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The Electronic Structure of Carbonium Ions. Alkyl Cations and Protonated Hydrocarbons

Teijiro Yonezawa, Hiroshi Nakatsuji, and Hiroshi Kato

Contribution from the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto, Japan.
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Abstract: The electronic structure of alkyl cations and some protonated hydrocarbons has been studied by a semiempirical SCF MO treatment for valence electron systems. It is found that the inclusion of electron repulsion and core repulsion terms is essential for the successful investigation of charged species. Good agreements of calculated ionization potentials of alkyl radicals with experiments are obtained. The electronic excitation energies and oscillator strengths of some alkyl cations are presented; the energy changes in some ionic reactions are calculated, and the results compare satisfactorily with experiment. The change of σ and π electron populations with structural change in alkyl cations is investigated, and the comparison of the electronic structure of CH_5^+ and CH_5^- is carried out. The stable configurations of $C_2H_5^+$ and $C_2H_3^+$ are also examined.

The chemistry of carbonium ions has been developed extensively in recent years. Until recently, one of the most general features of carbonium ions was their transient character. But recently, it has been possible to capture carbonium ions in the form of stable salts with very strong acids.[1]

Theoretical studies of carbonium ions have been largely limited to conjugated cations and thereby the behavior of σ electrons, perhaps essential for the study of positively charged species, was left unsolved.

Recently, Hoffmann developed the extended Hückel theory[2] and applied it to some carbonium ions.[3] This was the first attempt to treat carbonium ions extensively, considering all valence electrons of the constitutent atoms, and was very instructive. But one of the shortcomings of this treatment was that the electron interaction and nuclear repulsion terms were not taken into account explicitly.

In the present work, the electronic structures of some carbonium ions have been studied with our newly developed semiempirical ASMO SCF method for valence electron systems.[4] The carbonium ions investigated are some alkyl cations, such as methyl, ethyl, *n*-propyl, isopropyl, isobutyl, and *t*-butyl cations, and some protonated hydrocarbons, such as protonated methane, protonated ethylene, and protonated acethylene. We also examined the electronic structures of some alkyl anions and CH_5^- as a reference.

One of the main purposes of this study is to examine the effects of the electron repulsion term in charged species. It has been found that the inclusion of electron

(1) (a) N. C. Deno, *Progr. Phys. Org. Chem.*, 2, 129 (1964); (b) G. A. Olah and C. U. Pittman, *Advan. Phys. Org. Chem.*, 4, 305 (1966).
(2) R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963).
(3) R. Hoffmann, *ibid.*, 40, 2480 (1964).
(4) T. Yonezawa, K. Yamaguchi, and H. Kato, *Bull. Chem. Soc. Jap.*, 40, 536 (1967). In these calculations, one-center exchange integrals are further considered. See also H. Kato, H. Konishi, and T. Yonezawa, *ibid.*, 40, 1017, 2761 (1967).

repulsion is essential especially for the successful investigation of orbital energies.

Method and Parameters

The molecular orbitals (MO's), φ_i's, are taken as a linear combination of all valence atomic orbitals (AO's), χ_r's, centered on the various atoms of the molecule. Roothaan's SCF equation[5] for a closed shell molecule is

$$\sum_r Cir(Frs - Srs\epsilon_i) = 0 \qquad (s = 1, 2, \cdots) \qquad (1)$$

where

$$Frs = Hrs + \sum_u Ptu[(rs|tu) - {}^1/_2(rt|su)] \qquad (2)$$

$$Srs = \int \chi_r \chi_s \, d\tau \qquad (3)$$

$$(rs|tu) = \int \chi_r(\mu)\chi_s(\mu) \frac{e^2}{r_{\mu\nu}} \chi_t(\nu)\chi_u(\nu) \, d\tau_\mu d\tau_\nu \qquad (4)$$

The atomic integrals appearing in the above equations are evaluated by the approximations previously reported.[4]

The additional improvement introduced in the present calculations is the inclusion of one-center exchange integrals with the approximations[6]

$$(2s,2p\sigma|2s,2p\sigma) = (2s,2p\pi|2s,2p\pi) = 0.200(2s,2s|2p\sigma,2p\sigma) \qquad (5)$$

and

$$(2p\sigma,2p\pi|2p\sigma,2p\pi) = (2p\pi,2p\bar{\pi}|2p\pi,2p\bar{\pi}) = 0.0604(2p\sigma,2p\sigma|2p\pi,2p\pi) \qquad (6)$$

The Wolfsberg–Helmholtz parameter, K, introduced[4] in the calculations of off-diagonal elements of Hrs[7] in eq 2 is set at 1.1 and 1.08.[8]

The total electronic energy (E) of the valence electrons is written as

$$E = {}^1/_2\sum_{rs} Prs(Hrs + Frs) \qquad (7)$$

and the total energy (W) of the molecule is obtained by

$$W = E + \sum_{A>B}\sum Z_A Z_B / R_{AB} \qquad (8)$$

in which the nuclear repulsion energy $\sum_{A>B}\sum Z_A Z_B/R_{AB}$ is calculated by the hole approximation[9]

$$\sum_{A>B}\sum Z_A Z_B/R_{AB} = \sum_{A>B}\sum Z_A Z_B(2S_A,2S_A|2S_B,2S_B) \qquad (9)$$

where Z_A and $2S_A$ are the core charge and the 2S AO of the atom, A, respectively.

