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ON THE INTERACTION OF HEXAMETHYLENETETRAMINE AND SULFUR DIOXIDE

P. S. SANTOS and R. LIEDER
Instituto de Química da Universidade de São Paulo, São Paulo (Brasil)

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ABSTRACT

The interaction of hexamethylenetetramine(HMTA) and sulfur dioxide was investigated by means of Raman spectroscopy. It is shown that the interaction leads to the formation of an adduct not yet reported in the literature. The analysis of the Raman data suggests the presence of non-equivalent sulfur dioxide molecules in the adduct and shows the splitting of several HMTA degenerate modes, small frequency shifts on most of the HMTA bands and a dramatic variation of the HMTA band at 1042 cm^{-1} relative to the intensity of all the other Raman bands.

INTRODUCTION

Sulfur dioxide is acknowledged as one of the most serious atmospheric pollutants in industrial areas. Consequently a great deal of effort has been dedicated towards its detection and quantification. On the other hand, very little is presently known about its interaction with organic molecules, particularly those that are of biological relevance. There are some references in the literature about the interaction of sulfur dioxide with organic bases such as aliphatic and aromatic amines [1—10], pyridine and pyridine derivatives [11, 12] but in most of these studies only thermodynamic parameters were determined. The molecular complex formed by trimethylamine and sulfur dioxide is one of the few cases where a detailed structural investigation was undertaken, using X-ray crystallography [13] and vibrational spectroscopy [2].

Over the last few years there has been a renewed interest for investigating the interaction of sulfur dioxide with several substrates, both organic and inorganic. On the one hand, it was shown that some organic bases, such as *N,N*-dimethylaniline, are amongst the best solvents for the removal of sulfur dioxide from industrial effluents [14], and on the other, the excellent performance of lithium batteries was recently demonstrated using as electrolyte a solution of alkaline halides and sulfur dioxide in organic solvents [15]. In both cases it is known that molecular complexes are formed between an electron donor species and sulfur dioxide which can be classified as a relatively weak Lewis acid.

We then decided to undertake a study on the interaction of sulfur dioxide with organic bases, and in the present paper report the results obtained from a Raman spectroscopic investigation of the molecular complex formed by HMTA and sulfur dioxide. HMTA is of great interest for such investigation since its cage structure is a model of several macrocyclic systems of biological relevance and it has also been thoroughly investigated by X-ray crystallography and vibrational spectroscopy.

EXPERIMENTAL

HMTA was purified by sublimation in high vacuum and its purity was confirmed by elemental chemical analysis. Its Raman and infrared spectra are in excellent agreement with those reported in the literature [16]; the crystallographic parameters obtained coincides perfectly with the published data [17]. Sulfur dioxide with a minimum purity of 99% was used from a gas cylinder, precautions being taken to remove traces of water and other minor impurities.

The reaction vessel containing finely ground HMTA was thoroughly purged with dry nitrogen and sulfur dioxide was condensed over the solid. After ca. 15 min the excess sulfur dioxide was allowed to evaporate and the system was purged with dry nitrogen at room temperature to remove gaseous sulfur dioxide from the reaction vessel. The reaction product, a white powder with the same aspect of HMTA was transferred to a glass capillary inside a dry box and after sealing in a flame was used to obtain the Raman spectrum.

The Raman spectra were obtained using a Jarrell-Ash Raman laser spectrometer, employing the 514.5 nm radiation from a Spectra-Physics Ar^+ laser as the exciting radiation; spectra of samples submitted to different periods of vacuum and heating were also obtained, for reasons to be discussed shortly.

RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of pure HMTA(A) and of its SO_2-adduct(B); the corresponding frequency values are listed in Table 1. In the Raman spectrum of the adduct there are two new bands, at 1108 cm^{-1} and 1128 cm^{-1}, in the region expected for the symmetric S—O stretching. The lower frequency value compares well with 1096 cm^{-1} assigned for the symmetric S—O stretching in the trimethylamine · SO_2 adduct [18]. In principle, there are several possibilities that would explain the existence of two bands in this region. One could consider them as the symmetric and antisymmetric S—O stretching in the adduct, but this can be discarded since the difference between the frequency values is too small compared with that for SO_2 and several SO_2 complexes [19]. In this respect the infrared spectrum could be very useful, showing the band corresponding to the antisymmetric stretching

