SOME OBSERVATIONS ON CLATHRATE COMPOUNDS

V. M. BHATNAGAR[*]

Department of Chemistry, Punjab University, Chandigarh

In this paper the stability of Clathrate Compounds of Benzene, Thiophene, Pyrole and Pyridine has been studied under conditions of vacuum, heating and grinding by spectrum analysis.

The effects of evacuation, heat, grinding etc. have been observed in case of some clathrates of nickel cyanide ammonia group. The infrared spectra were recorded as Nujol mulls and in the region where the Nujol bands obscure the bands of the clathrate compounds, as Halocarbon oil[1] mulls. In the benzene clathrate[2,3] many of the bands due to the enclathrated molecule disappeared or became weak, showing that the clathrate had been decomposed. The benzene was found to escape in vacuo but only very slowly. The removal was not complete even after two months and fifteen days. The clathrate was placed under vacuum first for twelve days and after removing, the spectrum of this sample still showed benzene bands (though with smaller intensity). After two months and fifteen days, the sample showed pronounced reduction (Fig. 1) in the intensity of benzene. While the original composition of benzene clathrate was found to be C, 46·31%; H, 4·47%; N, 20·56%. Calc. : C, 46·60% ; H, 4·37%; N, 20·40%, the compositions of the sample after twelve days and two months and fifteen days were (C, 21·31%; H, 2·97; N, 29·24%) and (C, 21·19%; H, 2·71%, N, 29·66%) respectively.

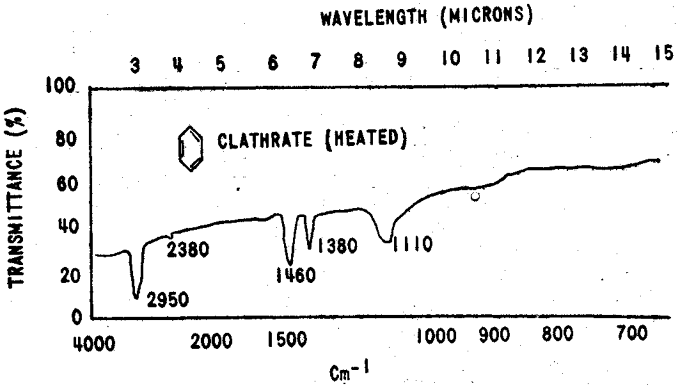

FIG. 1—Infrared spectrum of evacuated benzene clathrate.

A sample of benzene clathrate, from which the benzene had been removed by evacuation was exposed to a benzene vapour atmosphere. No reabsorption of benzene was

---

[*] Now at Instituto di Chimica, General ed Inorganica, Universita di Roma, Rome (Italy).

found. This was due to the fact that the crystal lattice had collapsed after liberation of benzene and it could not reshape itself. It has been shown by Aynsley *et al*[4] that when benzene was removed from the clathrate by evacuation, the cell dimensions showed a continuous variation.

The benzene clathrate was heated on a very low Bunen burner flame in a small glass tube for a very short time. A brown to yellow brown colour developed in clathrate and droplets of liquid benzene were observed on the sides of the glass tube. The spectrum of this heated sample (Fig. 2) was very different from the original clathrate. The percentage composition of the heated sample was found as C, 21. 69%; H, 1. 21% N, 25.02%. The melting point could not be determined since decomposition took place; before melting. The clathrate did not give off any smell of benzene after formation, but on applying a lighted match to a sample of the clathrate, the liberated benzene burnt.

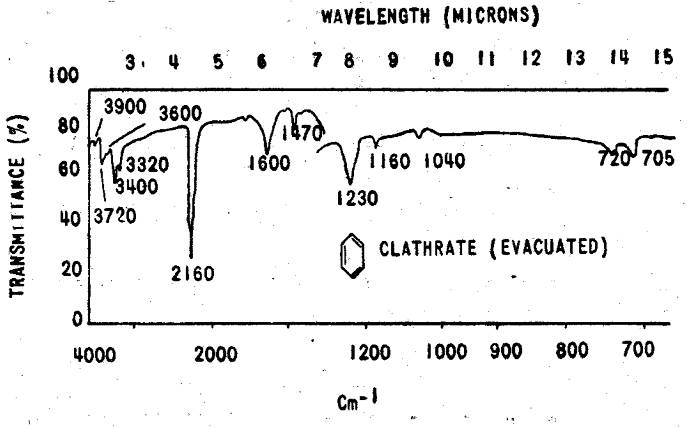

FIG. 2—Infrared spectrum of heated benzene clathrate.

Another sample of benzene clathrate was ground and its infrared spectrum (Fig.3) found to be different from that of the original clathrate. Analysis gave the following result for the ground sample C, 28. 25%; H, 3. 37%; N, 23. 78%.

