Structure of Croconic Acid

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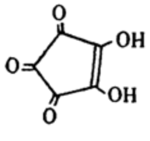
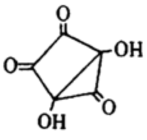
Croconic acid, $C_5H_2O_5$, is a yellow substance which has been known for a long time. It has a strong acidity and is sensitive to the sun light. However, there has been some ambiguity as regards its structure. So far, two structural formulas I[1] and II[2] have been forwarded; further it was suggested that there was an equilibrium involving the formula III[3] in an aqueous solution.


(I)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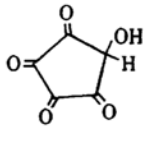
(III)

According to polarographic studies[4] of croconic acid which were done in recent years, it showed properties somewhat different from the typical enediolic compounds studied at the same time.

The properties of croconic acid were examined in order to elucidate its structure, and during the course of studies many interesting observations were obtained. Its ultraviolet spectrum differed from that expected from either structure I or II, the infrared spectrum showed a strong hydrogen bond, and its dipole moment was unusually large.

Methylation.—Since the two hydrogen atoms would naturally be expected to play a unique and important role in the characteristic properties of this acid, a methylation was first carried out. Treatment of the silver salt of the acid with methyl iodide yielded the dimethyl derivative, $C_5O_5(CH_3)_2$.

Ultraviolet spectrum.—Figs. 1—4 show the ultraviolet spectra of the croconic acid and dimethyl croconate. The solvent and the pH of the solution exert a strong influence on the spectra of croconic acid.

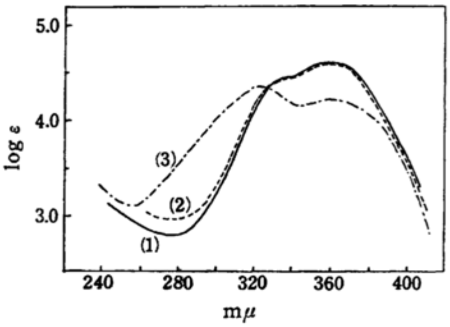

Fig. 1. Croconic acid in water.
(1): neutral; (2): 0.1 N NaOH;
(3): 0.1 N HCl.

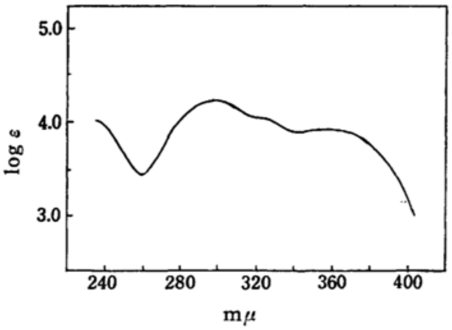

Fig. 2. Croconic acid in ethanol.

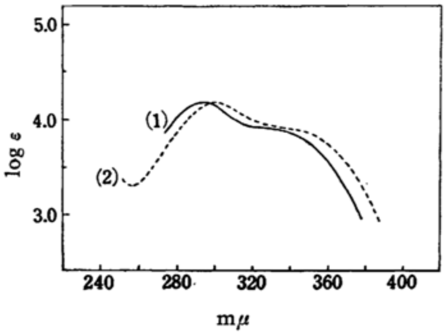

Fig. 3. Croconic acid.
(1): dioxane solution
(2): aqueous solution (9 N HCl)

In the first place, paying attention to the changes of the spectra caused by varying the solvent, we find that the spectrum in an aqueous solution substantially agrees with that in methanol,

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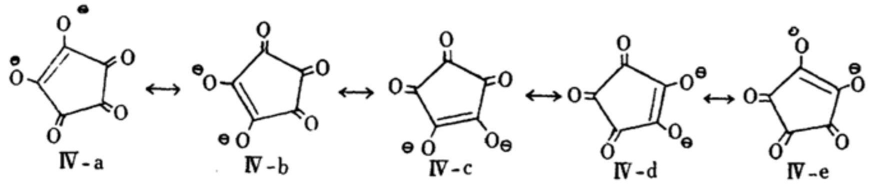
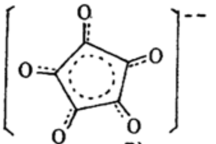
[1] R. Malachowski, *Chem. Ber.*, **71**, 2246 (1938).

