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The Basicities of Tropone and Tropolone

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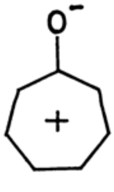
The ultraviolet absorption spectra of tropone (I) and tropolone (II) were measured with sulfuric acid solutions of various acidities. The accurate pK_a values, as determined by the proposed method, were -1.02 and -0.86 for I and II respectively. The Raman spectra of II were measured with sulfuric acid solutions of various acid concentrations. The bands in the 6 and 15 μ regions change sharply when the solvent acidity changes from 5 to 25%, corresponding well to the ultraviolet absorption change. The infrared absorption spectra of II were measured with the concentrated deuterosulfuric acid solution in the 6 μ region. The vibrationals mode of the protonated tropolone were discussed.

As evidenced by the facile production of their hydrochlorides, tropone and tropolone are known to be relatively stronger bases than most other unsaturated ketones.[1,2] We have shown theoretically in a previous paper[3] that this anomalously large basic character of tropone derivatives is attributable to the large (16%) contribution of the polar structure to the ground state. The



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[1] T. Nozoe, T. Mukai and K. Takase, *Sci. Rep. Tohoku Univ. Ser. I*, **39**, 164 (1956).

[2] T. Nozoe, "Non-benzenoid Aromatic Compounds," Interscience Publishers, New York (1959), p. 339.

[3] H. Hosoya, J. Tanaka and S. Nagakura, *Tetrahedron*, **18**, 859 (1962).

stabilities of tropone and tropolone hydrochlorides are also related to the stability of a unipositively charged seven-membered ring (the tropylium ion $C_7H_7{}^+$) system.

Recently Raman spectra have come to be used to study the structural change of organic bases in strong acidic media,[4,5] while ultraviolet absorption measurements have been shown to be suitable for the critical analyses of equilibria, even in strong acidic media.[4] Therefore, both methods were applied to the study of the protonations of tropone and tropolone.[6]

Experimental

Materials.—Tropone and tropolone were purified by the methods described in previous papers.[3,7] Concentrated sulfuric acid of a G. R. grade (95%) was used without further purification. Deuterosulfuric acid (97% acid concentration and 99% deuterium concentration) was purchased from the Showa Denko K. K.

Measurements.—A Cary recording spectrophotometer, model 14 M, was used for the ultraviolet absorption measurements. The ultraviolet absorption spectra of tropone and tropolone (ca. 10^{-4} M) were measured with sulfuric acid solutions of various acidities (H_0), fused quartz cells with a path length of 1 cm. being used. Because of its unstability, tropone was purified by distillation just before the solution was prepared. The numerical values for the acidity function (H_0) of the solvent sulfuric acid were taken from the table of Paul and Long (at 25°C).[8] The measurements were carried out in a temperature-controlled room adjusted at 20°C (±1°C). Since the temperature dependency of acidity functions is small, no temperature corrections to them were made.

The Raman spectra of tropolone (5—10 wt. %) in various acidities of sulfuric acid solutions were measured with the Cary model 81 recording Raman spectrophotometer located at the Government Chemical Industrial Research Institute, Tokyo.[9] The solution in the cell was warmed as high as about 40°C during the Raman spectral measurements.

The infrared absorption spectrum of tropolone in a concentrated deuterosulfuric acid solution was measured with a Hitachi EPI-2 infrared spectrophotometer, with a rock salt prism attached. Polyethylene bag cells were used for this purpose; the details have been described elsewhere.[10]

Results and Discussion

The Basicities of Tropone and Tropolone.—The ultraviolet absoprtion spectrum of tropolone consists of two parts. We have assigned that the longer wavelength bands (250—400 mμ, A and B bands in Ref. 3) are due to the tropone excitation (perpendicular to the C=O axis) perturbed by the hydroxyl group. The spectrum changes with the sulfuric acid concentration of the solvent, the change at about 360 mμ being the most prominent (Fig. 1). For solutions with sulfuric acid concentrations higher than 60% the absorption curve gradually shifts to shorter wavelengths, but its shape remains unchanged. The former change unequivocally corresponds to the following equilibrium (X=OH) between tropolone and its conjugated acid,[11] while the latter change is probably due to the solvent effects. We have shown that the latter effects can be eliminated from the pK determination by applying the least