In the present calculations, it is assumed that the cationic carbon of alkyl cation is in the trigonal state,[10] and that the bond distance between the sp^2 and sp^3 carbons is 1.50 Å. The bond distances between a carbon and a hydrogen atom and between sp^3 carbons are taken to be 1.09 and 1.54 Å, respectively.

Results and Discussion

In the present paper, we will discuss first the general results on the orbital energies and the electronic transitions of carbonium ions, and then enter into details of the electronic structures of alkyl cations and protonated hydrocarbons.

Orbital Energies. Carbonium ions are electron-deficient species compared with radicals or neutral molecules. Therefore, the destabilization due to the electron repulsion decreases in these species. Hence, the neglect of electron interaction and parametrization for neutral molecules will lead to too high orbital energies in carbonium ions. This is the case for the treatment of carbonium ions by the extended Hückel method. The orbital energies calculated for ethyl cation and staggered ethane by the extended Hückel method and the present method are compared in Table I. The ionization potentials (*IP*'s) of ethyl cation and ethane calculated by the extended Hückel method are 13.74 and 13.76 eV, respectively, and those calculated by the present method are 19.90 eV for $K = 1.1$, 19.42 eV for $K = 1.08$, and 12.09 eV for $K = 1.1$, 11.42 eV for $K = 1.08$, respectively. The *IP* of ethyl cation has never been reported, so far as we know, but it may be expected to be much larger than that of neutral molecule, which is compatible with the present results. On the other hand, the orbital energies of ethane calculated by the two different methods do not differ as much as in the case of the ethyl cation, and the *IP* calculated by our method agrees reasonably with the experimental value,[11] 11.65 eV. It seems therefore that the extended Hückel method may be approximately valid in the calculations of the neutral molecules, but invalid in those of the charged molecules such as cations and anions, where the term representing the electron interaction in eq 2 cannot be neglected.

Table I. Orbital Energies of Ethyl Cation and Staggered Ethane

	$C_2H_5^+$		Stag. C_2H_6	
	Hoffmann	Present, $K = 1.1$	Hoffmann	Present, $K = 1.1$
LV	−10.482	−8.696	3.212	13.917
HO	−13.744	−19.899	−13.763	−12.088
	−14.316	−20.222	−13.763	−12.589
	−15.295	−20.690	−14.126	−12.589
	−16.070	−22.677	−15.871	−14.918
	−21.231	−26.765	−15.871	−14.918
	−26.860	−30.563	−21.873	−19.757
			−26.711	−23.001

The orbital energies of methyl cation, methyl anion, and methane are compared in Table II. The changes of orbital energies are remarkable and their trends seem reasonable, for the lowest vacant (LV) and the highest occupied (HO) orbital energies correspond to the electron affinity and the *IP* of the referring molecules, respectively.

(5) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(6) H. Hinze and H. H. Jaffé, *J. Chem. Phys.*, **38**, 1834 (1963).
(7) The invariance of the Wolfsberg–Helmholtz approximation to rotation of the basis set in space is easily seen in eq 6 and 7 in ref 4, representing that Hrr's for $2p_x$, $2p_y$, and $2p_z$ AO's on the same atom become equal regardless of their orientation in space.
(8) The results obtained by adjusting K to 1.08 are almost parallel with those obtained by $K = 1.1$, so that we will show only the results obtained by $K = 1.1$.
(9) G. Del Re and R. G. Parr, *Rev. Mod. Phys.*, **35**, 604 (1963).
(10) Recently, Olah, *et al.*, substantiated the planar sp^2-hybridized structure of the simple alkyl cations in solution: G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964).
(11) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

Table II. Orbital Energies of Methyl Cation, Methane, and Methyl Anion

	CH_3^+, $K = 1.1$	CH_4, $K = 1.1$	CH_3^-, $K = 1.1$
LV	−9.661	11.740	18.878
HO	−21.618	−12.671	−0.290
	−21.618	−12.671	−3.371
	−29.053	−12.671	−3.371
		−20.137	−10.260

The ionization potential of a radical may be set approximately equal to the electron affinity of the corresponding cation.[12]

$$IP_{\text{radical}} = -\epsilon^{\text{LV}}{}_{\text{cation}} \tag{10}$$

But, in the above approximation, a further investigation should be required to adopt the energy of the LV orbital, since the LV orbital is not included in the SCF procedure.

An *IP* of a radical can also be calculated by

$$IP_{\text{radical}} = W_{\text{cation}} - W_{\text{radical}} \tag{11}$$

which is essentially a better approximation of the *IP* of a radical than eq 10, and may be used to check the validity of the LV orbital energy. The term, W_{radical}, appearing in eq 11 denotes the total energy of the referring radical and is calculated by the relation[13]

$$W_{\text{radical}} = W_{\text{anion}} + IP_{\text{anion}} \tag{12}$$

The *IP*'s of the alkyl radicals calculated by the above two methods are compared with the experimental values in Table III, where the *IP*'s calculated by eq 11 and 12

Table III. *IP*'s of Alkyl Radicals and Cations

	IP of radical		*IP* of cation,
	$K = 1.1$	Exptl[a]	$K = 1.1$
CH_3	9.661 (9.643)[b]	9.95	21.168
C_2H_5	8.696 (8.712)	8.78	19.899
n-C_3H_7	8.377	8.69	18.826
i-C_3H_7	7.410 (7.436)	7.90	19.423
i-C_4H_9	8.155	8.35	18.523
t-C_4H_9	5.885	7.42	19.513

[a] A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, **1**, 1 (1963). [b] The values in parentheses are calculated by eq 11.

are shown in parentheses. It is seen that the *IP* values calculated by both methods are very close and agree fairly well with experiments, and, hence, the validity of the LV orbital energies in SCF procedure may be assured.

