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An INDO-MO Study of the Conformations and Electronic Structures of $HCHOH^+$, CH_3CHOH^+, $(CH_3)_2COH^+$, $HCO_2H_2^+$, $CH_3CO_2H_2^+$, and $CH_3OH_2^+$

Katsutoshi Ohkubo, Toshiaki Yoshida, and Katsumi Tomiyoshi

Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860

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INDO-SCF calculations were performed on several protonated compounds, $HCHOH^+$ CH_3CHOH^+, $(CH_3)_2COH^+$, $HCO_2H_2^+$, $CH_3CO_2H_2^+$, and $CH_3OH_2^+$, and also on the corresponding parent molecules in order to investigate their conformations and electronic structures. Geometric optimization resulted in reasonable conformations as compared with the previous *ab initio* calculations and in sufficient magnitudes of the energy differences between the rotational isomers in comparison with the NMR observations. The change in the electronic structures of the parent molecules due to protonation is also discussed by paying attention to the polarization caused by electron delocalization, hybridization at the proton-bound oxygen atom, the protonation energy, and the ionization potentials.

Protonated weak bases formed quantitatively in low-temperature "magic acid" solutions have hitherto received considerable attention, because such cations are important as intermediates in acid-catalyzed hydrolysis reactions and in the determination of Brønsted base strengths. Concerning the structures of tautomers or rotational isomers of the protonated species, Olah *et al.*[1] have extensively studied the low-temperature NMR spectra of these substances.

However, the structures of protonated aldehydes, ketones, acids, and alcohols, which were investigated in the present work, have been the object of only limited investigations as regards their molecular orbital treatments. Only protonated formaldehyde, acetaldehyde, and formic acid have been studied in detail in a few *ab initio* calculations. The geometric optimization of CH_3CHOH^+ and $HCO_2H_2^+$ by Ros[2] with small Gaussian basis set (32/2) brought about an incorrect relative stability of their rotational isomers, and large Gaussian basis set (73/3) calculations performed by Csizmadia *et al.*[3,4] improved the discrepancy of this relative stability on the base of results obtained under geometric assumptions.

Recently, the present authors have undertaken a semi-empirical INDO-MO study of several protonated compounds with particular attention being paid to their optimized conformations, electronic structures, and the magnitude of the energy difference between tautomers or rotational isomers. The present INDO calculations with sufficient geometric optimization were almost successfully carried out so that the above subjects may be discussed without any need to consider the solvent effect on the protonated species in super-acid solutions.

Method of Calculation

The semi-empirical calculations of HCHO, CH_3CHO, $(CH_3)_2CO$, HCO_2H, CH_3CO_2H, CH_3OH, and their protonated species (unstable alkoxy-protonated species were neglected in the protonated acids) were carried out using the INDO-SCF method[5] which is considered to be reliable for bond angles, but less so for bond lengths.[6]

The bond lengths and angles which are to be optimized are shown in Fig. 1 in which most of the fixed lengths and angles were taken from the standard tables,[7] except for those of HCHO and CH_3CHO (which were taken from Ref. 2). The optimization of geometric parameters was carried out by means of a repeated SCF-procedure. This was performed first on the bond lengths for fixed bond angles, then in turn on the angles until the most

