The Infrared Spectra of *S*-Alkylisothiouronium Salts

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(Received January 6, 1966)

The infrared spectra of thiourea[1,2] and its metal co-ordination complex[3] have been examined by several authors. Kutzelnigg and Mecke made the vibration assignment of the isothiouronium ion.[4] Stam examined the crystal structure of *S*-methylisothiouronium sulfate by X-ray analysis.[5] However, no reports on the characteristic absorption bands of *S*-alkylisothiouronium salts and their deuterated compounds have yet appeared.

The infrared spectra of *S*-alkylisothiouronium salts  $\left(\mathrm{R{-}S{-}C}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{NH}\end{smallmatrix}\cdot\mathrm{HX}\right)$ have two characteristic absorption bands in the region from 1675 to 1420 cm^{-1}. On deuteration, they shift to a lower frequency, and two new bands appear in the region from 1198 to 1140 cm^{-1}. These bands were observed in almost the same region when the alkyl groups and salts of *S*-alkylisothiouronium compounds were substituted. Isothiouronium compounds are important as agents protecting against radiation and as the medium of the sulfur-containing compounds. In this note the characteristic absorption bands of *S*-alkylisothiouronium compounds will be presented.

Experimental

The Preparation of Compounds.—Most of the compounds used in this experiment were prepared by

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1) J. E. Stewart, *J. Chem. Phys.*, **26**, 248 (1957).

2) R. M. Badger and R. D. Waldron, ibid., **26**, 255 (1957).

3) A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

4) W. Kutzelnigg and R. Mecke, *Spectrochim. Acta*, **17**, 530 (1961).

5) C. H. Stam, *Acta Cryst.*, **15**, 317 (1962).

TABLE I. THE CHARACTERISTIC ABSORPTION BANDS OF *S*-ALKYLISOTHIOURONIUM SALTS (cm^{-1})*

Compound					
S-Methyl	iodide	1639 (s)	1427 (m)		
	deuterated	1577 (s)	1393 (m)	1189 (m)	1142 (m)
	difference	62	34		
S-Methyl	sulfate	1675 (s) 1642 (m)	1435 (m) 1420 (m)		
	deuterated	1587 (s)	1397 (m)	1182 (m)	—
	difference	88 55	38 23		
S-Ethyl	iodide	1642 (s) 1635 (sh)	1433 (m)		
	deuterated	1575 (s)	1391 (s)	1188 (m)	1155 (m)
	difference	67 60	42		
S-Ethyl	bromide	1645 (s) 1637 (sh)	1453 (m) 1431 (m)		
	deuterated	1563 (s)	1399 (s)	1198 (m)	1143 (m)
	difference	82 74	54 32		
S-Ethyl	chloride	1658 (sh) 1647 (s)	1447 (m) 1427 (m)		
	deuterated	1563 (s)	1399 (s)	1195 (m)	1143 (m)
	difference	95 84	48 28		
Ethylene-di-	bromide	1639 (s)	1435 (s)		
	deuterated	1565 (s)	1389 (s)	1192 (m)	1140 (m)
	difference	74	56		
1-Phenyl- propenyl	chloride	1645 (s)	1439 (s)		
	deuterated	1582 (s)	1391 (s)	1193 (m)	1140 (m)
	difference	63	48		
O-Methyl- isouronium	chloride	1692 (s)	1580 (m)		
	deutrated	1631 (s)	1543 (m)	1233 (m)	1067 (m)
	difference	61	37		

* (s); strong, (m); medium, (sh); shoulder

the method described in "Organic Syntheses."[6,7] Their purity was examined by elementary analysis. 1-Phenyl-propenylisothiouronium chloride and ethylenediisothiouronium bromide were obtained from Dr. Nishimura of this laboratory.[8] Deuterated compounds were obtained by the treatment with deuterium oxide in a sealed tube and by drying in vacuo.

Infrared Spectra.—The infrared spectra were recorded on a Perkin-Elmer model 21 infrared spectrophotometer, equipped with a sodium chloride prism, in the region from 5000 to 650 cm^{-1}. The spectra of crystals were measured in a potassium bromide disk. Deuterated compounds should be measured in either hexachlorobutadiene paste or Nujol mull, but the compounds used in this study did not disperse homogeneously in these media; therefore, the measurements of spectra were carried out in a potassium bromide disk which had been carefully prepared in a simple dry box.

