in equilibrium with the dimers (pinacolates).

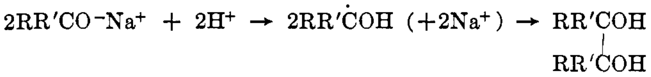


$$[RR'CO]^-Na^+ \rightleftharpoons \begin{array}{l} RR'CO^-Na^+ \\ \quad\;| \\ RR'CO^-Na^+ \end{array}$$

Attempts to demonstrate the existence of this equilibrium by purely chemical methods have not been entirely satisfactory. Hydrolysis of the ketyls by water or alcohol gave products which were consistent with the reaction

$$2RR'\,CO^-Na^+ + 2H_2O \rightarrow RR'CO + RR'CHOH + 2NaOH$$

indicating a monomeric formula for the ketyls (113). On the other hand, hydrolysis of sodium benzophenone with dilute acetic acid gave a quantitative yield of benzpinacol, and Bachmann (10) concluded that sodium benzophenone consists almost entirely of dimeric sodium pinacolate. It was supposed that the alkali conditions in previously reported hydrolyses had caused the pinacol initially formed to disproportionate to the ketone and the hydrol. A similar argument could, however, be applied to Bachmann's observation; the acid conditions might be responsible for the formation of a dimeric product, perhaps by

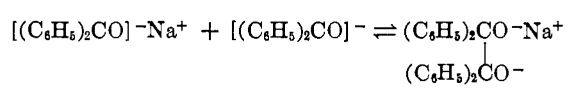


$$2RR'CO^-Na^+ + 2H^+ \rightarrow 2RR'\dot{C}OH\ (+2Na^+) \rightarrow \begin{array}{l} RR'COH \\ \quad\;| \\ RR'COH \end{array}$$

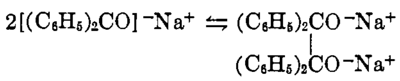
A further complication is that the *precipitation* of pinacol in the hydrolysis in ether solution might mean that the products do not indicate the equilibrium existing in solution (146). Hydrolysis in liquid ammonia, in which the pinacol is more soluble, yielded (146) a smaller proportion of pinacol than Bachmann obtained from the corresponding reaction in ether.

The results of electrical conductivity measurements on solutions of sodium benzophenone in liquid ammonia could not be (75) explained in terms of simple binary ionization, and Wooster (147) concluded that the following equilibria occur.

$$[(C_6H_5)_2CO]^-Na^+ \rightleftharpoons [(C_6H_5)_2CO]^- + Na^+$$



$$[(C_6H_5)_2CO]^-Na^+ + [(C_6H_5)_2CO]^- \rightleftharpoons \begin{array}{l} (C_6H_5)_2CO^-Na^+ \\ \qquad\quad\;| \\ (C_6H_5)_2CO^- \end{array}$$



$$2[(C_6H_5)_2CO]^-Na^+ \leftrightharpoons \begin{array}{l} (C_6H_5)_2CO^-Na^+ \\ \qquad\quad\;| \\ (C_6H_5)_2CO^-Na^+ \end{array}$$

No indication of these equilibria was, however, found from ebullioscopic determinations. Within the experimental error, the latter indicated monomeric ion pairs (4).

Measurement of apparent molar paramagnetic susceptibility has been used to determine radical content. No association was found in hydrocarbon AFR solutions (30), although it was found to be considerable in concentrated ketyl solutions (3, 37, 119). For example, the paramagnetic susceptibility indicated about

20% association in the case of a 15% solution of potassium benzophenone. Similar determinations have been made for many solid ketyls (95). Unfortunately, according to the method of preparation described (96), involving vacuum drying, it would seem probable that the solids contained occluded solvent (*cf.* 59, 114), and that factors other than the equilibrium constant for dimerization might determine the free-radical content of the sample.

For very dilute solutions, the amount of association is probably negligible. The variation of optical density with concentration has been studied for a number of ketyl solutions. It was found (28) that Beer's law holds—as it should do if there is no association—for 10^{-4} to 10^{-3} M solutions in dioxane. Deviations from Beer's law have been reported (17), however, for dilute solutions of sodium benzophenone in ether. The absence of appreciable amounts of pinacolate in dilute solutions of ketyls in dioxane is also indicated by the kinetics of their reactions with organic halides (27). Under pseudo-unimolecular conditions with excess halide, the plot of log (optical density) against time is accurately linear. This would not be found, as a rule, if equilibrium existed with appreciable concentrations of pinacolate.

AFR have been prepared from the triarylborons (46), by alkali metal reduction. These are isoelectronic with the corresponding triarylmethyl radicals and so are expected to have properties analogous to those of the latter, except in so far as the triarylboron AFR carry a negative charge. Like the triaryl methyl radicals, triarylboron AFR undergo dimerization, the extent of which depends on the nature of the aryl groups. Complete dimerization is found in the case of triphenylboron, and this may be compared with the nearly complete association of triphenylmethyl (110). Tri-α-naphthylboron and tri(β-methylnaphthyl)boron react in tetrahydrofuran solution with sodium to give paramagnetic solutions containing the monomeric AFR. This behavior may be compared with the incomplete association found in tri-β-naphthylmethyl solutions (110).

III. REACTIONS OF ANIONIC FREE RADICALS

Two classes of AFR reactions have been investigated in detail. These are (A) the reactions with organic halides and (B) the initiation of polymerization reactions.

A. REACTIONS WITH ORGANIC HALIDES

The reactions of dilute ($\sim 10^{-3}$ M) alkali and alkaline earth metal AFR derivatives have been studied, using an optical method of following the reactions (27, 84–86, 92). The reactions were shown to be second order, and the velocity constants were measured under pseudo-unimolecular conditions with excess halide.

