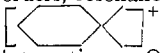


[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Hyperconjugation and Spectrum of the Benzenium Ion, Prototype of Aromatic Carbonium Ions¹BY NORBERT MULLER,^{2a} LUCY W. PICKETT AND ROBERT S. MULLIKEN^{2b}

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We have used the semi-empirical LCAO MO method to calculate the energy levels and spectrum, charge distribution, bond orders, resonance energy and hyperconjugation energy (HCJE), of the $C_6H_7^+$ ion, which we assume to have the structure  Throughout our computations, we included overlap for neighboring atoms, but neglected non-neighbor interactions. Our calculations indicate that the $C_6H_7^+$ ion should be colored, and that the contribution of hyperconjugation to the total net resonance energy is of the order of 0.6 e.v., larger than most non-aromatic conjugation energies.³ The results, surveyed in Sections 10-13, are probably fairly typical for aromatic (and aliphatic) carbonium ions and for the intermediates in aromatic substitution reactions.

It is shown that hyperconjugation in $C_6H_7^+$ creates relatively large π bond orders between the CH_2 carbon atom and the neighboring ring atoms, thus to a considerable extent restoring the otherwise lost aromatic character of the ring. The computed HCJE is already moderately large when electronegativity differences (between carbon atoms and the H_2 of the CH_2 group, and among carbon atoms which differ in charge, as they do in $C_6H_7^+$) are neglected; it is greatly increased when proper self-consistent allowance is made for a redistribution of charge to conform to these electronegativity differences. The possible application of a similar procedure to explain the ionization potentials of other hydrocarbon ions is briefly discussed. Relations of the charge distribution in $C_6H_7^+$ computed for the case that electronegativity difference effects are neglected, to considerations of Longuet-Higgins on the charge distribution in alternant hydrocarbon radicals and their cations, are discussed in Section 11. In Section 3 the choice of parameters for the theoretical treatment of hyperconjugation by the semi-empirical LCAO method is discussed, and a theoretical justification is given for the empirically established electropositive behavior of hydrogen quasi- π orbitals toward carbon π orbitals in hyperconjugation.

Introduction

1. **General Discussion.**—A number of authors⁴ have studied the equilibria in mixtures of aromatic hydrocarbons and strong acids, which may be written $Ar + H^+ \rightleftharpoons ArH^+$. Kilpatrick and Luborsky,^{4b} who investigated the reaction $Ar + HF \rightleftharpoons ArH^+ + F^-$ of the methylated benzenes, report that the equilibrium constant varies from 10^{-8} for $Ar =$ benzene to 10^{-2} for hexamethylbenzene. These results support the belief⁵ that cations of the type ArS^+ are formed as intermediates in electrophilic substitution reactions of aromatic hydrocarbons ($S =$ substituent; in our case the extra H functions as S).

The simplest such ion is $C_6H_7^+$, which may be called the benzenium ion.⁶ The following calcula-

(1) The calculations were begun by Lucy W. Pickett at Chicago in summer, 1951, continued at Mount Holyoke, and carried further by Norbert Muller in 1953.

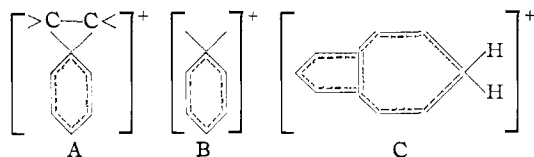
(2) (a) National Research Postdoctorate Fellow. Present address: Department of Chemistry, Purdue University, Lafayette, Indiana. (b) Fulbright Research Scholar. Permanent address: Department of Physics, University of Chicago, Chicago 37, Illinois.

(3) A preliminary account of this work has appeared in *J. Chem. Phys.*, **21**, 1400 (1953).

(4) (a) W. Klatt, *Z. anorg. Chem.*, **234**, 189 (1937); D. A. McCaulay and A. P. Lien, *THIS JOURNAL*, **73**, 2013 (1951); H. C. Brown and H. W. Pearsall, *ibid.*, **74**, 191 (1952). The spectra have been studied by V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952), and (see Section 10 below) by C. Reid. (b) M. Kilpatrick and F. E. Luborsky, *THIS JOURNAL*, **75**, 577 (1953). (c) H. C. Brown and W. J. Wallace, *THIS JOURNAL*, **75**, 6268 (1953).

(5) G. W. Wheland, *ibid.*, **64**, 900 (1942); M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949); V. Gold, *ibid.*, 2184 (1952); and related papers.

(6) D. J. Cram, *THIS JOURNAL*, **74**, 2129 (1952), has used the name *phenonium* ion for the species A. In a private communication he suggests that



ethylene-phenonium ion may be a better name for A; then phenonium could be used as a generic name for ions containing the grouping B. On the other hand, E. Heilbronner and M. Simonetta, *Helv. Chim.*

tions, based on the semi-empirical LCAO MO (Linear Combination of Atomic Orbitals Molecular Orbital) method, give the energy levels, charge distribution, bond orders and resonance energy of this ion. We find that hyperconjugation, neglected in previous computations,⁵ makes an important contribution to the resonance energy. We further find that two electronic transitions should occur in or near the visible, so that solutions containing benzenium ion should appear colored; this is in agreement with observations reported in reference 2 above.

Figure 1 shows the configuration assumed for these calculations.

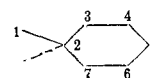


Fig. 1.

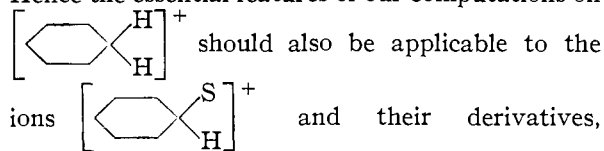
The six carbon atoms form a ring in a plane which also contains five of the hydrogen atoms, the other two hydrogens being symmetrically placed above and below it, so that the ion has C_{2v} symmetry. This is the geometrical model agreed on by most authors (*cf.* reference 3). Dewar⁷ has proposed a " π -complex" model in which the added proton is not bonded to any particular atom of the ring. He argues that otherwise "the ring would cease to be aromatic, and there would be a large decrease in resonance energy." The results of the present calculations seem to remove the force of such an argument.


With the model shown in Fig. 1, hyperconjugation should occur between the CH_2 group and the remaining π electrons of the ring. The case is simi-

Acta, **35**, 1049 (1952), in an article describing calculations similar to those of reference 3 for C and similar ions, use the name *azulenium*. We feel that it may be useful to give specific names to important particular aromatic carbonium ions, even though the generic name phenonium may be adopted for B and its derivatives.

(7) M. J. S. Dewar, "A Review of the π -Complex Theory," Paper presented at the Colloque International de Montpellier, 1951, and printed in *Bull. soc. chim. France*, [5] **18**, C71 (1951).

lar to that of cyclopentadiene $\square\text{CH}_2$.⁸ The theoretical treatment of hyperconjugation^{8b,9} shows that it should occur not only with CH_2 or CH_3 groups, but also (though no doubt to a somewhat different quantitative extent) when one or more of the H atoms is replaced by any substituent group S. Hence the essential features of our computations on



which are believed to exist as intermediates in electrophilic substitution reactions. (Ions of the type  should likewise be subject to the same kind of treatment.)