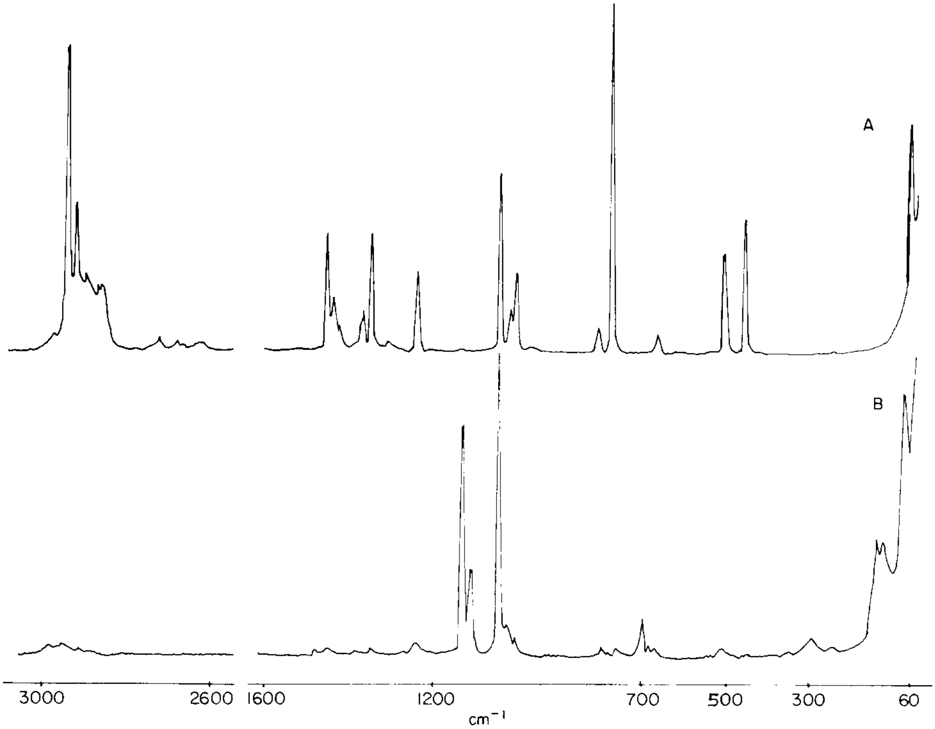

Fig. 1. Raman spectra of HMTA(A) and HMTA · $2SO_2$(B). See text for details.

as an intense one, but due to the overlapping with HMTA bands and more stringent sampling techniques it is not of great help. Another possible origin of the two bands could be a correlation splitting in the solid, although 20 cm^{-1} would be too much for such splitting. The remaining possibility is the existence of non-equivalent SO_2 molecules in the adduct. Both chemical and thermogravimetric analysis indicate the composition HMTA · SO_2, but on the other hand the measurements of absorbed SO_2 volume indicate a SO_2 to HMTA ratio very close to two. Finally, the analysis of the Raman spectra of samples submitted to different periods of vacuum or vacuum and heating is definitive for the interpretation of the apparently conflicting results mentioned previously. Figure 2 shows a series of Raman spectra obtained with samples of the adduct that were exposed to the forementioned conditions (see caption for details). One observes very clearly that the Raman band at 1128 cm^{-1} decreases in intensity with increasing vacuum periods and eventually disappears, while the band at 1108 cm^{-1} persists even after long periods of vacuum, and only disappears after subjecting the sample to vacuum at a temperature of ca. 80°C. It must also be mentioned that the Raman spectrum of the sample exposed to vacuum and heating, where the bands at 1128 cm^{-1} and 1108 cm^{-1} are absent, is absolutely identical to that

TABLE 1

Raman frequencies in cm^{-1} for HMTA and HMTA · $2SO_2$; relative intensities in parentheses

Assignment[a]	HMTA	HMTA · $2SO_2$	Assignment[a]	HMTA	HMTA · $2SO_2$	
	70(6,5)	68(8)	CNC def., A_1	1042(5)	1042(10)	
		120(4)			1108(4,5)	SO_2 sym.str.
		138(4)			1128(7)	
		248(0,1)	CN str., F_2	1238(2)	1240(0,1)	
		299(0,2)	E	1308(0,2)		
		352(0,1)			1338(sh)	
CNC def., E	463(4)	457(0)	CH_2 twist., E	1350(3,5)	1351(0,05)	
CNC def., F_2	512(3)	510(0,1)	CH_2 wag, F_2	1370(1)	1383(0)	
CNC def., F_2	672(0,5)	670(0,1)	E	1429(0,5)		
		683(0,1)	E	1442(1,5)		
		700(0,8)	CH_2 def., E	1454(3,5)	1451(0,05)	
		760(0,1)	sym. CH_2 str., F_2	2873(1,7)		
CN str., A_1	778(10)	779(0)	sym. CH_2 str., A_1	2882(1,7)		
CH_2 rock, F_2	812(0,5)	801(0,1)	A_1	2910(2,2)	2912(0)	
F_2	971(0)		asym. CH_2 str., F_2	2951(9)	2952(0,05)	
CN str., F_2	1005(2)	1003(0,1)	F_2	2992(0,3)	2990(0,05)	
CN str., F_2	1020(1)	1022(0,3)				