The stoichiometry (92) of the reaction of M^+X^- with a halide RY can be interpreted in terms of the following reactions

$$\mathrm{RY} + \mathrm{M^+X^-} \rightarrow \mathrm{M^+Y^-} + \mathrm{R\cdot} + \mathrm{X} \qquad \text{(Eq. 15)}$$

$$\mathrm{R\cdot} + \mathrm{X^-} \rightarrow (\mathrm{R{-}X})^- \qquad \text{(Eq. 16)}$$

or

$$\mathrm{R\cdot} + \mathrm{R\cdot} \rightarrow \mathrm{R{-}R} \qquad \text{(Eq. 17)}$$

Eq. 15 being the rate-determining step.

A wide range of reaction speed was found, which depended on the nature of the organic halide and the AFR. A reactivity scale of the AFR was set up as follows. If k_1 and k_2 are the velocity constants for Eq. 15 in the reactions of the AFR X_1 and X_2 with the same halide at the same temperature, the ratio of the reactivities R is defined to be

$$R(X_1)/R(X_2) = k_1/k_2$$

The reactivity of sodium fluorenone in dioxane solution was taken as standard, $R(X) = 1$.

The rate-determining step (Eq. 15) can probably be described as follows. In dioxane solution, the AFR exist in association with metal cations, as ion pairs. The halide molecule approaches the cation in M^+X^- until critical internuclear distances are reached, at which point electron transfer takes place. The process resembles the mechanism of electron transfer between sodium benzophenone and benzophenone molecules (2). Thus, the reaction can be represented as

$$\mathrm{X^-M^+} + \mathrm{Y{-}R} \rightarrow \underset{\text{transition state}}{\left\{\begin{array}{l} \mathrm{X^-M^+Y} \ldots . \mathrm{R} \\ \mathrm{X\ M^+Y^-\ \cdot R} \end{array}\right.} \rightarrow \mathrm{X} + \mathrm{M^+Y^-} + \mathrm{\cdot R}$$

This is similar to the scheme proposed for the gaseous phase reactions of sodium with organic halides (138).

$$\mathrm{Na\cdot} + \mathrm{Y{-}R} \rightarrow \left\{\begin{array}{l} \mathrm{Na\cdot Y} \ldots . \mathrm{R} \\ \mathrm{Na^+Y^-\ \cdot R} \end{array}\right. \rightarrow \mathrm{Na^+Y^-} + \mathrm{\cdot R}$$

In the latter case, the activation energy is simply related to the over-all heat of reaction. If a similar relationship holds for AFR–halide reactions, then changes in activation energy produced by changing the AFR would arise mainly through differences in electron affinity of the *gaseous* generators, since the other quantities which might effect differences in heats of reaction approximately cancel, provided that the same solvent and alkali metal are used (92). This conclusion was supported by the experimental results (85). Thus, graphs of log $R(X)$ *vs.* the orbital energy E_{N+1} are approximately linear (Fig. 1), as they should be if differences in rate constants are due primarily to differences in activation energy. The suggested (85) reason why the log $R(X)$, E_{N+1} points do not all lie on the *same* straight line is that the pre-exponential factors in the Arrhenius equation depend somewhat on the type of generator. Unfortunately, there is some uncer-

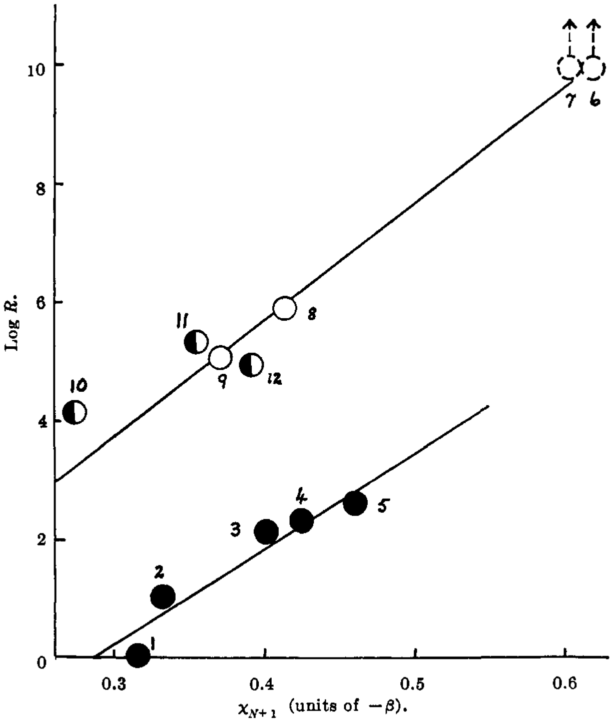


Fig. 1.—Dependence of reactivity of sodium compounds on orbital energy $\chi_{N+1}\beta$; generators are: 1, fluorenone; 2, benzil; 3, dibiphenyl ketone; 4, phenyl biphenyl ketone; 5, benzophenone; 6, naphthalene; 7, phenanthrene; 8, anthracene; 9, fluoranthene; 10, fluorenone anil; 11, fluorenone imine; 12, benzophenone anil.

tainty, because of the rather arbitrary choice of parameters in the calculation of E_{N+1} for heteroaromatic molecules.