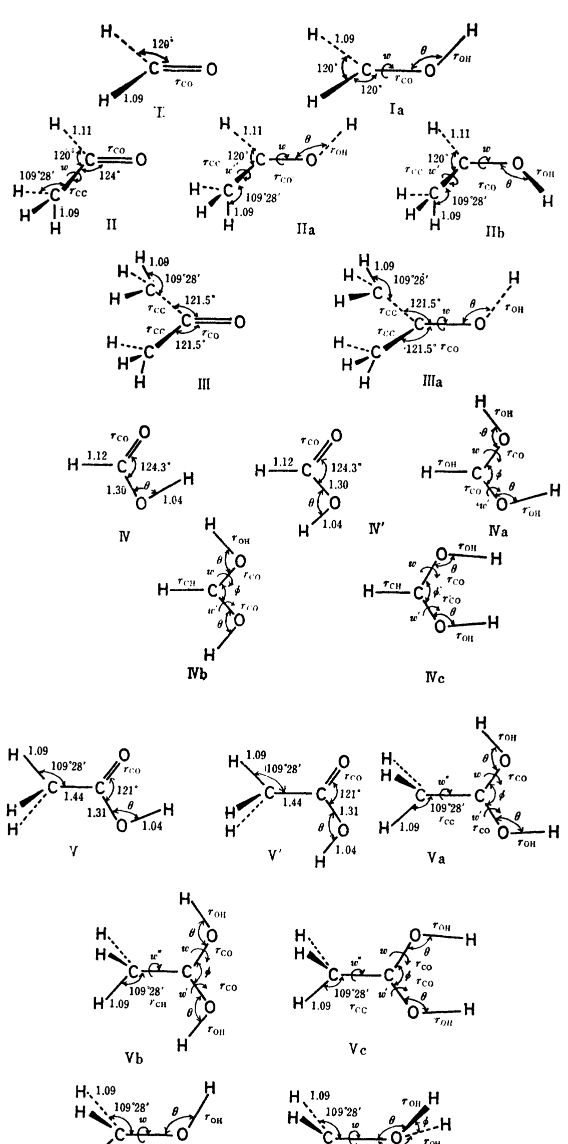

Fig. 1. Geometric parameters for parent molecules and protonated species.

stable conformations had identical bond lengths and angles, and finally the optimized geometries were recalculated by changing all their bond lengths and angles by the amounts of ±0.02 Å and ±2°, respectively, as a check on the reliability of the optimization results. In the cases of $HCO_2H_2^+$ and $CH_3CO_2H_2^+$, the optimized r_{CO}, r_{OH}, and r_{HC} (or r_{CC}) values in the energetically most stable *cis-trans* isomer (IVa or Va in Fig. 1) were commonly used for the other unstable isomers.

Results and Discussion

Optimized Conformations. Let us first examine the optimized conformations of the parent molecules before discussing those of the protonated species. The bond length of the C=O bond was calculated to be slightly longer than the experimental value by 0.02—0.04 Å for all the molecules, except CH_3OH, with an overestimation of the θ values for the acids to the extent of *ca.* 4°, while the value (1.36 Å) for CH_3OH was shorter by 0.074 Å than the experimental value (1.434 Å⁸⁾) with $r_{OH}=1.04$ Å (expt.⁸⁾$=0.937$ Å) and $\theta=107°$ (expt.⁸⁾$=105°56'$). Some parent molecules such as CH_3OH and HCHO have already been calculated by the INDO method without any geometric assumptions,⁵⁾ but the geometric assumptions used here did not show as serious defects in comparison with the complete optimization results,⁵⁾ so that the protonated species may be treated under same geometric assumptions as the parent molecules.

In regard to the rotations of the CH_3 group about the C–C bond (CH_3CHO) and about the C–O bond (CH_3OH), the rotational barriers obtained from the energy difference between the most stable staggered conformations (SII and SVI) and the most unstable eclipsed conformers (EII and EVI) were estimated to be 0.35 kcal/mol (expt.⁹⁾=1.16 kcal/mol) for CH_3CHO and 0.83 kcal/mol (expt.⁸⁾=1.07 kcal/mol; *ab initio*¹⁰⁾=1.59 kcal/mol) for CH_3OH (see Fig. 2). The INDO calculations resulted in smaller rotational barriers than those obtained from the experimental results, probably because the approximations involved in the INDO method neglect multiple-center (more than two-center) repulsion integrals.

Concerning two possible isomers of HCO_2H and CH_3CO_2H (Fig. 1), the *trans* forms (IV and V) of both the acids, which have smaller bond angles (θ) than the *cis* form by 1° were found to be more stable by 1.69

