Complexes of Bromine with Hexamethylphosphoric Triamide (HMPA) and with its Polymeric Analogue Poly-HMPA

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The equilibrium constant of complexation of bromine with hexamethylphosphoric triamide (HMPA) has been determined by ^{1}H n.m.r. spectroscopy by using a ' competitive complexation ' method. Solid adducts of bromine with poly-HMPA, a polymer analogue of HMPA, have been isolated from chloroform solutions.

HEXAMETHYLPHOSPHORIC TRIAMIDE (HMPA) has a strong tendency to form molecular complexes with electron acceptors.[1] Its donor properties have been attributed to the pronounced basicity of the oxygen of its PO group.[2] Though formation of charge transfer complexes between bromine and electron donors has been extensively investigated,[3,4] no information is available about its complexation with HMPA. Polymeric analogues of hexamethylphosphoric triamide (Poly-HMPA) were recently synthesized,[5] and it was observed that solid adducts precipitate upon addition of bromine to their chloroform solutions.[6] We decided, therefore, to investigate the interaction of bromine with HMPA and with poly-HMPA.

A convenient technique for the study of complexation reactions is provided by n.m.r. spectroscopy.[7] The hydrogen atoms in HMPA are, however, far apart from the interacting oxygen, and their chemical shifts are apparently very little affected by the interaction of HMPA with bromine. On the other hand, hydrogen bonding between HMPA and chloroform causes a pronounced shift in the position of the chemical shift of the chloroform hydrogen.[8,9] The competition between hydrogen bonding and complexation of HMPA with bromine may be used, therefore, as a convenient probe for the study of the latter reaction. The concentration of free HMPA in such systems can be evalu-

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[1] H. Normant, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1046; H. Normant, *Russ. Chem. Rev.*, 1970, **39**, 457.

[2] M. W. Hanson and J. B. Bouck, *J. Amer. Chem. Soc.*, 1957, **79**, 5631.

[3] O. Hassel, *Science*, 1970, **170**, 497.

[4] R. Foster, ' Organic Charge Transfer Complexes,' Academic Press, London and New York, 1969.

[5] A. Bello, W. Bracke, J. Jagur-Grodzinski, G. Sackmann, and M. Szwarc, *Macromolecules*, 1970, **3**, 98.

[6] Y. Ozari, Annual Progress Report submitted to the Israel Research Council, March 1972.

[7] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Progr. N.M.R. Spectroscopy*, 1969, **4**, 9.

[8] A. J. Dale, *Acta Chem. Scand.*, 1970, **24**, 3403.

[9] T. Olsen, *Acta Chem. Scand.*, 1970, **24**, 3081.

ated from the position of the chemical shift of chloroform hydrogen. A similar approach was recently applied to the quantitative study of complexation of bromine with ethers.[10]

EXPERIMENTAL

Chloroform (Frutarom, analytical) was washed with water to remove traces of alcohol, dried over $CaCl_2$, distilled in an argon atmosphere and kept in the dark under argon.

Bromine (Fluka, AnalaR), Dicyclohexyl-18-crown-6 (E. I. du Pont de Nemours, pure), and sodium bromide (Fisher, AnalaR) were used without further purification.

Hexamethylphosphoric triamide (Fluka, practical) was degassed on a high vacuum line, and kept for several days in contact with molecular sieves (Linde, 4A). The fraction distilling at 56 ± 1 °C and 10^{-1} mmHg was collected and again degassed for 48 h on a high vacuum line to remove last traces of dimethylamine.

The polymer analogue of HMPA (poly-HMPA), $[\eta]_{25}$ $(CHCl_3) = 0{\cdot}17$ dl g^{-1}, was synthesized, as described.[5]

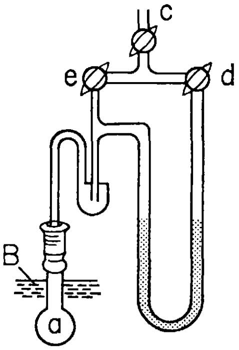

FIGURE 1

Crude polymer was purified by precipitating it from acetone solutions with a very small quantity of water (3·6 cm^3 per 100 cm^3 of a 30% solution of poly-HMPA in acetone). The water cross-linked polymer was redissolved in chloroform and dried over $CaCl_2$. Chloroform was evaporated and the residual polymer was dried in high vacuum. Poly-HMPA,Br_2 adducts were prepared by mixing chloroform solutions of bromine and poly-HMPA and centrifuging the precipitated adduct, or by exposure of poly-HMPA to bromine vapour.

