Bond Localization and the Hyperconjugative Effect in the Aromatic Carbonium Ions. I. Absorption Spectra of Benzenium-, Toluenium-, and Mesitylenium- Ions[1]

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Reid's measurements of the absorption spectra of methylbenzenes in anhydrous hydrogen fluoride-boron trifluoride indicate that the bands of the longest wave length which Reid attributed to those of carbonium ions of methylbenzenes shift toward violet with the increasing number of methyl substituents[2]. To investigate this phenomenon theoretically seems to be of much interest. In performing the theoretical treatment on these carbonium ions, it should be taken into account, whether the hyperconjugation takes place or not between the aromatic ring and the H_2 group constructed by the attached proton together with the hydrogen atom already present at the position of proton attack in the ring. Under the assumption of localization of the H_2—C bond with respect to the conjugated part of molecules, Gold and Tye[3] have calculated the π-electron energies of the carbonium ions of many hydrocarbons and have suggested the order of base strengths of hydrocarbons[4]. Heilbronner and Simonetta[5] have also carried out similar computations on azulenium- and methyl azulenium- ions from the standpoint of the same hypothesis. In addition, it seems to be reasonable that these carbonium ions correspond to the transition state intermediates in the electrophilic substitution reactions from the fact that in methylbenzenes, a parallel relation exists between the equilibrium constants for the carbonium ion

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[1] As to the review on the experimental results, see, L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

[2] C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954).

[3] V. Gold and F. L. Tye, *J. Chem. Soc.*, **1952**, 2184.

[4] For polymethyl benzenes which are the objects of the present study, calculations have not been carried out.

[5] E. Heilbronner and M. Simonetta, *Helv. Chim. Acta*, **35**, 1049 (1952).

formation and the rates of substitution in the electrophilic substitution reactions, with respect to the number of methyl substituents in the aromatics[6], and moreover the bond localization theory has gained much success in the interpretation of chemical reactivities[7-10], so that in the case of the aromatic carbonium ion also, the bond localization hypothesis will have much importance in the consideration of its behavior. On the other hand, Muller, Pickett, and Mulliken[11] have discussed the hyperconjugative effect of the H_2 group, and explained the absorption spectra of the benzenium ion. Generally speaking, it may be desirable to take the hyperconjugative effect of the H_2 quasi-atom into consideration. In the following, consequently, the experimental blue shifts are treated by the theoretical computation for benzenium-, toluenium- and mesitylenium- ions, using the semi-empirical LCAO MO method, from the point of the localization, on the one hand, and of the hyperconjugation, on the other, of the H_2—C bond.

Method of Calculation

Molecular Models. — The molecular models and the numbering in the present calculations are shown in Fig. 1 for the hyperconjugation and in Fig. 2 for the bond localization, in both cases (a), (b), and (c) being benzenium, toluenium, and mesitylenium ions, respectively. The attached proton at position 2 in the ring constructs the quasi-atom H_2 together with the hydrogen atom already present there, which takes part in hyperconjugation with the aromatic ring for the hyperconjugation model, but not for the bond localization one. The symmetry group to which these ions belong is C_{2v}. As for toluenium ion, there are other different models depending on the position at which proton attaches to the ring with respect to the methyl substituent, but only the C_{2v} type is adopted, because the selection rule is not applied to the molecules having attached proton at ortho- or meta-position with regard to the carbon atom linking to the methyl substituent, on account of lack of symmetry; furthermore it seems not bad to adopt the C_{2v} type from the analogy of the *p*- (and *o*-) orienting effect of the methyl substituent in the electrophilic substitution reaction of toluene.

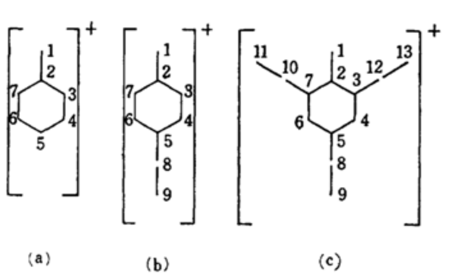

Fig. 1. Molecular models for the hyperconjugation.

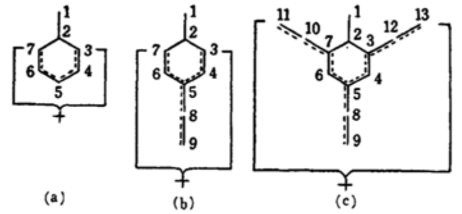

Fig. 2. Molecular models for the bond localization.