Further, the calculated *IP* values of the alkyl cations are summarized in Table III. The *IP*'s of alkyl cations seem not to have been observed and these values should be checked by experiment.

The Electronic Transitions. Some calculated transition energies and transition moments of various alkyl cations are shown in Table IV. It is seen from the table that the lowest transitions of alkyl cations are excitations of the $\sigma \rightarrow \pi^*$ type and their intensity will be rather small.

(12) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 901 (1955).
(13) In these calculations, the geometries of cations and anions are assumed to be the same.

Table IV. Calculated Transition Energies (ΔE) and Transition Moments (Q) of Alkyl Cations

Cation	Type of transition[a]	$K = 1.1$ $^3\Delta E$, eV	$K = 1.1$ $^1\Delta E$, eV	$K = 1.1$ Q, Å	$K = 1.08$ $^3\Delta E$, eV	$K = 1.08$ $^1\Delta E$, eV	$K = 1.08$ Q, Å
CH_3^+	$\sigma-\pi^*$	2.06	2.47	0.0	1.56	1.95	0.0
$C_2H_5^+$	$\sigma_1-\pi^*$	3.91	4.07	0.110	3.51	3.63	0.103
	$\sigma_2-\pi^*$	2.27	3.28	0.179	1.78	2.39	0.188
	$\pi-\pi^*$	4.88	6.04	0.684	4.16	5.07	0.684
n-$C_3H_7^+$	$\sigma_1-\pi^*$	4.06	4.23	0.095	3.14	3.26	0.040
	$\pi-\pi^*$	4.99	5.55	0.526	4.44	4.85	0.451
	$\sigma_2-\pi^*$	4.91	5.06	0.170	4.33	4.50	0.181
i-$C_3H_7^+$	$\sigma_1-\pi^*$	4.52	4.79	0.098	3.34	3.65	0.085
	$\sigma_2-\pi^*$	4.89	5.17	0.162	3.94	4.24	0.179
	$\pi-\pi^*$	6.41	7.24	0.849	5.32	6.03	0.786
i-$C_4H_9^+$	$\sigma_1-\pi^*$	4.57	4.64	0.052	3.69	3.77	0.091
	$\sigma_2-\pi^*$	4.71	5.06	0.271	4.01	4.35	0.233
	$\pi-\pi^*$	5.28	6.39	0.718	4.28	5.34	0.704
t-$C_4H_9^+$	$\sigma_1-\pi^*$[b]	6.26	6.56	0.002	4.73	5.05	0.010
	$\sigma_2-\pi^*$	7.73	7.79	0.002	6.33	6.37	0.001
	$\pi-\pi^*$	8.51	9.22	0.779	6.91	7.54	0.739

[a] π^* orbital is LV orbital in every case. σ_1 and σ_2 denote the highest and the next highest σ-type orbitals, respectively. [b] The HO orbital is doubly degenerate.

Table V. Some Orbitals of Ethyl Cation Calculated with $K = 1.1$

(A) HO orbital of ethyl cation[a]
$-0.294\pi'_{C1} + 0.562\pi'_{C2} - 0.236(h_3 - h_4) - 0.395(h_5 - h_6)$
(B) LV orbital of ethyl cation[b]
$0.992\pi_{C1} - 0.174\pi_{C2} + 0.119(h_5 + h_6) - 0.239h_7$
(C) Highest π-type orbital of ethyl cation[c]
$0.200\pi_{C1} + 0.573\pi_{C2} - 0.226(h_5 + h_6) + 0.452h_7$

[a] π and π' denote the pπ AO in and out of the molecular plane, respectively, and the numbering of the constituent atoms are shown in Table VII. [b] The geometry chosen for ethyl cation causes additional terms due to hyperconjugation, and these are: $-0.002s_{C1} - 0.003\sigma_{C1} + 0.001s_{C2} + 0.001(h_3 + h_4)$. [c] The additional terms due to hyperconjugation are: $0.002s_{C2} + 0.003\sigma_{C1} - 0.002s_{C2} + 0.001\sigma_{C2} - 0.001(h_3 + h_4)$.

These circumstances may be understood by referring to the natures of HO and LV orbitals of alkyl cations. As an example, the HO and LV orbitals of ethyl cation are listed in Table V. As will be seen in this example, the HO orbitals of alkyl cations are the σ-type orbitals consisting of AO's lying in the molecular plane, and, on the other hands, the LV orbitals of alkyl cations are the π-type orbitals which are almost localized on the cationic carbon atom.

Referring to Table IV, the strong transitions in alkyl cations which are expected to be found in the rather short wavelength region may be due to the excitation of a electron from the highest π-type orbitals to the LV orbitals. The highest π-type orbitals of mono-, di-, and trimethylcarbonium ions are constructed chiefly by the pseudo-π and -pπ AO's of the hyperconjugative methyl groups, as is shown by the example of ethyl cation in Table V.

