In conclusion, we propose the following mechanism for the photoxidation of sulfite

Initiation

$$SO_3^{2-} \xrightarrow{h\nu} SO_3^- + e_{aq}^- \, (+ O_2 \longrightarrow O_2^-) \qquad (7)$$

$$SO_3^- + O_2 \longrightarrow SO_5^- \qquad (12)$$

Propagation

$$SO_5^- + SO_3^{2-} \longrightarrow SO_4^- + SO_4^{2-} \qquad (25)$$

$$SO_4^- + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^- \qquad (19)$$

Termination

$$SO_5^- + SO_5^- \longrightarrow \qquad (24)$$

$$SO_4^- + SO_4^- \longrightarrow \qquad (26)$$

and other termination reaction (*e.g.*, $SO_5^- + O_2^- \rightarrow$). In the thermal autoxidation, the photochemical initiation is replaced by some other electron transfer, *e.g.*, to Cu^{2+}. This mechanism is applicable to systems where $[HSO_3^-]$ is small and the conversion of SO_4^- into OH can be ignored. Extension of the mechanism to include reactions of HSO_3^- and OH can account for the pH effect. In strongly alkaline solutions, SO_5^- and O^- are the main chain carriers of the autoxidation.

It is interesting to note that in alkaline solution the mechanism presented here bears some resemblance to the Haber mechanism[2] which involves the following chain-propagation reaction.

$$HSO_3 + O_2 + H_2O + SO_3^{2-} \longrightarrow 2SO_4^{2-} + OH + 2H^+ \qquad (27)$$

This reaction is the overall form (in acidic form) of reactions 12, 25, and 20.

Finally, it should be emphasized that we have no direct evidence for the role of SO_4^- in the autoxidation mechanism. Our efforts to detect its spectrum have failed. We believe that this is due to the low concentration of SO_4^- present in the system. If, for simplicity, we ignore the termination reactions and consider the steady concentrations of SO_5^- and SO_4^- in the system after the flash, then eq 25 and 19 lead to the relation $[SO_4^-] = (k_{25}/k_{19})[SO_5^-]$. There is no information on k_{25}, but because it involves oxygen transfer it is likely to be lower than k_{19}, *i.e.*, $[SO_4^-] < [SO_5^-]$. Both radicals have comparable extinction coefficient, and since the absorption of SO_5^- was rather weak (Figure 10), that of SO_4^- could have escaped detection. Here it is of interest to note that with their sensitive device to study the spectra of transient species produced in the steady photochemistry, Devonshire and Weiss[7] found some difference around 450 nm (λ_{max} of SO_4^-) between the spectra produced in oxygen and argon saturated solutions of Na_2SO_3.

Some Data on Oxyanions and Oxyradicals of Sulfur. Tables III and IV summarize some spectroscopic and kinetic data pertaining to the photochemistry of the oxyanions of sulfur. The following conclusions can be drawn from these tables. (a) The primary process occurring in ions with strong S–O bonds is electron ejection. (b) The single S–S and O–O bonds are readily ruptured. (c) The rate constants for the bimolecular recombination of the radicals SO_n^- decrease with increase in n.

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ω-Type Calculations on π-Electron Systems with Inclusion of Overlap Charges. III. π-Bond Energies, Heats of Formation, and Resonance Energies of Conjugated Hydrocarbons

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Abstract: The ω technique with inclusion of overlap charges, as described in previous papers of this series, has been extended to evaluate the π-bond energies, heats of formation, and resonance energies of some conjugated hydrocarbons. The success of the method has been supported by comparing the results with experimental data and with results obtained by others using Pople's SCF–MO method.

Generally quantum chemists have used the ω technique for π-electron systems with neglect of overlap charges. However, as reported in our previous papers,[1,2] we have have performed ω-type calculations on π-electron systems with inclusion of overlap charges and consequently ionization potentials and electron affinities have been calculated for some conjugated hydrocarbons. The results have been found to be in good agreement with the observed values.