The ^1H n.m.r. spectra were recorded on a Varian A-60 spectrometer. Solutions for n.m.r. measurements were prepared by adding stock solution of bromine to cold solutions of HMPA in chloroform.

The u.v. spectra were recorded on a Cary 15 spectrophotometer with 5 cm quartz optical cells.

Vapour pressure determinations were performed with a paraffin oil manometer, schematically shown in Figure 1. A sample of *ca.* 0·3 g of poly-HMPA,Br_2 was placed in a 3 ml round-bottomed flask (a) and cooled to 15 °C by immersion in a thermostatted bath (B). The system was evacuated on a high vacuum line and after a 10^{-3} mmHg pressure was attained, stopcock (e) was closed. The vapour pressure of bromine was read from the difference in the level of the paraffin oil meniscus in the two arms of the U-tube, after 3—5 min of equilibration. Reproducibility of the results was checked by alternating measurements at different temperatures. The bromine content of the adducts before and after vapour pressure determination was checked by an iodometric titration.

RESULTS AND DISCUSSION

Complexes of HMPA with Bromine and Chloroform.—As may be seen from the data listed in the Table, addition of bromine to solutions of HMPA in chloroform causes a large up-field shift in the position of the chemical shift of the chloroform hydrogen. For a very large excess of bromine, the position of the shift approaches that observed in pure chloroform. Obviously, the concentration of free HMPA decreases upon addition of bromine, and the hydrogen bonding equilibrium between chloroform and HMPA is shifted. This clearly indicates that bromine competes effectively with chloroform for the complexation with HMPA. Upon addition of carbon tetrachloride to such solutions, a bromine–HMPA complex may be indeed isolated from the system. A 1 : 1 Br_2 : HMPA stoicheiometry was established by iodometric titrations of such adducts.*

^1H N.m.r. chemical shifts of the chloroform hydrogen in the presence of HMPA and of bromine at 22 °C

Chloroform (mole fraction)	$(Br_2)_0$ (M)	$(HMPA)_0$ (M)	δ_x (p.p.m.)	Δ_B [a] (Hz)
1·000	None	None	7·283	
0·770	3·00		7·823	None
0·858	None	1·50	7·735	26·5
0·732	1·55		7·533	15·0
0·687	2·07		7·496	12·8
0·655	2·58		7·466	11·0
0·613	3·10		7·450	10·0
0·581	3·62		7·425	8·5
0·537	4·14		7·416	8·0
0·735	None	2·50	8·166	52·4
0·568	2·00		7·800	31·0
0·534	2·50		7·725	26·5
0·495	3·00		7·700	25·5
0·468	3·50		7·663	22·8
0·430	4·00		7·633	21·0
0·399	4·50		7·583	18·0
0·577	None	3·50	8·783	89·4
0·387	2·26		8·356	64·4
0·357	2·81		8·213	55·8
0·315	3·40		8·066	47·0
0·274	3·81		7·953	40·2
0·247	4·33		7·873	35·4

[a] Δ_B Is the increment in the chemical shift due to addition of HMPA to a chloroform solution.

In solutions, both the hydrogen bonding and Br_2–HMPA complexation equilibria must be simultaneously maintained. Hence,

$$P_e = \frac{(PC)}{C_e \cdot K_H} = \frac{(PB)}{B_e \cdot K_B} \qquad (1)$$

where K_H and K_B are the hydrogen bonding and bromine complexation equilibria respectively, $P_e =$

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* Bromine was in excess over HMPA in solutions from which such adducts were separated.

[10] E. Shchori and J. Jagur-Grodzinski, *Israel J. Chem.*, 1972, **10**, 935.