Measurements of electronic spectra of alkyl cations have been made by several investigators but decisive assignments of the observed spectra to alkyl cations seem not to have been completed.[14] However, the

(14) The ultraviolet absorption of alkyl cations was observed by J. Rosenbaum and M. C. R. Symons (*Mol. Phys.*, 3, 205 (1960)) in concentrated sulfuric acid and they reported that isopropyl and t-butyl cations have the absorption maxima at 296 and 293 mμ (ϵ_{max} 6.4 × 10^3), respectively. (The intensity of absorption was later corrected to be <2000; see ref 1b.) But Deno[1a] held a different view and suggested that they are entirely due to a mixture of cyclopentenyl and cyclohexenyl cations.

present calculations may suggest that the observed spectra of isopropyl cation at 296 mμ (4.19 eV) and of *t*-butyl cations at 293 mμ (4.25 eV) are assigned to the $\sigma \rightarrow \pi^*$ transition.

As shown in the previous paper,[4] the LV orbital energy depends comparatively on the Wolfsberg–Helmholtz parameter, *K*, and the greater the value of *K*, the higher the LV energy. Therefore, the calculated transition energy for $K = 1.1$ is larger than those for $K = 1.08$.[15] But the calculated transition moment is little influenced by this parameter, as is seen in Table IV.

Alkyl Cations. The total electronic energies, nuclear repulsion energies, and total energies calculated for alkyl cations are summarized in Table VI. It is seen in the table that the structural isomerizations of alkyl cations cause only small changes in total energies, in spite of the rather large changes in total electronic energies and nuclear repulsion energies.

Table VI. Total Electronic Energies (*E*), Nuclear Repulsion Energies (*NRE*), and Total Energies (*W*) of Alkyl Cations

Cation	*E*, $K = 1.1$	*NRE*	*W*, $K = 1.1$
CH_3^+ [a]	−287.79	128.67	−159.11
CH_3^+ [b]	−288.03	129.54	−158.50
$C_2H_5^+$	−802.84	475.38	−327.46
$n\text{-}C_3H_7^+$	−1493.10	986.80	−506.29
$i\text{-}C_3H_7^+$	−1482.95	976.58	−506.37
$i\text{-}C_4H_9^+$	−2352.73	1657.08	−695.65
$t\text{-}C_4H_9^+$	−2328.43	1632.48	−695.95

[a] Trigonal configuration. [b] Tetrahedral configuration.

Further, it may be noted that the experimentally observed order of stability between isomers ($i\text{-}C_3H_7^+$ and $t\text{-}C_4H_9^+$ are more stable than $n\text{-}C_3H_7^+$ and $i\text{-}C_4H_9^+$, respectively) should reflect those of the nuclear repulsion energy. Since the resultant isomerization energies seem rather small compared with experiment, a further improvement in the present treatment seems necessary.

The calculated populations of some alkyl cations and, for comparison, those of methane and staggered ethane are presented in Table VII. It is seen in Table VII that the charge of the cationic carbon distributes chiefly on the hydrogens of the adjacent methyl or methylene groups, and even to those of the terminal methyl group of the *n*-propyl cation. The average net charges of the hydrogen atom in methyl groups of isopropyl and *t*-butyl cations are +0.153 and +0.146 for $K = 1.1$ and these parallel the observed[10] chemical shifts of −5.06 and −4.35 ppm from tetramethylsilane, respectively. The population of the C–H bond lying in the plane perpendicular to the molecular plane is the smallest in every case, and it is expected that next fission of a hydrogen may occur at this bond. It is to be noted that the bonds between α-carbon and β-carbon are generally the weakest ones in the molecule, and that the bond population between the cationic carbon and α-carbon is exceptionally

Table VII. Atom Bond Populations of Alkyl Cations Calculated with $K = 1.1$

Alkyl cation	Atom	Population	Bond	
Methyl				
(i) the sp^2 form	C	+0.261	C–H	0.724
	H	+0.246		
(ii) the sp^3 form	C	+0.231	C–H	0.714
	H	+0.256		
Ethyl	1	+0.339	1–2	0.809
	2	−0.198	1–3	0.802
	3	+0.180	2–5	0.790
	5	+0.154	2–7	0.740
	7	+0.192		
n-Propyl	1	+0.372	1–2	0.897
	2	−0.142	2–3	0.714
	3	−0.212	1–4	0.822
	4	+0.152	1–5	0.812
	5	+0.153	2–6	0.769
	6, 7[a]	+0.175	3–10	0.813
	8, 9, 10[a]	+0.108		
Isopropyl	1	+0.362	1–2	0.866
	2	−0.209	1–4	0.840
	4	+0.135	2–5	0.795
	5	+0.137	2–6	0.790
	6	+0.180	2–7	0.746
	7	+0.143		
Isobutyl	1	+0.379	1–2	0.944
	2	−0.064	2–3	0.717
	3	−0.206	1–5	0.823
	5	+0.136	2–7	0.780
	7	+0.172	3–8	0.816
	8, 9, 10[a]	+0.108		
t-Butyl	1	+0.382	1–2	0.891
	2	−0.231	2–5	0.794
	5	+0.134	2–7	0.749
	7	+0.170		
Methane	C	−0.167	C–H	0.788
	H	+0.042		
Stag. ethane	C	−0.113	C–C	0.681
	H	+0.064	C–H	0.823