For the sake of simplicity in writing, the method has been abbreviated as the IOC-ω technique (inclusion of overlap charges in the ω technique) and, according to this method

$$H_{\mu\mu} = \alpha_0 + \omega\left[1 - \frac{1}{2}\sum_{\sigma}(p_{\mu\sigma}S_{\mu\sigma} + p_{\sigma\mu}S_{\sigma\mu})\right] \qquad (1)$$

$$H_{\mu\nu} = \frac{1}{2}KS_{\mu\nu}(H_{\mu\mu} + H_{\nu\nu}) \qquad (2)$$

Here α_0 is the core Coulomb integral which describes the energy of a π electron in a p_z atomic orbital in a

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(1) B. Krishna and S. P. Gupta, *J. Amer. Chem. Soc.*, **92**, 7247 (1970).
(2) B. Krishna and S. P. Gupta, *J. Chem. Soc. A*, 123 (1971).

widely separated carbon atom and thus is a constant for every carbon atom, K is a dimensionless constant, and ω is an empirical parameter. The overlap integral $S_{\mu\nu}$ is supposed to be zero unless μ and ν are directly bonded, in which case $S_{\mu\nu}$ is given a constant value, say S; for $\mu = \nu$, S is assumed to be unity. $p_{\mu\sigma}$ is defined as

$$p_{\mu\sigma} = 2\sum_{i}^{\text{occ}} C_{i\mu}C_{i\sigma} \tag{3}$$

$C_{i\mu}$ and $C_{i\sigma}$ being the LCAO–MO coefficients. Here $p_{\mu\sigma}$ is defined for all atoms, but for bonded atoms it is identical with the Hückel molecular orbital (HMO) bond order.[3]

The inclusion of overlap charges in the ω technique apparently approximates the SCF equation by bringing in an approximate correction for the two-center two-electron repulsion integrals also, while the ω technique approximates only one-center two-electron repulsion integrals.

The π-Bond Energy

The total π-bond energy, $E_{\pi\text{b}}$, of a molecule is defined as the energy required when isolated carbon atoms, each with a π electron, combine to form π bonds. In the SCF–MO theory this energy is given by[4]

$$\begin{aligned} E_{\pi\text{b}} = {} & \text{(total molecular orbital energy)} - \\ & \text{(total interelectron repulsion)} + \\ & \text{(total core repulsion)} - \text{(total energy of} \\ & \pi \text{ electrons in widely separated carbon atoms)} \end{aligned} \tag{4}$$

since the total molecular orbital energy includes twice the total interelectron repulsion. If the molecule is neutral, the Coulomb repulsion of the cores of the atoms should be more or less balanced by the Coulomb repulsion of the electrons attached to those cores. Since in the ground state the molecules as well as the atoms in them are supposed to be neutral, the total π-bond energy of a molecule may be given by

$$\begin{aligned} E_{\pi\text{b}} = {} & \text{(total molecular orbital energy)} - \text{(total energy of} \\ & \pi \text{ electrons in widely separated carbon atoms)} \end{aligned} \tag{5}$$

(Here it is noteworthy that in the SCF–MO method, the Hartree–Fock eigenvalues involve two types of repulsion integrals, Coulomb integrals ($J_{\mu\nu}$) and exchange integrals ($K_{\mu\nu}$). Now since the core repulsion cancels approximately only the Coulomb integrals and leaves the exchange integrals uncompensated for,[4] the total interelectronic repulsion in the SCF–MO method is not balanced by the total core repulsion. On the other hand, the IOC-ω technique in any case involves only Coulomb integrals and in no way involves exchange integrals, so the total interelectronic repulsion included in the total molecular orbital energy given by the IOC-ω technique is approximately completely canceled by the total core repulsion of the atoms.)

Therefore

$$\begin{aligned} E_{\pi\text{b}} = {} & \sum_{\mu}\sum_{\nu} p_{\mu\nu}H_{\mu\nu} - n\alpha_0 = \\ & n\alpha_0 + 2(kS\alpha_0 - \omega S)\sum\sum_{\mu<\nu} p_{\mu\nu} - \\ & k\omega S^2 \sum\sum_{\mu<\nu} \sum_{\lambda\neq\mu} \sum_{\sigma\neq\nu} p_{\mu\nu}(p_{\mu\lambda} + p_{\nu\sigma}) - \\ & n\alpha_0 = 2(kS\alpha_0 - \omega S)\sum\sum_{\mu<\nu} p_{\mu\nu} - \\ & k\omega S^2 \sum\sum_{\mu<\nu} \sum_{\lambda\neq\mu} \sum_{\sigma\neq\nu} p_{\mu\nu}(p_{\mu\lambda} + p_{\nu\sigma}) \end{aligned} \tag{6}$$