Inclusion of Overlap.—Effects of neglect and inclusion of overlap on the various quantities, such as π-bond order, π-electron density, dipole moment, resonance energy, hyperconjugation energy, and absorption wave length, have been discussed in the numerous hydrocarbons and heteromolecules. As regards bond lengths, dipole moments and resonance energies there are little differences between their magnitudes calculated with and without overlap[12-16]. Mulliken et al.[17] have found that explicit inclusion of overlap improves the agreement of the calculations with the observed hyperconjugation shift in the ultraviolet absorption spectra, and with hyperconjugation energies, whereas for these empirical data the calculations without overlap gain less success[18]. Consequently in the present treatment also, overlap integrals between adjacent atoms are included.

Molecular Orbitals and Secular Equations.—Molecular orbitals used are of the

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[6] H. C. Brown, and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

[7] G. W. Wheland, ibid., **64**, 900 (1942).

[8] M. J. S. Dewar, *J. Chem. Soc.*, **1949**, 463.

[9] C. A. Coulson, *Research*, **4**, 307 (1951).

[10] R. D. Brown, *Quart. Rev.*, **6**, 63 (1952).

[11] N. Muller, L. W. Pickett and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1400 (1953); *J. Am. Chem. Soc.*, **76**, 477 0 (1954).

[12] D. W. Davies, *Trans. Faraday Soc.*, **51**, 449 (1955).

[13] T. H. Goodwin and V. Vand, *J. Chem. Soc.*, **1955**, 1683.

[14] T. H. Goodwin, ibid., **1955**, 4451.

[15] R. H. Knipe, *J. Chem. Phys.*, **23**, 2089 (1955).

[16] G. W. Wheland, *J. Am. Chem. Soc.*, **63**, 2025 (1941).

[17] R. S. Mulliken and C. A. Rieke, ibid., **63**, 1770 (1941).

[18] R. S. Mulliken, C. A. Rieke and W. G. Brown, ibid., **63**, 41 (1941).

LCAO (linear combination of atomic orbitals) type $\psi_j=\sum_{\mu} x_{j\mu}\phi_\mu$, where ψ_j is the j'th MO (molecular orbital), ϕ_μ the AO (atomic orbital) on the μ'th atom, $x_{j\mu}$ the coefficient of the μ'th AO in the j'th MO, ψ_j. The energies of the π-electron levels are given by the roots of the secular equation[10,19],

$$|\beta_{\mu\nu}+S_{\mu\nu}\lambda_{\mu\nu}|=0,$$

where

$$\beta_{\mu\nu}=\gamma_{\mu\nu}-(1/2)S_{\mu\nu}(\alpha_\mu+\alpha_\nu),$$

$$S_{\mu\nu}=\int\phi_\mu\phi_\nu d\tau,$$

$$\lambda_{\mu\nu}=(1/2)(\alpha_\mu+\alpha_\nu)-\varepsilon_j,$$

and

$$\gamma_{\mu\nu}=\int\phi_\mu H\phi_\nu d\tau, \quad \alpha_\mu=\int\phi_\mu H\phi_\mu d\tau,$$

$$\varepsilon_j=\int\psi_j H\psi_j d\tau.$$

The coefficient of each atomic orbital in the molecular orbital is computed by solving linear equations under the normalization condition of the molecular orbital with the knowledge of the energy of the latter.

Assumptions and Choice of Semi-empirical Parameters.—In the semi-empirical method, appropriate values of the resonance and the Coulomb integrals must be chosen. As for the resonance integrals several authors[6,20,21] have used the assumption of the proportionality of the parameter γ to the overlap integral S. However, in the present work the parameter β introduced for the first time by Mulliken[22] is assumed proportional to S[23]. Values of overlap integrals are obtained from Mulliken et al.[24], and those used in the present calculation are like those in Table I. For the value of the corrected term δ for the Coulomb integral of H_3 or H_2, several authors have used the empirical values of -0.2[4,6,25-28] or -0.5[10,20,21]. The value used in the present work is -0.3 obtained by I'haya[29] through the theoretical calculations.

TABLE I

VALUES OF OVERLAP INTEGRALS USED IN THE PRESENT CALCULATIONS

Bonds	Values of overlap integrals
$C—H_2$ or $C—H_3$	0.541[a]
$C_{methyl}—C_{arom}$[b]	0.203[c]
C—C[d]	0.247

a). See, ref. 21), footnote 27. b). The bond between the methyl carbon and the neighboring carbon atom in the ring. c). The value corresponding to the interatomic distance of 1.51 Å. d). The bond between the adjacent carbon atoms in the benzene ring.