[2] R. Nietzki et al., ibid., **18**, 510, 1833 (1885).
G. E. Carpéni, *Compt. rend.*, **206**, 601 (1938).

[3] Y. Hirata et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*) **69**, 63 (1948).

[4] F. Petuely et al., *Monatsh.*, **83**, 80 (1952).
F. Arcamone et al., *Bull. soc. chim. France*, **1953**, 891.





(IV)[5]

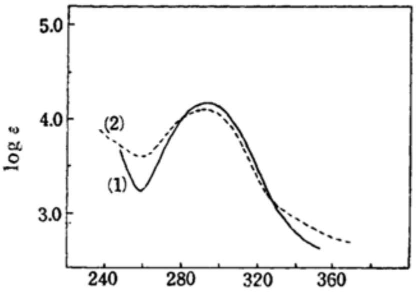


Fig. 4. (1): croconic acid in HCl gas saturated methanol
(2): dimethyl croconate in methanol

but that in ethanol there appears a new absorption in the short wave length region, and the intensity of the band common to aqueous and methanolic solution is lowered. Second, changes in pH lead to the following results; i. e., the spectra taken in a neutral and an alkaline solution are almost the same. On the other hand, when the solution is acidified, a new short wave length band appears. This new absorption is clearly different from the one observed in ethanol solution. Third, the two spectra taken in strong acidic aqueous solution (9 N hydrochloric acid) and in the non-polar dioxane agree with each other fairly well, but a general bathochromic shift of 8~10 mμ is apparent in the former solvent. Finally, though the spectrum of the dimethyl croconate taken in neutral methanol differed from that of the free acid taken in the same solvent, it showed a close similarity when the latter was taken in acidic methanol (compare Figs. 1 and 4).

This spectral behavior may be interpreted as follows. The intensities of the absorptions in Figs. 1—3, are strong enough to exclude the possibility that the absorptions originate from the assumed structures II or III, and, moreover, the absorptions in Figs. 1 and 2 can not be attributed to the enediolic keto form I.

At first, it may be noted that the two curves in Fig. 4, namely, the absorption of the acid in strong acidic methanol, and that of its dimethyl derivative in the neutral methanol show a close resemblance (the difference of two $\lambda_{\text{max.}}$ is 3 mμ). Then, considering the positions and the intensities, it is reasonable to conclude that these two absorptions are due to I, or, in other words, due to the chromophore of the enediolic keto structure. We next turn to the absorption maxima in the long wave length region. On account of the strong acidity of croconic acid, it should be almost completely dissociated in water or in methanol to give the dianion, the "croconate ion", which presumably exists in a highly resonating state IV[5], receiving contributions from the structures IVa to IVe. Accordingly, the absorption near 295 mμ due to structure I disappears and, instead, the characteristic absorption of the croconate ion appears around 365 mμ.

In the last place, Fig. 3 will be examined. As mentioned before, the two absorptions are quite similar except the fact that one is shifted by 8~10 mμ as compared to the other. The dipole moment[6] of the acid in dioxane supports structure I with the two hydroxyl groups lying in the plane of the five membered ring. The inference from the observation is that the acid is in an undissociated state in strongly acidic

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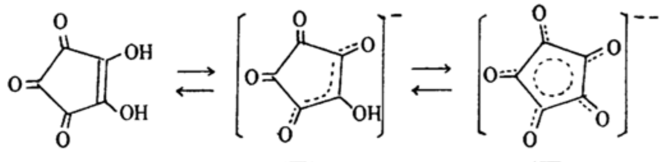
[5] The dotted lines in structure IV simply denote that the two electrons are distributed throughout the entire molecule, and certainly does not denote that the molecule is mesoionic.