The observed AFR reactivity depends on the nature of the positive counter ion. It was found (27, 86) that graphs of log R(X) *vs.* $1/(\mathcal{R} + 2)$ (where $\mathcal{R}$ is the crystal cationic radius) are linear, separate lines being found for the alkali and alkaline earth metals. There exists, however, another relationship with cationic parameters. Figure 2 shows the plot of log R(X) against the first ionization potential of the metal. This is approximately linear, and, moreover, all the points lie near the same straight line for the alkali and the alkaline earth series. This behavior would be expected for reactions of free metal atoms in the gaseous phase, and it perhaps implies that the activation energy depends on the energy needed to remove an electron from the unit M^+X^- containing a finite unpaired electron density on M^+.

B. POLYMERIZATION REACTIONS

1. *Mechanisms of Initiation*

The polymerization of styrene by the addition of sodium naphthalene was described by Szwarc (123) in 1956. Since that time, many papers (124) have appeared which deal with polymerizations catalyzed by AFR or in which AFR are expected to be formed as reaction intermediates. In much of this work, however, the interest lies in the production and properties of the resulting polymer rather than in the role of the AFR in the reaction. As such work provides little further insight into the physical chemistry of AFR, it will not be considered here.

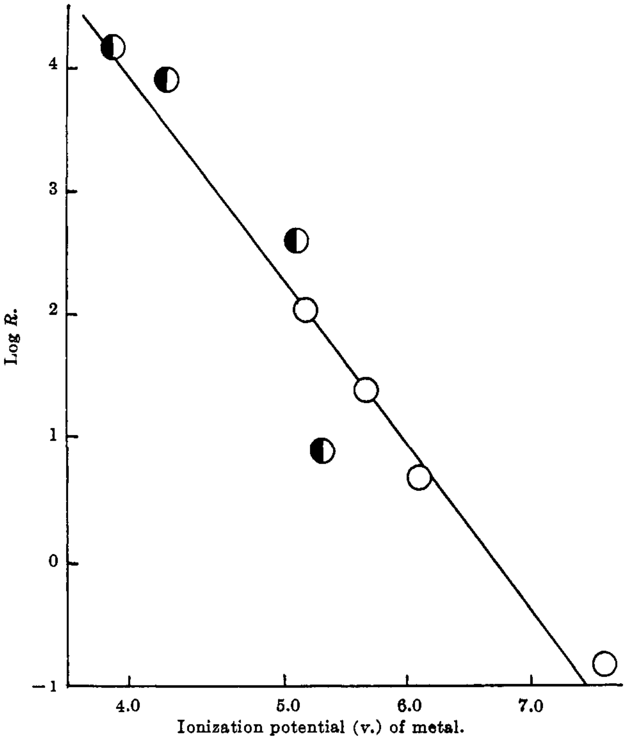


Fig. 2.—Dependence of reactivity of benzophenone AFR on the metal counter ion: ◐, alkali metals; ○, alkaline earth metals.

The polymerization of a monomer, M, by an AFR, X^-, may be initiated in several ways which depend on the nature of M and X^-. The following reactions occur.

(i) electron transfer from X^- to M

$$X^- + M \rightarrow X + M^- \qquad \text{(Eq. 18)}$$

This may be followed by dimerization[2]

$$2M^- \rightarrow (M{-}M)^{-2} \qquad \text{(Eq. 19)}$$

The resulting anion then polymerizes further molecules of M. Such a mechanism was proposed (123, 127, 128, 132) for the polymerization of styrene by sodium naphthalene.

(ii) bond formation between X^- and M (94).

$$X\cdot^- + M \rightarrow XM\cdot^- \qquad \text{(Eq. 20)}$$

$$2XM\cdot^- \rightarrow (XM{-}MX)^{-2} \qquad \text{(Eq. 21)}$$

The resulting anion then polymerizes further molecules of M. The polymerization of α-methylstyrene by sodium diphenylacetylene (131) appears to proceed through this mechanism, because (a) the absorption

(2) The formation of α-methylstyrene dimeric anion, by the slow addition of monomer to sodium emulsion, probably proceeds by the mechanism (76) $M^- + M \rightarrow (M{-}M)^- \xrightarrow{M^-} (M{-}M)^{-2}$

spectrum of the final product indicates that it contains a stilbene-like fragment derived from the diphenylacetylene, and (b) it is possible to explain, on this mechanism, the dependence of the equilibrium number-average degree of polymerization on the initial and equilibrium concentrations of monomer and sodium diphenylacetylene.

It is not necessary for Eq. 18 to be followed by Eq. 19. Thus, if M^- encounters a neutral molecule M, reaction may occur. In the case of styrene, for example, one might have (125)

$$[C_6H_5\underset{\cdot}{C}H—\underset{..}{C}H_2] + C_6H_5CH{=}CH_2 \rightarrow [C_6H_5\underset{\cdot}{C}H—CH_2—CH_2—\underset{..}{C}HC_6H_5] \quad \text{(Eq. 22)}$$

The resulting species differs from the AFR so far considered, in that it contains two unconjugated parts. One end is a "true" radical, with zero net charge, and the other end is a "true" carbanion with zero net electron spin. Such a dimer can now cause polymerization in two ways. Either the radical end may initiate polymerization, the behavior following the rules of the radical mechanism, or the anionic end may grow, according to the rules of the anionic mechanism.

The relative probability of occurrence of reactions 19 and 22 depends on the ratio of the concentrations of M^- and M. Relatively low concentrations of M^- would favor reaction 22, whereas higher concentrations would favor 19. In the homogeneous polymerization of styrene by sodium naphthalene, the initial electron transfer is virtually instantaneous and complete (123). Accordingly, a relatively high initial concentration of M^- is formed and reaction 19 is favored. On the other hand, in the slower, heterogeneous initiation of polymerization by a lithium suspension, it was shown (97, 98) that reaction 22 is important.

