Electronic Structures and Spectra of the Keto and Enol Forms of Acetylacetone

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Near and vacuum UV absorption spectra of acetylacetone were measured in the vapor phase and in several organic solvents at various temperatures. From the temperature dependence of the spectra, the equilibrium constant and enthalpy change between the keto and enol forms of acetylacetone were determined to be 25 at 20 °C and −4.3 kcal/mol, respectively, in the vapor phase. Rydberg excitation bands were observed at 47170 and 53300 cm^{-1} for the enol form, and ≈52000 cm^{-1} for the keto form. The estimated values of the quantum defect indicate that the Rydberg orbitals are 3s and 3p. A modified CNDO-CI method was applied to the valence-shell transitions. A weak band observed at ≈34000 cm^{-1} for the keto form was assigned to the first n-π^* transition, and relatively strong bands observed at 38020 and 56800 cm^{-1} for the enol form, to the first and second π-π^* transitions, respectively. Special attention was paid to the charge-transfer (CT) character pertinent to the intramolecular hydrogen bond in the excited states of the enol form. Configuration analysis of the wave functions revealed us that the first π-π^* band observed at 38020 cm^{-1} has the CT character.

Acetylacetone and its congeners in the enol form have a strong intramolecular hydrogen bond with the O···O distance of 2.38—2.55 Å as revealed from the X-ray diffraction[1] and gas-phase electron diffraction studies.[2,3] The electronic structures of the molecules in the ground states have been studied by the nonempirical[4-6] and semiempirical[6-8] calculations. The electronic absorption spectra of acetylacetone and its congeners in the near ultraviolet (UV) region have been measured by several authors[9-13] and have been compared with the spectra of their metal chelates.[12] The spectroscopic results so far obtained, however, are restricted only to the first allowed band and no spectral information is available for discussing the higher excitation bands of acetylacetone.

The charge-transfer (CT) mechanism of hydrogen bond between a proton donor and a proton acceptor is important.[14] Electronic structure of the symmetrical intramolecular hydrogen bond of the hydrogen maleate anion was investigated in previous papers[15,16] and the CT character pertinent to the hydrogen bond was discussed in detail for the ground and excited states from theoretical and experimental points of view.[16] For intermolecular hydrogen-bonded systems between acetic acid and some aliphatic amines, the CT band pertinent to the hydrogen bond was observed successfully in the vacuum ultraviolet (VUV) region by the present authors.[17]

In the present paper, in order to investigate the electronic structures of the keto and enol forms of acetylacetone, electronic absorption spectra in the near and vacuum UV (30000—61000 cm^{-1}) region have been measured with acetylacetone in the vapor phase and also in various solvents. The observed valence-shell transition and Rydberg excitation bands have been interpreted on the basis of theoretical results by a modified CNDO-CI method[18] and the configuration analysis[19] of the ground and excited states.

Experimental

Acetylacetone (Wako G. R. Grade) was distilled three times under reduced pressure immediately before use. Methanol (Kanto G. R. Grade) used as a solvent was purified by fractional distillation. Acetonitrile and heptane (Wako Spectro Grade) were fractionally distilled over diphosphorus pentaoxide and sodium metal wire, respectively. Perfluorohexane (Kishida G. R. Grade) was purified by vacuum distillation through a column filled with silica gel.

Near and vacuum UV absorption spectra were measured with a Cary recording spectrophotometer model 14, with a vacuum UV spectrophotometer constructed in our laboratory,[20] and in part with a JASCO VUV-3 recording spectrophotometer,[21] the cells of 0.1 mm—10 cm light path length being used. In the vapor phase measurement between 18—300 °C, temperature of the sample cell was regulated within ±0.5 °C by a thermoregulator.

Theoretical

The electronic structures of the keto and enol forms of acetylacetone and of its anion were calculated by the modified CNDO-CI method[18] to investigate the characters of the valence-shell transitions. The following one-center Coulomb repulsion integral (γ) and bonding parameter (β^0) were commonly used for all the 2s and 2p atomic orbitals (AO) of the methyl carbon atom of the enol form and the anion, and of all the carbon atoms of the keto form (molecular skeleton of which is not planar); $\gamma(C)=12.78$ eV and $\beta^0(C)=-15.4$ eV. The other semiempirical parameters used in the calculations were the same as reported previously,[16] the effect of excess formal charge in the anion being considered by the parametrization.[16] In the configuration interaction (CI) treatment, 80 singly excited π-π^* and σ-σ^* configurations and 70 singly excited π-σ^* and σ-π^* configurations were taken into account for the enol form and the anion, and 80 singly excited configurations, for the keto form.