since all the conjugated hydrocarbons belong to alternant systems for which $p_{\mu\mu} = 1$ and $p_{\mu\nu} = p_{\nu\mu}$. This equation can be simply written as

$$E_{\pi\text{b}} = -\left[\lambda_1 \sum\sum_{\mu<\nu} p_{\mu\nu} + \lambda_2 \sum\sum_{\mu<\nu}\sum_{\lambda\neq\mu}\sum_{\sigma\neq\nu} p_{\mu\nu}(p_{\mu\lambda} + p_{\nu\sigma})\right] \tag{7}$$

where

$$\lambda_1 = -2(kS\alpha_0 - \omega S) \tag{8}$$

$$\lambda_2 = +k\omega S^2 \tag{9}$$

Here λ_1 and λ_2 are treated as empirical parameters. However, even if they are treated as empirical parameters, a great difficulty arises in setting their values because no observed value is available for $E_{\pi\text{b}}$. Therefore, for this purpose we have to rely on some theoretical data. Dewar and Schmeising[5] have determined the $E_{\pi\text{b}}$ value for ethylene as 1.5894 eV as a function of bond length from a thermocycle. Using the same thermocyclic data (*i.e.*, σ-bond energies of 3.9562 eV (91.23 kcal) for C═C and 4.3590 eV (100.52 kcal) for C—H), we can manupulate the contribution of the π-bond energy to the observed value of heat of atomization of benzene and thus the $E_{\pi\text{b}}$ value for benzene comes out to be 7.270 eV. These two values of $E_{\pi\text{b}}$ for ethylene and benzene set our λ_1 and λ_2 equal to −0.9052 and −0.3421 eV, respectively. Now utilizing these values of λ_1 and λ_2 we have calculated $E_{\pi\text{b}}$ values for a number of conjugated hydrocarbons which are listed in Table I. The direct check on the correctness of these values is provided by the evaluation of heats of formation and reasonance energies for these compounds.

Heat of Formation and Resonance Energy

The heat of formation (heat of atomization) of a molecule in its equilibrium configuration is the additive sum of the bond energies. The total bond energy of a molecule is given by the sum of the total σ-bond energy, $E_{\sigma\text{b}}$, and the total π-bond energy, $E_{\pi\text{b}}$. In aromatic hydrocarbons, where carbon–carbon bond lengths are all very similar, a common value E_{C} can be used for the σ-bond energy for an aromatic σ bond. Therefore, if E_{C} and E_{H} (the bond energy of a C–H bond) are known, the following equation would provide a simple route to calculation of the heat of formation of an aromatic hydrocarbon in its ground state.

$$-\Delta H_{\text{f}} = NE_{\text{C}} + N_{\text{H}}E_{\text{H}} + E_{\pi\text{b}} \tag{10}$$

where N and N_{H} represent the numbers of C–C and C–H bonds, respectively, in the molecule. Since in the literature no reliable value has been ascribed for

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(3) Such bond orders are tabulated in A. Streitwieser, Jr., and C. A. Coulson, Ed., "Tables of π Electron Calculations," Pergamon Press, Elmsford, N. Y., 1965. To an approximation, these bond orders have been used in the present work.

(4) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 167.

(5) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); 11, 96 (1960).

Table I. π-Bond Energies, Heats of Formation, and Resonance Energies of Conjugated Hydrocarbons

Compound	$E_{\pi b}$, eV	Heat of formation, eV			Resonance energy, eV		
		This work	Dewar	Obsd[a]	This work	Dewar	Obsd[b]
Benzene	7.270	57.01	57.16	57.16	0.719	0.869	0.869
Naphthalene	12.653	90.53	90.61	90.61	1.237	1.323	1.323
Anthracene	17.979	123.98	123.89	123.93	1.698	1.600	1.639
Phenanthrene	18.189	124.70	124.22	124.20	1.908	1.933	1.908
Pyrene	21.049	138.71	138.62	138.88	2.087	1.822	2.350
Naphthacene	23.279	157.42	157.11	157.56	2.133	1.822	
3,4-Benzphenanthrene	23.581	157.72	157.77	157.48	2.435	2.478	
Chrysene	23.585	157.73	157.77	157.73	2.439	2.483	2.441
Triphenylene	23.623	157.76	157.94	157.76	2.477	2.654	2.472
Perylene	26.442	172.14	172.15	172.04	2.615	2.619	2.610
Biphenyl	15.100	109.55	109.75	109.76	1.501	1.699	
p-Terphenyl	22.162	162.13			2.312		
m-Terphenyl	23.001	162.17			2.353		
o-Terphenyl	23.006	162.18			2.358		
p,p-Diphenylbiphenyl	30.810	214.69			3.109		
p,m-Diphenylbiphenyl	30.806	214.68			3.109		
m,m-Diphenylbiphenyl	30.808	214.69			3.111		
Butadiene	3.802	41.98	42.05	42.05	−0.067	0.003	
Hexatriene	5.948	60.71	60.81		−0.105	0.000	
3-Vinylhexatriene	8.264	79.60			+0.027		
2,3-Divinylbutadiene	8.237	79.58			0.000		
3,4-Divinylhexatriene	10.520	98.42			0.082		