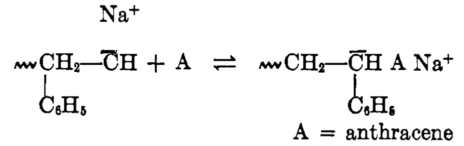
2. Energetic Factors Influencing the Initiation Reaction

The equilibrium in reaction 18 will only lie to the right-hand side if the electron affinity of M is greater than that of X. For a given monomer, the extent to which this reaction occurs increases as the electron affinity of X decreases. It was originally postulated (123) that reaction 18 is complete and instantaneous for the sodium–naphthalene-initiated polymerization of styrene. In this case, since all the initiating M_2^{-2} are formed at the same time and therefore have equal chances of forming polymer molecules, two conditions apply. (a) The polymer should be monodisperse, *i.e.*, the resulting polymer molecules should all have approximately the same size. The weight-average and number-average molecular weights should then be equal. (b) The degree of polymerization should be proportional to the ratio of the concentration of monomer to that of the catalyst.

Conditions a and b were found to hold approximately for the naphthalene⁻-initiated styrene polymer. The solution remaining after polymerization was, however, found (78) to give an e.s.r. spectrum identical with that of the naphthalene AFR, and this was shown to arise because reaction 18 does not quite go to completion.[3] The initial electron transfer should be more nearly complete if biphenyl, which has a lower electron affinity, were used in place of naphthalene, and it was found that the biphenyl⁻-initiated polymerization does give a more nearly monodisperse product (142, 143).

With AFR derived from generators having a high electron affinity, reaction 18 may not take place to any significant extent. This is one of the reasons for the observation that benzophenone⁻ will not polymerize styrene (68, 149).

It has been found (74) that, for the polymerization of styrene by hydrocarbon AFR, the ratio k_p/k_i (k_p and k_i are the velocity constants for propagation and initiation) is related to the reduction potential of the hydrocarbon, increasing as the latter increases. In the case of the polymerization by anthracene⁻, k_p/k_i has a much smaller value than expected. This is because anthracene forms a molecular complex (which can be detected spectroscopically) with the polystyrene anion. Thus, there is an equilibrium (5, 74, 77)

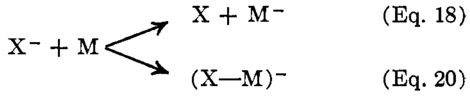


$$\sim CH_2—\bar{C}H(C_6H_5)\ Na^+ + A \rightleftharpoons \sim CH_2—\bar{C}H(C_6H_5)\ A\ Na^+$$

A = anthracene

for which $K \approx 10^6$ l. mole⁻¹. The small value of k_p/k_i is now understandable if it be assumed that the "complexed" negative end of the polymer is unable to propagate further polymerization (74).

An alternative to electron transfer is bond formation (129, 131).



$$X^- + M \rightarrow X + M^- \quad \text{(Eq. 18)}$$

$$X^- + M \rightarrow (X—M)^- \quad \text{(Eq. 20)}$$

The simple assumption may be made (*cf.* section II) that the behavior in any given case depends on the relative values of the π-electron energy changes for reactions 18 and 20.

Of the two unconjugated fragments X′ and M′ resulting in the bond-formation reaction 20, one is an anion and one is a free radical. By means of a treatment similar to that given in section II, it follows that, for this reaction (Eq. 20), the π-electron energy change is

$$\Delta\zeta_\pi = L_X + L_M - \lambda(X',M')\beta - \chi_{N+1}(X)\beta \quad \text{(Eq. 23)}$$

where L_X and L_M are the localization energies defined

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[3] There is also a time-dependent contribution to the e.s.r. spectrum arising through the decomposition of the polystyrene anion (116, 126).

in Eq. 12. The term $\lambda(X',M')$ is the smaller of the two values of χ_N' for X′ and M′, and arises because the negative fragment will be that which has the greater value of χ_N'. If both X and M are alternant hydrocarbons, $\lambda(X',M') = 0$.

For the electron-transfer reaction (Eq. 18)

$$\Delta\zeta_\pi = \chi_{N+1}(M)\beta - \chi_{N+1}(X)\beta \qquad \text{(Eq. 24)}$$

and the difference in π-electron energy changes of the bonding and electron-transfer reactions is

$$\Delta\zeta_\pi\,(\text{Eq. 20}) - \Delta\zeta_\pi\,(\text{Eq. 18}) = L_X + L_M - \lambda(X',M') - \chi_{N+1}(M)\beta \qquad \text{(Eq. 25)}$$

It has been suggested (130) that larger values of χ_{N+1} (X) would favor reaction 18 at the expense of reaction 20, but the present treatment indicates that this is not so, and that the mechanism of initiation with a given monomer is governed by the value of L_X for alternant hydrocarbon AFR.

IV. ELECTRONIC SPECTRA

A. EXPERIMENTAL RESULTS

All known AFR are colored. The absorption spectra of a number of hydrocarbon AFR were reported in 1956 (101),[4] and a qualitative interpretation was given (101). Subsequently, the spectra have been reported of the mono- and dinegative ions formed from condensed ring alternant hydrocarbons (14, 24, 64): biphenylene (66), polyphenyls (14, 35), 1,*n*-diphenylpolyenes (n = 1–6) (52), tetraphenylcumulenes (52), nitro compounds (73, 85), aromatic ketones (28), anils, and imines (85). A regular dependence on n of band frequencies in the spectra of 1,*n*-diphenylpolyenes was noted (52). The spectra of AFR are somewhat dependent on the nature of the positive counter ion, and a relationship has been found between the spectral frequencies and the cationic radius (28, 86). The effect of solvent on the spectra has been studied (40, 107). Owing to the high reactivity of many of the compounds, care has to be taken to identify spurious bands which sometimes arise through decomposition (23).