Geometrical structures were taken for the keto form from the gas-phase electron diffraction study[2] and for the enol form from the X-ray diffraction study of tetraacetylethane[1,22] (hydrogen-bonded O···O distance, 2.424 Å), a linear symmetrical hydrogen bond being assumed. The molecular geometry of the anion was assumed to be the same as that of the enol form, except for the fact that the hydrogen-bonded hydrogen atom was removed.

The configuration analysis[19] was applied to the ground and two excited (B_1 symmetry) states of the enol

form. In order to elucidate the electronic structures of the symmetrical intramolecular hydrogen bond, the 35 molecular orbitals (MO) of the anion and the 1s orbital of the hydrogen-bonded hydrogen atom were adopted as the reference MO's, as for the case of the symmetrical hydrogen bond of the hydrogen maleate anion.[16] The ground state of the enol form was analyzed by the ground and 101 singly excited π-π^* and σ-σ^* reference configurations (with A_1 symmetry) and by all the doubly excited reference configurations derived from the above configurations, and the excited states of the enol form were analyzed by 99 singly excited π-π^* and σ-σ^* reference configurations (with B_1 symmetry) and 99×101 doubly excited reference configurations.

Results and Discussion

Electronic Absorption Spectra of Acetylacetone. Figure 1 shows near and vacuum UV absorption spectra in the 30000—61000 cm^{-1} region measured with acetylacetone in the vapor phase and in perfluorohexane at room temperature. As pointed out by the NMR[23] and IR[24,25] spectroscopic studies, acetylacetone predominantly exists as the enol form in the vapor phase and in nonpolar solvents at room temperature. Therefore, both spectra shown in Fig. 1 are due to the enol form. The difference between them in the frequency region higher than 45000 cm^{-1} can be explained by the fact that Rydberg transition bands in the vapor phase disappear in the condensed phase, *i.e.*, in perfluorohexane.[26] From this point of view, a weak band at 47170 cm^{-1} and a moderately strong band at 53300 cm^{-1} are assigned to the Rydberg transitions of the enol form.

The Rydberg excitation energy is expected to satisfy the following formula;[26]

$$h\nu = I_p - 109737/(n-\delta)^2, \quad (1)$$

where $h\nu$ is the excitation energy (cm^{-1}), I_p is the ionization potential (cm^{-1}), n is the principal quantum number, and δ is the quantum defect. The equation was applied to the 47170 cm^{-1} (5.85 eV) and 53300 cm^{-1} (6.61 eV) bands of the enol form by the use of the first I_p value (9.00 eV) obtained by photoelectron spectroscopy.[27] δ was determined to be 0.92 for the former band, and 0.62 for the latter band, corresponding to $n=3$. This strongly suggests that the 47170 cm^{-1} and 53300 cm^{-1} bands are due to the transitions to the 3s and 3p Rydberg orbitals, respectively, from the highest occupied π orbital.

In addition to the Rydberg transition bands, the enol form has valence-shell transition bands at 38020 cm^{-1} (4.72 eV) in the vapor phase or at 36770 cm^{-1} (4.56 eV) in perfluorohexane and at 56800 cm^{-1} (7.04 eV) in perfluorohexane. From Table 1 which shows the observed and theoretical values of the transition energies and oscillator strengths of the valence-shell transition bands, we can see that the bands at 4.72 and 7.04 eV are assigned to the first and second π-π^* transitions of the enol form, respectively.

In such polar solvents as acetonitrile and water, the amount of the keto form increases and the intensity of the 4.72 eV band pertinent to the enol form decreases with an approximate linear correlation with the dielectric constants of solvents. Figure 2 shows the intensity change of the band in several solvents.

Figure 3 shows the vapor phase absorption spectra of acetylacetone measured at various temperatures (20—204 °C) in the 30000—54000 cm^{-1} region. We can see that in the vapor phase the fraction of the keto form increases at higher temperatures. From the temperature dependence of the spectra in the 30000—35000 cm^{-1} region in Fig. 3, a weak band due to the keto form was found at $\approx$34000 cm^{-1} ($\approx$4.2 eV) in the vapor phase. The observed transition energy and oscillator strength are compared with the theoretical values in Table 1. We can see that the band is safely assigned to the first n-π^* transition of the keto form (calculated at 3.97 eV).