[a] Reference 5. [b] M. J. S. Dewar, "Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 177.

E_C, we treat it as an empirical parameter and assign its value so as to best fit the experiment with $E_H = 4.4375$ eV, as recently ascribed by Dewar and de Llano.[6] For this purpose, we took the various assumed values of E_C, carried out the calculation for ΔH_f for several compounds, and compared the results every time with those obtained experimentally. Among the various assumed values for E_C, the one that gave the best results was as 3.8520 eV. This value of E_C gave, in most cases, results which were exactly the same as those obtained from experiment. Table I lists the values of ΔH_f calculated by us for several hydrocarbons with the appropriate values of E_C and E_H.

The heats of formation of benzenoid hydrocarbons calculated in this way are found to be uniformly larger than those predicted by the corresponding localized-bond model. This extra stability is of course responsible for the special chemical behavior of such compounds, and this extra stabilization, over and above that expected for a localized structure, has been termed the "resonance energy" by Dewar and de Llano.[6] It was originally introduced by Pauling[7] to describe the extra stability of certain molecules over and above that predicted by the localized bond model, while some authors[8] have used the term in a number of other ways, *e.g.*, to describe the differences between the heats of hydrogenation of molecules and those of arbitrary chosen reference structures. Since the quality of interest to chemists is the extra stability of compounds such as benzene in comparison with classical open-chain anologs rather than a comparison with idealized theoretical concepts, the definition of resonance energy given by Dewar and de Llano is more important than those given by other investigators. This resonance energy may be called the "Dewar–de Llano resonance energy."

If in a classical localized polyene the bond energy of a localized C—C bond is E_1 and that of a localized C=C is E_2, the heat of formation will be

$$-\Delta H_f' = N_1E_1 + N_2E_2 + N_HE_H \qquad (11)$$

where N_1 and N_2 represent the numbers of localized C—C and C=C bonds, respectively, in the polyene. Therefore, the resonance energy of the corresponding aromatic hydrocarbon will be given by the difference between $\Delta H_f'$ and ΔH_f, so that

$$E_R = NE_C - N_1E_1 - N_2E_2 + E_{\pi b} \qquad (12)$$

To calculate the resonance energy for any compound from eq 12 one must know the proper values of E_1 and E_2 even if the proper value of E_C is known. Since their values have not been generally quoted as exact values in the literature, E_1 and E_2 can be treated as empirical parameters. However, to avoid any type of inconsistency that might arise in our treatment by treating E_1 and E_2 as empirical parameters, we adopt the values recently given by Dewar and de Llano.[6] These values were calculated by plotting the total C–C bond energies for linear polyenes and radialenes against the number of single C–C bonds. The values found from these plots are $E_1 = 4.3499$ eV and $E_2 = 5.5378$ eV. Using these values of E_1 and E_2, the calculated values of the resonance energies for aromatic hydrocarbons are found to be in good agreement with the experimental values.

Results and Discussion

Table I lists the values for π-bond energies, heats of formation, and resonance energies for some conjugated hydrocarbons. Values calculated by us and by Dewar and de Llano, utilizing Pople's SCF-MO method, are given, along with observed values, where available. The comparison of calculated values for heats of formation and resonance energies with the corresponding observed values shows that our values are

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(6) M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969).