[a] Average value.

large, compared with that of the ethane C–C bond. These parallel the experimentally observed[10] bond-stretching frequencies of C–C and C–H bonds of the simple alkyl cations. In these, the small bond populations between the α- and β-carbons of *n*-propyl and isobutyl cations interpret the well-known β-fission rule.[16]

The change in charge at the cationic carbons with increasing number of methyl groups attached is of special interest. They are +0.261, +0.345, +0.362, and +0.382 for methyl, ethyl, isopropyl, and *t*-butyl cations, respectively.[17] More detailed analyses of these values are shown in Table VIII,[18] which also includes those of the populations on α-carbons. It is seen in Table VIII that the π population at the cationic carbon increases with increasing number of methyl groups linked to it. This is the same trend as that obtained by Muller and

Olah, *et al.*,[10] also observed a single weak absorption maximum around 290 mμ with a low extinction coefficient in antimony pentafluoride solution of some alkyl fluorides, and they assigned it to $\sigma \rightarrow \pi^*$ transition. But Olah and Pittman corrected their conclusion in their recent review[1b] and stated that this absorption is not due to alkyl cation but to impurity ions.

(15) From the calculations carried out for neutral molecules, the transition energies calculated by $K = 1.1$ may be recommended for the small molecules and those calculated by $K = 1.08$ for the large molecules, such as isobutyl and *t*-butyl cations (see ref 4).

(16) For example, see B. S. Greensfelder in "The Chemistry of Petroleum Hydrocarbons," Vol. 4, B. T. Brook, *et al.*, Ed., Reinhold Publishing Corp., New York, N. Y., 1954, Chapter 27.

(17) The corresponding values calculated by Hoffmann were +0.609, +0.571, +0.611, and +0.692, respectively, and their changes were not monotonous (see ref 3).

(18) We gave preliminary results on the electronic structure of cyclopropylmethyl cations calculated by the method which does not include one-center exchange terms in eq 5 and 6. Therefore, the values presented here differ a little from those in our earlier paper: T. Yonezawa, H. Nakatsuji, and H. Kato, *Bull. Chem. Soc. Jap.*, **39**, 2788 (1966).

Table VIII. AO Populations at Cationic Carbons and α-Carbons

Cation	Cationic carbon, $K = 1.1$ σ^a	π	$\sigma + \pi$	α-Carbon, $K = 1.1$ σ^a	π	$\sigma + \pi$
CH_3^+	3.739	0.0	3.739			
$C_2H_5^+$	3.512	0.150	3.661	3.152	1.046	4.198
n-$C_3H_7^+$	3.412	0.216	3.628	3.098	1.044	4.142
i-$C_3H_7^+$	3.342	0.296	3.638	3.143	1.066	4.209
i-$C_4H_9^+$	3.359	0.262	3.621	3.060	1.004	4.064
t-$C_4H_9^+$	3.225	0.393	3.618	3.140	1.093	4.232
Stag. C_2H_6				3.153	1.039	4.192

[a] σ-AO's in this table are the sums of s, pσ, and pπ′ AO's of the referring carbon atom.

Mulliken,[19] so that these delocalization of π electrons may be attributed to the hyperconjugative effect of the methyl group. On the other hand, σ electrons behave conversely compared with π electrons, namely, the σ population at the cationic carbon decreases with increasing number of methyl groups attached to it. This behavior of σ electrons is reasonable, since an increase of π population due to hyperconjugation will cause a decrease of σ population owing mainly to the one-center electron repulsion terms in eq 2.

The behavior of the AO populations at cationic carbon with increasing number of methyl groups attached is illustrated in Figure 1, which shows that, in spite of large changes in σ and π populations, the change of total population is surprisingly small. The trend of total population reflects that of the σ population, but is the reverse of that of the π population. Hence it may be stressed that the usual approximation of σ–π separation is inadequate in alkyl cations.

Further, Table VIII may indicate that the σ population of the "trigonal" carbon atom is larger than that of the adjacent sp^3 carbon atom. This would be the consequence of larger electronegativity of an sp^2 carbon than an sp^3 carbon.[20] However, interestingly, the AO population of the α-carbon in an alkyl cation suffers little change from those of the sp^3 carbon in ethane (Table VIII), so that the comparatively large σ population of the sp^2 carbon is due chiefly to the supply from hydrogens in the molecule. The σ and π populations at the cationic carbon of the n-propyl cation are between those of ethyl and isopropyl cations, and those of the isobutyl cation are between those of n-propyl and isopropyl cations. These facts may suggest the order of the electronic effect of alkyl substituents on the cationic carbon atom.

The π AO bond populations between cationic carbon and α-carbon calculated with $K = 1.1$ are 0.094, 0.090, and 0.081 for $C_2H_5^+$, i-$C_3H_7^+$, and t-$C_4H_9^+$, respectively, which shows that the π-bond population decreases with increasing number of methyl groups linked to the cationic carbon. Further, those of n-$C_3H_7^+$ and i-$C_4H_9^+$ are calculated with $K = 1.1$ to be 0.120 and 0.133, respectively.

Protonated Hydrocarbons. Proton Affinities and Heat of Reactions in Some Ionic Reactions. A protonated hydrocarbon is a proton adduct of a hydrocarbon, and the energy which is released in this process is the proton affinity of a hydrocarbon. The calculated total energies of protonated hydrocarbons are listed in

(19) N. Muller and R. S. Mulliken, *J. Amer. Chem. Soc.*, **80**, 3489 (1958).
(20) W. Moffitt, *Proc. Roy. Soc.* (London), **A202**, 534, 538 (1950).

