Infrared Spectra of Troponoid Compounds. I : Tropone and Tropolone

Infrared Spectra of Troponoid Compounds. I
Tropone and Tropolone

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Synopsis

The systematic studies on the infrared spectra of troponoid compounds* are being conducted in this laboratory. As the first step, tropone, tropolone, tropolone methyl ether and hinokitiol have been examined at their gaseous states and some discussions on the result have been made.

I. Introduction

Many studies on the infrared spectra of troponoid compounds having tropone or tropolone skeleton have been reported. Namely, in 1950, Aulin-Erdtman and Theorell[1] examined the characteristic absorption bands of natural tropolones, and Scott and Tarbell[2] those of colchicine and its derivatives, respectively. In the next year, Koch[3] made discussion on the chemical constitution of synthesized tropolone from its absorption spectra. Moreover, in 1952, Kuratani *et al.*[4] made some considerations from absorptions of tropolone and its some derivatives. And in 1954, Bryant *et al.*[5] reported on the effect of substituents on absorption bands of carbonyl group of tropone nucleus. Many of these reports discussed on the absorption bands of carbonyl group which being the functional group common to tropones and of tropolone hydroxyl group.

It will be necessary to examine systematically the infrared absorption of troponoid compounds including the seven membered aromatic systems. As its first step, the absorptions of tropone and tropolone have been measured. It will have important meaning to compare the absorption bands of tropone and tropolone because interesting difference between chemical constitutions of the two compounds has been found.

The absorption of tropone has been reported by Dauben[6], Doering[7] and Nozoe[8] respectively and that of tropolone has been discussed by Koch[3] and Kuratani. These spectra have been measured in the states of solids, liquids and solutions

* Troponoids is the general term of tropone, tropolone, and their derivatives.

(1) G. Aulin-Erdtman and H. Theorell, Acta Chem. Scand., **4** (1950), 1490.
(2) G. P. Scott and D. S. Tarbell, J. Am. Chem. Soc., **72** (1950), 240.
(3) H. P. Koch, J. Chem. Soc., **1951**, 512.
(4) K. Kuratani, M. Tsuboi and T. Shimanouchi, Bull. Chem. Soc. Japan, **25** (1952), 250.
(5) B. E. Bryant, J. C. Pairaud and W. C. Fernelius, J. Org. Chem., **19** (1954), 1889.
(6) H. J. Dauben and H. J. Ringold, J. Am. Chem. Soc., **73** (1951), 876.
(7) W. Von Doering and F. L. Detert, ibid., **73** (1951), 876.
(8) T. Nozoe, T. Mukai, K. Takase and T. Nagase, Proc. Japan Acad., **28** (1952), 477.

of the compounds. For examining the absorption of these compounds released from association, infrared absorption spectra of tropone, tropolone, tropolone methyl ether and hinokitiol in gaseous state have been obtained.

II. Experimental

The measurement of infrared absorptions was conducted by using a Perkin-Elmer Model 21 recording infrared spectrophotometer with a NaCl prism. For solid substances, KBr disk method was adopted, and for solution, NaCl liquid cell having 0.504 mm path length was used. For the measurement of gases, a heatable cell shown in Fig. 1 was specially prepared and used. A hard glass tube of 23 mm in inner diameter and 50 mm in length was made in the form of (1), and two KCl plates (2) were attached to both the ends of the tube with glyptal resin. After putting about 50 mg of the sample in (3), the cell was evacuated (1/100~1/1000 mmHg) and fused at the salient part (4). Outer side of the cell was covered with a hard

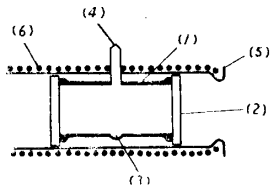


Fig. 1. Heatable cell.