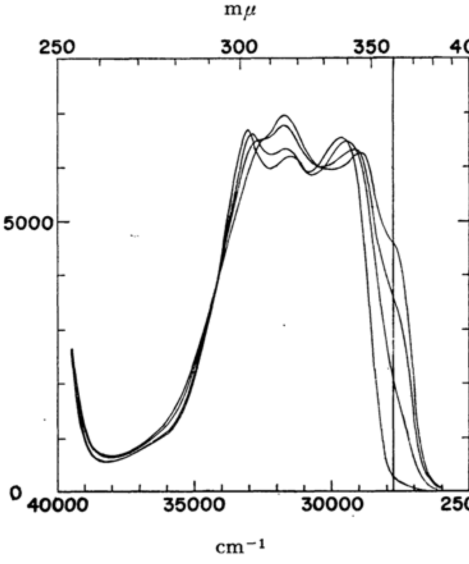

Fig. 1. Ultraviolet absorption spectra of tropolone in sulfuric acid of various concentrations.
The acidity constants H_0's of the solvents are -0.02, -0.48, -1.24, and -3.38 (from the top to the bottom at 360 mμ).

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[4] H. Hosoya and S. Nagakura, *Spectrochim. Acta,* **17**, 324 (1961).

[5] N. C. Deno and M. J. Wisotsky, *J. Am. Chem. Soc.*, **85**, 1735 (1963).

[6] In the course of preparing this paper, we found that Kende and his collaborators measured the pK_a value of tropone to be -0.6 ± 0.3 with the change in ultraviolet absorption spectra. Since Kende did not report the temperature and the detailed method of the pK_a determination, no discussion was made for the discrepancy between his and our pK_a values. A. Kende, "Advances in Chemical Physics," Vol. 8, Interscience Publishers, London (1965), p. 133.

[7] We thank Professor Yoshio Kitahara and Professor Kozo Doi, Tohoku University, for their kindness in giving us the samples of tropolone and cycloheptatriene.

[8] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

[9] We thank Mrs. Michiko Fukuyama for measuring the Raman spectra.

[10] H. Hosoya and S. Nagakura, This Bulletin, **37**, 249 (1964).

[11] The X-ray analysis of tropolone hydrochloride showed that protonation occurs at the carbonyl oxygen atom. Y. Sasada, K. Osaki and I. Nitta, *Acta Cryst.*, **7**, 113 (1954).

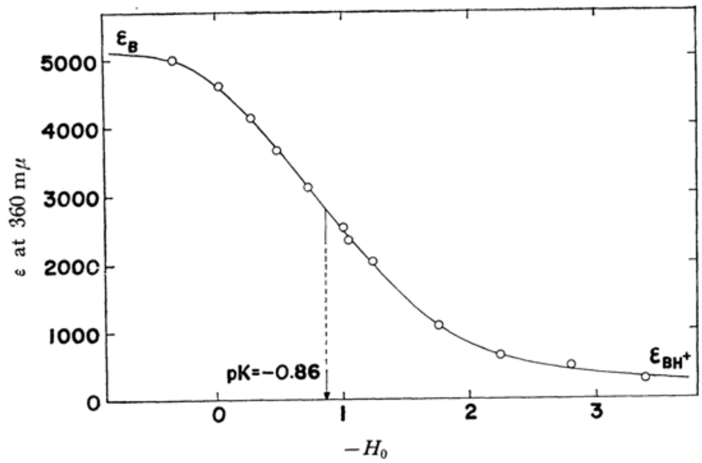


Fig. 2. Acidity dependency of the molar extinction coefficients at 360 mμ of tropolone in sulfuric acid. The vertical line and dots represent the inflection point of the sigmoid curve giving the pK_a value.

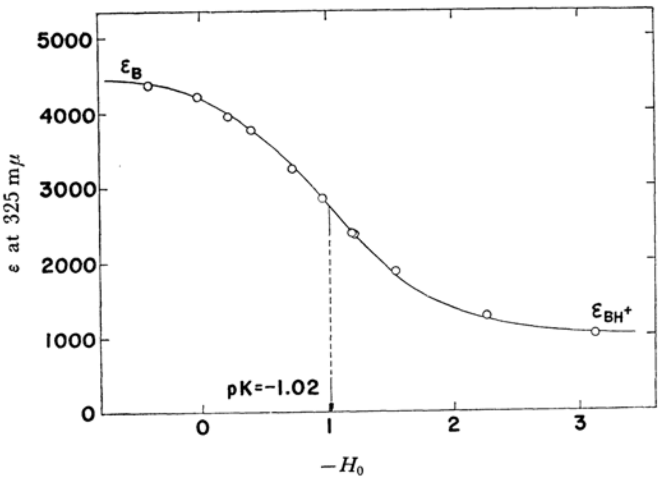
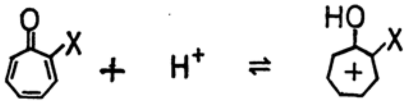


Fig. 3. Acidity dependency of the molar extinction coefficients at 325 mμ of tropone in sulfuric acid.