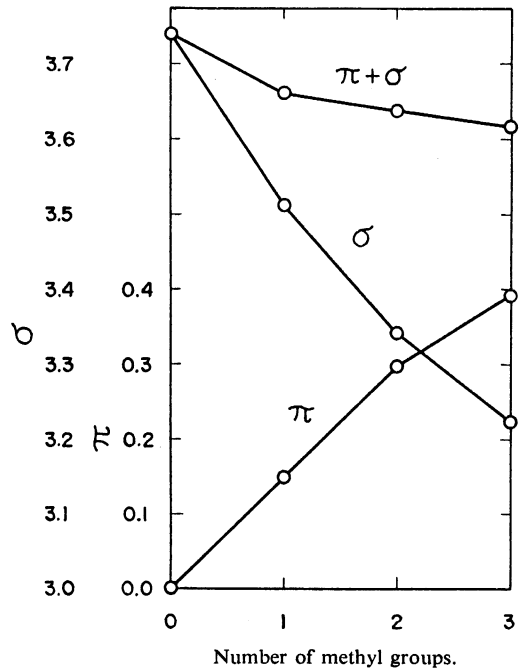


Figure 1. Changes of AO populations at the cationic carbon with increasing number of methyl groups attached.

Table IX, which also includes those of the parent hydrocarbons. Calculated proton affinities of CH_4, C_2H_4, and C_2H_2 are shown in Table X, together with the calculated energy changes for the reactions

$$CH_5^+ \longrightarrow CH_3^+ + 2H$$

$$CH_4 \longrightarrow CH_3^+ + H$$

and

$$C_2H_6 \longrightarrow C_2H_5^+ + H$$

Table IX. Calculated Total Energies of Protonated Hydrocarbons and Their Parent Hydrocarbons

Species	$K = 1.1$	Species	$K = 1.1$
CH_5^+	−192.07	CH_4	−186.15
$C_2H_5^+$		C_2H_2	−285.53
A form	−327.48	C_2H_4	−320.31
A′ form	−328.00	C_2H_6	−356.79
B form	−326.86		
$C_2H_3^+$			
A form	−290.68		
B form	−291.19		

Table X. Calculated Energy Changes for Some Reactions

Reaction	Exptl	Calcd, $K = 1.1$
$CH_4 \longrightarrow CH_3^+ + H + e$	14.39[a]	13.44
$CH_5^+ \longrightarrow CH_3^+ + 2H$	≥5.7[a]	5.76
$CH_5^+ \longrightarrow CH_4 + H^+$	4.95 ~ 5.58[b]	5.92
$C_2H_3^+ \longrightarrow C_2H_2 + H^+$	5.93[c]	5.67
$C_2H_5^+ \longrightarrow C_2H_4 + H^+$	6.6[d]	7.68
$C_2H_6 \longrightarrow C_2H_5^+ + H + e$	12.9[e]	15.19

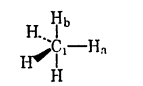
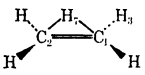
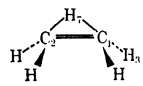
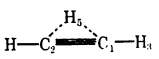
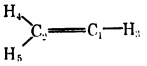
[a] Reference 21. [b] Reference 25. [c] Estimated value from ΔH_f-$(C_2H_3^+)$ = 283 kcal/mol.[30] [d] Reference 16. [e] J. L. Franklin and H. E. Lumpkin, *J. Chem. Phys.*, **20**, 745 (1952).

In calculating the values shown in Table X, we used the total energy of the most stable conformation expected for

the referring cation, which will be discussed below. The agreement with experiment seems satisfactory, and the more detailed discussions about Table X will be seen in the corresponding sections which follow.

Protonated Methane and Its Negative Isomer. The assumed geometry of protonated methane is a trigonal bipyramid with a carbon–hydrogen bond of 1.05 Å.[21] This model may be considered as an adduct of two hydrogen atoms on both ends of the vacant π AO of the methyl cation. The calculated atom bond populations are shown in Table XI, which indicates that the three hydrogens (H_a's) of the parent methyl group are bound more tightly than the other two hydrogens (H_b's). Interestingly, the charge of the central carbon is more negative than that of methane, and the net charge of this cation is completely distributed to hydrogens in molecule.

Table XI. Atom Bond Populations of Protonated Hydrocarbons Calculated with $K = 1.1$

Protonated hydrocarbon	Atom	Population	Bond	
Protonated methane				
	1	−0.348	1-a	0.702
	a	+0.231	1-b	0.613
	b	+0.328		
Protonated ethylene				
(i) the A form[a]	1	+0.060	1-2	0.885
	3	+0.162	1-3	0.823
	7	+0.233	1-7	0.313
(ii) the A′ form[b]	1	+0.028	1-2	0.801
	3	+0.168	1-3	0.817
	7	+0.274	1-7	0.423
(iii) the B form[a]	1	+0.034	1-2	0.862
	3	+0.170	1-3	0.815
	7	+0.252	1-7	0.310
Protonated acetylene				
(i) the A form	1	+0.120	1-2	1.478
	3	+0.238	1-3	0.775
	5	+0.285	1-5	0.278
(ii) the B form	1	+0.248	1-2	1.288
	2	+0.062	1-3	0.743
	3	+0.268	2-4	0.752
	4	+0.211		
Ethylene	C	−0.155	C-C	1.225
	H	+0.078	C-H	0.827
Acetylene	C	−0.135	C-C	1.828
	H	+0.135	C-H	0.794

[a] The distance between H_7 and the center of the C–C bond is 1.2 Å. [b] The distance between H_7 and the center of the C–C bond is 0.8 Å.