$[\mathrm{HMPA}]_e$, $C_e = [\mathrm{CHCl_3}]_e$, $B_e = [\mathrm{Br_2}]_e$, $(PC) = [\mathrm{HMPA,CHCl_3}]_e$ and $(PB) = [\mathrm{HMPA,Br_2}]_e$.

For a fast exchange beteeen free and hydrogen bonded species, the experimentally observed chemical shift, δ_x, is given [11] by

$$\delta_x = \delta_{(PC)} \cdot f_{(PC)} + \delta_c \cdot f_C \qquad (2)$$

$$\delta_x = (\delta_{(PC)} - \delta_C) f_{(PC)} + \delta_C \qquad (2a)$$

where f_C, δ_C and $f_{(PC)}$, $\delta_{(PC)}$ are molar fractions and chemical shifts of the free and of the hydrogen bonded chloroform respectively.

If one denotes $\Delta_0 = \delta_{(PC)} - \delta_C$ and $\Delta_B = \delta_x - \delta_C$, equation (2a) yields equation (2b).

$$\Delta_B = \Delta_0 f_{(PC)} \qquad (2b)$$

Since $f_{(PC)} = (PC)/C_0$,

$$\Delta_B = \Delta_0 (PC)/C_0 \qquad (2c)$$

where the total concentration of chloroform $C_0 = C_e + (PC)$.

Hence: $$\frac{C_e}{(PC)} = \frac{\Delta_0}{\Delta_B} - 1 \qquad (2d)$$

It follows from equations (1) and (2d) that

$$P_e = \frac{1}{K_H\left[\dfrac{\Delta_0}{\Delta_B} - 1\right]} \qquad (3)$$

Since the sums of free and complexed bromine and HMPA remain constant and equal to the initial concentrations of the reagents, it follows from equation (2c) and from the right hand side of equation (1) that:

$$K_B = (PB)/\{P_e[B_0 - (PB)]\} \qquad (4)$$

where $$(PB) = P_0 - P_e - (C_0\Delta_B/\Delta_0) \qquad (4a)$$

The equilibrium constant of complexation K_B between HMPA and bromine may, therefore, be calculated from the initial concentrations of the reagents and from the values of Δ_B if K_H and Δ_0 are known.

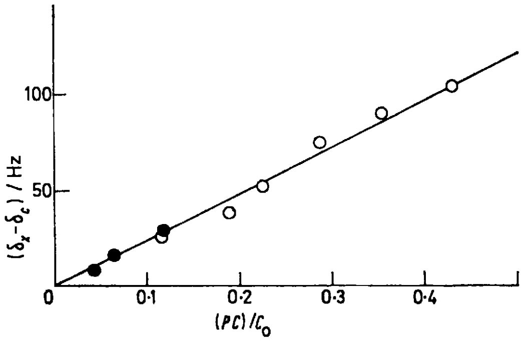

FIGURE 2 Chemical shifts of the chloroform hydrogen *vs.* $(PC)/C_0$; ○, HMPA–$\mathrm{CHCl_3}$ system, the linear fit corresponds to $K_H = 0{\cdot}31$ l mol^{-1}, $\Delta_0 = 240$ Hz; ●, Poly-HMPA–$\mathrm{CHCl_3}$ system, the linear fit corresponds to $K_H = 0{\cdot}08$ l mol^{-1}, $\Delta_0 = 240$ Hz

Because of limitations imposed by the solubility characteristics of the HMPA,$\mathrm{Br_2}$ complex, we were compelled to use chloroform both as a reagent and as a solvent.

Chemical shifts of the chloroform hydrogen after addition of HMPA or poly-HMPA were analyzed accordingly to the treatment proposed by Creswell and Allred.[11] The linear plot of $(\delta_x - \delta_C)$ *vs.* $(PC)/C_0$ shown in Figure 2 yields $\delta_{(PC)} = 11{\cdot}283$ p.p.m. ($\Delta_0 = 240$ Hz), $K_H^{22°} = 0{\cdot}31$ l mol^{-1} for HMPA and $K_H^1 = 0{\cdot}08$ l mol^{-1} for poly-HMPA. The value of $K_H^{22°}$ in our system is lower than that determined by Dale [8] for the hydrogen bonding between HMPA and chloroform in $\mathrm{CCl_4}$ solutions ($K_H^{20°} = 3{\cdot}0$ l mol^{-1}). This may be explained by self-association of chloroform in its concentrated solutions. On the other hand, the large chemical shift is apparently due to the increased polarity of the complex in such media.