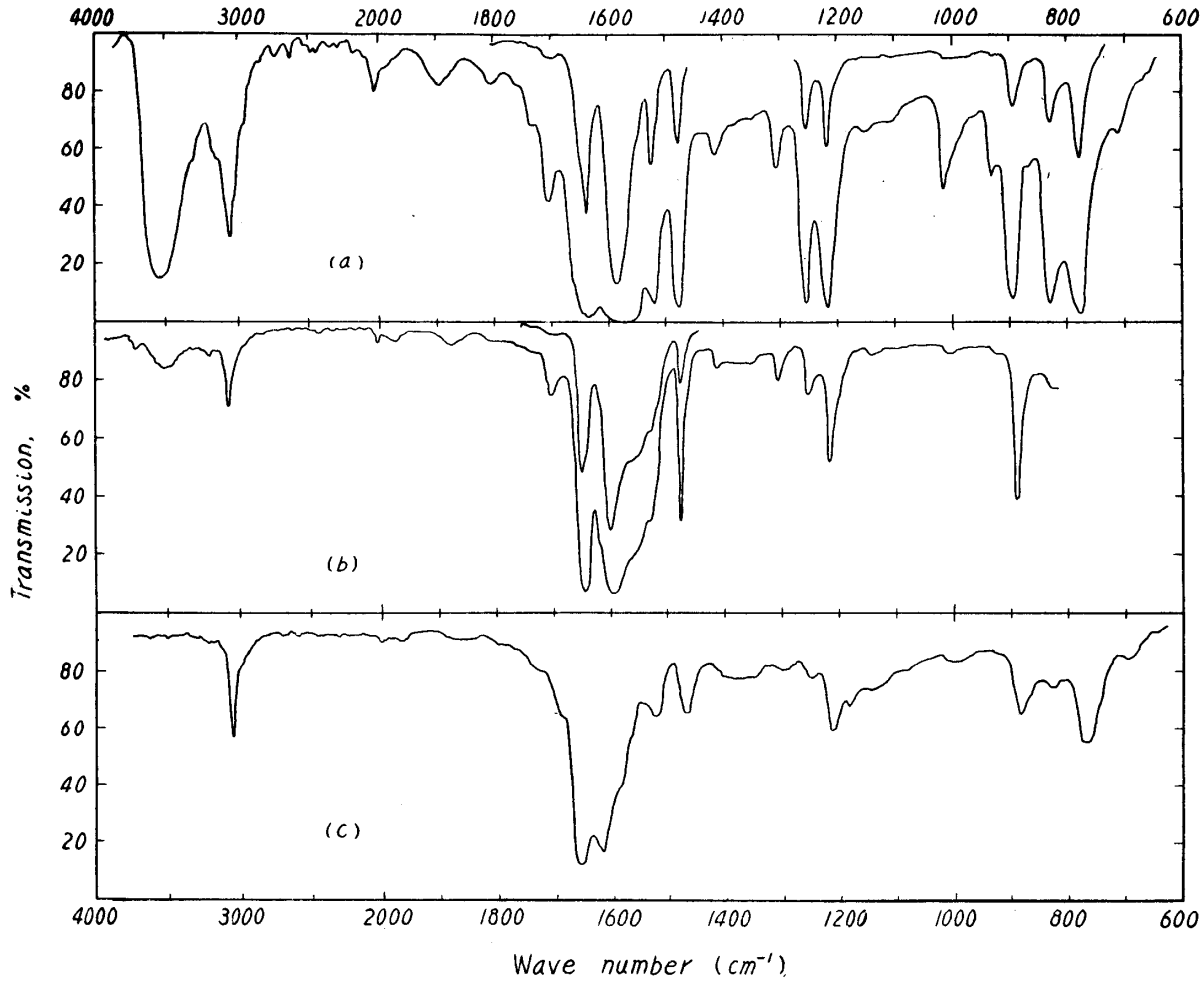


Fig. 2. Infrared spectra of tropone.
(a) liquid, (b) carbon tetrachloride solution, (c) gas.

glass (5) and asbestos, and then winded with nichrome wire (6) for heating. Temperature of the heated cell was measured with a thermocouple. When the cell was gradually heated to about 80°C, it was observed that liquid condensed at the salient part. By keeping the temperature of the cell at 105~110°C, the cell was filled with vapor giving suitable condition for getting proper absorption spectra.