The nature of the carbon–hydrogen bond in protonated methane is of special interest, and we summarized the calculated AO and AO-bond populations of CH_5^+ in Table XII, which also includes those of methane, ethylene, and acetylene. The value of the ratio of the AO-bond populations, $(p\sigma_C\text{–}h)/(s_C\text{–}h)$, in Table XII, which may be considered to represent the hybridized state of the referring carbon atom, undergoes a great change from methane to ethylene, and from ethylene to acetylene. These values of the C–H_a and C–H_b bonds in CH_5^+ are remarkably different from each other, although the assumed bond lengths are 1.05 Å for both bonds, and it may be concluded that the s character of C–H_b bond is greater than that of the C–H_a bond.

(21) (a) J. R. Hoyland and F. W. Lampe, *J. Chem. Phys.*, 37, 1066 (1962); (b) J. Higuchi, *ibid.*, 31, 563 (1959).

Table XII. AO and AO-Bond Populations in CH_4, C_2H_4, C_2H_2, CH_5^+, and CH_5^- [a]

Species	s_C–h	$p\sigma_C$–h	C–H bond population	H atom population	$(p\sigma_C\text{–}h)/(s_C\text{–}h)$
CH_4	0.207	0.581	0.788	0.958	2.81
C_2H_4	0.285	0.542	0.827	0.922	1.90
C_2H_2	0.376	0.418	0.794	0.865	1.11
CH_5^+					
H_a	0.164	0.538	0.702	0.769	3.28
H_b	0.186	0.427	0.613	0.672	2.29
CH_5^-					
H_a	0.272	0.533	0.805	1.175	1.96
H_b	0.049	0.417	0.466	1.405	8.51

[a] The values in this table are calculated with $K = 1.1$.

The LV orbital of CH_5^+ calculated with $K = 1.1$ is[22]

$$\varphi^{LV}_{CH_5^+} = 0.100s_C + 0.552(h_{a1} + h_{a2} + h_{a3}) - 0.889(h_{b1} + h_{b2})$$

This is bonding between s_C and h_a AO's but antibonding between s_C and h_b AO's. The orbital energy calculated with $K = 1.1$ is −1.429 eV and is extraordinarily higher than the LV orbital energies of usual alkyl cations and protonated hydrocarbons ($-6 \sim -10$ eV; see also Table III). Also the electron affinity of CH_5^+ may be expected to be very small,[23] and will be the order of magnitude of those in neutral molecules.[24] We examined further the occupied orbitals of CH_5^+ and found that all the occupied orbitals are bonding between the C–H_b bond.

The proton affinity of methane was observed[25] to be in the range 4.95–5.58 eV, and the present calculation gave 5.92 eV by $K = 1.1$ and 4.68 eV by $K = 1.08$ as shown in Table X.

We also calculated the electronic structure of CH_5^-, which may be assumed to be a model compound resembling the transition state of the SN2 reaction. The calculated AO and AO-bond populations and the ratio, $(p\sigma_C\text{–}h)/(s_C\text{–}h)$, are also summarized in Table XII. It may be noted that the difference between the bond populations of the C–H_a and C–H_b bonds increases remarkably from CH_5^+ to CH_5^-. This means that the C–H_b bond becomes much weaker than the C–H_a bond in CH_5^-. Further, the s_C–h bond population is nearly zero in CH_5^-, indicating that the C–H_b bond in CH_5^- is formed by almost pure p AO of the central carbon atom. Thus, the H_b–C–H_b bond of CH_5^- may properly be called a three-center bond. The ratio, $(p\sigma_C\text{–}h)/(s_C\text{–}h)$, of the C–$H_a$ bond in CH_5^- approaches to the value of ethylene.

(22) The appropriateness of this LV orbital may be checked by the HO orbital of CH_5^- (see below).

(23) The electron affinity of CH_5^+ calculated by eq 11 is 1.446 eV and agrees fairly well with the estimated value (1.429 eV) from the LV orbital energy of CH_5^+.

(24) For example, the observed electron affinity of methyl radical is 1.1 eV. See also H. O. Pritchard, *Chem. Rev.*, 52, 529 (1953), and N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, 51, 600 (1955).

(25) V. L. Tal'rose and E. L. Frankeritch, *J. Amer. Chem. Soc.*, 80, 2344 (1958).

The HO orbital of CH_5^- which corresponds to the LV orbital of CH_5^+ is

$$\varphi^{HO}_{CH_5^-} = 0.059s_C + 0.560(h_{a1} + h_{a2} + h_{a3}) - 0.884(h_{b1} + h_{b2})$$

and its energy is +6.367 eV, which is very large and is extraordinarily higher than that of the usual anions, since the HO orbital energy of an anion may be set approximately equal to the electron affinity of the corresponding radical.[24] Further, because of the instability of the HO orbital of CH_5^- the total energy of CH_5^- (−187.148 eV) is larger than that of CH_5^+ (−192.069), and this is also exceptional, referring to those of alkyl cations and anions.