(1)

(X=H, OH)

squares calculation.[4,12] Namely, the H_0 value for the inflection point of the ε_λ—H_0 curve is just the pK value wanted, where ε_λ is the extinction coefficient subjected to the correction of solvent effects at the wavelentgh λ.

As is shown in Fig. 2, the observed ε values, at 360 mμ, for instance, change with the sulfuric acid concentration (H_0). The iterative calculation for determining simultaneously the pK_a, ε_B, and ε_{BH^+} values was executed following the method previously described.[4,12]

$$pK_a = -\log([B][H^+]/[BH^+]) \qquad (2)$$

After repeating the least squares calculations for twelve pairs of data, we found the pK_a value of tropolone to be -0.86.

The same method was applied to the tropone-sulfuric acid system, ε's at 325 mμ being used. The pK_a value was thus found to be -1.20 (see Fig. 3); namely, tropone is less basic than tropolone. The existence of the equilibrium 1 was confirmed by the H_0— $\log[(\varepsilon-\varepsilon_{BH^+})/(\varepsilon_B-\varepsilon)]$ plots, with slopes of 0.96 and 0.89 for tropolone and tropone respectively (Fig. 4).[4]

The pK_a value of -1 means that the concentrations of a base, B, and its conjugated acid, BH$^+$

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12) The quantity in the summation of the last term in each of the three Eqs. 14 in Ref. 4 should be multiplied by ε.

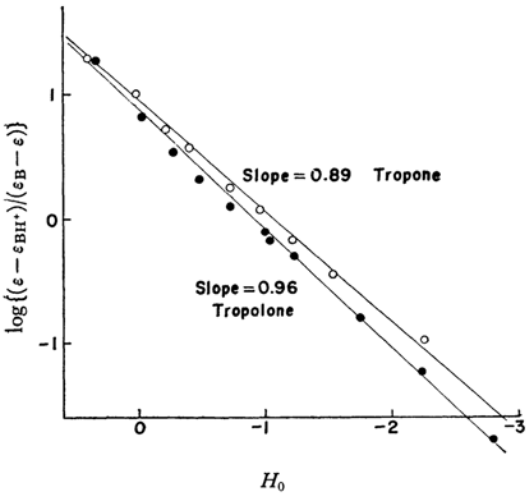

Fig. 4. Check of the existence of the equilibria 1. Open and filled circles stand, respectively, for tropone and tropolone.

are almost equal in a 20% sulfuric acid solution (4.7 N), while the sigmoid ε - H_0 curve observed shows that in sulfuric acid solutions more concentrated than 40% (the same acid concentration as the concentrated hydrochloric acid), these compounds are completely protonated. However, a host of carbonyl compounds, such as aromatic and aliphatic ketones, aldehydes and carboxylic acids, have their pK_a values in the −6—−7 range (in 70—80% sulfuric acid half-protonated).[13] This anomalously basic character of the carbonyl groups of troponoid compounds is due to the stability of the tropylium cation, as derivatives of which the protonated tropone or tropolone have been described. This is also the case for the anomalously basic cyclopropenone derivative.[6,14]

The dilution of the sulfuric acid solutions of these compounds with water gives almost the same spectra for their respective aqueous solutions, within an accuracy of about five per cent. This fact suggests the fair stabilities of these two compounds in concentrated sulfuric acid and the reversivility of the protonation processes.

Changes in Vibrational Spectra.—The infrared and Raman spectra of tropolone and its conjugated acid have characteristic but complicated features in the 1400—1650 cm^{-1} region, making a plausible assignment difficult.[15] Although the absolute intensities of the Raman spectra were not obtained accurately, therefore, a good reproducibility was obtained in each run. Thus, we have reproduced the spectra in various concentrations of sulfuric acid solutions on a logarithmic scale. Figure 5 shows the acicity dependency of the Raman spectra of this system in the 14 and 6—7 μ regions. It may be noticed that the relative intensities of several bands within each run greatly change in the concentration range of sulfuric acid between 5 and 25 per cent. Namely, the 1539 cm^{-1} band (II) has the weakest intensity in the 6—7 μ region spectra of tropolone in sulfuric acid with a concentration lower than 5 per cent, while the 1553 cm^{-1} band (II′), the shifted band of the 1539 cm^{-1} band, has an intensity comparable to the strongest 1490 cm^{-1} band (III′) in the spectra of the solutions with concentrations of sulfuric acid higher than 25 per cent. The same tendency is also seen for the two bands in the 14 μ region. It should be remembered that the ultraviolet absorption data shows that the sharpest transference of the equlibrium 1 occurs at about a 20 per cent sulfuric acid solution. Thus, it may be concluded that the changes in the Raman spectra shown in Fig. 5, namely, the shifts of the bands to the respective bands, are caused by the protonation of tropolone.