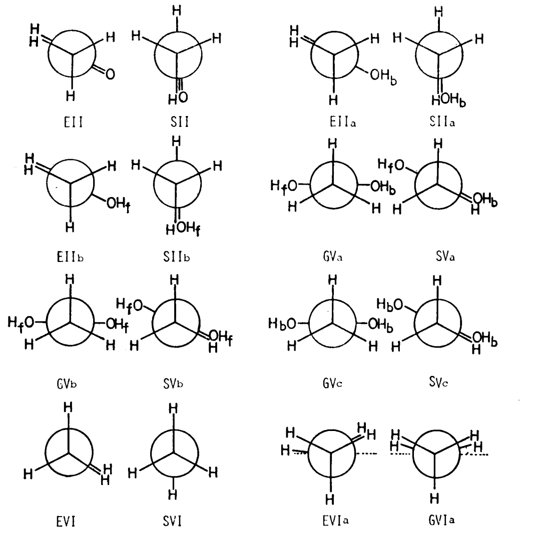

Fig. 2. Energetically most stable and unstable conformations of the protonated species during the CH_3 rotation around the C–C or C–O bond. (The subscripts of b and f mean the back and the front respectively.)

Table 1. Optimized values for the geometric parameters

Species	$r_{C=O}$	r_{CO}	r_{OH}	r_{CC}	θ	ϕ	ω	ω'	ω''	r_{HC}
I	1.25(1.21)									
Ia		$1.28(\underline{1.27})$	$1.05(\underline{\underline{0.985}})$		$121°(\underline{120°})$		$90°(\underline{\underline{90°}})$			
II	1.26(1.22)			1.44(1.50)						
IIa		$1.29(\underline{\underline{1.27}})$	$1.04(\underline{\underline{0.985}})$	$1.41(\underline{\underline{1.50}})$	$119°(\underline{121°})$		$0°(\underline{\underline{0}}°)$	$0°(\underline{\underline{0}}°)$		
IIb		$1.29(\underline{\underline{1.27}})$	$1.04(\underline{\underline{0.985}})$	$1.42(\underline{\underline{1.50}})$	$119°(\underline{118.5°})$		$0°(\underline{\underline{0}}°)$	$0°(\underline{\underline{0}}°)$		
III	1.27(1.24)			1.45(1.55)						
IIIa		1.31	1.04	1.43	118°					
IV	1.26(1.25)				112°(107.8°)					
IV′	1.26(1.25)				$113°(\underline{\underline{118°}})$					
IVa		$1.30(\underline{1.31})$	$1.04(\underline{\underline{0.98}})$		$118°(\underline{118°})^{a)}$	$118°(\underline{\underline{124°}})$	$0°(\underline{\underline{0}}°)$	$0°(\underline{\underline{0}}°)$		$1.12(\underline{\underline{1.09}})$
IVb		$1.30(\underline{1.31})$	$1.04(\underline{\underline{0.98}})$		$118°(\underline{118°})$	$114°(\underline{\underline{124°}})$	$0°(\underline{\underline{0}}°)$	$0°(\underline{\underline{0}}°)$		$1.12(\underline{\underline{1.09}})$
IVc		$1.30(\underline{1.31})$	$1.04(\underline{\underline{0.98}})$		$120°(\underline{121°})$	$125°(\underline{\underline{124°}})$	$0°(\underline{\underline{0}}°)$	$0°(\underline{\underline{0}}°)$		$1.12(\underline{\underline{1.09}})$
V	1.27(1.25)				112°(107.8°)					
V′	1.27(1.25)				113°(107.8°)					
Va		1.31	1.04	1.44	117°	113°	0°	0°	0°	
Vb		1.31	1.04	1.44	118°	109°	0°	0°	0°	
Vc		1.31	1.04	1.44	119°	120°	0°	0°	0°	
VI		1.36(1.434)	1.04(0.937)		107°(105°56′)		0°			
VIa		1.39	1.04		121°	65°	0°			

Bond lengths are in Å units. Values in parentheses are experimental,⁷⁾ optimized²⁾ (underlined), and assumed values²⁾ (doubly underlined). a) 116° has been given for the other C–O–H angle.