Let us turn to the Rydberg transition band of the keto form. In the region of 50000—54000 cm^{-1} in which the Rydberg transition bands of acetylacetone appear, spectral intensity increases at $\approx$52000 cm^{-1} with increasing temperature, whereas the bands at 47170 and 53300 cm^{-1} pertinent to the enol form decrease in intensity (see Fig. 3). This indicates that the band at $\approx$52000 cm^{-1} is ascribed to the keto form. By the aid of the equilibrium constant mentioned later, the 50000

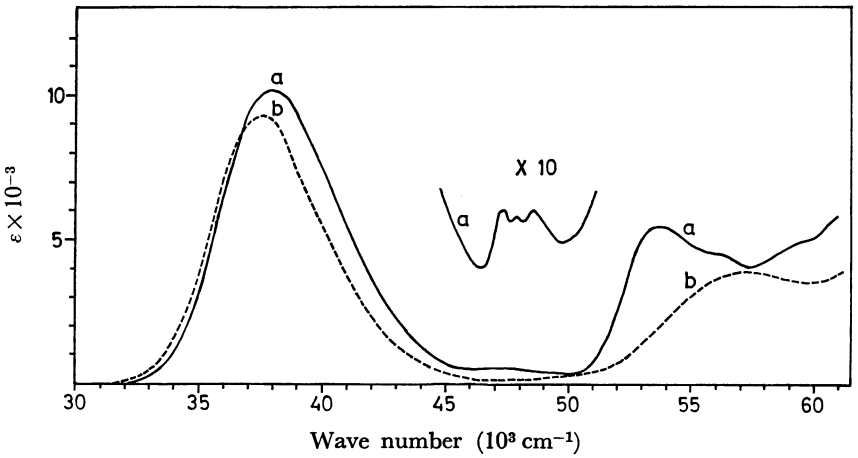

Fig. 1. Near and vacuum UV absorption spectra of acetylacetone measured (a) in the vapor phase and (b) in perfluorohexane at room temperature.

TABLE 1. TRANSITION ENERGIES ($^1\Delta E$(eV)) AND OSCILLATOR STRENGTHS (f) OBSERVED AND CALCULATED FOR THE ENOL AND KETO FORMS OF ACETYLACETONE

Assignment	Enol form					Keto form			
	Obsd		Calcd		Main[a] config.	Obsd		Calcd	
	$^1\Delta E$	f	$^1\Delta E$	f[b]		$^1\Delta E$	f	$^1\Delta E$	f[c]
σ-π^*			2.85	0.000_2 (z)	20-21	≈4.2[d]	≈0.007[d]	3.97	0.000_2 (z)
π-π^*	4.72[d]	0.24[d]	4.47	0.120 (x)	19-21			4.00	0.000 (y)
σ-π^*			5.31	0	20-22			7.30	0.207 (x)
σ-π^*			6.89	0	18-21			7.99	0.002 (y)
π-π^*	7.04[e]	≈0.13[e]	7.20	0.216 (y)	19-22			8.02	0.014 (z)
σ-π^*			7.61	0.017 (z)	(16, 13)-21			8.22	0.000_3 (y)
					18-22				
π-σ^*			8.00	0.025 (z)	19-(23, 25)			8.81	0.031 (z)
σ-σ^*			8.38	0.002 (x)	20-23			8.97	0.106 (y)
π-π^*			8.46	0.120 (y)	17-21			9.15	0.024 (xz)[f]
σ-π^*			8.58	0.004 (z)	(16, 13)-21			9.16	0.042 (y)
π-σ^*			8.60	0.009 (z)	19-26			9.35	0.013 (y)
σ-σ^*			8.93	0.022 (y)	20-(27, 24)			9.52	0.018 (z (x))[g]
π-σ^*			9.00	0	19-(27, 24)			9.54	0.023 (z)
σ-σ^*+π-π^*			9.02	0.685 (x)	20-26			9.94	0.008 (y)
					14-21				
σ-π^*			9.06	0	15-21				
π-σ^*			9.78	0.019 (z)	19-(28, 23, 25)				
σ-σ^*			9.94	0.045 (x)	20-(25, 23)				