Protonated Ethylene. Protonated ethylene is an isomer of ethyl cation and is sometimes postulated to represent the true configuration of $C_2H_5^+$.[26] In order to study the stable configuration, we calculated the total energies of protonated ethylenes with some configurations which are shown in Table XI. In the A form in Table XI, the proton adds symmetrically to planar ethylene. In the B form, the terminal carbon–hydrogen bonds are bent in the tetrahedral angle; in both cases, the C—C bond lengths are assumed to be 1.44 Å. As a first step, the distance from the adding proton to the center of the C=C bond is assumed to be 1.2 Å[3] and the results with $K = 1.1$ and $K = 1.08$ predict that the A form will be more stable than the B form by 0.61 and 0.52 eV, respectively. When this length in the A form is varied, the total energy minimum is obtained about 0.8 Å (the A′ form in Table XI) by $K = 1.1$. But this value may be rather small, and may not represent the real configuration of protonated ethylene, since the approximation introduced in eq 9 may underestimate the nuclear repulsion energy when the interatomic distance becomes small.

Comparing the total energy of the A′ form with that of ethyl cation of the geometry shown in Table VII, the present calculation may suggest that the stable configuration of $C_2H_5^+$ will be protonated ethylene type of the A′ form.

The atom bond populations of the A, A′, and B forms are illustrated in Table XI. The charge of the adding proton is well distributed, and the bond population between this proton and carbon atom is relatively large. The π-AO population of the carbon atom is 0.790 in the A′ form and is remarkably small, compared with the value 1.00 for ethylene. Further, the C–C bond population of ethylene calculated by $K = 1.1$ is 1.225. This bond in protonated ethylene is considerably weakened by protonation.

The proton affinity of ethylene and the heat of formation of $C_2H_5^+$ from ethane, which are shown in Table X, are calculated based on the A′ form which is expected to be the most stable form of $C_2H_5^+$. The appearance potentials of CH_3^+ from CH_4 and of $C_2H_5^+$ from C_2H_6 were observed to be 14.39 and 12.9 eV, respectively, and the stabilization energy[27] of $C_2H_5^+$ relative to CH_3^+ was expected to be 1.5 eV. But we failed in calculating the stabilization energy of $C_2H_5^+$, and this is due to the overestimation of off-diagonal core Hamiltonian matrix elements (*Hrs* in eq 2) by the weight *K*.[4,28]

Protonated Acetylene. Protonated acetylenes of two configurations, symmetrical and unsymmetrical, illustrated in Table XI are considered. In the A form, the distance between the adding proton and the center of the C–C bond of acetylene is assumed to be 1.20 Å, in the B form, one of the terminal carbons is assumed to be in the sp^2 state, and C–C bond lengths of both forms are assumed to be 1.27 Å. As shown in Table IX, the B form which may be regarded as the product of the dehydride reaction of ethylene is expected to be more stable than the A form by 0.514 eV, and this is the same trend as reported by Hoffmann.[3] However, both methods involve some approximations, and further investigations would be necessary to draw a final conclusion.

The atom bond populations of protonated acetylene are shown in Table XI, which shows also that the net charge of the adding proton distributes in the molecule. Further, the atom population of the sp carbon in the B form is remarkably small and this is due to the small value (0.115 by $K = 1.1$) of the π'-AO population of this carbon atom.

The LV and next LV orbitals of the B form are[29]

LV

$$0.995\pi'_{C1} - 0.114\pi'_{C2} - 0.248(h_4 - h_5)$$

Next LV

$$0.742\pi_{C1} - 0.902\pi_{C2}$$

and their orbital energies are −8.58 and −7.05 eV,[30] respectively. These results may suggest that the protonated aceylene of the B form has two stable unoccupied orbitals, one of which lies in the molecular plane and the other lies in the plane perpendicular to the molecular plane.

The proton affinity of acetylene estimated from the observed[30] heat of formation of $C_2H_3^+$ is 5.93 eV and is less than the observed value for ethylene. The calculated proton affinity of acetylene, based on the B form, is 5.67 eV and is also less than the calculated value of ethylene, as shown in Table X. The agreement of the calculated value with the estimated values is excellent.

Acknowledgment. The calculations were carried out on an HITAC 5020 E computer at the computation center of the University of Tokyo, whom the authors wish to thank.

(26) L. G. Connell and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, 78, 5812 (1956).

(27) See Table X, footnote *e*.

(28) By improving the overestimation of off-diagonal core Hamiltonian matrix element, we succeeded in calculating the stabilization energy. Namely, the appearance potentials of CH_3^+ from CH_4 and of $C_2H_5^+$ from C_2H_6 are calculated by the improved method as 13.43 and 12.40 eV, respectively. More details about this improvement will be published in the near future.

(29) In the LV orbital, the group orbital $(h_4 - h_5)$ is antibonding with π'_{C1}, and bonding with π'_{C2}.

(30) The *IP* of the vinyl radical was observed to be 9.45 eV: A. G. Harrison and F. P. Lossing, *J. Amer. Chem. Soc.*, 82, 519 (1960). But the observed configuration of vinyl radical is different from that of the B form in the present calculation: R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1963).