2. Outline of the Computations.—We treat the C_6H_7^+ ion as if it had six π -electrons, in orbitals made by combining the six $2p_{\text{C}}$ AO's (atomic orbitals) and a quasi- π orbital ($1s_{\text{H}} - 1s_{\text{H}}$) on the H_2 quasi-atom. In the customary way,¹⁰ the energy levels and the ratios of the LCAO coefficients are obtained by solving seven linear equations and the corresponding secular equation after equating to zero the matrix elements representing interactions between non-neighbor atoms.

Because of the C_{2v} symmetry, the orbitals may be divided into two groups, those of a_2 symmetry, with coefficients $c_3 = -c_7$, $c_4 = -c_6$, $c_1 = c_2 = c_5 = 0$, and those of b_1 symmetry with $c_3 = c_7$, $c_4 = c_6$. If these conditions on the coefficients are substituted into the linear equations (this brings about a transformation to symmetry orbitals) it is found that the energies of the a_2 orbitals are the roots of the secular equation

$$D(a_2) = \begin{vmatrix} x_3 & \beta_{34} + \frac{1}{2}S_{34}(x_3 + x_4) \\ \beta_{34} + \frac{1}{2}S_{34}(x_3 + x_4) & x_4 \end{vmatrix} = 0 \quad (1)$$

while the energies of the b_1 orbitals are the roots of $D(b_1) = 0$, where

$$D(b_1) = \begin{vmatrix} x_1 & \beta_{12} + \frac{1}{2}S_{12}(x_1 + x_2) & 0 & 0 & 0 \\ \beta_{12} + \frac{1}{2}S_{12}(x_1 + x_2) & x_2 & 2\beta_{23} + S_{23}(x_2 + x_3) & 0 & 0 \\ 0 & \beta_{23} + \frac{1}{2}S_{23}(x_2 + x_3) & x_3 & \beta_{34} + \frac{1}{2}S_{34}(x_3 + x_4) & 0 \\ 0 & 0 & \beta_{34} + \frac{1}{2}S_{34}(x_3 + x_4) & x_4 & \beta_{45} + \frac{1}{2}S_{45}(x_4 + x_5) \\ 0 & 0 & 0 & 2\beta_{45} + S_{45}(x_4 + x_5) & x_5 \end{vmatrix} \quad (2)$$

In these determinants, $x_i = \alpha_i - \epsilon$ (ϵ = orbital energy), with the electronegativity parameters $\alpha_i = \int \psi_i H \psi_i d\tau$; the resonance integrals $\beta_{ij} = \gamma_{ij} - \frac{1}{2}S_{ij}(\alpha_i + \alpha_j)$, where $\gamma_{ij} = \int \psi_i H \psi_j d\tau$; and S_{ij} is the overlap integral $\int \psi_i \psi_j d\tau$.

3. The Choice of Semi-empirical Parameters.—We began by using the Slater-AO value $S_{\text{CC}} = 0.25$

(8) (a) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); (b) R. S. Mulliken, C. A. Rieke and W. G. Brown, *THIS JOURNAL*, **63**, 41 (1941); see footnote 30 of reference 9 for a correction which affects the quantitative though not the qualitative conclusions of the 1941 paper.

(9) R. S. Mulliken and R. G. Parr, *J. Chem. Phys.*, **19**, 1275 (1951), footnote 26.

(10) *Cf., e.g.*, C. A. Coulson, "Valence," Oxford Univ. Press, London, 1952, p. 238.

(11) R. S. Mulliken and C. A. Rieke, *THIS JOURNAL*, **63**, 1770 (1941); R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949), eq. 29, 85.

for all carbon-carbon overlap integrals, and taking the corresponding β 's as all equal. With the procedure used by Mulliken, *et al.*,¹² to find group overlap integrals, we computed the CH_2 quasi- π overlap integral, S_{12} , for several assumed values of the H-C-H angle and of the C-H distance. Typical results were

| $\angle\text{H-C-H}$ | $R\text{CH}, \text{\AA}$ | S_{12} |
|----------------------|--------------------------|----------|
| 105° | 1.09 | 0.491 |
| 120° | 1.14 | .512 |

As it happened, we made the first calculations using the second value, and then retained it for consistency; it is clear that a value near 0.5 is about right and that the exact value does not matter much. In accordance with the assumption of the approximate proportionality of β to S , β_{12} was taken to be twice β_{CC} .¹³

Here it may be worthwhile to pause to emphasize the following points. (1) The much larger value of β for the quasi- π bond, which together with a quasi- σ bond forms the $\text{C}=\text{H}_2$ quasi-double bond, is directly related to the fact that the $\text{C}=\text{H}_2$ bond (corresponding as it does, if one uses localized bond orbitals, to two strong C-H σ bonds) is much stronger than a C=C double bond. (2) The difference between hyperconjugation and ordinary conjugation or resonance is dependent precisely on the larger value of β_{12} than of β_{CC} ; if $\beta_{12}/\beta_{\text{CC}}$ could be increased at will, hyperconjugation would progressively diminish in strength.

A single value of x , called x_0 , was used for all the carbon atoms in the first approximate calculations, and the x value of the H_2 quasi-atom was written as $x_0 + \delta\beta_{\text{CC}}$, so that a positive value of δ indicates greater electronegativity.¹⁴

In the first computations on the MO theory of hyperconjugation, Mulliken, Rieke and Brown^{8b} set $\delta = 0$ after preliminary work indicated that the results were not very sensitive to δ .¹⁵ Later^{13c} Mulliken and Roothaan, in computations on hyperconjugation in twisted ethylene, reasoned that δ (δ/β in their notation) must be positive, since the hydrogen atom $1s$ electron is surely

(12) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1258 (1949).

(13) (a) R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 265 (1942), footnote 14; further, G. W. Wheland, ref. 5 above, who, however, assumed a different parameter γ to be proportional to S (regarding the relation of β to γ , see text and ref. 9 above); (b) R. S. Mulliken, *J. chim. phys.*, **46**, 675 (1949), section 28; (c) R. S. Mulliken and C. C. J. Roothaan, *Chem. Revs.*, **41**, 219 (1947). Here calculations were made with each of two trial values of $\beta_{12}/\beta_{\text{CC}}$, namely, 2.0 and 1.5.

(14) Heilbronner and Simonetta (see ref. 6) included the hyperconjugative effect of the methyl group in calculations on methylated azulonium ions. They used $\delta = -0.2$ for the H_2 quasi-atom, $\delta = 0$ for the carbon of the methyl group, and $\delta = -0.1$ for the ring carbon bearing the methyl group. These authors also recognized the need for the inclusion of hyperconjugation with the H_2 quasi-atom, but they made no calculations of this effect.

(15) For extensive computations by the same method on radicals, see J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1948).

more electronegative than the carbon atom $2p\pi$ electron.¹⁶

Pullman and co-workers¹⁷ have assumed $\delta = -0.2$, and $\beta_{CH} = 2\beta_{CC}$, for either $C=H_2$ or $C\equiv H_3$ hyperconjugation, and similar parameters have been used by Wheland⁵ for toluene and by others.^{14,18}

More recently Coulson and Crawford,¹⁹ in papers on hyperconjugation especially in methylated benzenes and ethylenes, have cited chemical and dipole moment evidence which makes it fairly certain that δ is negative, and perhaps in the neighborhood of -0.5 .