a) Main electron configurations of the respective excited states are shown. (i,j)-k denotes the singly excited configurations, i-k and j-k, and i-(k,l), the singly excited configurations, i-k and i-l. b) The direction of the transition moment is shown in the parentheses, the x-axis being taken to be parallel to the O···H···O bond within the molecular (x-y) plane. c) The main component of the transition moment is shown in the parentheses, the x-axis being taken to be parallel to the C_2–C_4 line within the C_2–C_3–C_4 (x-y) plane (see Fig. 6(a)). d) Estimated from the observed intensity measured at 20 °C in the vapor phase by the aid of the equilibrium constant, K. e) Observed value in perfluorohexane. f) x- and z-components of the transition moment contribute comparably with the same sign to each other. g) x-Component of the transition moment contributes appreciably with the opposite sign to z-component.

—54000 cm^{-1} band can be resolved into the Rydberg bands of the keto form (≈52000 cm^{-1}) and the enol form (53300 cm^{-1}); the resolved spectra are also shown in Fig. 3. Equation 1 was applied to the ≈52000 cm^{-1} band of the keto form. From the first I_p value (9.60 eV) of the keto form,[27] δ was determined to be 0.92 corresponding to $n=3$, suggesting that the ≈52000 cm^{-1} band is due to the transition to the 3s Rydberg orbital from the highest occupied n orbital.

The UV absorption spectrum of the acetylacetonate anion[28] was also measured in 0.1 M NaOH aqueous solution; the result is shown in Fig. 2. Theoretical result tabulated in Table 2 clearly shows that the 34190 cm^{-1} (4.24 eV) band of the anion can be assigned to the first π-π^* transition calculated at 4.60 eV.

Electronic Structure of the Intramolecular Hydrogen Bond. Figure 4 shows the energy levels calculated by the modified CNDO-CI method for some low-lying π-π^* and σ-σ^* excited states of the enol form. In the figure, i–j represents a singly excited configuration caused by the one-electron excitation from the i-th occupied MO to the j-th vacant MO. The shapes of the MO's of the enol form are schematically shown in Fig. 5. The CT band characteristic of the intramolecular hydrogen bond, O···H···O corresponds to the transition from the nonbonding orbital to the antibonding orbital in the hydrogen bond. The 20–26 configuration corresponds to this transition. As is illustrated in Fig. 4, the 20–26 CT configuration interacts significantly with the 19–21 and 14–21 π-π^* configurations, and contributes to the first (calculated at 4.47 eV) and sixth (calculated at 9.02 eV) excited states. The 4.47 eV band is mainly composed of the 19–21 π-π^* (83.3%) and 20–26 CT (9.8%) configurations. The main configurations in other excited states of the enol form are also given in Table 1.

The character of the intramolecular hydrogen bond of acetylacetone can be clarified quantitatively by the configuration analysis; the results for the ground and the first π-π^* excited (calculated at 4.47 eV) states are tabulated in Table 3, together with the result for the first σ-σ^* excited (predicted at 8.38 eV) state. In the ground state, the hydrogen bond is composed of the symmetric covalent structure III (≈45.1%), the ionic structure V (≈42.9%), and the symmetric ionic structure I (≈11.0%). As is shown in a previous paper,[16] the CT structure corresponds to the antisymmetric covalent structure IV and antisymmetric ionic structure II. The antisymmetric covalent and ionic structures contribute fairly (≈9.7%) to the first π-π^* excited state, but contribute only little (≈1.4%) to the first σ-σ^* excited state predicted at 8.38 eV.