B. MOLECULAR ORBITAL TREATMENT OF ALTERNANT HYDROCARBON ANIONIC FREE RADICAL SPECTRA

The spectra arise through $\pi \rightarrow \pi$ transitions. The π-orbital ψ_i values may be approximated by Eq. 1, and orbital energies E_i are found from the secular equation

$$\det|H_{\mu\lambda} - ES_{\mu\lambda}| = 0 \qquad \text{(Eq. 26)}$$

where

$$S_{\mu\lambda} = \int \bar{\varphi}_\mu \varphi_\lambda d\tau$$

$$H_{\mu\lambda} = \int \bar{\varphi}_\mu H \varphi_\lambda d\tau \qquad \text{(Eq. 27)}$$

H is the Hamiltonian operator for the π-electrons and is not further specified. It has been shown that this simple MO treatment is much more reliable for alternant hydrocarbon AFR than it is for the generators themselves (11). Hence this method has been used successfully in the interpretation of the spectra of AFR (12).

The excitations responsible for absorption by AFR in the visible and near-visible regions are represented in Fig. 3. For an alternant hydrocarbon, there exists a pairing relationship between the bonding and the antibonding orbitals; to each energy level $\alpha + \chi\beta$, there corresponds a level $\alpha - \chi\beta$. Hence

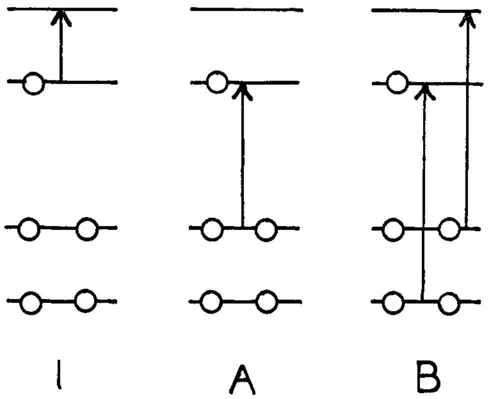

Figure 3.

$$E_l - E_N = E_{N+1} - E_k, \text{ if } l = 2N + 1 - k$$

The singly excited configurations and their energies relative to the ground state are thus

$$\begin{array}{ll} {}^2\psi_A = {}^2\chi_{N\rightarrow N+1} & E_A = -2\chi_N\beta \\ {}^2\psi_I = {}^2\chi_{N+1\rightarrow l} & E_I = (\chi_l - \chi_{N+1})\beta \\ \left.\begin{array}{l} {}^2\psi_{B1} = 2\chi_{k\rightarrow N+1} \\ {}^2\psi_{B2} = {}^2\chi_{N\rightarrow l} \end{array}\right\} & E_B = (\chi_{N+1} - \chi_k)\beta \quad (l = 2N + 1 - k) \\ {}^2\psi_0 & E = 0 \end{array}$$

The configuration B is degenerate, and there is important first-order configuration interaction between ${}^2\psi_{B_1}$ and ${}^2\psi_{B_2}$. Since the $(N + 1)$th level contains an unpaired electron in the ground state, a two-electron excitation ${}^2\chi_{(N+1\rightarrow l;N\rightarrow N+1)}$ also gives a configuration, say ${}^2\psi_{B_3}$, with energy E_B, and configuration interaction between ${}^2\psi_{B_1}$ ${}^2\psi_{B_2}$, ${}^2\psi_{B_3}$ must be allowed for in the calculations. Hence there will be three excited states, Ψ_{Ba}, Ψ_{Bb}, Ψ_{Bc}, whose wave functions are formed by taking linear combinations of the Slater determinants for ${}^2\psi_{B_1}$, ${}^2\psi_{B_2}$, ${}^2\psi_{B_3}$. The other configurations are usually nondegenerate, and, as a first approximation, ${}^2\psi_A$ and ${}^2\psi_I$ represent the wave functions for the excited doublet states Ψ_A and Ψ_I although configuration interaction calculations involving ${}^2\psi_A$ and ${}^2\psi_I$ have been performed (12).

The intensity of a spectroscopic band is related to the dipole strength of the transition

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(4) The spectrum assigned to the mononegative tetracene ion in ref. 101 is actually that of the dinegative ion (14).

$$D = M^2/e^2 \qquad \text{(Eq. 28)}$$

where, for a transition between two states X and Y

$$M = e\int \Psi_X \mathbf{r} \Psi_Y \mathrm{d}\tau \qquad \text{(Eq. 29)}$$

r being the electronic position vector. D is determined experimentally from the equation

$$D = 3.99 \times 10^{-4} \int \frac{\epsilon}{\nu} \mathrm{d}\nu \qquad \text{(Eq. 30)}$$

where ϵ is the molar extinction coefficient at frequency ν(in Å.$^{-1}$), and the integral is evaluated graphically.

The above treatment, simplified by means of the Pariser–Parr approximations (100), has been applied to a number of hydrocarbon AFR (12). Typical results for a number of strong bands are given in Table III.

