

Study of interaction between microclusters of silver and arsenious trisulphide

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Abstract. Interaction between clusters of silver and arsenious trisulphide have been investigated using electron diffraction and EDAX. The results of the study show the possibility of bulk reactions when clusters of two different materials are brought in contact. The chances of formation of complexes between the clusters are also considerable.

Keywords. Electron diffraction; clusters; chemisorption; bulk reactions; lattice contraction.

1. Introduction

The study of physical and chemical properties of microclusters of materials and the variation of these properties with respect to the bulk values has become the focus of considerable attention in recent years (Brus 1986). Chemical reaction studies provide a useful probe into the structural make up of clusters and also yield information regarding the mechanism of breaking and making of chemical bonds on the cluster surfaces (Riley 1989). Parent and McElvany (1989) obtained evidence for two structural forms of carbon cluster ions, from their differing reactivities with HCN. Reaction studies of Fe and Co clusters with N₂ have shown sharp variation in reactivity with cluster size (Jarrold and Bower 1989).

The interactions involving metal clusters can be characterized as either surface chemisorption reactions or bulk reactions (Riley 1989). In the former, reactions involve the formation of surface adsorbate bonds which are either physical or chemical. Bulk reactions are characterized by more extensive breakage of metal–metal bonds and the formation of a bulk compound having metal–nonmetal bonds. The chemisorption reactions of Fe clusters with ammonia and water and that of nickel clusters with ammonia have been reported by Riley (1989). These reaction studies represent fundamental chemical processes that are promoted by the interaction between adsorbate and metal atoms and an understanding of their detailed sequence of steps will provide us with valuable information about the unique properties of metal surfaces. Chemisorption and chemical reaction studies on size selected clusters have made possible the estimation of activation barriers for chemisorption on the cluster surfaces (Jarrold and Bower 1989).

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Although chemisorption reactions of clusters have been studied in detail there has not yet been much effort focused on the possibility of bulk reactions between clusters. Freundlich and Moor (1924) studied the interaction of silver and As_2S_3 sols and indicated the possibility of formation of the compound Ag_3AsS_3 . We report here the study of the feasibility of bulk chemical reactions between microclusters of silver and arsenious trisulphide, using electron diffraction and EDAX. The results of the study show that even though bulk chemical reactions are highly probable, the chance of formation of complexes between silver and arsenious trisulphide is considerable.

2. Experimental

Aqueous suspensions of silver used for the present study are prepared by Bredig's method by striking an arc between two silver electrodes immersed in distilled water (Weiser 1949) and using a suitable stabilizer. The concentration of silver suspension thus prepared is 0.129 g/l. Arsenious trisulphide suspension of concentration 0.6888 g/l is prepared by the literature method (Jirgensons and Straumanis 1964). The two suspensions are allowed to interact by titrating the suspension of arsenious trisulphide against the suspension of silver until precipitation occurs. This precipitate, which may contain Ag_3AsS_3 or complexes between Ag and As_2S_3 particles as the product of interaction, and unreacted Ag and As_2S_3 particles, is removed, washed repeatedly with water and redispersed in distilled water. The clusters of Ag, As_2S_3 and that of the product of interaction are subjected to TEM and selected area electron diffraction studies by placing a drop of the respective suspension on the grid of the Philips EM 301 TEM and allowing the liquid to evaporate off. From the TEM micrographs the average particle size is found to be about 16 nm for Ag and 8 nm for As_2S_3 clusters. The electron diffraction patterns of Ag and As_2S_3 clusters are found to be spotty (figures 1a and 1b), whereas that of the product of interaction shows diffused and broadened rings (figure 1c) with reflection corresponding to unreacted Ag. The interplanar spacings calculated for Ag and As_2S_3 clusters indicate lattice contraction. A portion of the precipitate is subjected to X-ray analysis and the diffraction pattern (figure 2) does not contain any sharp peaks, indicating the absence of crystallinity. Chemical analyses of different samples of the precipitate were done by EDAX. The atomic percentages of Ag, S and As do not indicate stoichiometric reaction in any of the cases. A typical EDAX result is given in table 1.