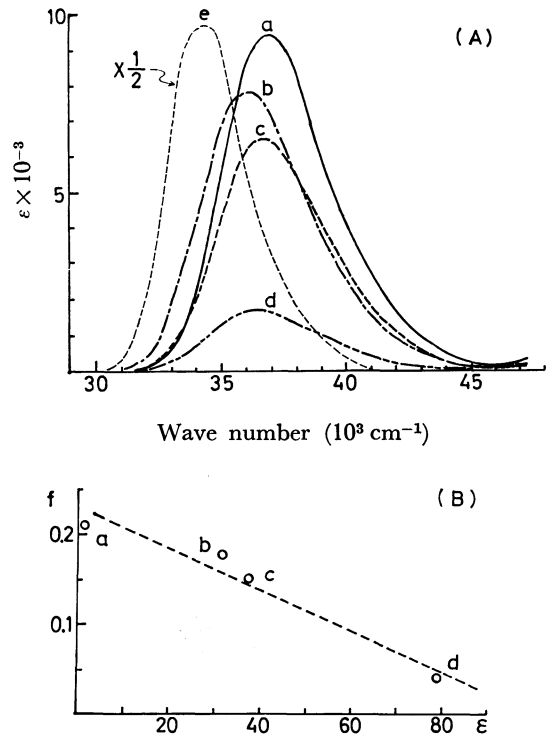

Fig. 2. (A) UV absorption spectra of acetylacetone measured at room temperature in (a) heptane, (b) methanol, (c) acetonitrile, (d) water, and (e) 0.1 M NaOH aqueous solution.
(B) Dependence of the oscillator strength (f) observed with the 36000—37000 cm^{-1} band in (a) heptane, (b) methanol, (c) acetonitrile, and (d) water upon the dielectric constant (ε) of the solvent used.

Electron Densities. Figure 6 shows electron densities for the ground states of the keto and enol forms of acetylacetone, and of its anion. The carbon and oxygen atoms in the five membered ring of the enol form are more polarized than the corresponding atoms in the keto form. By the removal of the hydrogen-bonded proton, electron densities in the anion increase in the whole region of the molecule compared to the corresponding ones in the enol form. Dipole moments of the keto and enol forms of acetylacetone were calculated to be 4.93 and 3.18 Debye, respectively, being in good agreement with the observed value for the enol form in the vapor phase (3.0 Debye).[29]

Table 2. Transition energies ($^1\Delta E$(eV)) and oscillator strengths (f) observed and calculated for the acetylacetonate anion

Assignment[a]	Obsd		Calcd[a]	
	$^1\Delta E$	f	$^1\Delta E$	f[b]
σ-π*			2.92	0.000$_2$ (z)
σ-π*			3.60	0
π-π*	4.24	0.37	4.60	0.234 (x)
σ-π*			6.01	0
π-π*			6.27	0.249 (y)
σ-π*			6.46	0.027 (z)
π-σ*			6.83	0.024 (z)
π-π*			7.30	0.042 (y)
σ-σ*			7.40	0.001 (x)
π-σ*			7.51	0
σ-σ*			7.65	0.015 (y)
σ-π*			7.98	0
π-σ*			8.26	0.009 (z)
σ-π*			8.53	0.001 (z)
σ-σ*			8.67	0.011 (x)
π-π*+σ-σ*			8.84	0.276 (x)

a) The molecular structure was assumed to be the same to the one of the enol form of acetylacetone except for the fact that the hydrogen-bonded proton was removed.
b) The direction of the transition moment is shown in the parentheses, the x-axis being taken to be parallel to the O···O line within the molecular (x-y) plane.

Equilibrium Constant Between Keto and Enol Forms of Acetylacetone. The equilibrium constant (K) between the keto and enol forms of acetylacetone;

$$K = [\text{enol}]/[\text{keto}] \quad (2)$$

was determined in the vapor phase from the temperature dependence of the absorption spectrum shown in Fig. 3. As already mentioned, gaseous acetylacetone

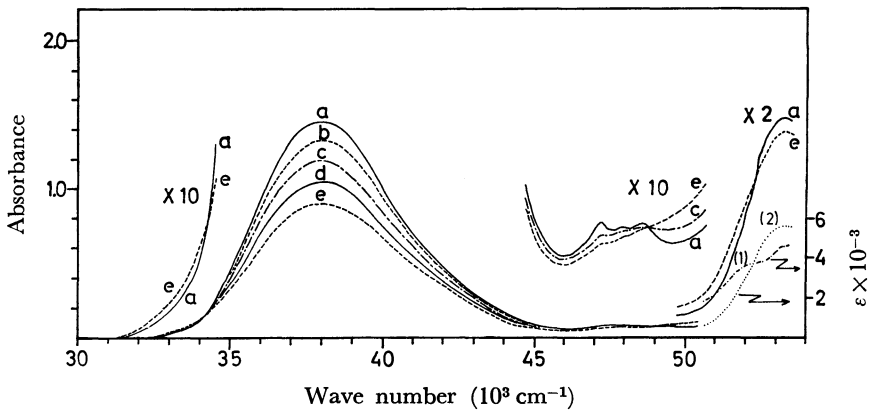

Fig. 3. Absorption spectra of acetylacetone in the vapor phase measured at (a) 20°, (b) 98°, (c) 120°, (d) 169°, and (e) 204 °C. From the mole fraction of the enol form, absorption spectrum in the 50000—54000 cm^{-1} region was resolved into two spectra ascribed to (1) the keto form and (2) the enol form of acetylacetone.