kcal/mol for HCO_2H or by 5.33 kcal/mol for CH_3CO_2H than the other forms. The experimentally determined energy difference between *trans* (IV) and *cis* (IV′) HCO_2H (IV is more stable than IV′), 2.0 kcal/mol, is well reflected in the computed value of 1.63 kcal/mol, even though previous *ab initio* calculations of IV and IV′ gave overestimated energy differences of 8.1 kcal/mol (for (32/2) basis sets)[2] and 9.46 kcal/mol (for (73/3) basis sets).[3] The energy difference (1.69 kcal/mol) between IV and IV′ of $H_aC(=O_a)OH_b$ can be roughly explained using the Coulomb attraction or repulsion energy estimated from $0.5292Q_AQ_B/r_{AB}$ (Q_A and Q_B=formal charges of A and B atoms; r_{AB}=nuclear distance between A and B). As a result, the difference in the Coulomb attractions (IV—IV′=3.34 kcal/mol for the O_a–H_b and −1.29 kcal/mol for the negatively charged H_a-positively charged H_b attractions) makes IV more stable than IV′ by 2.05 kcal/mol. The energy difference between V and V′ for $CH_3C(=O_a)OH_a$ was also explained similarly by the O_a–H_a attraction and the CH_3–H_a repulsion. It is noteworthy here that, in the *trans* isomers of both the acids, hydrogen bonding cannot be expected between the O_a and H_b (or H_a) atoms (overlap populations were negative).

Now, let us focus on the optimized conformations of the protonated species (Table 1). Protonation on the oxygen atom resulted the C–O bond length being increased by 0.03—0.04 Å with respect to the r_{CO} of the parent molecule. The magnitude of the C–O bond stretching was in good agreement with that expected from *ab initio* calculations of $HCO_2H_2^+$ and $CH_3CO_2H_2^+$,[2] but the r_{OH} value of 1.04 Å given consistently for all the protonated species except $HCHOH^+$ (r_{OH}= 1.05 Å) appears to be considerably overestimated in comparison with r_{OH}=0.985 Å of $HCO_2H_2^+$ calculated by Ros.[2]

In regard to the bond angles, the C–O–H bond angle (θ) fell in the range from 117° (Va) to 121° (VIa), and those of Ia and Va, b, c, were found to be almost identical for both the INDO and *ab initio*[2] calculation results. Interestingly, the O–C–O bond angles (ϕ) which were assumed to be 124°[2] or 120°[3] in the previous *ab initio* calculations are different for the three isomers of the protonated acids. They increased systematically for a decrease in the distance between the two hydrogen atoms of the O–H bonds, that is, with increasing H–H repulsion. However, the magnitude of the change in the ϕ value (11°) appears to be too large, nevertheless the INDO calculation tends to underestimate the electron-electron repulsions.[5,11]

Here, we will discuss the CH_3 rotation about the C–C bond for the two isomers of CH_3CHOH^+ and the three isomers of $CH_3CO_2H_2^+$ and about the C–O bond for $CH_3OH_2^+$. As can be seen from Fig. 2, the staggered (SIIa, SIIb, SVa, SVb, and SVc) and gauche-like (GVIa) conformations having minimum H–H repulsions or maximum H–O attractions were found to be the most stable, while the eclipsed (EIIa, EIIb, and EVIa) structures possessing maximum H–H repulsion and the gauche structures (GVa, GVb, and GVc) having minimum H–O attraction were the most unstable. The rotational barriers falling in the range of 0.005—0.48 kcal/mol indicate free CH_3 rotations in the above protonated species except for *trans*-CH_3CHOH^+ (barrier=0.86 kcal/mol). Therefore, the CH_3 rotation, especially that in $CH_3CO_2H_2^+$, does not appear to play an important role in the determination of the relative stability of the protonated isomers.

Charge Densities, Protonation Energies, Dipole Moments, and Ionization Potentials. The change in the electron distributions for protonation will be discussed first by noticing the charge densities of the parent molecules and the energetically most stable protonated conformers (Fig. 3). Ros[2] has already pointed out on the basis of the results of his *ab initio* calculation that there is a general shift (polarization) of electrons from the terminal carbon-bound hydrogens (but not from the proton-bound oxygen) towards the incoming proton. This trend was also observed from the change in the charge distributions estimated by the present INDO calculations. The computed charge distributions appear reliable in view of the fact that the computed dipole moments of the parent molecules (those of the protonated species are unknown) are in satisfactory agreement with the experimental values.[12–16]