[a] Assignment according to ref. 16; in case of combination bands or overtones, only the symmetry species are indicated.

of pure HMTA. In addition, the reverse experiment was also undertaken, i.e. a series of Raman spectra were obtained from a sample of HMTA exposed to SO_2 in a closed system for increasing periods of time; the results confirm completely those obtained in the previous experiments.

On the basis of such results the Raman bands at 1108 cm^{-1} and 1128 cm^{-1} can be assigned to the S—O symmetric stretching of two non-equivalent SO_2 molecules in the adduct; the band at 1108 cm^{-1} is assigned to the SO_2 molecule that is more tightly bound to HMTA, while the band at 1128 cm^{-1} is assigned to the SO_2 molecule that is more loosely bound, since it is much more easily removed and its frequency value is quite close to that observed for the symmetric stretching of SO_2 in non-polar solvents, reported at 1144 cm^{-1}. It is worthwhile comparing the frequency assigned here to the weakly bound SO_2 molecule with that reported for SO_2 in the hydroquinone clathrate, at 1148 cm^{-1} [20]. In the latter the value is practically coincident with the one for gaseous SO_2, indicating that the interaction is almost negligible, while in the case of the HMTA adduct the interaction albeit small is not negligible, even for the loosely bound SO_2 molecule. It seems that the HMTA · SO_2 adduct is solvated by an additional SO_2 molecule, originating a solvate that is unstable and easily loses the "solvent" molecule. Such an interpretation would explain the apparent conflict in the chemical analysis results and is reinforced by comparison with the value 1125 cm^{-1} found in the KSCN sulfur dioxide solvate [21], where SO_2 is solvating the SCN^- anion.

Finally, additional evidence in favour of this interpretation was given by

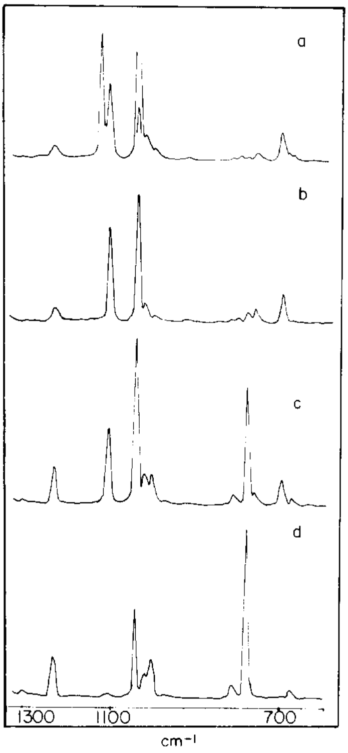

Fig. 2. Raman spectra in the range 600 cm^{-1} to 1300 cm^{-1} of the adduct (a) without exposition to vacuum; (b) after 30 min at 10^{-3} Torr; (c) after 60 min at 10^{-3} Torr; (d) after 60 min. at 10^{-3} Torr and 80°C. See text for details.

the Raman spectrum of the solid that precipitates when SO_2 is bubbled in a chloroform or acetonitrile solution of HMTA. This spectrum is identical with the one in which all the loosely bound SO_2 has been removed, i.e. it shows only the band at 1108 cm^{-1}, demonstrating that the solvation energy must be very small, leading to the "extraction" of the loosely bound SO_2 by the polar solvents.

There are still other aspects in the Raman spectrum of the adduct that deserve to be mentioned. The vibrational spectrum of HMTA was investigated in great detail by Bertie and Solinas [16], who performed a normal coordinate analysis, assuming a T_d symmetry for the molecule. Our Raman data for HMTA are in excellent agreement with those reported by the mentioned authors. The comparison of the Raman spectra of HMTA and of its adduct shows the splitting of several HMTA bands assigned to degenerate modes, as expected from the lower symmetry in the adduct. It is also observed that the coordination to SO_2 causes, in general, small shifts in the HMTA frequencies; in particular the bands at 1042 cm^{-1} and 778 cm^{-1}, assigned to the C—N—C deformation and C—N stretching respectively, do not shift significantly. Since these frequencies are expected to be particularly sensitive to the coordination, one is led to the conclusion that the interaction with SO_2 should be defined as rather weak. In the case of the HMTA adduct, HMTA · BH_3, the X ray data show that the C—N bond involved in the coordination is lengthened by 0.05 Å [22]. Considering that SO_2 is a much weaker Lewis acid than BH_3, it is to be expected that the variations in the HMTA geometrical parameters induced by its coordination to SO_2 must be very small. On the other hand it is known that the SO_2 vibrational frequencies, particularly of the stretching modes, are very sensitive even to minor variations in the molecular geometry, as is the case of the SO_2 solvates of alkaline halides, where despite the weakness of the interaction there are non-negligible frequency shifts in both the symmetric and antisymmetric stretching modes [21].