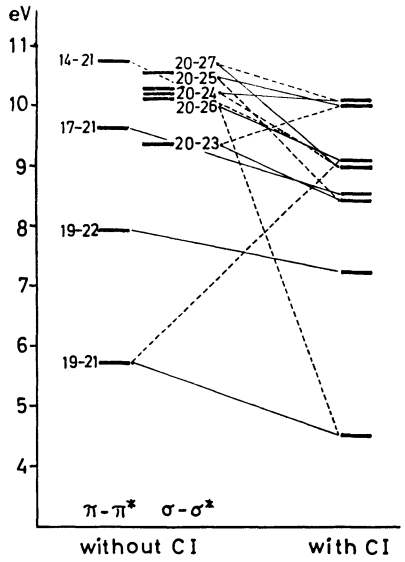

Fig. 4. Energy levels calculated with and without CI treatment for some lower π-π^* and σ-σ^* excited states of the enol form of acetylacetone.

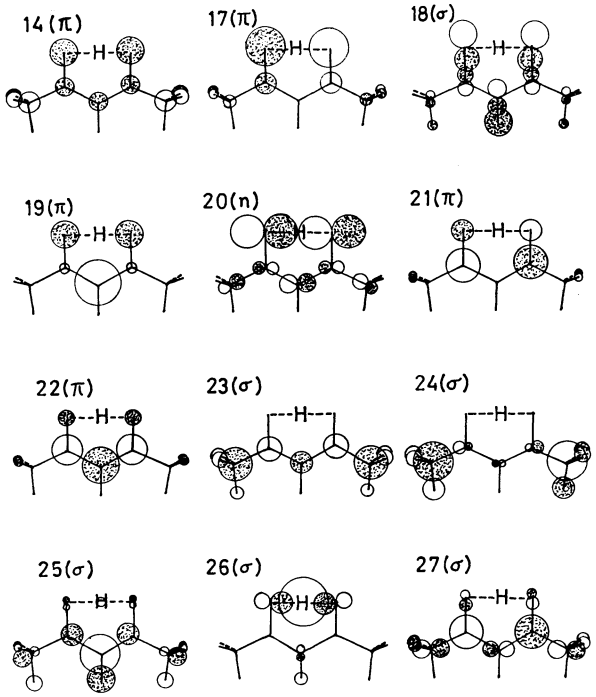

Fig. 5. Schematic shapes of some occupied and vacant MO's of the enol form of acetylacetone. The 20th MO is the highest occupied one.

at room temperature exists almost completely as the enol form. Strictly speaking, however, it may contain slightly the keto form. In view of this, we tried to determine accurately the mole fraction of the enol form and the K value from a linear relationship between $\ln K$ and $1/T$. In actuality, we evaluated K at 68, 120, 169, and 204 °C by combining the observed absorption intensity (at each temperature) at 38020 cm^{-1} and the molar extinction coefficients at the same wave number derived from several appropriate mole fraction values of the enol form at 20 °C, 90.0, 95.0, 96.2, 97.0, and 100%. The values of $\ln K$ obtained thus at 20—204 °C are plotted against $1/T$ (Fig. 7). We can see that the linear relationship is most satisfactorily held for the mole fraction of 96.2%. The K values for this case

Table 3. Results of the configuration analysis (weights) for the ground and the first π-π^* and σ-σ^* excited states of the enol form of acetylacetone