Thus empirically, a negative δ seems to be required, but it seemed desirable also to seek a theoretical explanation since, according to theoretical reasoning mentioned above, δ should be positive. The following argument appears to give at least a rough basis for such an explanation. The electronegativities which we wish to compare are those of a carbon $2p\pi$ orbital and an H_2 quasi- π group orbital of the form $1s-1s$. In the theoretical reasoning used earlier, it was assumed that it would be adequate to set the electronegativity of the $1s-1s$ group orbital equal to that of a hydrogen atom. But more recent calculations show that the overlap integral S_{HH} for the two $1s$ orbitals making up $1s-1s$ is about 0.26 (for a normal CH_2 group with 120° H-C-H angle), which tends to indicate that these orbitals interact strongly. This interaction would be an antibonding one, which would make the orbital $1s-1s$ less tightly bound than $1s_H$ alone. According to LCAO MO theory,²⁰ the binding energy (or ionization potential I) of a $1s-1s$ MO should be given approximately by

$$-I_{1s-1s} \approx -I_H - \beta_{HH}/(1 - S_{HH})$$

with $-\beta_{HH}$ about 2.05 e.v.²¹ Then setting $I_H = 13.6$ volts, I_{1s-1s} is found to be 10.8 volts, which is slightly smaller than $I_{2p\pi}$ (11.2 volts) for the $2p\pi$ AO for carbon¹⁶ in its proper valence state. Hence if electronegativity is given¹⁶ by $(I + E)/2$, and if E in each case is assumed proportional to I (this assumption should probably be satisfactory, especially since both E 's are near zero anyway), the quasi π $1s-1s$ H_2 MO should be less electronegative than the $2p\pi$ carbon AO, in agreement with the assumption of a negative δ value by Pullman and by Coulson and Crawford.²²

(16) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934). In that paper the use of $(I + E)/2$ was proposed as an absolute measure of electronegativity (I = ionization potential, E = electron affinity, for detachment or attachment of an electron in a particular orbital—pure or hybrid as the case may be—the atoms and ions being in appropriate valence states).

(17) B. Pullman, M. Mayot and G. Berthier, *ibid.*, **18**, 257 (1950), and references given there.

(18) Longuet-Higgins and Sowden, *J. Chem. Soc.*, 1404 (1952); C. A. Coulson, *Proc. Phys. Soc.*, **45**, 933 (1952); H. H. Jaffe, *J. Chem. Phys.*, **20**, 778 (1952).

(19) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953); V. A. Crawford, *ibid.*, 2058 (1953); 2061 (1953). It may be noted that these authors have largely overlooked refs. 11 and 13, which are of some relevance. Also, Coulson and Crawford have followed Mulliken, Rieke and Brown in an error (*cf.* ref. 8b) which may somewhat (although not seriously) affect their quantitative conclusions.

(20) R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949), § 6 and 7.

(21) R. S. Mulliken, *ibid.*, **46**, 675 (1949), Table XX.

(22) While the reasoning above is qualitatively satisfactory, it is not clear how α values are related quantitatively in general to electronegativities. According to some studies by Mulliken (*J. chim. phys.*, **46**, 497 (1949), Tables III, IV, and *ibid.*, **46**, 675 (1949), Table XVIII,

As has been mentioned above, the appropriate formulation of the $C=H_2$ double bond in the discussion of hyperconjugation involves not only a quasi- π bond between a $2p\pi_C$ AO and a $1s-1s$ H_2 MO, but also a quasi- σ bond. The latter is between a *digonal* carbon AO $2d_{iC}$ [of form $2^{-1/2}(2s_C + 2p\sigma_C)$] and a $1s + 1s$ quasi- σ H_2 MO. To supplement the foregoing discussion of the relative electronegativities of the $2p\pi_C$ and the $1s-1s$ of H_2 , it seems desirable here to give a corresponding discussion of the relative electronegativities of $2d_{iC}$ and $1s + 1s$ of H_2 .

Proceeding as above, the bonding energy of $1s + 1s$ of H_2 should be given approximately by

$$-I_{1s+1s} \approx -I_H + \beta_{HH}/(1 + S_{HH})$$

which with I_H and β_{HH} as given above, gives I_{1s+1s} as about 15.2 volts. On the other hand, $I_{2d_{iC}} = 1/2(I_{2s} + I_{2p\sigma})$, for the proper valence state of carbon, is about 16.14 volts,¹⁶ indicating that in the quasi- σ bond as well as in the quasi- π bond, H_2 should be somewhat electropositive to carbon. This would indicate that the H_2 group as a whole in CH_2 would be somewhat electropositive to carbon. A preliminary examination indicates that these conclusions would probably not be strongly modified using $(I + E)/2$ as a measure of electronegativity.

NOTE ADDED IN PROOF.—In the preceding discussion, it would have been better to have added to each of the equations for $-I_{1s-1s}$ and $-I_{1s+1s}$, and *also* to $-I_{2p\pi}$ for carbon, a term ω which would affect the results very considerably (for bonding MO's at least, ω is usually positive, though sometimes negative: *cf.* ref. 20, Tables IV–VI).

4. Energy Levels.—We carried through the present calculations with trial δ values of -0.5 , -0.25 , 0 , 0.25 and 0.5 . The results are shown in Table IA.

All the b_1 levels decrease in energy with increasing electronegativity of the hydrogen, while the a_2 energies are unaffected. That is, increasing δ leads to lower total energy (but smaller resonance energy, see below) and to lowering of the calculated frequency of the longer wave length transition. The position of the second transition is relatively insensitive to changes of δ . Hyperconjugation causes a considerable migration of positive charge to the hydrogen (*cf.* Table IIA), mainly from the 3, 5 and 7 carbons; this effect decreases for increasing δ , as one would expect.

5. Charges and Bond Orders.—The charges and bond orders (Table IIA) were computed from the coefficients of the occupied MO's. The *relative* values of the coefficients in the j^{th} MO are found by substituting the corresponding energy into the linear equations; the *absolute* values may then be found from the normalizing condition on the LCAO wave function, $\sum_{r,s} c_{rj} c_{sj} S_{rs} = 1$. Here c_{rj} is the coefficient in the j^{th} LCAO MO of an AO on atom r . A measure of the fraction of the total electronic

semi-empirical α 's), $-\alpha$ lies in general between I and $(I + E)/2$, but usually nearer I . This suggests that usually α may be *roughly proportional to I* or to $(I + E)/2$, which is all that is necessary for our argument. Reasons for preferring a quantity proportional to $(I + E)/2$ rather than to I as a measure of electronegativity are given in ref. 16 but when E is small as for both C and H atoms (and probably for $1s-1s$ of H_2 here), the difference may be unimportant.