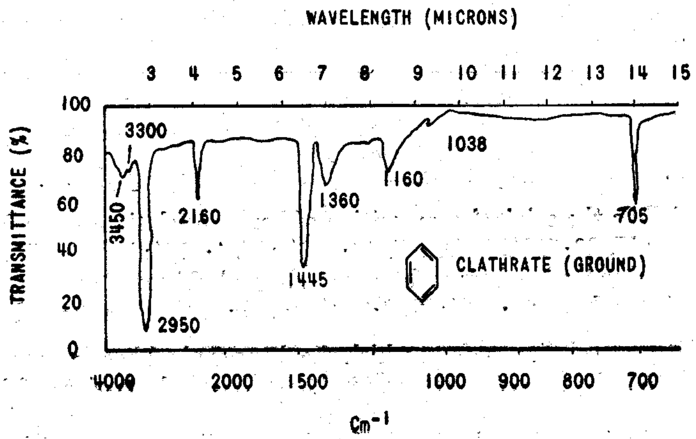

FIG. 3—Infrared spectrum of ground benzene clathrate.

The clathrates were found to be insoluble in most solvents but it is in the nature of the clathrate compounds that they can not be dissolved as such. One of the easiest ways of destroying the benzene clathrate (and similar other clathrates) is by its "solubility" in strong warm ammonia solution. When the clathrate "dissolved", it was found to decompose. In this case, the nickel cyanide complex must break down to something smaller and the benzene would no longer be associated with it.

In the ground sample of thiophene clathrate, the peak at 712 cm.$^{-1}$ was very weak as compared to its position in original spectrum. The bands at 1035 and 1080 cm.$^{-1}$ were also absent from the spectrum of the ground sample. It may be assumed that the replacement of strong and medium bands (or elimination of bands) on grinding, evacuating of any other similar process must be due to some amorphous form or decomposition. The clathrate on pelleting, evacuating etc. may be decomposed to some extent but still every molecule of the compound would not deteriorate, so that some would be able to absorb.

Pyrrole clathrate was also not stable under ordinary laboratory conditions. A sample of the clathrate was placed in air for about five days. The clathrate showed some decomposition as was evident from the spectrum and the following analysis C, 18. 46%; H, 2. 77%; N, 24. 42%. The percentage composition for the original clathrate is found to be C, 36, 45%; H, 4.17%;N, 28.52%. Calc. C, 36. 92%; H, 4.10%; N, 28.76%. The clathrate was deep violet in colour before exposure. The residue showed grey appearance after exposure in air.

The ground sample of this clathrate also showed a quite different infrared spectrum from the original (unground sample).

The effect of heat on pyrrole clathrate was investigated by heating the clathrate in the same way as benzene clathrate. Brown to grey colour developed in the clathrate and the vapours of pyrrole condensed on the sides of the glass tube. The composition of this heated sample was C, 22. 32%; H, O. 89%:; N, 25.20%.

During heating, grinding etc., it is assumed that the continued association between the cage and the enclathrated molecule was broken and the supply of energy from outside helped in pushing apart the system of atoms in the cage so as to provide holes large enough for escape of the enclosed pyrrole.

One sample of pyrrole clathrate was evacuated first for twenty days and later for about two months. The compositions of the samples were C, 29.72%; H ,3.81%; N, 28.97%. and C, 21.52%; H, 2.71%; N, 27.24% respectively.

The infrared transmission curve studies for two months evacuated sample showed that most of the pyrrole frequencies were effected to a great extent and only very weak absorption occurred at 752 and 1170 cm^{-1} . This was the case when the pyrrole was driven out of the walls of the enclosing cage. The walls of the caging material are composed of a system of atoms and the latter still clearly showed their presence, e.g. 2160 cm.$^{-1}$ C=N stretch, 1600 cm.$^{-1}$ antisymmetrical NH_3 deformation and 1230 cm.$^{-1}$ symmetrical NH_3 deformation were all present.

In the ground sample of pyridine clathrate, most of the pyridine bands were effected except the band at 685 cm.$^{-1}$ which in contrast to the 690 cm^{-1} band in the original pyridine clathrate, appeared here with more strong absorption. The other strong bands of pyridine at 991, 1030, 1068,1148 and 1217 cm.$^{-1}$ appeared, as weak (999 and 1215 cm.$^{-1}$) and medium bands (1035, 1062 and 1142 cm^{-1} in the ground sample.

ACKNOWLEDGEMENT

I am deeply indebted to Dr. A. R. H. Cole, University of Western Australia, for his kind advice, discussions and encouragements during my stay in Australia. I express my sincere thanks to Prof. R. C. Paul, Punjab University, for providing facilities in the department.

REFERENCES

1. CROCKET, D. S. & HAENDLER, H. M., *Anal. Chem.*, 31, 626 (1959).
2. RAYNER, J. H. & POWELL, H. M., *J. Chem. Soc.*, 319 (1952).
3. BHATNAGAR, V. M. & FUJIWARA, S., *Chem. & Ind.*, 1471 (1962).
4. AYNSLEY, E. E., CAMPBELL, W. A. & DODD, R. E., *Proc. Chem. Soc.*, 210 (1957).