TABLE III

Generator	N[a]	Transition[b]	D_{calcd}[c]	D_{obsd}[d]	ν_{calcd} (1000 cm.$^{-1}$)	ν_{obsd} (1000 cm.$^{-1}$)
Anthracene	7	8 → 9	1.01	0.95	12.0	14.0
Tetracene	9	10 → 11	2.04	1.01	9.9	12.6
Phenanthrene	7	8 → 10	0.92	0.34	11.0	9.3
Pyrene	8	9 → 13	4.72	1.89	23.6	20.3
Perylene	10	10 → 11	6.48	1.75	19.6	17.2
Biphenyl	6	7 → 10	1.84	0.30	12.5	15.7

[a] $2N$ is the number of carbon atoms. [b] The numbering refers to Hückel energy levels in order of increasing energy, components of degenerate levels being assigned different numbers. [c] Dipole strengths calculated according to Eq. 28 and 29. [d] Experimental dipole strengths, calculated from Eq. 30. Because of the overlapping of bands, there are sometimes contributions to D_{obsd} of weaker transitions which are not indicated in the table.

For molecules other than alternant hydrocarbons, the interpretation of the AFR spectra is more difficult. There is uncertainty about the best way of applying the MO theory, and of the values of the parameters used in the calculation. Moreover, the assumption of a planar framework in which all the bond lengths are equal is no longer justified. Some progress has been made in the calculation of the frequencies in the ketyl spectra by a self-consistent field method (89).

Recently, it has been found that *cationic* free radicals, formed by the *removal* of an electron from an alternant hydrocarbon molecule, give electronic spectra which are almost identical with those of the corresponding AFR (1, 16, 56). This is an obvious consequence of the pairing property of the Hückel π-orbitals for alternant hydrocarbons, and the identity is also indicated by a more detailed analysis (90, 91).

C. RELATIONSHIP WITH SPECTRA OF GENERATORS AND DINEGATIVE IONS

The spectra of generators and dinegative ions arise through singlet excitations from singlet ground states, and so configurations corresponding to $^2\psi_{B_1}$ do not arise. In the dinegative ion, transitions A and B$_1$ are forbidden by the Pauli principle. The transitions I do not occur in the generator. Otherwise, the treatments of the spectra of generators (34) and dinegative ions (13) are similar to the treatment of AFR spectra. Detailed comparison of the three types of spectra has been made for benzene, coronene, and triphenylene (50) and for some polyacenes (55, 57).

When terms are included in the Hamiltonian for the repulsion between π-electrons, the energies of the excited states relative to the ground state are expressible in terms of the energies $\chi_i\beta$ and the integrals $K_{j,l}$ between molecular orbitals.

$$K_{j,l} = \iint \bar{\psi}_j(1)\bar{\psi}_l(2)\frac{e^2}{r_{12}}\psi_j(2)\psi_l(1)\mathrm{d}\tau(1)\mathrm{d}\tau(2) \qquad \text{(Eq. 31)}$$

The dipole strengths are expressible in terms of the quantities

$$\mathfrak{D}_{j,l} = m^2/e^2 \text{ where } m = e\int \psi_j \mathbf{r} \psi_l \mathrm{d}\tau \qquad \text{(Eq. 32)}$$

For the hydrocarbons pyrene, perylene, and the lower polyacenes, it has been shown (57) that the ratios between the integrals $K_{N,N+1}$, $K_{N,l}$, and $K_{N+1,l}$, are roughly constant. In this case, approximate general expressions have been derived for the energies and dipole strengths in the electronic excitations of the molecules X and the ions X$^-$ and X^{-2} (55, 57).

Transitions I

$$\begin{array}{lll l}
X^- & E_I & = (\chi_l - \chi_{N+1})\beta & D = \mathfrak{D}_{N+1.l} \\
X^{-2} & E_I & = (\chi_l - \chi_{N+1})\beta + K_{N+1,l} & D = 2\mathfrak{D}_{N+1.l}
\end{array}$$

Transitions A

$$\begin{array}{lll l}
X & E_A & = -2\chi_N\beta + K_{N.N+1} & D = 2\mathfrak{D}_{N,N+1} \\
X^- & E_A & = -2\chi_N\beta & D = \mathfrak{D}_{N,N+1}
\end{array}$$

Transitions B

$$\begin{array}{lll l}
X & E_{B^-} & = (\chi_l - \chi_N)\beta - {}^3/_4K_{N,l} & D = 0 \\
 & E_{B^+} & = (\chi_l - \chi_N)\beta + {}^{11}/_4K_{N,l} & D = 4\mathfrak{D}_{N.l} \\
X^- & E_{B_a} & = (\chi_l - \chi_N)\beta - K_{N.l} & D \approx 0 \\
 & E_{B_b} & = (\chi_l - \chi_N)\beta + {}^1/_2K_{N,l} & D \approx \mathfrak{D}_{N.l} \\
 & E_{B_c} & = (\chi_l - \chi_N)\beta + {}^5/_2K_{N.l} & D \approx 2\mathfrak{D}_{N,l} \\
X^{-2} & E_B & = (\chi_l - \chi_N)\beta + K_{N.l} & D = 2\mathfrak{D}_{N,l}
\end{array}$$

From these equations, the following can be deduced (55, 57): (1) Since $K_{N,l} > 0$, the A-band in X$^-$ occurs at a longer wave length than the A-band in X and has about half the intensity of the latter. (2) A similar relationship exists between the I-bands of X$^-$ and X^{-2}. (3) There are three B-bands in X$^-$, increasing in intensity in the order of increasing frequency. The strongest of these, B_c, occurs at about the same wave length as the stronger B-band of the generator and has about half the intensity of the latter. The intensity of B$_c$, is also the same as the intensity of the single B-band of X^{-2}.