The choice of the auxiliary inductive parameter, δ_{ind}, for the Coulomb integral of the carbon atom with which the H_3 or H_2 quasi-atom binds is considerably arbitrary and its decision is essentially empirical, although Goodman and Shull[30] have pointed out the possibility of finding the reasonable values from the experimental transition- and ionization-energy shifts due to this effect. Various values of this parameter have been used, such as $\delta_{ind}/\delta=1/4\sim1/10$[31], $1/2$[25], $1/5$[20], $1/8$[32,33] and $1/3\sim1/5$[34]. In the present treatment $\delta_{ind}/\delta=1/3$ is used in accordance with many investigators' arguments[35-37]. The use of this parameter is limited to the case of the bond localization calculations.

The Hyperconjugation Energy

The hyperconjugation energy, for example, of benzenium ion, is obtained as follows. (1) The π-electron energies of the hyperconjugation and of the bond localization model are calculated. (2) The vertical hyperconjugation energy is obtained by subtracting the ground state π-electron energy of the hyperconjugation model from that of the bond localization one. (3) The correction of the compressional energies[38] is carried out assuming that the bonds are distorted harmonically, taking the values of force constants,

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[19] L. Lofthus, ibid., **79**, 24 (1957).

[20] C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, **1953**, 2052.

[21] Y. I'haya, This Bulletin, **28**, 376 (1955).

[22] R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949).

[23] R. S. Mulliken, ibid., **46**, 675 (1949).

[24] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[25] B. Pullman, M. Mayot and G. Berthier, ibid., **18**, 257 (1950).

[26] H. C. Longuet-Higgins and R. G. Sowden, *J. Chem. Soc.*, **1952**, 1404.

[27] C. A. Coulson, *Proc. Phys. Soc.*, **45**, 933 (1952).

[28] H. H. Jaffé, *J. Chem. Phys.*, **20**, 778 (1952).

[29] Y. I'haya, ibid, **23**, 1165 (1955).

[30] L. Goodman and H. Shull, *J. Chem. Phys.*, **23**, 33 (1955).

[31] G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

[32] P. O. Löwdin, *J. Chem. Phys.*, **19**, 1323 (1951).

[33] H. H. Jaffé, *J. Am. Chem. Soc.*, **76**, 3527 (1954).

[34] Y. I'haya, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 314 (1956).

[35] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry" Prentice-Hall, Inc., New York, 1941.

[36] V. Gold, *Trans. Faraday Soc.*, **46**, 326 (1950).

[37] H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 778, 1554 (1952); **21**, 415 (1953); *J. Am. Chem. Soc.*, **77**, 274 (1955).

[38] Lennard-Jones, *Proc. Roy. Soc.*, A **158**. 280 (1937); D. F. Hornig, *J. Am. Chem. Soc.*, **72**, 5772 (1950); C. A. Coulson, and S. L. Altmann, *Trans. Faraday Soc.*, **48**, 293 (1952).

TABLE II

ELECTRIC STATES AND TRANSITION PROCESSES

Carbonium ions	Ground state	Lowest excited state	Transition	Polarization
Benzenium	$(1b_1)^2(2b_1)^2(1a_2)^2$	$(1b_1)^2(2b_1)^2(1a_2)^1(3b_1)^1$	$A_1 \rightarrow B_2$	y
Toluenium	…………… $(3b_1)^2(1a_2)^2$	…………… $(3b_1)^2(1a_2)^1(4b_1)^1$	$A_1 \rightarrow B_2$	y
Mesitylenium	………………………………… $(4b_1)^2(2a_2)^2$	…………………… $(1a_2)^2(4b_1)^2(2a_2)^1(5b_1)^1$	$A_1 \rightarrow B_2$	y

TABLE III

THE FIRST TRANSITION ENERGIES CALCULATED FOR TWO MODELS AND EXPERIMENTAL VALUES

Carbonium ions	For hyperconjugation model (unit of $-\beta$)	For bond localization model (unit of $-\beta$)	Absorption wave length observed (A)	Oscillator strength observed
Benzenium	0.87083	0.80193	4170	0.15
Toluenium	0.87902	0.81574	4000	0.15
Mesitylenium	0.81801 0.81445	0.76018	3900	0.27