TABLE IA

SUMMARY OF RESULTS OF ENERGY CALCULATIONS WITH VARIOUS TRIAL VALUES OF δ , ASSUMING $\omega = 0$ AND UNIFORM α 'S AND β 'S FOR THE RING ATOMS^a

| | $\delta = -0.50$ | $\delta = -0.25$ | $\delta = 0.00$ | $\delta = 0.25$ | $\delta = 0.50$ | |
|--|--|------------------|-----------------|-----------------|-----------------|---------|
| Orbital energies w_i for delocalized model, in units of $-\beta$: $w_i = (\epsilon_i - \alpha)/-\beta$ | 5b ₁ | 7.4318 | 7.3580 | 7.2883 | 7.2241 | 7.1638 |
| | 4b ₁ | 2.6294 | 2.5988 | 2.5703 | 2.5440 | 2.5200 |
| | 2a ₂ | 1.3333 | 1.3333 | 1.3333 | 1.3333 | 1.3333 |
| | 3b ₁ | 0.1356 | 0.0654 | 0.0000 | -0.0594 | -0.1124 |
| | 1a ₂ | -0.8000 | -0.8000 | -0.8000 | -0.8000 | -0.8000 |
| | 2b ₁ | -1.0582 | -1.0910 | -1.1214 | -1.1477 | -1.1694 |
| | 1b ₁ | -1.4552 | -1.4973 | -1.5539 | -1.6275 | -1.7187 |
| Sum (E) of orbital energies for occupied π -orbitals, in units of $-\beta$ | E (delocalized model) | -6.6268 | -6.7766 | -6.9506 | -7.1504 | -7.3762 |
| | E (semi-localized model) | -6.1940 | -6.4284 | -6.6629 | -6.9286 | -7.1940 |
| | E (localized model) | -5.3766 | -5.6110 | -5.8455 | -6.1112 | -6.3766 |
| | E (benzene, deloc. model) ^d | | | -5.8667 | | |
| | E (benzene, loc. model) ^d | | | -4.8000 | | |
| Vertical HCJE (hyperconjugation energy) | $E_{\text{semiloc.}} - E_{\text{deloc.}}$ ^b | 0.4328 | 0.3482 | 0.2877 | 0.2218 | 0.1822 |
| | kcal./mole ^c | 26.0 | 20.9 | 17.3 | 13.3 | 10.9 |
| Vertical resonance energy | $E_{\text{loc.}} - E_{\text{deloc.}}$ ^b | 1.2502 | 1.1656 | 1.1051 | 1.0392 | 0.9996 |
| | kcal./mole ^c | 75.0 | 69.9 | 66.3 | 62.4 | 60.0 |
| Vertical resonance energy of benzene for comparison: ^d | | | 1.0667 | | | |
| Compressional energies (in kcal./mole) ^e | Delocalized model | 26.5 | 23.4 | 20.6 | 18.3 | 16.5 |
| | Semi-localized model | 13.1 | 13.1 | 13.1 | 13.1 | 13.1 |
| | Net (deloc. - semiloc.) | 13.4 | 10.3 | 7.5 | 5.2 | 3.4 |
| | Net HCJE (kcal./mole) ^{e,g} | 12.6 | 10.6 | 9.8 | 8.1 | 7.5 |
| | Net resonance energy (kcal./mole) ^{e,f} | 48.5 | 46.5 | 45.7 | 44.1 | 43.5 |

^a β is defined in the last paragraph of section 2, δ in the second paragraph of section 3, ω in section 9. ^b These energies are in units of $-\beta$. ^c Figures given in kcal. are computed using $\beta = -60$ kcal. per mole (see last paragraph of section 9). ^d See last paragraph of section 7. ^e Net HCJE = vertical HCJE minus net (deloc. - semiloc.) compression energy. ^f Net resonance energy = vertical resonance energy minus compression energy of delocalized model.

TABLE IB

SUMMARY OF RESULTS OF ENERGY CALCULATIONS WITH α 'S AND β 'S MADE SELF-CONSISTENT FOR THREE TRIAL VALUES OF ω , TAKING $\delta = 0$

| | $\omega = 0$ | $\omega = 2$ | $\omega = 4$ | |
|--|--|--------------|--------------|---------|
| Orbital energies w_i for delocalized model, in units of $-\beta_0$: $w_i = (\epsilon_i - \alpha_0)/-\beta_0$ | 5b ₁ | 6.619 | | |
| | 4b ₁ | 2.546 | | |
| | 2a ₂ | 1.369 | | |
| | 3b ₁ | 0.000 | -0.3708 | -0.6750 |
| | 1a ₂ | -0.813 | -1.0937 | -1.3765 |
| | 2b ₁ | -1.116 | -1.4005 | -1.6877 |
| | 1b ₁ | -1.520 | -1.7791 | -2.0616 |
| Sum (E) of orbital energies ^a for occupied π -orbitals | E (delocalized model): | -6.898 | -8.547 | -10.252 |
| | E (semi-localized model): | -6.680 | -8.202 | -9.796 |
| Vertical HCJE | $(E_{\text{semiloc.}} - E_{\text{deloc.}})$ ^a | 0.218 | 0.345 | 0.456 |
| | kcal./mole ^b | 13.1 | 20.7 | 27.4 |
| Net compressional energy correction (kcal./mole)(deloc. - semiloc.) ^b | | 7.2 | 7.2 | 7.2 |
| Net HCJE (kcal./mole) ^b | | 5.9 | 13.5 | 20.2 |

^a Energies are in units of $-\beta_0$. ^b In kilocalories per mole, $-\beta_0 = 60$.

charge which is associated with atom γ would then be $2 \left\{ \sum_j c_{rj}^2 + \sum_j \sum_{s \neq r} 1/2 c_{rj} c_{sj} S_{rs} \right\}$. The factor 2 occurs because MO is doubly occupied.

A less tedious procedure, which leads here to almost identical results, is to renormalize the coefficients by requiring that $\sum_r c_{rj}^2 = 1$ and then to use

$2 \sum_j c_{rj}^2$ as a measure of the negative charge on atom r . The first procedure corresponds to a division of the charge distribution into "atomic" and "overlap" charge, with the overlap charge subsequently divided between the corresponding pairs of atoms.

The second, approximate procedure involves a division of the distribution directly into atomic charges only; this method was used to derive the charges in Table IIA and also in Table IIB. The same coefficients as were used to find the charges were then used to find the bond orders, $p_{rs} = 2 \sum_j c_{rj} c_{sj}$.²³

6. Conjugation and Hyperconjugation.—In order to obtain resonance and hyperconjugation energies we considered, in addition to our delocalized model, a localized and also a semi-localized one. In the localized model, four π -

(23) Cf. Coulson, reference 10, p. 251.