	Structure	Reference configuration[a,b]	State		
			Ground	1st π-π^*	1st σ-σ^*
I	$(OH^-O^+)+(O^+H^-O)$[c]	i,j-36, 36	0.1101	—	—
II	$(OH^-O^+)-(O^+H^-O)$	i,j-36, 36	—	0.0320	0.0045
III	$(O\text{-}H\cdots O)+(O\cdots H\text{-}O)$	i-36	0.4166	—	—
		i-36 + π-π^*[d]	0.0194	0.3627	0.0386
		i-36 + σ-σ^*[d]	0.0153	0.0081	0.3628
		(Total for sym. covalent structure)	(0.4513)	(0.3708)	(0.4014)
IV	$(O\text{-}H\cdots O)-(O\cdots H\text{-}O)$	i-36	—	0.0605	0.0085
		i-36 + π-π^*[d]	—	0.0028	0.0004
		i-36 + σ-σ^*[d]	—	0.0019	0.0003
		(Total for antisym. covalent structure)		(0.0652)	(0.0092)
V	$O^{-1/2}H^+O^{-1/2}$	G^0 [e]	0.3942	—	—
		π-π^*[f]	0.0184	0.3433	0.0365
		σ-σ^*[f]	0.0153	0.0082	0.3460
		i,j-k,l	0.0013	0.0232	0.0297
		(Total for $O^{-1/2}H^+O^{-1/2}$ structure)	(0.4292)	(0.3747)	(0.4122)
		Total	0.9906	0.8427	0.8273

a) i and j denote the 20 occupied MO's of the anion, and k and l, the 15 vacant MO's of the anion. The 1s orbital of the hydrogen-bonded hydrogen is numbered as the 36th vacant orbital. b) i-k and i,j-k,l denote the singly and doubly excited reference configurations, respectively. c) The ionic structure, $((O^+H^-O)+(OH^-O^+))$, is also involved. d) Doubly excited configurations, i,j-k,36. e) The ground reference configuration coincides with the ground state of the anion. f) Singly excited configurations, i-k.

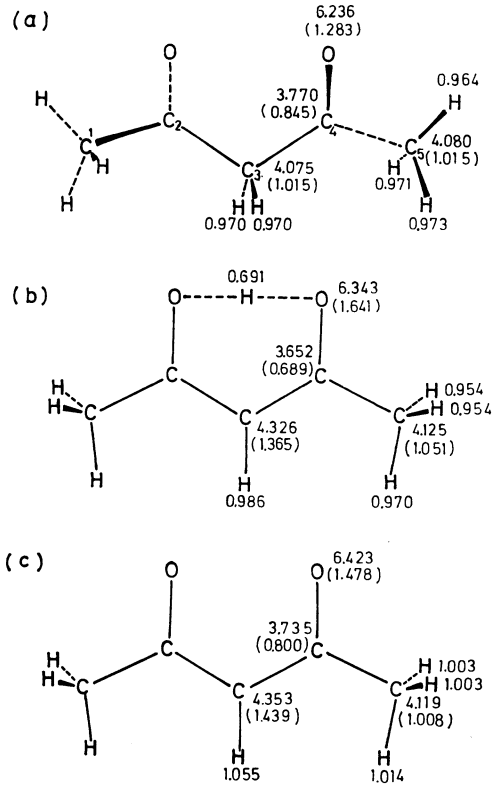

Fig. 6. Total and π-(in parentheses) electron densities calculated for the ground states of (a) the keto form, (b) the enol form, and (c) the anion of acetylacetone.

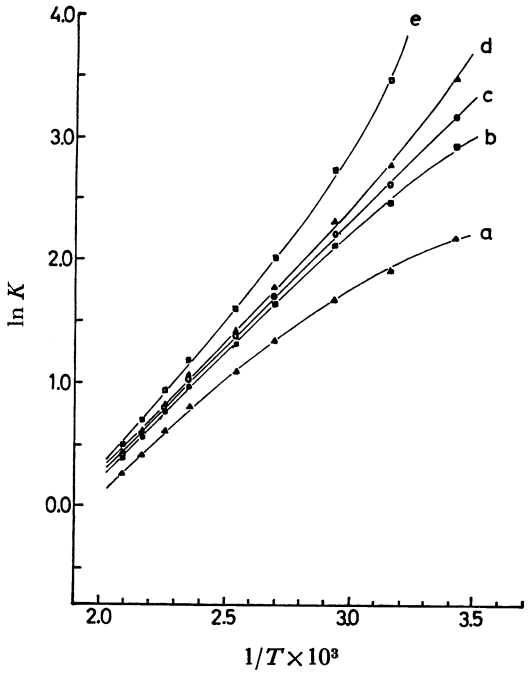

Fig. 7. Plots of $\ln K$ *versus* $1/T$ for acetylacetone in the vapor phase. The assumed mole fraction of the enol form at 20 °C is (a) 90.0%, (b) 95.0%, (c) 96.2%, (d) 97.0%, and (e) 100%.

are 25 at 20 °C, 9.5 at 68 °C, 4.03 at 120 °C, 2.25 at 169 °C, and 1.51 at 204 °C. From the slope of the straight line (c) in Fig. 7, the enthalpy change ($\Delta H°$) between the keto and enol forms in the vapor phase was evaluated to be −4.3 kcal/mol, being in good agreement with the result by an IR study in the vapor phase ($\Delta H° = -3.9$ kcal/mole) by Mecke and Funck.[30] From the mole fraction of the enol form, the ε_{max} and f values of the 38020 cm^{-1} band were calculated to be 10600 and 0.24, respectively.