TABLE IV

THEORETICAL DATA FAITHFUL TO REID'S EXPERIMENTS

Carbonium ions	Model	Singlet-triplet separations assumed (eV)	Longest absorption wave length (A)	Oscillator strength
Benzenium	Bond localization	1.77	4168	0.31
Toluenium	Bond localization	1.95	3999	0.20
Mesitylenium	Hyperconjugation	2.10	3909	0.32

TABLE V

THE SECOND TRANSITIONS CALCULATED FOR TWO MODELS

Carbonium ions	Transition	Polarization	Transition energies for hyperconjugation (unit of $-\beta$)	Transition energies for bond localization (unit of $-\beta$)
Benzenium	$A_1 \rightarrow A_1$ $(2b_1 \rightarrow 3b_1)$	z	1.18005	1.21308
Toluenium	$A_1 \rightarrow A_1$ $(3b_1 \rightarrow 4b_1)$	z	1.09208	1.09131
Mesitylenium	$A_1 \rightarrow A_1$ $(4b_1 \rightarrow 5b_1)$	z	1.09661	0.93919

4.50×10^5, 9.57×10^5, and 4.80×10^5 dyne/cm. for C—C, C=C, and C—H bonds[39], respectively, and calculating π-bond orders by the following relations of Chirgwin and Coulson[40],

$$p_{\mu\nu} = (1/2)\sum_{j=1}^{m} n_j (x_{j\mu} y_{j\nu} + x_{j\nu} y_{j\mu}),$$

$$\nu, \mu = 1, 2, \cdots\cdots n, ; \nu \neq \mu,$$

$$y_{j\mu} = \sum_{\nu=1}^{n} S_{\mu\nu} x_{j\nu},$$

n_j : number of electrons occupying the j'th MO,

m : number of occupied molecular orbitals,

bond lengths being obtained by the correlation between the bond length and the total bond order[41]. Calculations show 10.28 kcal/mole[42] for the hyperconjugation energy.

It will be noticed here that this value is too large for the hyperconjugation energy itself, which is usually of the order of a few kcal./mole. Positive δ values indicate smaller hyperconjugation energies[10], but from the electronegativity consideration of the H_2 quasi-atom compared with the $2p\pi$ carbon negative values of δ will be accepted[10]. The value —0.3

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[39] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", B. Van Nostrand, New York, N. Y. 1945, p. 193.

[40] B. H. Chirgwin and C. A. Coulson, *Proc. Roy. Soc.*, A **201**, 196 (1950).

[41] C. A. Coulson, ibid., A **169**, 413 (1939).

[42] Energies are expressed by the unit of β, the resonance integral including overlap between the neighboring carbon atoms in benzene molecule, and in converting those into the unit of kcal. $\beta = -60$ kcal./mole is used. See, C. C. J. Roothaan and R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).

for δ gives the smaller hyperconjugation energy than the value -0.5 does[10]. However, the difference between both cases is small and, in addition, $\delta=-0.5$ is adequate to account for the dipole moment and the spectral shift as well as the hyperconjugation energy of toluene[20,21]; consequently, it will not be of importance which value of these will have to be chosen. Matters will probably be otherwise; in fact the improved calculations by means of the self-consistent technique by Muller, Pickett, and Mulliken[10] show the smaller hyperconjugation energy, 5.9 kcal./mole. In relation to this, it will be very interesting to carry out the ASMO calculations.

The Spectra

Calculated results on the spectra and comparisons with experiments are indicated in Tables II, III, IV and V.

Table II shows the electronic states and transition processes for the first transitions. For these three aromatic carbonium ions, the manner in which electron transitions occur is the same, namely one electron elevates from the a_2 to the b_1 orbital, transition process being $A_1 \rightarrow B_2$, and polarization is in the y direction which is perpendicular to the molecular axis, z, and lies in the molecular plane.