Results and Discussion

Several spectra of *S*-alkylisothiouronium salts are illustrated in Fig. 1, while the observed frequencies of the characteristic absorption bands of *S*-alkylisothiouronium salts are shown in Table I.

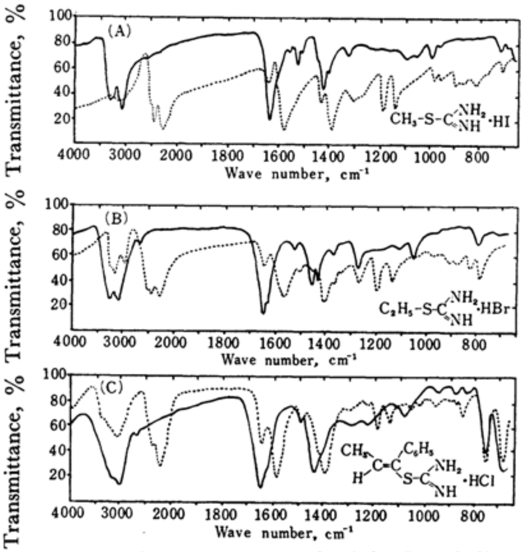

Fig. 1. Infrared spectra of, (A) *S*-methylisothiouronium iodide, (B) *S*-ethylisothiouronium bromide, and (C) 1-phenylpropenylisothiouronium chloride; ——, normal comound, ----, deuterated compound.

The two characteristic absorption bands of *S*-alkylisothiouronium salts were observed in the 1675—1635 cm^{-1} and 1455—1420 cm^{-1} regions. On deuteration, they shift to the lower frequency regions of 1590—1565 cm^{-1} and 1400—1390 cm^{-1} respectively, as is shown in Table I. The band

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[6] E. Brand and F. C. Brand, "Organic Syntheses," Coll. Vol. III, 440 (1955).

[7] F. Kurzer and A. Lawson, ibid., Coll. Vol. IV, 645 (1963).

[8] H. Nishimura, *J. Pharm. Soc. Japan (Yakugaku Zasshi)*, **84**, 930 (1964).

observed at about 1650 cm^{-1} may correspond to the two kinds of NH_2 scissoring vibrations, one of which is coupled with the out-of-phase N–C–N stretching vibration because it is shifted by only 50—90 cm^{-1} on deuteration. The increase in frequency of the out-of-phase N–C–N stretching vibration compared with that (A_2, 1470 cm^{-1}) of thiourea[3] may be explained as resulting from the greater double-bond character of the N–C–N bond; this has been confirmed by X-ray analysis in *S*-methylisothiouronium sulfate.[5] In the metal thiourea complex, the above situation has been reported for the same vibration.[3]

The band observed at about 1440 cm^{-1} may correspond to the band of thiourea at 1417 cm^{-1} (A_1), which has been assigned to the NH_2 rocking vibration coupled with the N–C–N and C=O stretching vibrations. For some compounds, each of the two characteristic absorption bands described above splits into two components, as Table I shows. A quantitative discussion of the nature of these characteristic vibrations could be made possible only by an appropriate normal coordinate treatment. The deuterated compounds give a pair of new bands with a medium intensity at around 1190 cm^{-1} and 1140 cm^{-1}; these bands can be assigned to the ND_2 scissoring vibrations.

Both characteristic absorption bands of *S*-alkylisothiouronium compounds exist in a narrow frequency region when their alkyl groups and their salts are replaced by other groups and salts. *S*-Alkylisothiouronium salt can be distinguished from *O*-alkylisouronium salt, which gives these characteristic absorption bands at slightly higher frequencies. An examination has been made by means of infrared absorption measurements as to whether an interaction of those compounds with alkali halide takes place. However, no change was found in the spectra when those compounds were mixed with alkali halides.

Though only a limited number of compounds were examined, it can be concluded that *S*-alkylisothiouronium salts have their characteristic absorption bands in the 1675—1635 cm^{-1} and 1455—1420 cm^{-1} regions. On deuteration, they shift to 1590—1565 cm^{-1} and 1400—1390 cm^{-1}, and give the two bands in the 1200—1180 cm^{-1} and 1155—1140 cm^{-1} regions. These characteristic absorption bands are expected to be useful for the determination of the *S*-alkylisothiouronium group involved in unknown compounds.

The authors wish to express their gratitude to Drs. Shinsuke Ose, Hideji Takamatsu and Kiyoshi Nakamura of this laboratory for their encouragement. We are also grateful to Dr. Haruki Nishimura for supplying some of the materials.