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References

1) J. P. Schaefer and P. J. Wheatley, *J. Chem. Soc., A*, **1966**, 528.
2) A. H. Lowrey, C. George, P. D'Antonio, and J. Karle, *J. Am. Chem. Soc.*, **93**, 6399 (1971).
3) A. L. Andreassen, D. Zebelman, and S. H. Bauer, *J. Am. Chem. Soc.*, **93**, 1148 (1971); A. L. Andreassen and S. H. Bauer, *J. Mol. Struct.*, **12**, 381 (1972).
4) J. E. Del Bene and W. L. Kochenour, *J. Am. Chem. Soc.*, **98**, 2041 (1976).
5) G. Karlström, H. Wennerström, B. Jönsson, S. Forsén, J. Almlöf, and B. Roos, *J. Am. Chem. Soc.*, **97**, 4188 (1975); G. Karlström, B. Jönsson, B. Roos, and H. Wennerström, *ibid.*, **98**, 6851 (1976).
6) A. D. Isaacson and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 4453 (1975).
7) P. Schuster, *Chem. Phys. Lett.*, **3**, 433 (1969).
8) M. S. Gordon and R. D. Koob, *J. Am. Chem. Soc.*, **95**, 5863 (1973).
9) P. Grossman, *Z. Phys. Chem.*, **109**, 305 (1924).
10) R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).
11) B. Eistert and W. Reiss, *Chem. Ber.*, **87**, 108 (1954); B. Eistert, E. Merkel, and W. Reiss, *ibid.*, **87**, 1513 (1954).
12) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).
13) G. S. Hammond, W. G. Borduin, and G. A. Guter, *J. Am. Chem. Soc.*, **81**, 4682 (1959).
14) For the discussion about the CT mechanism of the hydrogen bond, see for example, C. A. Coulson, *Research*, **10**, 149 (1957); S. Bratož, "Advances in Quantum Chemistry," Vol. 3, ed by P. O. Löwdin, Academic Press, New York (1967), p. 209; R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York (1969).
15) S. Nagakura, *J. Chim. Phys.*, **61**, 217 (1964).
16) H. Morita, K. Fuke, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **50**, 645 (1977).
17) H. Nakanishi, H. Morita, and S. Nagakura, *J. Mol. Spectrosc.*, **65**, 295 (1977).
18) H. Morita, K. Fuke, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **49**, 922 (1976).
19) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50**, 2078 (1968).
20) K. Kaya and S. Nagakura, *J. Mol. Spectrosc.*, **44**, 279 (1972).
21) A. Kuboyama, S. Matsuzaki, H. Takagi, and H. Arano, *Bull. Chem. Soc. Jpn.*, **47**, 1604 (1974).
22) The molecular geometries of acetylacetone determined by vapor-phase electron diffraction studies by different authors[2,3] differ appreciably to each other. The result of

tetraacetylethane by X-ray diffraction study[1] is intermediate between the above two results.

23) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

24) J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.*, **73**, 4553 (1951).

25) R. Mecke and E. Funck, *Z. Electrochem.*, **60**, 1124 (1956).

26) M. B. Robin, "Higher Excited States of Polyatomic Molecules," Vol. 1, Academic Press, New York (1974).

27) A. Schweig, H. Vermeer, and U. Weidner, *Chem. Phys. Lett.*, **26**, 229 (1974).

28) F. Hashimoto, J. Tanaka, and S. Nagakura, *J. Mol. Spectrosc.*, **10**, 401 (1963).

29) C. T. Zahn, *Physik. Z.*, **34**, 461 (1933); A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco (1963), p. 143.

30) R. Mecke and E. Funck, "Hydrogen Bonding," ed by D. Hadži, Pergamon Press, London (1959), p. 433.