Table III indicates the experimental values and the calculated transition energies for the first transitions. The experimental values of the absorption wave lengths in the fourth column are taken from the paper of Reid[11] and experimental oscillator strengths in the last column are determined roughly by the author on the basis of the experimental extinction curves by Reid through the following relation[43],

$$f=4.32\times10^{-9}\int\varepsilon_{\nu}d\nu,$$

where f is the oscillator strength, and ε_{ν} the extinction coefficient of the observed absorption of frequency ν. The calculated transition energies for the case of the bond localization model are those obtained using $\delta=-0.3$ as well as the auxiliary inductive parameter, $\delta_{\text{ind}}=-0.1$, while those for the hyperconjugation model correspond to the values obtained using only $\delta=-0.3$, except the second value of mesitylenium ion, the calculation of which includes $\delta_{\text{ind}}=-0.1$ also. All these are mean values of the transition energies to the singlet and the triplet excited states; consequently, in order to compare these calculated values with observed ones, an additional factor must be taken into account, e.g. the singlet-triplet separation in the excited state. Here, if it is assumed that the singlet-triplet splittings of these three molecules are not the same in general, but may not differ very much from each other, then it seems safe to let the calculated mean transition energies have the same tendency as the absorption shifts observed among these three substances. According to Table III, and from the view point just mentioned, the calculated mean transition energies for these three ions can explain the experimental "blue-shifts" in terms of neither the hyperconjugation nor the bond localization, although only the "blue-shift" of toluenium relative to benzenium ion is predicted by both models. At this point, if the bond localization rather than the hyperconjugation model is preferably chosen for benzenium and toluenium ion, while the hyperconjugation rather than the bond localization model, for mesitylenium ion, then there will be no contradiction between theories and experiments. However, this remains only to be an arrangement of the calculated results, so as to be faithful to Reid's measurements, and the critical discussion on this point will be performed in the following section.

The theoretical data arranged so as to be faithful to Reid's experiments are indicated in Table IV. When the values of siglet-triplet separations are assumed to be such as those shown in the third column and for the purpose of obtaining only the transition energies to the singlet excited states, a half of those values are added to the mean transition energies; the absorption wave lengths thus calculated may accord with the experimental values (compare the fourth column of Table IV with the fourth column of Table III). The theoretical oscillator strengths in the fifth column are computed by the relation[44],

$$f=1.085\times10^{11}\nu D,$$

$$D=Q^2,$$

$$\vec{Q}=\sqrt{2}\sum_{\mu}x_{i\mu}x_{j\mu}\vec{r}_{\mu},$$

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[43] J. R. Platt and H. B. Klevens, *Rev. Mod. Phys.*, **16**, 182 (1944).

[44] R. S. Mulliken and C. A. Rieke, *Reports on Progress in Physics*, **8**, 231 (1941).

where, ν is the absorption frequency (in cm.$^{-1}$); D, the dipole strength; $x_{i\mu}$, $x_{j\mu}$, coefficients of μ'th atom in the molecular orbitals, i and j, respectively, which are concerned with the electron jump; $\vec{r}_\mu$, the position vector of the μ'th atom with respect to some convenient origin. Oscillator strengths calculated and observed agree satisfactorily with each other.

Calculated results for the second transitions are shown in Table V. One electron concerning this transition elevates from the b_1 to the b_1 molecular orbital, and the polarization is in the direction of the molecular axis, z.

Discussion

In the preceding section the bond localization model is assumed for benzenium- and toluenium- ions and the hyperconjugation one for mesitylenium ion. This assumption is, however, only having put a finger on one possibility of the π-electron structures of these ions, and must be verified also from other criterions, which, however, unfortunately are not available at present.

Our calculation is only very approximate. The more rigorous approximation[11] including the self-consistent technique can not either determine distinctly which of the bond localization and the hyperconjugation model is suitable to benzenium ion, and further complicated factors, besides those pointed out by Coulson and Dewar[45], will have to be taken into account, such as configuration interactions, which are useful in predicting the absorption spectra, and screening effects by the electron distributions enhanced through the existence of the methyl substituents in the aromatic nucleus; it is difficult to carry out calculations including the former factor in the simple LCAO MO treatments on these systems in question[46]; furthermore, reasonable computations including the latter factor are difficult in the present step. Because our calculation is only rough, jumping from one model (bond localization) to the other (hyperconjugation) may be probably open to suspicion. Generally speaking, whenever the H_2 or H_3 group exists in conjugated systems, it may be adequate to assume the presence of its hyperconjugation[47].

In order to avoid these difficulties mentioned above, we assume that the hyperconjugation always occurs but its extent is different in each case of these ions in question; then it may be said that benzenium as well as toluenium is less hyperconjugated than mesitylenium ion, if we admit the simple theory and Reid's experiments. If, as in the preliminary report[48], the eigenfunction Φ of these ions is written by the linear combination of the eigenfunctions Φ_{HCJ} of the perfect hyperconjugation and Φ_{BL} of the bond localization model, Φ is the so-called hybrid and has commonly the lower energy than both models, while now we assume that Φ has the intermediate energy between the two extreme models, namely bond localization and perfect hyperconjugation models. In this respect there have been some confusions in the preliminary report.