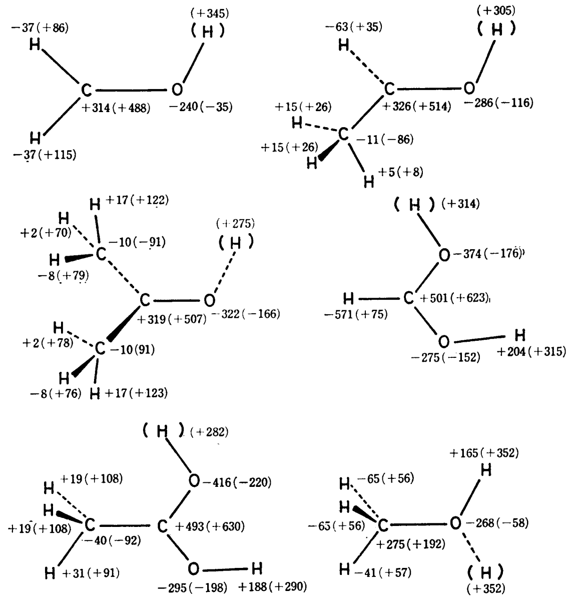

Fig. 3. Change in the charge distribution on the protonation. (Values in parentheses are those of the most stable protonated conformers, and all the values are in units of 10^{-3} electrons.)

The protonation also brought about a change in the electronic properties of the parent molecule, especially in the bond between the carbon and the proton-bound oxygen. The protonation decreased the overlap population of the above C–O bond by from 7.9% (HCHO) to 12.4% (CH_3CO_2H). The decrease in the π-type overlap population (16.8% for HCHO–35.5% for CH_3CO_2H) was found to be more marked than for the σ-type (5.0% for CH_3CHO–6.8% for CH_3CO_2H). The remarkable change in the π-conjugation of the C–O bond on the protonation is ascribed not only to the stretching of the C–O bond but also to the change in the hybridization at the proton-bound oxygen atom,

TABLE 2. ELECTRONIC PROPERTIES OF THE PARENT AND PROTONATED SPECIES

Species	Dipole moment/eV		*PA*/kcal mol^{-1}		*IP*/eV		Overlap population of C–O		
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	π	σ	Total
I	2.10	2.27[a]	227	166[f]	13.92	10.87[f]	0.198	0.701	0.899
Ia	3.13				26.21		0.165	0.664	0.829
II	2.86	2.72[a]	308	183[f]	13.26	10.28[f]	0.185	0.679	0.864
IIa	7.62				23.57		0.137	0.645	0.782
IIb	4.65				24.24		0.139	0.644	0.783
III	2.26	2.90[b]	328	202[g]	12.79	9.92[h]	0.174	0.655	0.829
IIIa	3.18				22.42		0.118	0.618	0.736
IV	1.68	1.42[c]	310	175[g]	13.63	11.05[i]	0.173	0.692	0.865
IV′	4.36				13.49		0.173	0.693	0.866
IVa	2.46				24.94		0.118 (0.120)	0.643 (0.647)	0.761 (0.767)
IVb	2.47				24.65		0.119	0.647	0.766
IVc	4.70				25.08		0.119	0.647	0.766
V	1.80	1.50[d]	334	188[g]	12.87	10.35[i]	0.162	0.668	0.830
V′	4.89				12.73		0.162	0.668	0.830
Va	2.44				23.86		0.105 (0.106)	0.623 (0.627)	0.728 (0.733)
Vb	3.95				23.35		0.105	0.634	0.739
Vc	2.74				24.15		0.105	0.627	0.732
VI	1.75	1.83[e]	273	180[g]	14.30	10.85[i]	0.036	0.601	0.637
VIa	6.39				24.57		0.021	0.562	0.583

Values in parentheses are those for the *trans* C–O bond with respect to the H–C bond. a) Ref. 12. b) Ref. 13. c) Ref. 14. d) Ref. 15. e) Ref. 16. f) Ref. 18. g) Ref. 19. h) Ref. 20. i) Ref. 21.