[6] M. Washino et al., This Bulletin, **31**, 520 (1958).



(I) (V) (IV)

aqueous solutions and takes the form of I⁽⁷⁾. The details of the spectra in ethanol and weakly acidic aqueous solution are illustrated in the experimental part.

Acidity.—As is apparent from the synthetic method, croconic acid is a strongly acidic compound and for this reason its purification is not easy. Since this strong acidity had already been well known qualitatively, the spectrophotometric method was applied for the measurement of pK_a.

Since two isosbestic points are present, as shown in Fig. 5, it may be inferred that two equilibrium systems exist; one is $I \rightleftarrows V$ in the low pH range, and the other is $V \rightleftarrows IV$ in the high pH range. But from the facts that the first isosbestic point (305 mμ) is incomplete and that there exist several absorption curves at intermediate pH's which deviate from both points, it can be deduced that the dissociations do not proceed stepwise and that the croconate ion IV is formed already in the range of low pH. The nature of the monoanion V will be considered next. The monoanion as well as the dianion is stabilized by resonance (Va, Vb); however, the extent of stabilization is smaller with the monoanion.

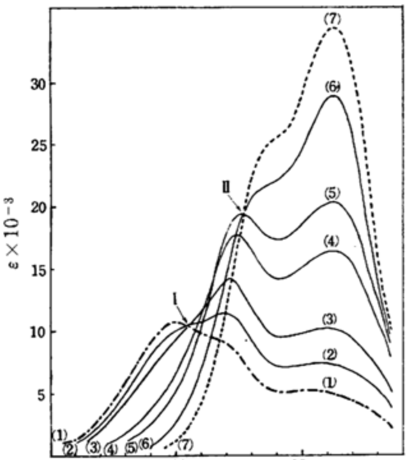
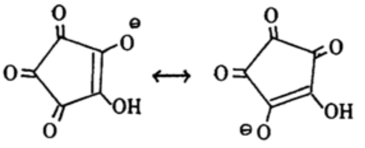


Fig. 5. Isosbestic points.
I: 305 mμ (ε=10400),
II: 327 mμ (ε=19300).
pH: (1) 0.2, (2) 0.3, (3) 0.5, (4) 1.0,
(5) 1.3, (6) 2.0, (7) ca. 6.0.



V-a V-b

Based on this consideration, one may account for the experimental facts as follows; the second dissociation occurs to produce the more stable croconate ion before the neutral acid molecule I is completely dissociated into the monoanion. When measuring pK_a values spectrophotometrically, the ultraviolet spectrum of each molecular species must be known⁽⁸,⁹⁾. For example, with the β-diketone compounds studied by B. Eistert et al.⁽⁸⁾, the pK_{a1} and pK_{a2} were determined from the spectra of the three species, i. e., the enol oxonium cation, the neutral enol and the enol anion. In the case of croconic acid, the dissociations are not stepwise, and it is impossible to obtain the absorption curve of the monoanion. Furthermore, the curve of the undissociated acid can not be obtained under the conditions studied.

Thus the values of pK_{a1} and pK_{a2} in aqueous solution can not be measured, but it may be deduced that the first and the second dissociations both occur in the region below pH 2⁽¹⁰⁾.

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7) The following is worthy of notice; although the acid has the structure I both in strongly acidic aqueous solution and in acidic methanolic solution, the absorptions in these two solutions are different from each other (Fig. 3-(2), Fig. 4-(1)). One possible interpretation of this phenomenon is that in the acidic aqueous solution the lone pair electrons of the hydroxyl groups are able to conjugate with the annular π-electrons, whereas this is not the case in the acidic methanolic solution. However, the exact nature of the role played by solvents is not clear.

8) B. Eistert et al., *Chem. Ber.*, **87**, 108, 1513 (1954).