TABLE II

CALCULATED ATOMIC CHARGES AND π BOND ORDERS

A. Approximate Delocalized Model, assuming $\omega = 0$ and uniform α 's and β 's for ring atoms, for several trial values of δ (based on calculations for Table IA)

| | Atom | $\delta = -0.50$ | $\delta = -0.25$ | $\delta = 0.00$ | $\delta = 0.25$ | $\delta = 0.50$ |
|----------------------|------------|------------------|------------------|-----------------|-----------------|-----------------|
| Charges ^a | 1 | 0.5212 | 0.3988 | 0.2580 | 0.1068 | -0.0448 |
| | 2 | -.0618 | -.0370 | .0026 | .0616 | .1376 |
| | 3 or 7 | .2010 | .2240 | .2472 | .2684 | .2854 |
| | 4 or 6 | -.0176 | -.0102 | -.0012 | .0068 | .0132 |
| | 5 | .1740 | .2108 | .2478 | .2814 | .3098 |
| π Bond orders | Bond | | | | | |
| | 1-2 | .7003 | .7743 | .8423 | .8955 | .9261 |
| | 2-3 or 2-7 | .4547 | .4132 | .3668 | .3163 | .2651 |
| | 3-4 or 6-7 | .7289 | .7370 | .7435 | .7505 | .7580 |
| | 4-5 or 5-6 | .6426 | .6261 | .6078 | .5912 | .5770 |

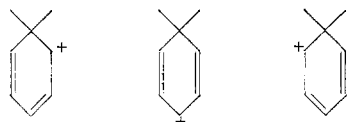
B. Improved Delocalized or Semi-localized Model, for $\delta = 0$ but with α 's and β 's made self-consistent for three trial values of ω (based on calculations for Table IB)

| | Atom | Delocalized model | | |
|----------------------|------------|-------------------|--------------|--------------|
| | | $\omega = 0$ | $\omega = 2$ | $\omega = 4$ |
| Charges ^a | 1 | 0.212 | 0.172 | 0.161 |
| | 2 | .004 | .076 | .090 |
| | 3 or 7 | .254 | .184 | .169 |
| | 4 or 6 | -.002 | .093 | .117 |
| | 5 | .280 | .198 | .175 |
| π Bond orders | Bonds | | | |
| | 1-2 | | 0.86 | 1.00 |
| | 2-3 or 2-7 | | .34 | 0.00 |
| | 3-4 or 6-7 | | .75 | .77 |
| | 4-5 or 5-6 | | .60 | .57 |

(Calcd. bond orders were approximately the same for all three ω values)

^a In units of $+e$.

electrons are in two-center orbitals on some four of the five ring atoms, corresponding to the two ordinary double bonds in any one of the three structures



The energy of these four electrons is $4(\alpha + 0.800\beta)$. Further, we must consider the two single C-H bonds of the CH_2 group as replaced by a quasi- σ and a quasi- π bond,²⁴ and include here the energy of the two quasi- π electrons, which is given by twice the lower root of the minor $\begin{vmatrix} d_{11} & d_{12} \\ d_{21} & d_{22} \end{vmatrix}$ of $D(b_1)$ in eq. 2, where $d_{11} = x_1$, $d_{12} = \beta_{12} + \frac{1}{2}S_{12}(x_1 + x_2)$, etc. This quasi- π energy of course depends on the value of δ . The total π -resonance energy is the difference between the π -electron energy of this model and that of the delocalized one.²⁵

The semi-localized model is that assumed by Wheland, Dewar and Gold³; in their calculations, however, overlap was neglected. Four π -electrons are placed in orbitals spread over five of the carbon atoms; the energies are given by the lower root of $D(a_2)$ above and the lowest root of the minor $\begin{vmatrix} d_{33} & d_{34} & d_{35} \\ d_{43} & d_{44} & d_{45} \\ d_{53} & d_{54} & d_{55} \end{vmatrix}$ of $D(b_1)$. The sixth carbon is consid-

(24) Cf. discussion of H_2O in reference 12.

(25) But see the discussion of R. S. Mulliken and R. G. Parr, *J. Chem. Phys.*, **19**, 1271 (1951), section 3.

ered to be part of a normal CH_2 group, and *hors-de-combat* as far as π interactions are concerned; hence the energy of the electron pair in the two-center quasi- π orbital, which must also be included, is the same as that in the localized model. We evaluated these energies, including overlap between neighboring atoms in the computations. The energy difference between the semilocalized and the delocalized models is the *vertical* hyperconjugation energy (HCJE).²⁶ The energy remaining after correcting for compressional energy changes (see below) we call the *net* HCJE.

It is not strictly accurate to compare the resonance energies of the different models without making allowance for the fact that a somewhat different value of β should be used for each one. Nevertheless, an average value of about -60 kcal. for β (see section 9 below) may be used without very serious error, and the vertical HCJE is then found to be 11 kcal. for $\delta = 0.5$, or 26 kcal. for $\delta = -0.5$.

7. Compressional Energies (CE).—To estimate the net HCJE it is of course necessary to include an energy correction for bond stretching and compression in passing from one model to another.²⁷ We estimated this using very rough formulas derived on the assumption that the bonds are distorted harmonically. For the $\text{C}=\text{H}_2$ bond further assumptions are needed; our procedure was as follows. If the quasi- π bond order is found to be z ,

(26) Our *vertical* resonance energy is what Coulson and Altmann, *Trans. Faraday Soc.*, **48**, 293 (1952), have called a *quantum-mechanical* resonance energy.

(27) Cf. reference 26 above for review, discussion and references.

the total bond order will be $1 + z$, assuming a single quasi- σ bond. We then considered the C=H₂ link, for the purpose of finding the CE, to consist of two single C-H bonds each of order $\frac{1}{2}(1 + z)$, and assumed further that the C-H distance could then be computed by taking the bond distance-bond order variation to be similar to that of a C-C single bond. The C=H₂ contribution to the total CE is small enough so that the errors in this procedure should be unimportant.

Using an observed bond distance-bond order relation²⁸ and force constants²⁹ of 4.50×10^5 dyne/cm. for C-C, 9.57×10^5 dyne/cm. for C=C, and 4.80×10^5 dyne/cm. for C-H, we obtained the formulas for estimating the CE corrections

$$\left. \begin{aligned} \text{C-C: CE} &= 324(0.29 - 0.33p + 0.04p^2)^2 \text{ kcal./mole;} \\ \text{C=C: CE} &= 689(0.50 - 0.33p + 0.04p^2)^2 \text{ kcal./mole;} \\ \text{C=H}_2\text{: CE} &= 110(1 - \frac{1}{2}p)^2 \text{ kcal./mole} \end{aligned} \right\} \quad (3)$$

where p is the total bond order.

Much of the error entailed by the use of these crude formulas can be expected to cancel in comparing the CE's of the semi-localized and delocalized models. The net HCJE (Table IA) is 12.6 kcal. for $\delta = -0.5$ and 7.5 kcal. for $\delta = 0.5$; these values are somewhat smaller than those given in our original Letter,¹ since at the time we underestimated the importance of the CE corrections. Still, either value is larger than most non-aromatic conjugation energies. The first value is very probably the better (see fourth paragraph of section 3 above).

We have included in Table IA a delocalized energy of benzene, and a localized energy corresponding to the energy of a single Kekulé form. These values, computed with $S = 0.25$ and $\delta = 0$, may be compared with the corresponding quantities calculated for the benzenium ion. The net conjugation energy of benzene, 39.4 kcal., is less than the over-all net resonance energy found for the benzenium ion with any of our trial values of δ .

Improved Calculations

8. Adjustment of the β 's to Self-consistency.—

As a first improvement in the approximation, we included a variation of β with interatomic distance, with the latter again inferred from the bond orders using the above-mentioned empirical relation.²⁸ The (Slater) overlap integrals at various distances are known,³⁰ and may be related to the bond orders by the approximate formula

$$S(p) = 0.080p + 0.115 \quad (4)$$

Assuming β proportional to S ,¹³ we now write

$$\beta(p) = \beta_0 S(p)/0.25 \quad (5)$$

β_0 being the β -value appropriate to the interatomic distance 1.39 Å., where the overlap is 0.25. For the carbon-hydrogen quasi- π bond, we retained the assumption that $S_{12} = 0.512$ and $\beta_{12} = 2\beta_0$ for both semi-localized and the delocalized model. A probably minor modification that should have been included would have been to use the same empirical distance-bond order relation as was used for finding

the CE's, evaluate the new S taking account both of the C-H distances and of the H-C-H angle (which in turn should depend somewhat on the bond order), and then take β proportional to S .