The absorption spectra of tropone and tropolone at their various states were shown in Figs. 2 and 3, respectively. And those of tropolone methyl ether and hinokitiol (4-isopropyltropolone) taken at the gaseous states were shown in Figs. 4 and 5, respectively. When the cell was cooled, the gas thus obtained condensed to liquid or solid on the KCl plates (2), giving the same absorption of the compounds in liquid or solid states. By heating the cell again the sample gave the same absorption with the gaseous state.

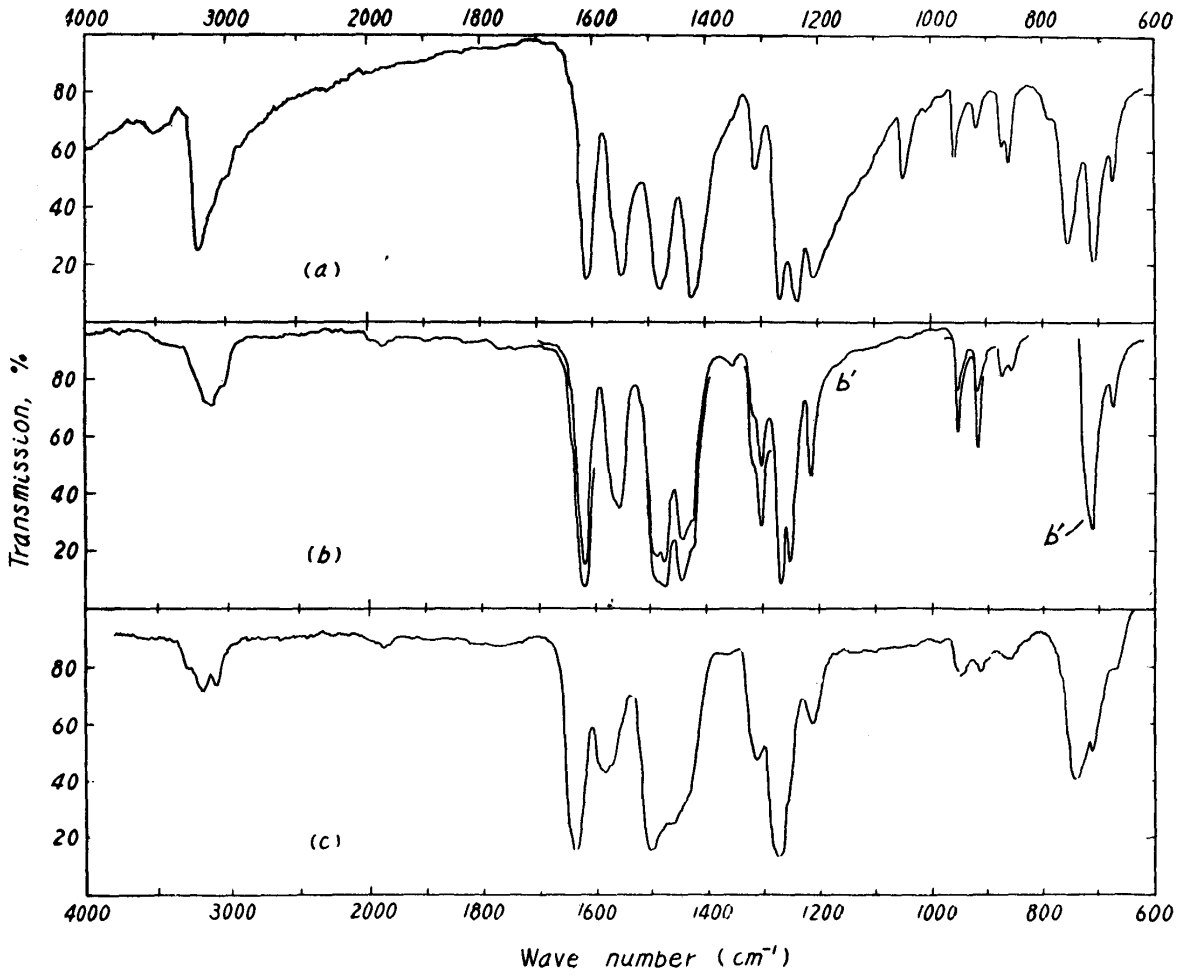


Fig. 3. Infrared spectra of tropolone.
(a) solid,
(b) carbon tetrachloride solution (ca. 1%) 0.504 mm,
(b') carbon tetrachloride solution (ca. 10%) 0.026 mm,
(c) gas.

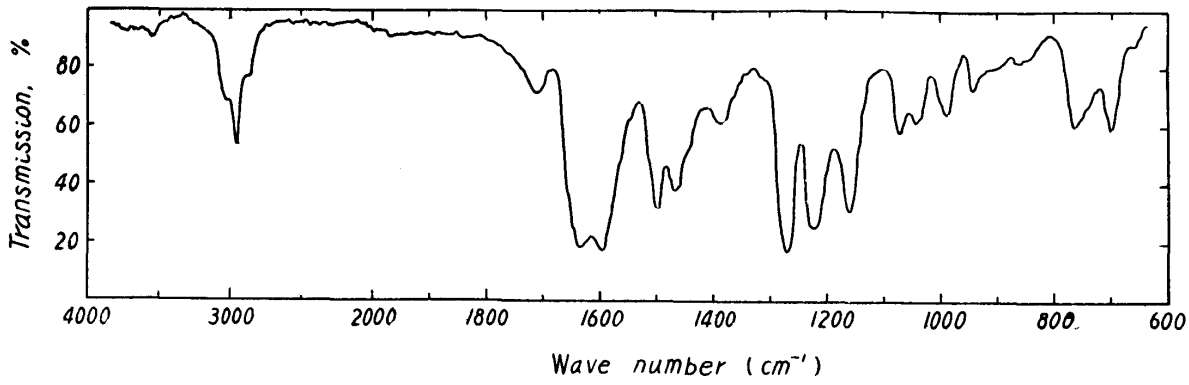


Fig. 4. Infrared spectrum of tropolone methyl ether in gaseous state.

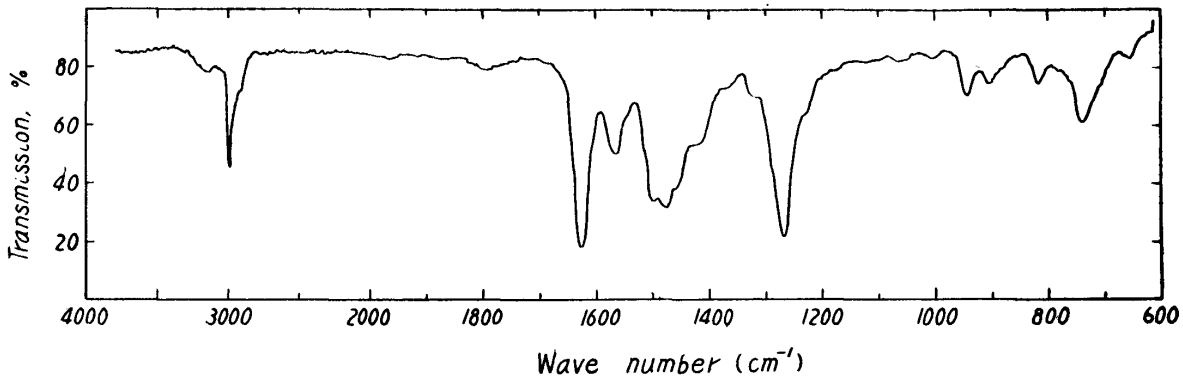


Fig. 5. Infrared spectrum of hinokitiol (4-isopropyltropolone) in gaseous state.