9) J. E. DeVries et al., *J. Am. Chem. Soc.*, **76**, 1008 (1954).

10) The pK_a can be obtained by plotting the absorbance against the pH at a suitable wave length (315 mμ). The curve obtained is distorted from the usual sigmoid shape on accout of the abnormal dissociations, and the estimation of the acidities is difficult. However, it is roughly estimated that the first dissociation occurs below pH 1 and the second one between pH 1~2.

Dipole moment.—The dipole moment of croconic acid is 9 to 10 D in dioxane. This large value is explicable only on the assumption that it has structure I. The dimethyl croconate has a dipole moment of 5.7∼6.0 D and this is also illustrated on the basis of structure I. For further details, see following report on dipole moment measurements.

Infrared spectrum.—(i) The infrared spectra of croconic acid are shown in Fig. 6-(1) and -(2). A broad band is observed around 3000 cm^{-1}, which is located at a higher frequency (3500 cm^{-1}) in potassium bromide than in Nujol (2600 cm.$^{-1}$); this band disappears when the wet method of potassium bromide is applied. In the region of 1500∼1800 cm.$^{-1}$, the bands taken in Nujol are somewhat different from those in potassium bromide, and their relative intensities are also different in both cases. The main bands are as follows: 1755, 1720 (w), 1655, 1630, 1540 (in Nujol); 1755, 1720, 1665, 1640, 1600, 1560 (shoulder), (in potassium bromide).

In the finger-print region, the spectra in potassium bromide and in Nujol have little resemblance. It is worth while to

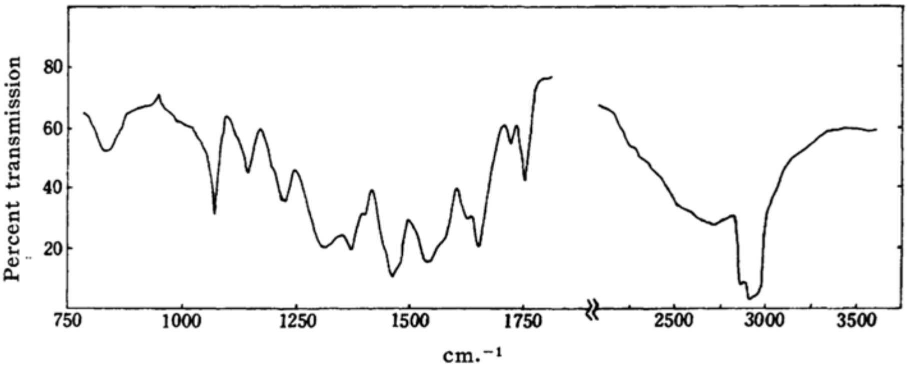


Fig. 6-(1). Croconic Acid (Nujol).

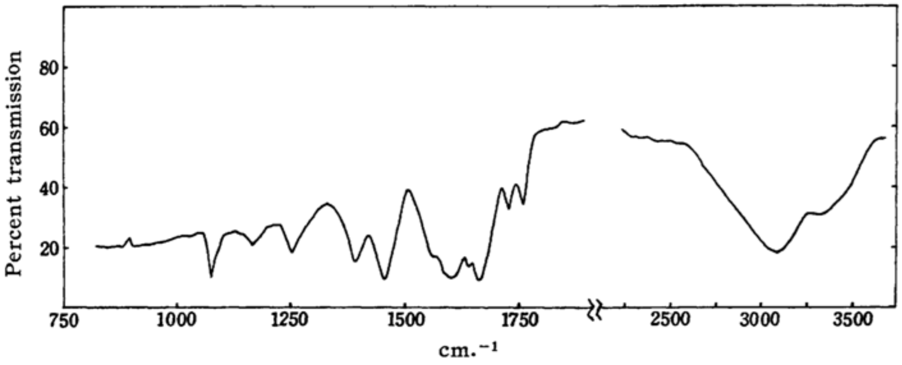


Fig. 6-(2). Croconic Acid (KBr).