The procedure used was to begin with a set of β values corresponding to an assumed set of bond orders and to calculate new bond orders, repeating the process to self-consistency, for both the semi-localized and the delocalized model, each separately. This was done only with $\delta = 0$; the results are summarized in the $\omega = 0$ columns of Tables IB and IIB.

The effect of this adjustment of the β 's is a rather large decrease in the HCJE, as may be seen by comparing the first column of Table IB with the central column of Table IA. The figures in Table IA corresponding to $\delta \neq 0$ should undergo a similar change if the β 's there were likewise made self-consistent.

9. Adjustment of the α 's.—According to Table IIA the carbon atoms in the ring differ considerably in charge. Theoretically, the integral represented by α should depend linearly on the valence-state ionization potential.³¹ It therefore cannot be independent of charge, so that the initial assumption that the α 's of all the carbon atoms are equal is inconsistent with the non-uniform charge distribution found. In order to work toward self-consistency, we decided to assume that the α 's depend linearly on the charges, so that the α of the r th atom, with charge q_r , becomes $\alpha_0 + \omega\beta q_r$.³² We may set an approximate upper limit to ω as follows: if $\alpha = \frac{1}{2}(I + E)$,^{17,22} the difference between the α values for the neutral atom and the positive ion ($q_r = 1$) should be approximately equal to the difference between the first and the second ionization potentials of carbon, which is about 12 e.v. If $\beta = -2.6$ e.v. (see below), this requires $\omega = 4.6$. As a result of polarization of the σ orbitals, the q 's calculated from the π electrons alone will certainly exceed the "real" q 's; use of a smaller value for ω should compensate this. We adjusted the α 's (and the β 's simultaneously) to self-consistency for the two trial ω values 2 and 4, with $\delta = 0$ and with the α of the H₂ pseudo-atom, as a function of its charge, treated like those of the carbons. This was done for both the semi-localized and the delocalized model, each separately. The results are shown in the second and third columns of Table IB and in Table IIB. The orbital energy decreases with increasing ω for both the semi-localized and the delocalized model, but more so for the latter; this differential effect represents a strong increase in the HCJE.

The foregoing adjustment of the α 's (and β 's) leads to an increase in the HCJE which for a reasonable value of ω more than compensates for the decrease resulting when the β 's alone are changed. (Calculations now in progress involving hyperconjugation stabilization of simple alkyl radicals and their ions indicate that a value of ω near 1.4 gives the best agreement with experiment.) The bond orders (Table IIB) are only very slightly affected

(28) For example, C. A. Coulson, *Proc. Roy. Soc. (London)*, **169A**, 413 (1939).

(29) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," New York, N. Y., 1945, p. 193.

(30) R. S. Mulliken, *et al.*, reference 9, Table III.

(31) R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949), especially equations 38 and 42.

(32) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949), made a similar adjustment, but assumed the special value $\omega = 1$.

by the inclusion of ω . The charge variation from atom to atom is considerably smoothed out (Table II).

Including the α adjustment for the cases with $\delta \neq 0$ of Table IA should alter the results in much the same way as for those with $\delta = 0$.

The energies in Table IB are in units of β_0 except where kcal. are indicated. The conversion to kcal. or e.v. was made using a spectroscopic value of -2.6 e.v., or -60 kcal., for β_0 .³³ The calculations of reference 33 are based on assumptions similar to those used here, that is, including S for nearest neighbors but neglecting non-neighbor interactions.

Survey and Discussion of Results

10. **The Spectrum.**—The two lowest predicted excited states of the benzenium ion result if an electron is transferred from either the $1a_2$ or the $2b_1$ level to the $3b_1$ level (see Tables I and III). For the former, the polarization will be parallel to the symmetry axis, and for the latter perpendicular to it and in the plane of the molecule. The calculated excitation energies lead to wave lengths near 6000 \AA. and 4300 \AA. , respectively, the precise values depending rather more on the choice of values of δ or ω than on the use of the semi-localized *versus* the delocalized model (see Table IIIB); in other words, they are not greatly affected by hyperconjugation. These wave lengths correspond to the mean of the singlet and triplet excited state in each transition, so that the predicted frequencies are subject to the additional uncertainty resulting from the singlet-triplet separation. If one assumes the latter to amount to 2.0 e.v. in both cases, the predicted wave lengths for transition to the singlet states become 4000 and 3200 \AA. , respectively.

TABLE III

FREQUENCIES OF CALCULATED SPECTRAL TRANSITIONS (IN UNITS OF $-\beta = 60 \text{ KCAL./MOLE}$)

A. Approximate Delocalized Model, assuming $\omega = 0$ and uniform α 's and β 's for ring atoms, for several trial values of δ . (From results at top of Table IA)

| Transition | $\delta = -0.50$ | $\delta = -0.25$ | $\delta = 0.00$ | $\delta = 0.25$ | $\delta = 0.50$ |
|---------------|------------------|------------------|-----------------|-----------------|-----------------|
| $3b_1 - 1a_2$ | 0.9356 | 0.8654 | 0.8000 | 0.7406 | 0.6876 |
| $3b_1 - 2b_1$ | 1.1938 | 1.1564 | 1.1214 | 1.0883 | 1.0570 |

B. Improved Delocalized and Semi-localized Models, for $\delta = 0$ but with α 's and β 's made self-consistent for three trial values of ω . (Based on calculations for Table IB)

| Transition | $\omega = 0$ | $\omega = 2$ | $\omega = 4$ |
|------------------------------------|--------------|--------------|--------------|
| Delocalized model $3b_1 - 1a_2$ | 0.813 | 0.723 | 0.702 |
| $3b_1 - 2b_1$ | 1.116 | 1.030 | 1.013 |
| Semi-localized model $3b_1 - 1a_2$ | 0.821 | 0.691 | 0.655 |
| $3b_1 - 2b_1$ | 1.196 | 1.084 | 1.059 |

The intensities of the two transitions may be estimated from the same coefficients as were used to compute the charges and bond orders. Following Mulliken and Rieke,³⁴ we use as a measure of the intensity the dipole strength D defined by

$$D = Q^2; \vec{Q} = \int \psi_i \sum_{\text{electrons}} \vec{\gamma}_e \psi_j d\tau \cong \sqrt{2} \sum_m c_{mi} c_{mj} \vec{\gamma}_m$$

(33) R. S. Mulliken and C. C. J. Roothaan, *J. Chem. Phys.*, **16**, 118 (1948).

(34) R. S. Mulliken and C. A. Rieke, *Reports on Progress in Physics*, **8**, 231 (1941), pp. 232, 256, especially eq. 35. In eq. 35 a factor $\sqrt{2}$ (see eq. 29) was unfortunately omitted; this is included here.

for the transition from electronic state ψ_i to ψ_j , where \vec{r}_m is the position vector of the m^{th} atom in some convenient reference system and the c 's are LCAO coefficient derived with the normalizing relation $\sum_m c_{mi}^2 = 1$.