III. Discussion

Comparing with the absorption spectra of the compounds in the states of solid, liquid or solution, those of the gaseous state obtained by the above described method are comparatively simple and broad, and noticeable changes are observed in the relative intensity. The absorption bands clearly observed by tropone and tropolone are shown in Tables 1 and 2, respectively.

In the case of liquid tropone, a broad intense absorption band is observed near 3530 cm^{-1} [9] (3425 cm^{-1} by Doering[7]), which becomes very weak in a carbon tetrachloride solution and a weak absorption appears near 3700 cm^{-1} at the same time. These absorptions are not, however, observed when the substance changes into gaseous state. The same tendency is also observed in tropolone methyl ether. Considering in connection with the fact that tropolone methyl ether takes easily the water of crystallization from the atmosphere the band of 3530 cm^{-1} will be due to the water associated with tropone. This association will affect on many absorption bands of tropone.

The absorption bands of tropolone and hinokitiol corresponding to ν(O–H) appear in 3140 cm^{-1} in the case of the gaseous state, which is shifted to lower wave number by about 60 cm^{-1} than the case of solid, and is supposed to have intra-

(9) P. L. Pauson, Chem. Rev., **55** (1955), 21.

Table 1. Absorption bands of tropone (cm^{-1})

Liquid	CCl_4 solution	Gas
	3700	
3530	3500	
3040	3040	3048
1702	1699	
1635	1645	1651
1580	1595	1613
1523		1516
1475	1474	1465
1411		
1304	1302	1305
1253	1251	1251
1217	1212	1208
1150		
1014		
930		
892	887	882
870		
828		827
778		767
708		703

Table 2. Absorption bands of tropolone (cm^{-1})

Solid	CCl_4 solution	Gas
3200	3110	3140
	3055	3055
	3015	3030
1613	1618	1628
1548	1555	1573
1480	1490	1490
	1476	
	1443	1450
1425	1425	
	1355	
1310	1304	1305
1266	1267	1265
1238	1252	
1208	1214	1208
1049		
958	953	940
919	917	908
874	874	
860	858	
789		
754		738
708	714	710
672	677	

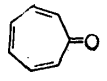
molecular hydrogen bond[4]. Also the wave number is less than 3175cm^{-1} of chelated 1-hydroxy-2-naphthyl aldehyde[10], for example, showing comparatively lower frequency of ν(O-H) band due to intramolecular hydrogen bond.

Absorption bands corresponding to ν(C=O) and ν(C=C) in tropone and tropolone were compared in solid (liquid in tropone), solution and gaseous states and the results were shown in Table 3. Carbonyl bands of tropolone methyl ether and hinokitiol in gaseous state were observed at 1635 cm^{-1} and 1625 cm^{-1}, respectively.

Table 3. Comparison of ν(C=O) and of ν(C=C) of tropone and tropolone

	Tropone		Tropolone		$\Delta\nu$	
	ν(C=O)	ν(C=C)	ν(C=O)	ν(C=C)	$\Delta\nu$(C=O)	$\Delta\nu$(C=C)
Solid or liquid	1635	1581	1613	1548	22	33
CCl_4 solution	1645	1595	1618	1555	27	40
Gas	1651	1613	1628	1573	23	40

The absorption bands of carbonyl in troponoid compounds appear generally in lower wave number than 1651 cm^{-1} of gaseous tropone. Also the absorption band corresponding to ν(C=C) is comparatively wide and is seen at the side of the lower wave number of carbonyl absorption band. When tropone (I) and tropolone (II) are compared in gaseous state, $\Delta\nu$(C=O) (23 cm^{-1}) corresponds to the shift of carbonyl