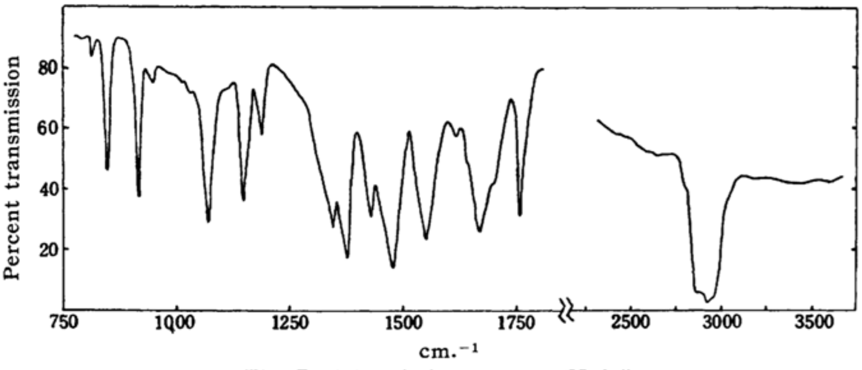


Fig. 7. Dimethyl croconate (Nujol).

notice the sharp band at 1075 cm^{-1}. This band is observed not only in the acid, but in the dimethyl derivative in Fig. 7.

(ii) As expected, there is no absorption band near 3000 cm^{-1} in the spectrum of the dimethyl derivative (Fig. 7). The main bands in the 1500$\sim$1800 cm^{-1} region are as follows: 1757, 1695 (shoulder), 1655, 1610, 1550. All the bands are sharp in comparison with those of the acid, and in the finger-print region, there is no band corresponding to the band of the acid except the band at 1075 cm^{-1} described before.

(iii) The spectra of the various metallic salts of the acid were measured (Fig. 8), in order to examine croconic acid in the ionic state. A strong broad band in the region of 1300$\sim$1700 cm^{-1} was common to all samples, and besides this, a few weak bands were observed. The bands in the finger-print region are small in number and weak.

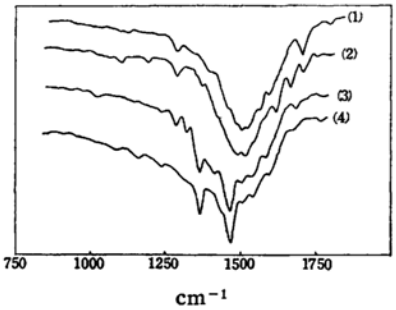
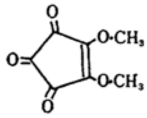


Fig. 8. Metallic salts of croconic acid.
(1) K (2) Ba (KBr)
(3) Ag (4) Cu (Nujol)

(iv) Some of the deductions from these spectra are as follows. Since the molecule is a compact system of conjugated groups in which intense coupling is expected to be present, the assignment of bands to specific groups is almost impossible. Nevertheless, assignments to a limited extent are possible. The band at 1755 cm^{-1} observed in both the acid and the dimethyl croconate is considered to originate from the $>$C=O groups. From the position of this band, the possibility is excluded that the acid might have the three-membered ketonic structure II. A four-membered ring ketone[11] absorbs at 1775 cm^{-1}, and if II is the actual case, the absorption would be expected to be even higher. Because of the broad bands of the acid, an exact comparison of the bands between the acid and the dimethyl croconate is difficult. However, approximate correspondences in their positions and intensities are observed, when the bands in the carbonyl region are compared.

The structure of the dimethyl croconate is believed to be VI, (see the section of ultraviolet spectrum and the report[6] on dipole moment measurement), and the similarity of the bands in the carbonyl region of the two compounds leads to the inference that the acid has structure I in its crystalline state.



(VI)

The broad band[12] near 3000 cm^{-1} is considered to be one due to a strong hydrogen bond. The band position of the hydrogen bond changes when the spectrum is taken in Nujol and in potassium bromide. The position of the hydrogen-bonded $\nu_{\mathrm{O\text{-}H}}$ band suggests a stronger bond in the sample mulled in Nujol.