Using the coefficients for $\delta = 0$ and the simplest approximation, we find that for the $a_2 \rightarrow b_1$ transition the predicted dipole strength is about 0.72 , while for the $b_1 \rightarrow b_1$ transition it is about 1.48 , in units of 10^{-16} cm.^2 . The corresponding oscillator strengths or f values, given by eq. 2 of reference 34 as $f = 1.085 \times 10^{11} \nu D$ (cm.^2), are 0.2 and 0.5 , if the transitions are assumed to be at 4000 and 3200 \AA. , respectively. However, according to section 7(g) of reference 34, the observed f 's may be expected to be considerably smaller than (perhaps about 0.3 as large as) the calculated values.

Recently C. Reid,³⁵ has studied the absorption spectra of benzenium, toluenium and other aromatic carbonium ions. For the benzenium and toluenium ions he observed the first absorption transition at about 4200 \AA. , followed by a second stronger one with maximum (not reached) somewhat below 3000 \AA. , and with respective f values of roughly 0.15 and perhaps 0.4 . The agreement with the predictions made above is fairly satisfactory, considering the uncertainties in the latter.

11. **Charges and π Bond Orders.**—Figure 2 shows the computed charges and π bond orders corresponding to some of the various approximations or assumptions used above (see Table II for further values).

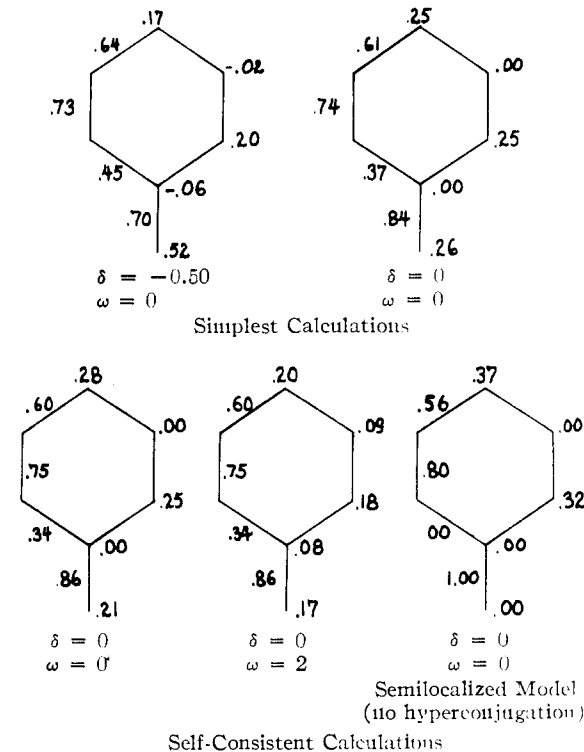
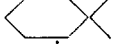



Fig. 2.—Charges and π bond orders.

(35) C. Reid, *This Journal*, **76**, 3264 (1954).

It is seen that the calculated π bond orders of the 2-3 and 2-7 bonds (see Fig. 1 for numbering) are greatly increased by the inclusion of hyperconjugation, in part at the expense of that of the C=H₂ bond. It is also seen that hyperconjugation permits a considerable migration of negative charge from the H₂ into the ring (even for $\delta = 0$).

The charge distributions in Fig. 2 have, for the case $\delta = 0$, $\omega = 0$, an interesting relation to some considerations of Longuet-Higgins³⁶ on zero-energy orbitals in alternant hydrocarbon radicals. The ion C₆H₇⁺ is the cation of the cyclohexadienyl free radical  (C₆H₇). This radical may be said to be hyperisoaromatic with the benzyl radical , which is an alternant hydrocarbon. That is to say, it has the same number of π electrons, arranged geometrically in the same way, as the benzyl radical, provided we count the quasi- π electron of the H₂ group in cyclohexadienyl as equivalent to the π electron on the carbon atom of the methylene group of the benzyl radical. As a consequence, provided $\delta = 0$ and $\omega = 0$, Longuet-Higgins' considerations should be applicable to the cyclohexadienyl radical and its cation. Accordingly, the last electron in the radical should be in a zero-energy orbital, with its LCAO coefficients zero on atoms 2, 4 and 6, and given by

$$\sum_n \beta_{ns} c_s = 0 \quad (6)$$

on atoms 1, 3, 5 and 7 (c_s = LCAO coefficient, $s = 1, 3, 5, \text{ or } 7$; β_{ns} = resonance integral (see section 2) between s and any of its next-neighbors n). In agreement with these considerations, $c_2 = c_4 = c_6 = 0$ is found according to our calculation for $\delta = 0$, $\omega = 0$, independently of the values of the β 's.

If all the β_{cc} 's are assumed equal and β_{12} is $2\beta_{cc}$ (cf. Section 3), eq. 6 leads to $c_1 = c_3 = c_5 = c_7 = 0.50$. Now if the zero-energy electron is removed from the radical to form C₆H₇⁺, the resulting positive charge should be c_s^2 on each atom, that is, zero on atoms 2, 4, 6, and 0.25 on atoms 1, 3, 5, and 7. As can be seen from Fig. 2 or Table II for the case $\delta = 0$, $\omega = 0$, with all β_{cc} 's taken equal ("simplest calculations"), this is in almost exact agreement with the results of our calculations. (The slight discrepancies may probably be attributed to the fact that we did not assume S_{12}/S_{cc} exactly equal to β_{12}/β_{cc} ; Longuet-Higgins assumed all β 's proportional to the corresponding S 's.) It will also be noted that the orbital energy of the 3b₁ MO in Tables IA and IB (the 3b₁ in C₆H₇⁺ is the lowest unoccupied MO, which would be occupied by the odd electron in C₆H₇), is precisely zero for $\delta = 0$, $\omega = 0$, in agreement with the considerations of Longuet-Higgins.

12. Hyperconjugation Energy.—The best value of the net HCJE within the scheme adopted here would correspond probably to $\omega \cong 1.4$ and $\delta = -0.5$, and would be about 14.5 kcal. This would probably be somewhat increased by the use of self-consistent-field rather than Slater S values, since with the assumption that β is proportional to S , the SCF S 's lead to a smaller value for β_{12}/β_0 , which is

(36) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 275 (1950), in particular the equation $\sum_{s \neq r} \beta_{rs} c_s^0 = 0$ and related discussion.

more favorable for hyperconjugation (cf. Section 3). In any event, the predicted hyperconjugation energy of the benzenium ion is of the same order of magnitude as usual resonance energies, and should approximately restore the ring conjugation energy which in the previous calculations⁹ seemed to have been largely lost.

We wish to draw attention to the fact that the present calculations lead to this extraordinarily large HCJE even though the parameters are given about the same values as those used in previous computations for other molecules^{8b, 13a, 18} where HCJE's an order of magnitude smaller were found.