because the magnitude of the decrease in the π-type overlap population for a simple expansion of the C–O bond length without the incoming proton is markedly different from that for protonation. For example, the simple stretching of r_{CO} in HCHO from 1.25 Å (the optimized r_{CO} for HCHO) to 1.28 Å (the r_{CO} for $HCHOH^+$) decreased the π overlap population from 0.198 to 0.187, while protonation decreased it from 0.198 to 0.165. This trend can also be recognized in the other species, even in CH_3OH which has a pseudo π-conjugation at the C–O bond (π bond-orders=0.223 in CH_3OH and 0.139 in $CH_3OH_2^+$). The change in the hybridization at the oxygen atom upon protonation results in a protonation energy (proton affinity), because hybridization of the oxygen lone-pairs (defined by the %s or %p character) correlates linearly with the proton affinity (PA).[17] In this sense, the incoming proton predominantly interacts not only with the highest-occupied (HO), nonbonding oxygen-lone-pair-orbital expanding perpendicularly to the C–O bond axis, but also with the oxygen lone-pair orbital conjugating with the carbon pi-orbital at the lower MO (next to the HOMO). In this respect, the order of the computed *PA* values which correspond consistently to one half of the magnitude of the observed results[18,19] was well reflected in that of the observed *PA* values (Table 2). Protonation at the oxygen atom also decreased the electron density predominantly on the HO oxygen-lone-pair orbital and lowered the ionization potential (*IP*) of the parent molecule. As can be seen from Table 2, the IP values of the parent molecules became markedly large due to the protonation, and the computed *IP* values, IP_{calcd}, were found to be systematically overestimated in comparison with the observed *IP* values,[20,21] IP_{obsd}, ($IP_{obsd}/IP_{calcd}\approx 0.8$).

Relative Stability between the Rotational Isomers. In CH_3CHOH^+, $HCO_2H_2^+$, and $CH_3CO_2H_2^+$, two keto-protonated isomers have been proposed for each species as the result of NMR spectroscopic investigations:[1] IIa and IIb, IVa and IVb, and Va and Vb in Fig. 1. The relative stabilities determined using the present INDO calculations, the previous *ab initio* computations,[2–4] and by the NMR spectra[1] are summarized in Fig. 4. In regard to the energy difference (1.85 kcal/mol) between IIa and IIb, the present INDO result is in good agreement with the experimental value (about 1 kcal/mol) and with the *ab initio* calculations for large Gaussian basis sets[3] (1.15 kcal/mol), although small basis sets of Gaussian exponents (32/2)[2] failed in the estimation of the relative stability between IIa and IIb (IIa was computed to be less stable than IIb). The Coulomb repulsion of H_a–H_b in $CH_3CH_aOH_b^+$ (1.55 and 2.41 kcal/mol for IIa and IIb, respectively) and of CH_3–H_b (6.29 and 6.98 kcal/mol for IIa and IIb, respectively) makes the *cis* isomer (IIa) more favorable energetically than the other isomer (IIb) by 1.55 kcal/mol, a value which roughly corresponds to the energy difference between IIa and IIb. A remark should be made about the H_a–H_b repulsion: a value (2.41 kcal/mol for IIb) larger than this value (1.55 kcal/mol for IIa) was given by the larger positive charge of H_a (0.074) in IIb ($Q_{H_b}=+0.303$; $r_{H_a-H_a}=2.976$ Å) as compared with that of H_a (0.035) in IIa ($Q_{H_b}=+0.305$; $r_{H_a-H_a}=2.284$ Å). In this respect, the energy contribution terms listed in Table 3 indicate that IIa has smaller nuclear repulsions and larger one-electron attractions than IIb.

The relative stabilities of the protonated isomers of $HCO_2H_2^+$, IVa>IVb>IVc, was in agreement with the