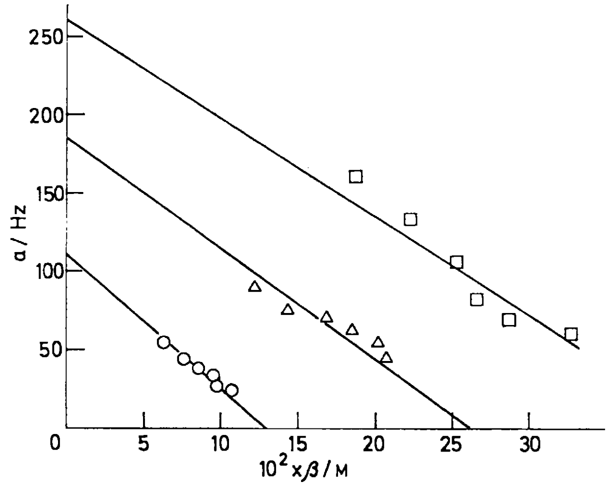

FIGURE 3 α *vs.* β calculated for $K_H = 0{\cdot}31$ l mol^{-1}, $\Delta_0 = 240$ Hz, $K_B/K_H = 9{\cdot}4$ □, $[\mathrm{HMPA}]_0 = 3{\cdot}5$M; △, $[\mathrm{HMPA}]_0 = 2{\cdot}5$M; ○, $[\mathrm{HMPA}]_0 = 1{\cdot}5$M

Using thus determined values of K_H and Δ_0 and data listed in the Table, one calculates from equations (3), (4), and (4a) that, at 22 °C, the equilibrium constant of complexation of bromine with HMPA $K_B = 2{\cdot}9 \pm 0{\cdot}5$ l mol^{-1}. An algebraic rearrangement of equations (3), (4), and (4a) yields:

$$\alpha = P_0\Delta_0 K_H - \Delta_0 K_B \beta \qquad (5)$$

where

$$\alpha = \Delta_B\{K_H C_0 + [\Delta_0/(\Delta_0 - \Delta_B)]\} \text{ and}$$

$$\beta = B_0 \Big/ \left(\frac{\Delta_0}{\Delta_B} + \frac{K_B}{K_H} - 1\right)$$

Plots of α *vs.* β shown in Figure 3, for constant initial concentrations of HMPA, permit us to check the self consistency of the results over a broad concentration range. For 1·5; 2·5, and 3·5M concentrations of HMPA, intercepts of the nearly parallel lines obtained for $\Delta_0 = 240$ Hz, $K_H = 0{\cdot}31$ l mol^{-1} and $K_B/K_H = 9{\cdot}4$, yield $\Delta_0 K_H = 74{\cdot}4$ Hz l mol^{-1}, while their slopes yield $\Delta_0 K_B = 730 \pm 110$ Hz l mol^{-1}.

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[11] C. J. Cresswell and A. L. Allred, *J. Phys. Chem.*, 1962, **66**, 1469.

Certain deviation of the experimental points (*cf.* Figure 3) from the expected straight and parallel lines should not be, however, attributed to the experimental scatter only. The implicit assumption, used in our treatment, that the activities of the reagents remain constant in spite of a large change in their concentrations, certainly represents an over-simplification in case of such concentrated solutions.