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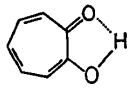

II

(10) I. M. Hunsberger, J. Am. Chem. Soc., **72** (1950), 5626.

absorption band due to intramolecular hydrogen bond of tropolone, and $\Delta\nu$(C=C) (40 cm^{-1}) may be assumed to be due to the decrease of double bond character by the chelation. The wave number of carbonyl group of tropone is less than that of *p*-benzoquinone (ν(C=O), 1667 cm^{-1})[11] having $\alpha\beta$, $\alpha'\beta'$unsaturated ring ketone like tropone. In the case of tropolone, it is slightly less than that of 10-hydroxy -9-phenanthrencarboxaldehyde (ν(C=O), 1637 cm^{-1})[12], which is conjugated to K-region of phenanthrene nucleous and chelated, and of 1-hydroxyanthraquinones (ν(C=O), 1640~1620 cm^{-1})[13], which are fused in the ring and chelated. This fact may be taken as one of specialities of troponoid compounds.

Comparing with tropone, strong absorption is observed in the region of 1300 ~1200 cm^{-1} in tropolone, which will be due to C-OH group in the compound. The most intense absorption at 1238 cm^{-1} observed in the solid becomes comparatively weak in the more dilute solution and is observed at 1252 cm^{-1}. In the gaseous state, it is observed merely as shoulder near the position. This fact is taken to be due to hydrogen bond formation of tropolone and generally observed in tropolone derivatives. For example, in hinokitiol fair differences are observed in the absorption in this region according to the states, i. e., solid, liquid and solution, as reported by Kuratani, *et al*[4]. In the absorption of the gaseous state shown in Fig. 5, the tendency became sparse and a strong absorption was observed at 1267 cm^{-1}.

On the other hand, gaseous tropolone methyl ether gave three strong absorptions at 1270 cm^{-1}, 1222 cm^{-1} and 1160cm^{-1}, among them 1270 cm^{-1} and 1222 cm^{-1} were separated further into two peaks respectively in the states of liquid and solution. For example, they are separated into 1280 cm^{-1}, 1266 cm^{-1} and 1233 cm^{-1}, 1215 cm^{-1}, respectively, in the liquid state. It is assumed that there should naturally be absorption, among the three absorption bands of the gaseous state, corresponding to the vibration of two C-O bonds in aralkyl ether. The two absorption bands of 1270 cm^{-1} and 1160 cm^{-1} are situated in slightly lower frequencies than the case of aralkyl ethers.[14]

In addition to this research it is desirable to study in detail on the absorption bands of tropone, tropolone and their derivatives. Studies on their halogen substituted compounds and amino-derivatives are also in progress.

Summary

(1) As tropone, tropolone, tropolone methyl ether and hinokitiol are easily vaporized, a measuring method was described.

(2) When spectra of a compound in the states of gas, solution, solid or liquid are compared, some differences are observed in positions and relative intensities of the absorption bands. Many of them are assumed to be due to the effect of

(11) M. L. Josien, N. Fuson, J. M. Lebas and T. M. Gregory, J. Chem. Phys., **21** (1953), 331.
(12) I. M. Hunsberger, R. Ketcham and H. S. Gutowsky, J. Am. Chem. Soc., **74** (1952), 4839.
(13) M. St. C. Flett, J. Chem. Soc., **1948**, 1441.
(14) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, (Methuen, 1954), 102.

hydrogen bond formation and association in the intra- or inter-molecules.

(3) The absorption at 3530 cm^{-1} observed in the case of liquid tropone, is also observed equally in tropolone methyl ether, which is assumed to be due to the absorbed water.

(4) Some discussions were made on ν(C=O) of tropone and tropolone and on the absorptions in the region of 1300~1150 cm^{-1} of tropolone derivatives.

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