There will be an additional way of treating these intermediate systems; that is, the systems having intermediate energies between those of the perfect hyperconjugation and bond localization models. Namely, by attributing different values to the resonance integrals between atoms 2 and 3 (Fig. 1 or Fig. 2) in these three molecules in question, computations on the spectra may be carried out. However, in so far as the approximation made is rough, the calculated results here also remain only to point out one possibility of the π-electron structures of these aromatic carbonium ions.

Recently Kilpatrick and Hyman[49] have measured the absorption spectra of benzene, mesitylene, and hexamethylbenzene in the various acids including anhydrous hydrogen fluoride. They have indicated the loss of fine structure at 260 mμ band of benzene due to the effect of the acidic environment and have been unable to detect the presence of the protonated benzene. They entertain a doubt on the absorption band which Reid attributed to that of benzenium ion[50]. Further Kilpatrick and Hyman have shown that the bands of protonated hexamethylbenzene shifts towards red compared to those of

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[45] C. A. Coulson and M. J. S. Dewar, *Discussions Faraday Soc.*, **2**, 54 (1947).

[46] As regards some alternant hydrocarbons, for example, polyacenes, inclusion of configuration interactions in the simple molecular orbital calculations, is possible. See, W. Moffitt, *J. Chem. Phys.*, **22**, 1820 (1954).

[47] The author wishes to express his sincere thanks to Professor R. S. Mulliken (University of Chicago) for his critical advice on these points (private communication to the author).

[48] T. Morita, *J. Chem. Phys.*, **25**, 1290 (1956).

[49] Private communication to Dr. S. Nagakura.

protonated mesitylene. This fact may suggest that the band of mesitylenium ion shifts towards red compared to that of toluenium ion. If so, our calculations may predict this red shift in terms of both the bond localization and the hyperconjugation models. Unfortunately measurements on toluene in anhydrous hydrogen fluoride have not been shown. Probably protonated toluene (and/or benzene) will occur in the system of anhydrous hydrogen fluoride and toluene (and/or benzene), but on account of its small quantity the absorption band of this carbonium ion seems not to exhibit itself.

Because of these experiments contrary to Reid's and because of the ambiguity of the absorption bands of benzenium and toluenium ions, we reserve making any conclusion about the calculated results. At any rate, at present, experimental facts are scarce, and the performance of experiments from various view points may be desirable.

Summary

The semi-empirical LCAO MO treatment on the spectra of benzenium, toluenium, and mesitylenium ions have been carried out. Neither the localization nor the hyperconjugation of the H_2—C bond with respect to the aromatic ring can explain the blue-shifts of the experimental spectra by Reid with the increasing number of methyl substituents. If, however, benzenium and toluenium ions are assumed to be less hyperconjugated than mesitylenium ion, the spectroscopic behaviors of these aromatic carbonium ions are understandable. However, if the mesitylenium band is assumed to shift towards red compared with toluenium by the analogy of the case of protonated hexamethylbenzene and mesitylenium ion, whose absorption spectra have been measured by Kilpatrick and Hyman, our theoretical calculations will predict well the case of mesitylenium and toluenium ion in terms of both the bond localization and the hyperconjugation models. Unfortunately, however, the measurement on toluene in acid medium have not yet been made. Further the case of benzenium ion is yet open to question. Consequently we reserve making any distinct conclusions on these three aromatic carbonium ions.

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50) Here see, H. Luther, and G. Pockels, *Z. Electrochem.*, 59, 159 (1955). Luther and Pockels' measurements of the absorption spectra of the system, benzene-$Al_2Br_6 \cdot HBr$(or -$Al_2Cl_6 \cdot HCl$) and toluene-$Al_2Br_6 \cdot HBr$(or -$Al_2Cl_6 \cdot HCl$), indicate different absorption wave lengths from those of Reid, and the absorption wave lengths are time-dependent, but the tendency of the blue-shifts of the spectra through the presence of the methyl substituents exists. However, it is questionable whether $[ArH]^+$, where Ar is the aromatic molecule, is responsible for these spectra. See also the paper by E. L. Mackor [*Chem. Weekblad*, 52, 240 (1956)], who suggested the presence of the more complicated complexes.