Although a more detailed discussion about the frequency assignment for the adduct would require a normal coordinate analysis, it can be seen in Fig. 1, that, apart from the SO_2 bands there are two new bands in the spectrum of the adduct, in the region of low frequencies, at 120 cm^{-1} and 138 cm^{-1}. In a Raman spectroscopic study of the trimethylamine · SO_2 adduct [23], the strong Raman band at ca. 180 cm^{-1} was assigned to the N—S stretching, and on a comparative basis one could tentatively assign one of these two bands to the N—S stretching in the HMTA adduct.

Another point that is immediately noticed when comparing the Raman spectra of HMTA and of its SO_2 adduct is the dramatic variation of the intensity of the band at 1042 cm^{-1} relative to the intensities of all other bands. Such variation is particularly outstanding, when one compares the bands at 778 cm^{-1} and 1042 cm^{-1}; the band at 778 cm^{-1} is the most intense in the HMTA Raman spectrum and almost vanishes in the Raman spectrum of the adduct. Moreover, examining Fig. 2 one can see that this intensity variation occurs continually from (a) to (d). The inversion in the intensity of the bands at 778 cm^{-1} and 1042 cm^{-1} was also observed in the Raman spectra of a series of HMTA adducts with weak Lewis acids such as $CHBr_3$, CBr_4, CHI_3, etc. [24], where despite the very small frequency shifts on complexation, enormous variations in the relative intensities of the mentioned bands occur. Such an effect deserves to be investigated in more detail; at present it is not possible to propose an interpretation for it.

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REFERENCES

1 L. C. Bateman, E. D. Hughes and C. K. Ingold, J. Chem. Soc., (1944) 243.
2 C. S. Sass and B. S. Ault, J. Phys. Chem., 88 (1984) 432.

3 A. B. Burg, J. Am. Chem. Soc., 65 (1943) 1629.
4 J. A. Moede and C. Curran, J. Am. Chem. Soc., 71 (1949) 852.
5 J. Grundnes and S. D. Christian, J. Am. Chem. Soc., 90 (1968) 2239.
6 H. W. Foote and J. Fleischer, J. Am. Chem. Soc., 56 (1934) 870.
7 W. E. Byrd, Inorg. Chem., 1 (1962), 762.
8 A. E. Hill and T. Fitzgerald, J. Am. Chem. Soc., 57 (1935) 250.
9 J. R. Bright and W. C. Fernelius, J. Am. Chem. Soc., 65 (1943) 637.
10 J. D. Childs, D. van der Helm and S. D. Christian, Inorg. Chem., 14 (1975) 1386.
11 Z. Pawelka, G. Maes and Th. Zeergen-Huyskens, J. Phys. Chem., 85 (1981) 3431.
12 C. L. Gardner and R. W. Day, Can. J. Chem., 62 (1984) 986.
13 D. van der Helm, J. D. Childs and S. D. Christian, Chem. Commun., (1969), 887.
14 R. L. Benoit and E. Milanova, Can. J. Chem., 57 (1979) 1319.
15 R. V. Moshtov and P. Zlatilova, Electrochim. Acta, 27 (1982) 1107.
16 J. E. Bertie and M. Solinas, J. Chem. Phys., 61 (1974) 1666.
17 ASTM microfiche 3-0135, 1978.
18 P. S. Santos and R. Lieder, paper presented at the 36th meeting of SBPC, 1984, São Paulo, Brasil.
19 G. J. Kubas, Inorg. Chem., 18 (1979) 182.
20 P. S. Santos and P. C. Isolani, Chem. Phys. Lett., 67 (1979) 487.
21 E. R. Lippincott and F. Eugene Welsh, Spectrochim. Acta, (1961) 123.
22 F. Hanic and V. Subrtová, Acta Crystallogr., Sect. B, 25 (1969) 405.
23 T. Hata and S. Kinumaki, Nature, 203 (1964) 1378.
24 P. S. Santos, unpublished results.