Reduction of the Alkali and Alkaline Earth Halides by Active Hydrogen

IN the course of investigations on the reduction of metal halides by atomic hydrogen, using apparatus previously described[1,2], I have found that the halides of lithium, sodium, potassium and caesium are all reduced to metal and hydrogen halide, resulting in the formation of metal mirrors on the walls of the reaction tube. The reaction apparently takes place in the vapour state during sublimation of the halides which is caused by the rise in temperature due to atomic recombinations. Unreduced sublimed halide may co-deposit with the metals or be deposited separately depending on temperature and relative volatility. It is possible to derive relative reaction rates for the halides: these are shown below:

LiF	12·8	NaF	4·0	KF	1·74		
LiCl	33	NaCl	7·0	KCl	1·86	CsCl	2·56
LiBr	48	NaBr	8·8	KBr	1·0	CsBr	2·4
LiI	86	NaI	13·0	KI	1·3		

It will be seen that the reaction rate decreases with increasing atomic number of the metal atom. With minor anomalies for KBr and KI it increases with increasing atomic number of the halogen atom and thus corresponds to the decrease in heat of formation. The extent of reaction, under conditions not yet optimized, varies from 70 per cent for LiI to 1–2 per cent for KBr and KI.

There is a marked difference in the behaviour of the alkaline earth metal halides. Here, under controlled conditions, reduction gives rise to deposits of metal and dihalide in equimolar proportions, the overall chemical composition therefore being expressible as *MX*. Except in the case of fluorides, where the metal is so finely dispersed in the halide that no characteristic metal lines are obtained, X-ray analysis confirms the presence of metal and dihalide. All the evidence points to the formation of monohalides of the metals beryllium, magnesium, calcium and barium, which disproportionate readily on contact with the walls of the reaction tube, yielding metal and dihalide.

The results of these and related investigations will be described and discussed in more detail elsewhere.

F. K. McTAGGART

C.S.I.R.O. Division of Mineral Chemistry,
Fishermen's Bend,
Victoria,
Australia.

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BIOPHYSICS

X-ray Diffraction Patterns of Liquid Crystalline Solutions of Poly-γ-benzyl-L-glutamate

THE X-ray diffraction patterns of liquid crystalline solutions of poly-γ-benzyl-L-glutamate in various solvents have been observed by Luzzati *et al.*[1] for a range of concentrations. They report four phases, namely, isotropic, cholesteric, paracrystalline and complex; the patterns are observed with unoriented materials and reflexions corresponding to equatorial reflexions only are recorded. In some cases, several reflexions are observed which apparently index on a hexagonal lattice. In the cholesteric phase, observed in *m*-cresol at concentrations between about 20–36 parts by weight of polymer per 100 parts of solution, one diffuse reflexion only is seen. Luzzati *et al.* calculate the length of the residue translation *h* of the polypeptide chain assuming that this diffuse reflexion may be regarded as the 10 reflexion of a hexagonal net and (implicitly) that the whole of the polymer has the corresponding mean inter-chain distance. For the cholesteric phase in *m*-cresol they obtain a value $\sim 2{\cdot}0$ Å for the residue translation *h* and suggest that this is evidence that the chain conformation is the 3_{10} helix (for which *h* is 2·0 Å).

Since orientation is easily induced in the liquid crystalline phase by flow[2,3] evidently information concerning the helix pitch could be got by observing the layer line streaks in the fibre diffraction pattern of an oriented sample. These will be weak compared with the diffuse scatter from the solvent, and clearly it is desirable to minimize this scatter by using nearly monochromatic radiation.

We have recently constructed a point-focusing X-ray diffraction camera in which copper $K\alpha$ radiation is reflected by a toroidal gold surface and most of the white and $K\beta$ radiation is removed[4]. This camera has been used in conjunction with a cell in which the polymer solution is oriented by shear. The polymer solution is contained between two thin parallel beryllium windows of 1 in. diameter, separated by about 0·5 mm. One window is fixed while the other is rotated at constant speed, producing a shear gradient in the solution, and good fibre diffraction patterns have been observed. One of these is shown in Fig. 1, where a meridional arc corresponding to a spacing 5·23 Å may be seen. Over a concentration range from 11 to 36 per cent wt. by wt. the spacings lie between 5·23 and 5·26 Å; the variation is random and due to errors of observation. This is almost identical with the spacing of the strongest reflexion on the layer line in the solid polymer (Bamford, Hanby and Happey[5], 5·26 Å; Parsons and Martius[6], 5·25 Å). It has been shown recently by Elliott, Fraser and MacRae[7] that in the solid polymer there are no sharp reflexions on the layer lines, which are streaks; the polymer is in fact paracrystalline.

The identity of the 'spacing' of the meridional arc in Fig. 1 with that of the point of maximum intensity in the streak on the 'turn' layer line (for which the reciprocal space co-ordinate in the fibre axis direction is $1/5{\cdot}4$ Å^{-1}) is convincing evidence that in the cholesteric phase the polymer is in the α-helix form. The 'turn' layer line of the 3_{10} helix has a reciprocal space co-ordinate $1/6{\cdot}0$ Å^{-1}; we have not observed any reflexions which might be associated with this.

That the chain conformation is the α-helix and not the 3_{10} helix in this phase is put beyond doubt by observations

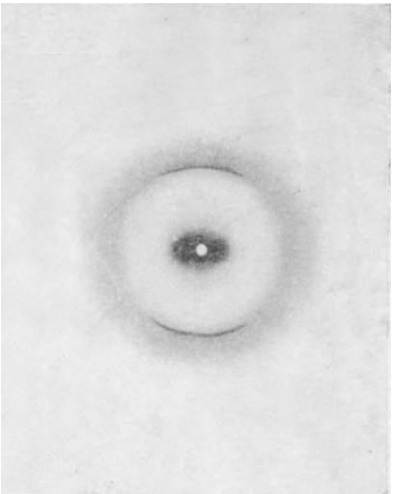

Fig. 1. X-ray diffraction photograph of cholesteric phase in poly-γ-benzyl-L-glutamate in *m*-cresol, under constant shear (degree of polymerization about 1,450), concentration 0·23 g/g solution. Copper $K\alpha$ radiation, partially monochromatized, 250 μamp, 50 kV, 3·63 cm specimen to film distance. Direction of shear vertical. Exposure time 1·5 h. Unit magnification. Meridional reflexion 5·23 Å, equatorial reflexion 27·2 Å