D. ASSIGNMENT OF THE OBSERVED BANDS TO TRANSITIONS

The obvious method of assignment of bands in a spectrum is to compare the frequencies calculated for various transitions with the observed spectrum. The assignment can be checked by comparison of the observed and calculated dipole strengths. Although, for various reasons, the absolute values of the latter are unreliable, reasonably good estimates of the relative values for different transitions can be obtained by calculation.

An independent method of assignment utilizes the dichroism induced in glassy solutions of AFR and dinegative ions by irradiation with plane polarized light. The dichroism arises through electron ejection (38, 58, 121) such as

$$X^{-2} \rightarrow X^{-} + e$$

or

$$X^{-} \rightarrow X + e$$

For example, in the case of a dinegative hydrocarbon ion such as anthracene^{-2}, of symmetry D_{2h}, the allowed transitions are polarized along two mutually perpendicular symmetry axes in the plane of the nuclei. If the wave length of the plane polarized exciting light corresponds to an x-polarized transition, then electron ejection will tend to occur in those ions which have their x-axes parallel to the polarization of the incident light, and mononegative ions will be formed with this orientation. The remaining dinegative ions will, on the average, be oriented with their x-axes perpendicular to this direction. By comparing the extinction coefficients for light polarized perpendicular to, and parallel to, the electric vector of the primary radiation, the directions of polarization of the electronic transitions can be determined (36, 58). The spectral assignments obtained by this method generally agreed with those found in earlier work, although a reinterpretation of the naphthalene AFR spectrum was shown to be necessary (55).

V. ION-PAIR FORMATION

Observations on the stereochemistry of certain reactions (113) led to the suggestion that there is a covalent carbon–metal linkage in compounds formed by the alkali metals and AFR generators. For example, addition of CO_2 to the dialkali metal stilbenes, followed by hydrolysis, gave a dicarboxylic acid which, in the case of the lithium compound, was resolvable into two optical isomers, whereas, with the sodium and potassium compounds, only the *meso* derivative was formed (113).

The physical properties, in particular the electronic spectra and the electrical conductivity, indicate, however, that the compounds exist as *ion pairs*, and the stereochemistry must be interpreted by assuming that in some compounds the cations are highly localized with respect to the anions.

It has been supposed (28) that the ion pairs are *contact* pairs, consisting of an AFR and a cation in close contact, and surrounded by a solvation shell. Subsequently, it was pointed out (35) that a better interpretation of the properties of hydrocarbon derivatives could be obtained if it were assumed that the AFR and the cation are separated by a layer of solvent molecules.

A. ELECTRON SPIN RESONANCE STUDIES OF ION-PAIR FORMATION

1. *Dissociation Constants*

The hyperfine splitting in the e.s.r. spectra of aromatic hydrocarbon radicals arises through the interaction of the unpaired electron with the protons attached to the aromatic system. For a system containing n groups of a_r equivalent nuclei, each nucleus having a spin I_r, it can be shown that the e.s.r. spectrum contains $\prod_{r=1}^{n} (2a_r I_r + 1)$ lines. Thus, for naphthalene$^-$, which contains two groups of four equivalent protons, one expects 25 lines.

In dimethoxyethane (DME) solution, sodium naphthalene gives the expected 25 lines (8). In tetrahydrofuran (THF) solution at room temperature, however, each line is further split into four components of equal intensity, arising from the interaction with the Na nucleus of spin $^3/_2$. These observations indicate that the AFR exist as free ions in DME, whereas in THF they exist as ion pairs.

At temperatures below −70°, the e.s.r. spectrum of the THF solution is the same as that of the DME solution. At intermediate temperatures, there is a superposition of the "split" and the "unsplit" spectra, and from the relative intensities of these, equilibrium constants, K_D, were derived for the dissociation of the ion pairs. By this method, the following values were obtained (8) for the dissociation in THF solution: $\Delta H° = -7.5$ kcal. mole^{-1}, $\Delta S° = -51.6$ cal. deg.$^{-1}$ mole^{-1}, and $\Delta G° = 8.0$ kcal. mole^{-1}, at 296°K.

The free energy of dissociation of ion pairs is related to the interionic distance, r_0. An approximate equation (32b), which applies for small values of K_D is

$$\Delta G° = Ne^2/r_0 D \qquad \text{(Eq. 33)}$$

where N is the Avogadro number, e the electronic charge, and D the dielectric constant of the solvent. For THF, $D = 7.5$, hence, $r_0 = 5.5$ Å., which is of the expected order of magnitude. A similar result is obtained from the value $K_D = 1.01 \times 10^{-4}$ for sodium benzophenone in liquid ammonia solution, as found from conductivity measurements (147).

2. *Exchange Reactions*

The shape of an e.s.r. line associated with a transition between a pair of states depends on the mean lifetime of the states. When naphthalene is added to a sodium naphthalene solution, a broadening of the hyperfine components occurs (136, 137), the extent of the broadening depending on the amount of added hydrocarbon. This effect arises through the occurrence of the exchange reaction: naphthalene$^-$ + naphthalene → naphthalene + naphthalene$^-$, which lowers the lifetime of any one naphthalene$^-$ radical. From the broadening, the rate constant for this reaction was determined, using several solvents. The results (137) for sodium naphthalene are: in DME, $k \approx 10^9$ l. mole^{-1} sec.$^{-1}$; in THF, $k \approx 10^7$ l. mole^{-1} sec.$^{-1}$, the values not being greatly temperature-dependent. These results imply (6) entropies of activation ΔS^* of about -4.5 and -13.5 cal. deg.$^{-1}$ mole^{-1} for DME and THF, respectively. The difference arises because, in the first case, the electron-transfer reaction involves free ions, whereas in the second, it involves ion pairs. In the second case, electron transfer is likely only when the Na^+ ion lies between the two hydrocarbon systems in the collision complex. The greater degree of order thus required leads to the more negative value of ΔS^*. As a result of this type of electron transfer, the cation changes partner at the same time as the unpaired electron (6). This type of exchange has also been found for the reaction of benzophenone with sodium benzophenone (2).