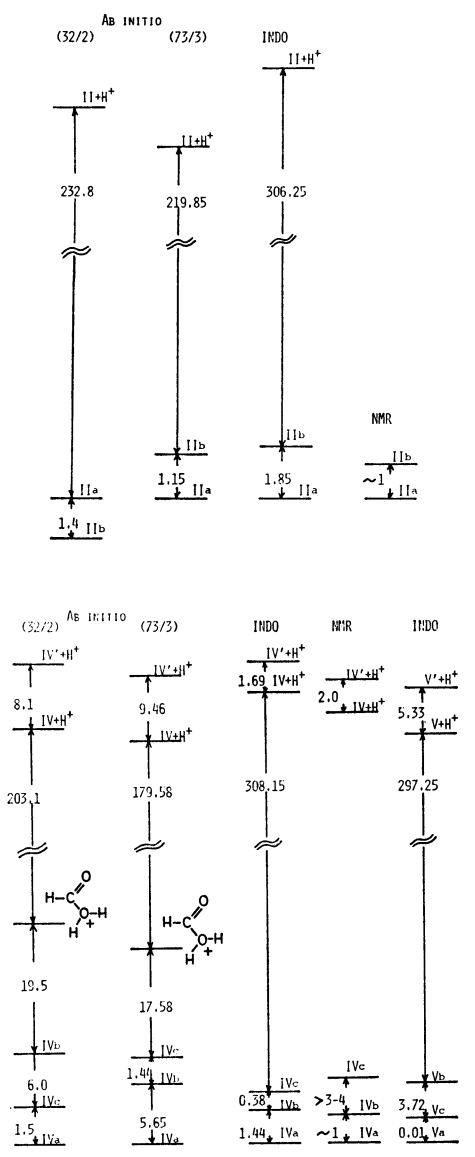

Fig. 4. Energy difference between the protonated isomers. (Values are in units of kcal/mol.)

TABLE 3. ENERGY CONTRIBUTION TERMS FOR PARENT AND PROTONATED SPECIES

Species	Total energy a.u.	One-electron energy a.u.	Inter-electronic repulsion a.u.	Nuclear repulsion a.u.
II	−34.1955	−130.4510	57.0996	39.1559
IIa	−34.6863	−137.3585	58.2054	39.1559
IIb	−34.6833	−135.9006	56.5944	44.6223
IV	−43.3811	−148.0520	65.7870	38.8839
IV′	−43.3784	−147.4676	65.4633	38.6259
IVa	−43.8749	−152.4360	64.4880	44.0731
IVb	−43.8726	−152.2294	64.3953	43.9615
IVc	−43.8720	−152.1936	64.3338	43.9878
V	−51.8375	−217.5575	97.8508	67.8691
V′	−51.8290	−217.5589	97.8074	67.9225
Va	-52.3699_2	−222.7850	96.4307	73.9844
Vc	-52.3699_0	−222.5534	96.3056	73.8779
Vb	−52.3640	−222.6517	96.3570	73.9307

NMR results[1)] and with the results of the *ab initio* calculation obtained by Csizmadia *et al.*[3)] (Ros's data: IVa>IVc>IVb). Although the energy difference (1.44 kcal/mol) between IVa and IVb corresponds approximately to that (about 1 kcal/mol) of the NMR results, the difference (0.38 kcal/mol) between IVb and IVc is too small for comparison with the experiment (3—4 kcal/mol).[1)] This may be attributable to an underestimation of the electron-electron repulsions. As can be seen from Table 3, the small repulsion terms, especially the electron repulsions, which favor IVc and IVb rather than IVa, were overcome by the one-electron energy term, and the relative stabilities follow the order: IVa>IVb>IVc.

Concerning the isomers of $CH_3CO_2H_2^+$, a discrepancy between the order of relative stabilities calculated by the INDO calculations (Va>Vc>Vb) and that found from the NMR spectra (Va>Vb≫Vc)[1)] was observed. This discrepancy may also be ascribed to an underestimation of the electron repulsion in view of the fact that the electron repulsion, in addition to the nuclear repulsion, makes Vc most favorable, even though a reasonable order (Va>Vb>Vc) can be obtained from the attraction term. It should be stressed here that the *cis-trans* conformers (IVa and Va) in both the acids were not stabilized by the hydrogen bonding between the *cis*-oxygen and the *trans*-hydrogen atoms because the appreciable long distances between the two atoms (about 2.40 Å in IVa and about 3.31 Å in Va) brought about negative overlap populations (—0.0008 for IVa and —0.0002 for Va), even though the effect of the hydrogen bonding has been demonstrated on the basis of the IR spectroscopic investigation of protonated carboxylic acids.[22)]

At any rate, the present INDO calculations of the protonated isomers brought about sufficient results for the determination of their relative stabilities in contrast with the previous *ab initio* calculation results.[2–4)]

The calculations were carried out on a FACOM 230-75 computer at the Data Processing Center of Kyushu University.

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