Large HCJE's are also found in observations³⁷ and calculations in progress on alkyl radicals and especially their ions. Large computed HCJE's have also been found^{13c} for twisted ethylene, a neutral molecule with two three-center hyperconjugated systems in mutually perpendicular planes. In both these cases parameter values similar to those of the present paper were used.³⁸

Observations such as those of reference 36a provide an experimental test of the methods used in the present paper. Such a check is unfortunately not available for the benzenium ion itself, since it would be necessary to predict the equilibrium constant for the reaction C₆H₆ + H⁺ \rightleftharpoons C₆H₇⁺, and such a prediction would be subject to a large uncertainty arising from the lack of a reliable method of estimating the solvation energies involved.

13. Charge Transfer and Hyperconjugation.—Comparison of the calculated HCJE's in Table IA for different δ values, and of those in Table IB for different ω values, shows that while the HCJE for C₆H₇⁺ is relatively large in any case, it is much increased when hyperconjugation is accompanied by the partial equalizations of charge distribution which occur if $\delta < 0$ (as it is believed to be) and when allowance is made for the fact that $\omega > 0$. One might claim that all the stabilization resulting from charge redistribution should be attributed to an "inductive" (better, a "charge transfer") effect. This, however, is not justified. Without hyperconjugation (that is, if the CH₂ group remained insulated from the π electrons of the remaining ring atoms), there would indeed be a considerable amount of inductive stabilization among the ring atoms; but there is *additional* stabilization, here called HCJE (namely, the energy difference between the semi-localized and delocalized models in Tables IA and IB) when this insulation is removed; and this additional stabilization is greater for $\delta < 0$ and/or $\omega > 0$ than if $\delta = \omega = 0$ is assumed. It can of course still be argued that the excess of HCJE which appears for $\delta < 0$ or $\omega > 0$ is not *pure* HCJE, but belongs to a *joint* inductive-hyperconjugative (or charge transfer-hyperconjugative) effect; but by the same argument, this excess can also at any rate not be considered as pure inductive or charge-transfer energy. The argument reduces

(37) (a) Cf. Franklin and Lumpkin, *J. Chem. Phys.*, **20**, 745 (1952); Halpern, *ibid.*, **20**, 744 (1952); (b) cf. also calculations by J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

(38) It may be noted that all these cases where large HCJE's have been found are associated with *odd numbers* of centers bearing π or quasi- π electrons, whereas the more familiar cases with HCJE's an order of magnitude smaller are associated with *even numbers* of centers.

to a matter of definitions. We believe that it is appropriate and convenient to define, as we have done, the whole of the *increased* energy stabilization which results when hyperconjugation is taken into account as HCJE. (Similar problems of definition arise in some cases for ordinary conjugation or resonance, especially frequently where ions are concerned.)

Large shifts in ultraviolet N,V spectra on methylation are known, even for simple neutral molecules of the alternant hydrocarbon type, such as ethylene, butadiene and benzene, which can be accounted for by hyperconjugation^{13a,18} using parameter values similar to those of the present paper. For the same molecules, methylation causes

changes (decreases) of still larger magnitude in ionization potential. A fraction of the observed decrease can be accounted for^{13a} by hyperconjugation in the ion without charge transfer (*i.e.*, assuming $\delta = 0$, $\omega = 0$). In view of the great increase in computed HCJE found in the present paper in the case of $C_6H_7^+$ when allowance is made for charge transfer, it seems likely that the remainder of the observed decreases in ionization potential on methylation could be accounted for in terms of hyperconjugation with charge transfer, using self-consistency procedures as in the present paper. Such computations, however, have not yet been made.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Sorption of Acetylene by Silver Nitrate

BY F. W. KIRSCH AND K. A. KRIEGER

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Silver nitrate catalysts important in the low temperature oxidation of acetylene have been studied as they function in oxidation and in the chemisorption stage which is an essential precursor to oxidation. Primary emphasis was given to phenomena occurring below 130°, which is the maximum temperature at which sorption is not complicated by oxidation. Measurement of sorption rates revealed an inverse relation between rate and acetylene pressure. This observation has been interpreted as an "autopoisoning" effect, which produces a layer of acetylene polymer resistant to penetration. Sorption rate can be correlated with the amount of free acetylene and of available surface, but regularly occurring discontinuities strongly suggest critical changes in the sorbent during sorption. Oxidation, with products identified as carbon dioxide, water, nitric oxide, nitrogen and possibly silver, proceeds at temperatures above 149° after a critical amount of acetylene sorption.

Introduction

A study of the low temperature oxidation of acetylene as catalyzed by silver nitrate supported on alumina revealed some steps in the process worthy of separate and more detailed research.¹ Foremost among these phenomena is the removal of acetylene from acetylene-air mixtures in a continuous process without a concomitant evolution of carbon dioxide in the product stream. This occurrence prompted efforts to clarify further the reaction mechanism with particular emphasis on the sorption step believed to be a prerequisite for oxidation.

In this study the sorption of acetylene on pure silver nitrate at temperatures between 96 and 170° was investigated in a closed system without gaseous oxygen. Preliminary tests having shown acetylene sorption by alumina to be immeasurably slow below 200°, the method of this research offered a somewhat simplified scheme for elucidating the sorption mechanism. Rates of sorption were measured in the lower temperature range; and, although oxidation complicates the picture somewhat at higher temperatures, it was found possible to elicit additional information on the sorption process.

Experimental

A. Materials.—The silver nitrate was prepared from C.P. grade salt by grinding and sizing through 200-mesh silk screens. At all times the sorbent was protected as much as possible from air and light before use.

Acetylene from commercial cylinders was passed suc-

cessively through aqueous solutions of sodium bisulfite and sodium hydroxide and then dried before use.

B. Analyses.—Gas analyses were carried out with samples between 0.02 and 0.2 cc. (STP) by absorption in ammoniacal cuprous sulfate solution and measurement of acetylene by a colorimetric method.² For larger samples from experiments involving oxidation, CO₂, NO, C₂H₂ and CO were determined by differential absorption in standard reagents.

C. Apparatus and Procedure.—The apparatus used in this study was a constant volume, static system in which the sorption rates were quantitatively determined by following the decrease in gas pressure as a function of time.

Essentially the sorption system consisted of a furnace-enclosed Pyrex cylinder, to which a Zimmerli gage was attached. Pressures were read from the gage with a cathetometer. The sorption system proper, the product removal line, and the gas storage section were evacuated prior to sorption by an oil pump and a single-stage mercury diffusion pump, which produced a residual pressure of 4 to 9 × 10⁻⁶ mm.

Between the gas-storage section and the sorption system, a doser-bulb contained the acetylene before it was admitted for sorption.

Constant furnace temperatures were maintained by a Thyatron regulator within about ±0.25°, and sorption temperatures were determined by a Chromel-Alumel couple inserted in a thermowell extending from the outer end to the center of the sorption tube.

A sampling line, separated from the sorption section by a stopcock, contained a manually operated Töpler pump to assist in the removal of residual gas after completion of the process.

D. Reversibility of Sorption and Attainment of Equilibrium.—When excess acetylene was admitted to samples of silver nitrate which had been thoroughly out-gassed at pressures of the order of 9 × 10⁻⁶ mm., a rapid decrease in pressure occurred. Additional quantities of acetylene admitted subsequently experienced no decrease in pressure

(1) W. T. M. Johnson and K. A. Krieger, *THIS JOURNAL*, **76**, 4782 (1954).

(2) T. A. Geissman, S. Kaufman and D. Y. Dollman, *Anal. Chem.*, **19**, 919 (1947).