Complexes of Bromine with Poly-HMPA.—Amorphous, orange-coloured, non-hygroscopic adducts precipitate from chloroform solutions upon mixing of poly-HMPA with bromine. The ratio of Br_2 to $\geqslant$P=O is less than 1 : 2, if a dilute bromine solution is slowly added to an excess of poly-HMPA. A much larger quantity of bromine is found in the complex if the order of mixing of the reagents is reversed. The bromine to poly-HMPA ratio in the complex also increases after the precipitated adduct has been left for a prolonged time in contact with bromine or its solutions in chloroform. Measurements of the vapour pressure of bromine, over adducts in which $\geqslant$P=O : $Br_2 > 2{\cdot}0$ indicates that the activity of bromine in the adduct is low. Its vapour pressure is several orders of magnitude lower than that of free bromine (*cf.* Figure 4). A much higher activity of bromine is observed when $1{\cdot}0 <$ $\geqslant$P=O : $Br_2 < 2{\cdot}0$. The very high vapour pressure of bromine, in the case of Br_2 : $\geqslant$P=O $> 1{\cdot}0$ ($P_{15^\circ} > 50$ mmHg) indicates that the additional bromine is simply occluded in the complex.

It may be concluded from the vapour pressure data that both 2 : 1 and 1 : 1 stoicheiometry for the polymer–bromine interaction is possible. Judging by the relative hydrogen bonding abilities of poly-HMPA and HMPA (*cf.* Figure 2), the equilibrium constants of complexation of bromine with poly-HMPA cannot be expected to be very high. It seems that the nearly quantitative precipitation of the complex from diluted solutions is due to its very limited solubility. A low Br_2 : polymer ratio found in some adducts precipitated from diluted solutions indicates that it may be sufficient to cross-link poly-HMPA chains with only few Br_2 molecules to render it insoluble. In order to estimate the solubility of the poly-HMPA–bromine complex, we reduced the concentrations of free bromine in chloroform until no precipitates were formed upon addition of poly-HMPA. This was achieved by converting bromine into a tribromide complex (by addition of dicyclohexyl-18-crown-6 + sodium bromide). The very low concentrations of free bromine in such systems can be calculated from the spectroscopically determined concentration of the tribromides ($\varepsilon = 4{\cdot}8 \times 10^4$), since the values of the equilibrium constant for this complexation reaction was recently reported.[12]

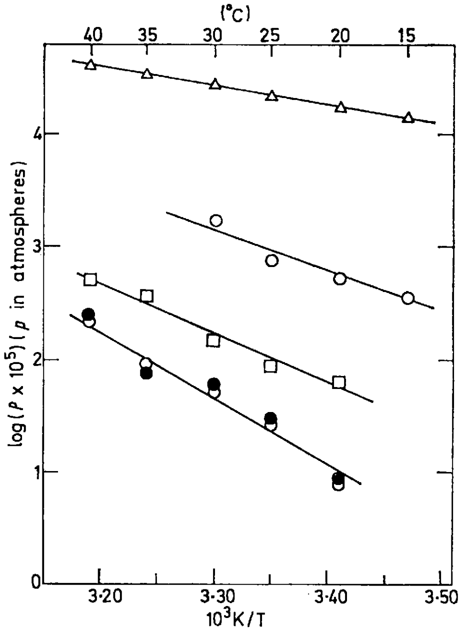

FIGURE 4 Equilibrium vapour pressure of bromine in poly-HMPA–bromine complexes *vs.* reciprocal absolute temperature; △, free bromine (data from Handbook of Chemistry and Physics, Chemical Rubber Co., 1971—72); ⊙, 37·1% Br_2 ($\geqslant$P=O/Br_2 = 1·2); □, 36·9% Br_2 ($\geqslant$P=O/Br_2 = 1·6); ○, 35·2% Br_2 ($\geqslant$P=O/Br_2 = 1·7); ●, 8·2% Br_2 ($\geqslant$P=O/Br_2- = 10·0)

On the basis of such measurements and assuming $K_B^{\mathrm{HMPA}} \simeq K_B^{\mathrm{poly\text{-}HMPA}}$ we estimate that the solubility of the poly-HMPA–bromine complexes in chloroform at room temperatures is *ca.* 10^{-8}—10^{-7} g l^{-1}. Because of a very slow release of bromine from the complex into the chloroform solutions it may perhaps be advantageous to use it as a mild brominating agent. Studies of the kinetics of such reactions will be reported elsewhere.

[2/1535 *Received, 3rd July,* 1972]

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[12] E. Shchori and J. Jagur-Grodzinski, *J. Amer. Chem. Soc.*, 1972, **94**, 7957.