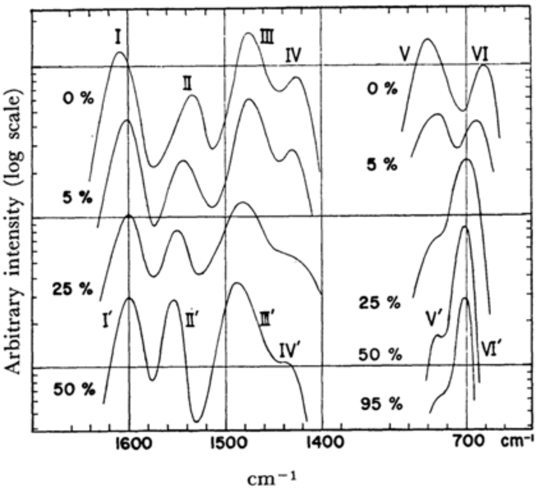

Fig. 5. Raman spectra of tropolone in sulfuric acid of various concentrations. The peak wave numbers of the characteristic bands of the neutral and protonated tropolone are, respectively, 1608 (I) and 1539 (II), and 1598 (I′) and 1553 (II′) cm^{-1}.

The Assignments of the Vibrational Spectra of Tropolone and the Protonated Tropolone in the 6—7 μ Region.

—As has been mentioned above, the vibrational spectrum of tropolone has several bands in the 6—7 μ region which have not yet been given conclusive assignments. Among these, the two bands near 1610 cm^{-1} (Band I) and 1540 cm^{-1} (Band II) have been recognized as having a mixed character C=C and C=O stretching vibrational modes. Recently Ikegami[16] showed

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[13] E. M. Arnett, "Progress in Physical Organic Chemistry," Vol. 1, Interscience Publishers, New York (1963), p. 223.

[14] Y. Amako, private communication.

[15] See the references cited in L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London (1958), p. 151.

[16] Y. Ikegami, This Bulletin, **35**, 972 (1962).

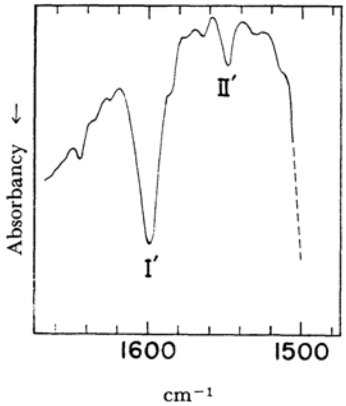

Fig. 6. Infrared absorption spectra of tropolone in a concentrated deuterosulfuric acid solution. The peak wave numbers are 1598 and 1547 cm^{-1} for I′ and II′, respectively.

that the infrared absorption band, II, is more liable to be influenced by the solvent change than Band I. As is evident in Fig. 5, the acidity dependency of the Raman Band II is the most prominent among the four in the 6—7 μ region. The intensity of the Raman Band II′ (1553 cm^{-1}) is increased to almost the same value as that of Band I′ (1598 cm^{-1}) for the protonated tropolone spectrum. Contrary to this, the infrared Band II′ (1547 cm^{-1}) of tropolone in a deuterosulfuric acid solution is much weaker than Band I′ (see Fig. 6). They have almost equal intensities in the spectrum of neutral tropolone.

Since the band pertinent to the C=O stretching vibration is expected to be sensitive to the protonation, Band II of tropolone may be assigned as largely due to the C=O stretching, and partly due also to the ring C=C stretching. The reverse is the case for Band I.

The protonated tropolone was shown by the X-ray crystal analysis technique to have two nearly equal C–OH bonds.[11] Therefore, it may be expected that absorption bands corresponding to the symmetrical and antisymmetric C–O stretching vibrations will appear. Band II′ may be assigned as due to symmetrical C–O stretching, because the intensity of Band II′ relative to that of Band I′ is stronger in the Raman spectrum than in the infrared spectrum.