The metallic salts show besides the very strong and broad band near 1500 cm^{-1} only several weak absorptions. This experimental result is explained by consideration of a symmetric structure IV for the croconate ion. In this structure, all bonds exist in a state more or less intermediate between that of single and double bonds, and the strong broad band at 1500 cm^{-1} is presumably a summation of the absorptions arising from these intermediate $>\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ bonds. It is well known that the absorptions of simple compounds with highly symmetrical structures are simple, i. e., the tropylium ion[13], and this interpretation is probably applicable to the present case also.

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[11] Whiffen et al., *J. Chem. Soc.*, **1946**, 1005.

[12] In carboxylic dimers, bands at $\simeq$1400 and $\simeq$1300 have been assigned to the coupling of in plane O-H bending and C-O stretching vibrations, and a band at $\simeq$940 to the out of plane O-H bending vibration (Sheppard and Hadži). Similar sets of bands are present in the spectra of dimedone and 2-hydroxy-1, 4-naphthoquinone, and accordingly it is presumed that somewhat analogous strong dimer rings are present in these two compounds. Croconic acid shows bands at 1455, 1245 and 800 cm^{-1} (in potassium bromide), and 1462, 1235 and 820 cm^{-1} (in Nujol), whereas these bands are absent in the spectrum of the dimethyl croconate (the band at 1430 cm^{-1} is probably due to $-\mathrm{CH_3}$). It would be intriguing to assume the presence of a similar dimerization (intermolecular hydrogen bond) tentatively in the case of croconic acid.

[13] W. v. E. Doering et al., *J. Am. Chem. Soc*, **76**, 3203 (1954).

Results

(A) State in solution.—In solution, croconic acid takes three different forms; the undissociated molecule I, the monoanion V and the dianion IV. The position of the equilibrium depends on the pH and the solvent used, as summarized roughly in Table I.

TABLE I

CROCONIC ACID IN SOLUTION

	Alkaline	Neutral	Acidic	Strong Acidic
Water	IV	IV	I, IV, V	I
Methanol	IV	IV	I, IV, V	I
Ethanol	IV	I, IV, V	I, IV, V	I

The undissociated molecule, the structure of which turned out to be I on the basis of the ultraviolet spectrum of dimethyl croconate VI exists only in strongly acidic solution. There seem to be two types of ultraviolet spectra corresponding to the undissociated molecule and this seems to suggest some effect of the lone pair belonging to the oxygen atoms of hydroxyl groups (Figs. 3-(2) and 4-(1)). Little is known about the monoanion V, existence of which is noticed from the ultraviolet spectrum. Finally, the croconate ion IV is a stable and highly symmetrical dianion, and absorbs strongly at a higher wave length than the undissociated molecule in the ultraviolet spectrum[14]. A similar bathochromic shift in the symmetric ion is observed in the β-diketone system. Namely, the absorption of the highly symmetrical enolate ion occurs at a wave length higher than that of less symmetrical enol[8]. The great stability of the croconate ion accounts for the strong acidity of the two hydroxyl groups.

It is presumed that the keto-form III, if it exists at all, is contained only to a negligible extent.

(B) Solid state.—The dipole moment and the ultraviolet spectrum of the dimethyl croconate support structure VI for this compound. Moreover, structure I for the free acid becomes favorable from the similarity of infrared spectra of the acid and the dimethyl croconate. The characteristic feature of the infrared spectrum of the acid is the strong hydrogen-bonded band and a set of bands similar to those observed with dimeric carboxylic acids, which disappear upon methylation. The three-membered ketonic structure II is excluded from the C=O band at 1755 cm^{-1}. The croconate ion is formed in the metallic salt, and only a few bands are observed because of the symmetrical structure of this ion.