3. Effect of the Cation on Charge Distribution in Anionic Free Radicals

From the spacings of the lines in the e.s.r. spectrum, the coupling constants Q_μ for the interaction of the unpaired electron with nuclei μ can be derived (67). For the interaction with a proton attached to an aromatic system, it has been shown that the coupling constant Q_μ is proportional to the unpaired electron density ρ_μ at the aromatic carbon atom contiguous to the proton. Thus, $Q_\mu = \mathcal{Q}\rho_\mu$, where $\mathcal{Q} \backsimeq 25$ gauss. Hence, the distribution of the unpaired electron can be obtained.

The proton coupling constants for sodium naphthalene in DME (*i.e.*, the free naphthalene anion) have approximately the same values as the corresponding ones found in THF solution (ion pairs); *i.e.*, the presence of the cation has little effect on the proton coupling constants. Hence, the charge distribution in the naphthalene AFR is not greatly altered by the presence of the cation. This perhaps indicates that the cation spends most time above the plane of the carbon nuclei and on or near to the symmetry axis, since minimum polarization would be caused by the cation in this position. An alternative explanation is that the two ions are separated by a sheath of solvent molecules (35). Both effects may be operative.

The AFR formed by electrolytic reduction are, of course, free ions, and comparison of the e.s.r. spectra of electrolytically formed AFR with those of the alkali metal compounds yields information about ion pairing. A detailed comparison has been made in the case of dinitrobenzene AFR.

The electrolytically formed AFR exhibit (82), as expected, spin distributions having the molecular symmetry. With the exception of the *o*-dinitrobenzene anion, the AFR formed by alkali metal reduction have a different charge distribution, in which the charge is mainly concentrated at one nitrogen atom at the expense of the other. This effect is obviously due to a strong polarization by the cation (134, 136), which, on energetic grounds, is expected to be localized near one of the nitro groups. The equivalence of the two nitrogen atoms in potassium *o*-dinitrobenzene probably arises because the two nitro groups are sufficiently close together for the cation to occupy a symmetrical position with respect to them.

B. MOLECULAR ORBITAL TREATMENT OF ION PAIRS

When a cation is in the neighborhood of the AFR, a term must be included in the Hamiltonian in Eq. 27 for the interaction of the cation with the π-electrons. It is reasonable to assume that, for alkali metal cations, this is $-e^2/r$, where r is the distance of the electron from the center of the cation. This will be true whether or not a solvent molecule separates the positive and negative ions. It may be shown (88) that

$$\int \frac{\varphi_\mu \varphi_\nu}{r} \mathrm{d}\tau \approx \frac{2S_{\mu\nu}}{r_\mu + r_\nu} \qquad \text{(Eq. 34)}$$

where r_μ and r_ν are the distances of the center of the cation from the nuclei μ and ν, and $s_{\mu\nu}$ is the overlap integral between φ_μ and φ_ν. Hence, for the AFR in the presence of the cation, Eq. 26 becomes

$$\det|H_{\mu\nu} - S_{\mu\nu}(E - 2e^2)/(r_\mu + r_\nu)| = 0 \qquad \text{(Eq. 35)}$$

The differences between the eigenvalues (E_i, say) of Eq. 35 and those (E_i^0, say) of Eq. 26 permit the calculation, according to the Hückel theory, of (a) the energy of electrostatic interaction between the positive and negative ions, and (b) the effect of the cation on the electronic spectrum of the AFR.

The total energy of the anion is obtained by summing over all the occupied molecular orbitals, and, assuming an unpolarized distribution of "core" electrons, the electrostatic energy E of the interaction between the cation and the anion is

$$E = 2\sum_{i=1}^{N} (E_i - E_i^0) + E_{N+1} - E_{N+1}^0 + \sum_{\mu=1}^{2N} e^2/r_\mu \qquad \text{(Eq. 36)}$$

The final summation in this equation arises from the coulomb repulsion between $2N$ nuclei (each having an effective charge of $+e$) and the cation. The set of values r_μ for the most stable ion-pair configuration will be those which give the numerically greatest energy of interaction compatible with a minimum distance of approach of the two ions. Calculations (88) indicate that the center of the cation will lie in a plane above the plane of the nuclei, and there is probably some oscillation about a position of minimum energy (35, 88). Approximately (88) $E = -e^2/r_0$, where r_0 is the perpendicular distance from the center of the cation to the plane of the nuclei.

The effect of the cation on the energy of the transition $i \rightarrow j$ is to alter it by an amount

$$\Delta_{ij} = (E_j - E_j^0) - (E_i - E_i^0) \qquad \text{(Eq. 37)}$$

It may be shown that, approximately (88)

$$\Delta_{ij} = 0.29 \frac{e^2}{r_0^2} \sum \rho_\mu (c_{\mu j}^2 - c_{\mu i}^2) \qquad \text{(Eq. 38)}$$

where ρ_μ is the distance of nucleus μ from the projection of the center of the cation in the plane of the nuclei. Equation 37 or 38 permits the calculation of the shift in a spectral band caused by a cation and the effect of altering the cation for one of different radius. Calculations of this type have been carried out for ketyls (88), polyphenyls (35), and condensed ring hydrocarbons (65).

ACKNOWLEDGMENT. The author is indebted to Dr. D. B. Hartley for assistance with the section on polymerization.

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