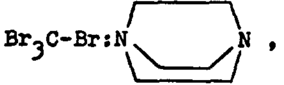
Tetrahedron Letters No. 27, pp. 2511-2512, 1971. Pergamon Press. Printed in Great Britain.

A CRYSTALLINE COMPLEX OF CARBON TETRABROMIDE AND 1,4-DIAZABICYCLO[2.2.2]OCTANE

John P. Lorand, Department of Chemistry, Boston University,
Boston, Massachusetts 02215 U.S.A.

(Received in USA 6 April 1971; received in UK for publication 8 June 1971)

Tetrahalomethanes have been observed to act as n- and π-acceptors in charge transfer complexes,[1] and a crystalline complex (m 53°) of p-xylene and carbon tetrabromide has been characterized by x-ray diffraction methods.[2] Complexes with amines have, however, been observed only in solution,[1] with the exception of a crystalline 1:1 complex of iodoform and hexamethylenetetramine.[3] CBr_4 and hexamethylenetetramine did not form a stoichiometric complex.[4] We now report the ready isolation of a stable 1:1 complex of carbon tetrabromide and DABCO (1,4-diazabicyclo[2.2.2]octane, "triethylenediamine").


, "CBr_4-DABCO"

Nearly saturated solutions of carbon tetrabromide (crude, m.p. 90.5-91.5°, lit 92°, 9.0 g, 28 mmols) and DABCO (m.p. 158-160°, lit 162°, 3.0 g, 28 mmols) in chloroform (15 and 10 ml, respectively) were mixed at room temperature. A yellow-green solid precipitated within seconds, and the temperature rose about 10°. The air dried solid amounted to 9.9 g; concentration of the filtrate yielded 1.2 g; total crude yield 11.1 g, 91% of theory. Recrystallized from chloroform as thin plates or needles, the product did not melt, but turned dark brown from 140-170°, and one sample exploded weakly at 170°.

Analysis: For $C_7H_{12}N_2Br_4$ (M = 443.82), calc: C, 18.94; H, 2.73; N, 6.31; Br, 72.02; found: C, 18.86; H, 2.71; N, 6.42; Br, 72.32.

The elemental analysis thus supports the formulation of the product as a 1:1 complex of the components. Other observations show that the components are strongly associated, although probably structurally intact:

(1) The complex is completely odorless, although both components are pungent, and

colored although the components are colorless.

(2) Trituration with 15% aq. HCl completely bleached the complex instantly, leaving pure CBr_4 (m 90-91°) in 81% recovery. Trituration with hot distilled water did not cause bleaching, although DABCO is water-soluble.

(3) The nmr spectrum of the complex (saturated solution, c.5% in $CHCl_3$), $\delta = 2.78$ ppm, singlet, coincided precisely with that of DABCO at the same concentration, indicating perhaps a low degree of association. From the yellow color of the saturated solution, however, association clearly occurs: broad absorption extends to 400 nm at 0.01<u>M</u>, although CBr_4 absorbs only to 350 nm.

Preliminary x-ray diffraction data[8] from single crystals indicate that these are monoclinic, with four "molecules" per unit cell. The cell dimensions are $a = 6.15$ Å, $b = 16.85$ Å, and $c = 12.41$ Å; $\beta = 101°55'$ and $\rho = 2.34$ g cm^{-3}. The complete structure is currently being determined.

DABCO also forms complexes with CCl_4, $BrCCl_3$, and $HCBr_3$, but none precipitate on mixing the components. The first is white and loses all its CCl_4 in one hour at 25°. The others are stable and are under investigation.

The isolation of CBr_4-DABCO contrasts with the behavior of CBr_4 and hexamethylenetetramine, which may be isomorphous. Our observation further emphasizes the ease with which amine bases associate with halogen compounds.[5] In line with previous comments,[6] we urge caution in such measurements as association constants of processes involving amines[7]—and presumably other n-donors—in perhalomethane solvents.

References

1. D. P. Stevenson and G. M. Coppinger, <u>J. Am. Chem. Soc.</u>, <u>84</u>, 149 (1962).
2. F. J. Streiter and D. H. Templeton, <u>J. Chem. Phys.</u>, <u>37</u>, 161 (1962).
3. T. Dahl and O. Hassel, <u>Acta Chem. Scand.</u>, <u>22</u>, 2036 (1968).
4. T. Dahl and O. Hassel, <u>ibid.</u>, <u>22</u>, 372 (1968).
5. S. Dunstan and H. B. Henbest, <u>J. Chem. Soc.</u>, 4905 (1957); P. Datta and G. M. Barrow, <u>J. Am. Chem. Soc.</u>, <u>87</u>, 3053 (1965).
6. W. Partenheimer, T. D. Epley, and R. S. Drago, <u>ibid.</u>, <u>90</u>, 3886 (1968).
7. M. M. Kreevoy, H. B. Charman, and D. R. Vinard, <u>ibid.</u>, <u>83</u>, 1978 (1961).
8. We are indebted to Professor Clarence E. Pfluger, Syracuse University, for these data.