(7) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(8) (a) E. Hückel, *Z. Phys.*, **70**, 204 (1931); (b) R. S. Mulliken and R. G. Parr, *J. Chem. Phys.*, **19**, 1271 (1951).

relatively better than those obtained by Dewar and de Llano. For most of the compounds, *e.g.*, phenanthrene, chrysene, and triphenylene, our values for both heats of formation and resonance energies come out to be identical with those obtained experimentally. Moreover, in several cases, *e.g.*, naphthacene and pyrene, the differences between calculated and observed values, which are significant in the work of Dewar and de Llano, have been minimized in our work. The success of the IOC-ω technique is indicated here, and the heats of formation and resonance energies indicate the correctness of the $E_{\pi b}$ values.

Further, in the case of polyphenyls, the calculation shows that their resonance energies are approximately integral multiples of the resonance energy of benzene. For example, the resonance energy of biphenyl (1.501 eV), where two benzene rings are joined by a C–C bond, is nearly twice that of benzene (0.719 eV); similarly, in the case of terphenyls, where three benzene rings are joined by two C–C bonds in various manners, the resonance energies are approximately three times that of benzene, etc. This proves that the bonds joining the benzene rings in polyphenyls are essentially single, localized bonds.

Further light is thrown on the case of open-chain classical polyenes where all C—C and C═C bonds are localized. The E_R values for those polyenes according to definition and expectation should be equal to zero. However, our calculation suffers in this case for two reasons: (1) the value of E_C has been assumed to be the same for all σ bonds in an aromatic hydrocarbon, while it should be a function of bond length, and (2) in the polyenes, unlike aromatic hydrocarbons, the differences between the lengths of C—C and C═C bonds are significant. The E_R values for these polyenes generally are slightly different from zero. However, the differences are so small (irrespective of sign) that they signify nothing except that that value of E_C is not appropriate in the case of polyenes, and that E_C should be a function of bond length. The above results and discussion lead to the conclusion that the IOC-ω technique, on being properly handled, is quite successful in accounting for experimental facts and theoretical predictions.

Polarization and Overlap Population. A Reanalysis of Molecular Orbital Theory of SN2 Reactions[1]

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Abstract: The effects of charge polarization on Mulliken overlap populations are analyzed. The results show that a bond population change cannot be accounted for by simply summing the effects of empty MO's mixed in and filled MO's mixed out, except in special cases. It is possible for an empty MO which is antibonding in a given bond to be mixed in, in a way to strengthen that bond. A reanalysis of the SN2 reaction shows how the charge polarization to the leaving atom, due to an approaching negative base, results in a weakening of the bond to the leaving atom and a strengthening of the bonds to the other hydrogens of methane. The calculations indicate that C–H bonds at tetrahedral carbons should generally be strengthened or weakened as they are polarized negative or positive, respectively. It is argued that effects of charge transfer on bond strengths also require consideration of more than contributions due to gain or loss of electron population in individual MO's of the separated molecules.

Consider the attack by a hydride ion on a methane molecule. Let the hydride ion approach along a C_3 axis (a C–H bond axis) from the carbon side (*i.e.*, "backside" attack). This system is a model for SN2 reactions. As an aid in predicting the stereochemical nature of SN2 reactions, one can ask which bonds in the methane molecule will be strengthened or weakened by the interactions with hydride. Two potentially important interactions may be cited: polarization of methane induced by the charged hydride, and, at fairly close approach, some transfer of electronic charge from hydride to methane.

In an earlier paper,[2] we analyzed the ways in which filled and empty MO's of methane or methyl fluoride are intermixed to effect charge polarization due to approach by negative bases. We found that the empty MO's mixed in are antibonding predominantly in the bond to the leaving group, while loss of the filled MO's occurs mainly in MO's which are bonding for that bond. It was argued from this that polarization by the negative base, in driving charge to the backside atom, simultaneously weakens the bond to that atom. This general approach further predicts that the bonds to the three front-side hydrogens should also be weakened although to a much lesser extent.

This approach has great intuitive appeal. It has also been applied in a limited way to the process of charge transfer in SN2 reactions.[3] Nevertheless, as we show below, it is not generally a complete approach and *can lead to predictions that bonds should be weakened when calculated bond orders show them to be strengthened and vice versa*. It was just such disagreements that led us to examine the problem more closely.

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) J. P. Lowe, *J. Amer. Chem. Soc.*, **93**, 301 (1971).

(3) For a clear review, see L. Salem, *Chem. Brit.*, **5**, 449 (1969).