Experimental

The ultraviolet spectra were measured with a Hitachi Spectrophotometer. Infrared spectra were measured with a Hilger H 800 Model, equipped with rock-salt prisms.

Croconic acid.—Glyoxal was used as the starting material, and the sample was recrystallized twice (for details of synthesis, see the following paper[15]).

Ultraviolet spectra of croconic acid.—Table II shows the positions and intensities of the absorptions of croconic acid and its dimethyl derivative. The dimethyl croconate, easily hydrolyzed even in the air, was weighed as rapidly as qossible and dissolved in methanol; once in solution, it is stable. When the solution was placed under the sun light, the intensity of the whole absorption was somewhat weakened, but the extent was not as considerable as in the case of croconic acid (croconic acid is decomposed rapidly by the sun light). The solvent methanol used for the dimethyl croconate was free from water (using metallic calcium) and distilled.

TABLE II

Solvent	Neutral		Alkaline		Acidic		Strong acidic	
	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
	(mμ)		(Croconic acid)					
Water	365	4.6	365	4.6	323 363	4.3 4.2	300	4.2
Ethanol	365	4.6	363	4.6	—	—	296	4.16
Methanol	298 360	4.2 3.9	—	—	—	—	—	—
Dioxane	295	4.16	—	—	—	—	—	—
			(Dimethyl croconate)					
Methanol	292	4.1	—	—	—	—	—	—

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[14] The calculation[6] based on the molecular orbital method agrees with this experimental fact.

[15] K. Yamada et al., This Bulletin, **31**, 550 (1958).

[16] B. O. Heston et al., *J. Am. Chem. Soc.*, **56**, 1462 (1954).

Two absorption peaks are clearly present in the weakly acidic aqueous solution and the ethanol solution of the croconic acid. These absorption curves differ from that of the croconate ion measured in water or in methanol. Croconic acid is presumed to exist as an equilibrium mixture among the neutral molecule and the ions (mono- or di-ion). The "solvent basicity" increases in the sequence of ethanol, methanol, and water[16], and thus the equilibrium is shifted towards the ions to a greater extent in the same order. The curves in Figs. 1-(3) and 2 are a composite of the three species.

Isosbestic point of croconic acid.—A stock solution containing 3.638 mg. of croconic acid in 50 ml. of water was prepared. Various solutions having different pH (about 0.1～2.5) were prepared as follows. One normal solution of hydrochloric acid was diluted suitably to make a solution having the desired pH. The ionic strength of every solution was adjusted to that of 1 N hydrochloric acid by adding the proper quantity of 1 M sodium chloride solution. The stock solution (1 ml.) was exactly added to 9 ml. of the solution prepared as noted above. The curve 7 in Fig. 5 was measured in 1 M sodium chloride solution. The absorption curve at pH 2.4, though not shown in Fig. 5, almost coincides with that in the neutral solution. As described previously in this paper, the isosbestic point at 305 mμ (ε=10400) is incomplete and the curves at pH 0.2, 0.3, 0.5, do not intersect at one point strictly. The absorption curves taken in the pH range of 0.6～1.2 pass neither of the isosbestic points. There thus exists an eqilibrium of three components in this pH region.

Metallic salts of croconic acids.—Various metallic salts were obtained easily from croconic acid. Potassium salt and barium salt were obtained during the synthetic process, or adding potassium hydroxide or barium hydroxide (or chloride) to the aqueous solution of croconic acid. The potassium salt loses the crystal water (2 moles) in a desiccator (yellow crystal), but this is easily absorbed again when placed in the air (orange crystal). Cupric salt, lead salt, etc., were obtained from the chloride or nitrate of the metal and the aqueous solution of croconic acid. The silver salt was prepared from silver nitrate. On account of the strong reducing property of croconic acid, the silver nitrate was partly reduced, and metallic silver was deposited. The silver salt was filtered at once under protection from the sun light.

Summary

The structure of croconic acid in solution and in the solid state has been studied. The undissociated molecule is represented by structure I and the ion by structure IV.

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