3. Discussion

Since small clusters are composed predominantly of surface atoms, their chemical properties may well reflect the macroscopic details of surface activity. It has been observed that in many cases the activity of a surface is highest at steps and other faults where the bonding is presumably strained (Richtsmeir *et al* 1985), as would be expected for small clusters, which are under surface stress due to high surface-to-volume ratio. It has been shown through electron diffraction studies in the case of fine particles of platinum and gold that a decrease in the lattice parameter, proportional to the reciprocal of the particle size, occurs and that this contraction is evidence for the existence of surface stress (Poppa *et al* 1971; Solliard and Flueli 1985). The electron

diffraction photographs of both Ag and As₂S₃ clusters in the present study indicate that the lattice contraction is larger for As₂S₃ clusters, which are smaller in size than Ag clusters. It may be expected that both Ag and As₂S₃ clusters are in a state of surface stress and, hence, there may be a tendency to release the resultant strain. As a result, when suspensions of clusters of Ag and As₂S₃ are brought into contact, in addition to the mutual or co-precipitation of the suspensions, a chemical reaction may ensue between them, which may release the strain. On meeting, there may be diffusion between the atoms and molecules constituting the Ag and As₂S₃ clusters, and subsequent rearrangement. The establishment of metal–nonmetal bonds may occur leading to the formation of clusters of the compound of the two earlier clusters,

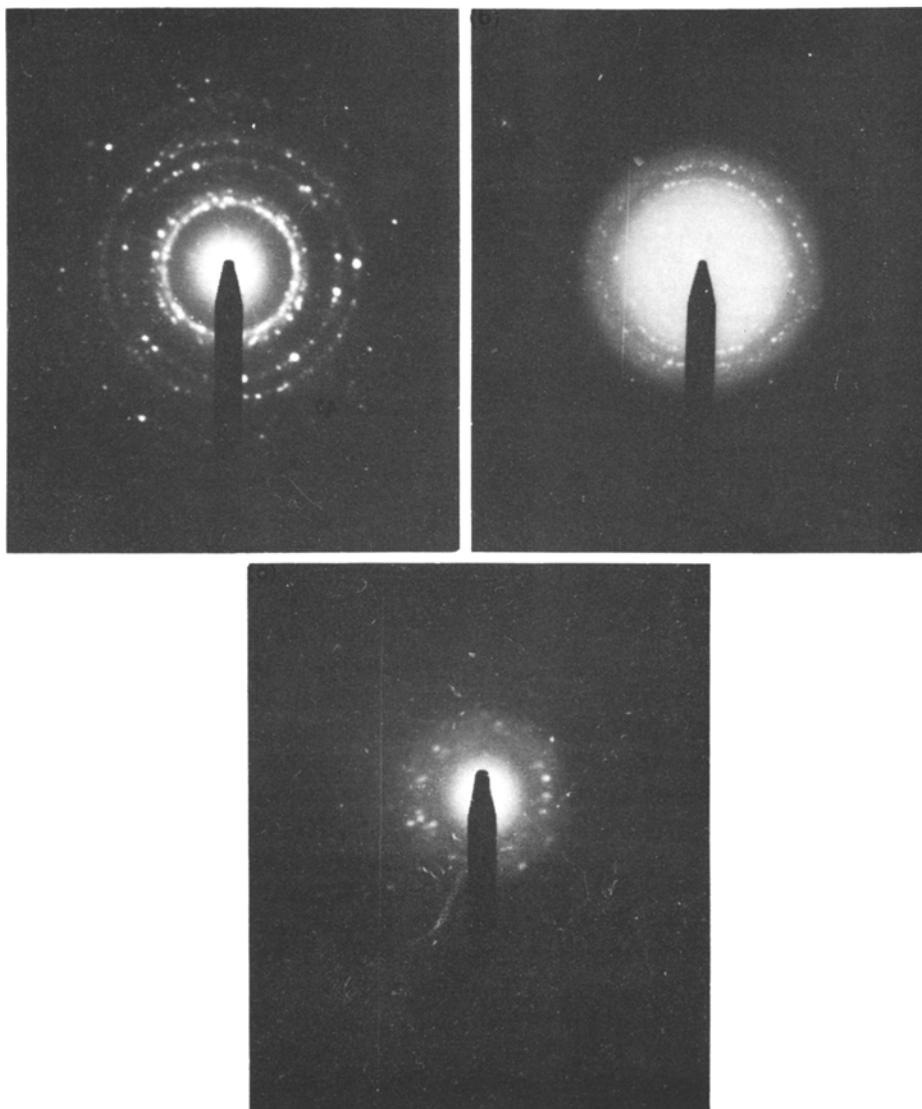


Figure 1. Electron diffraction photographs of aggregates of clusters of silver (a), arsenious trisulphide (b), and the product of interaction between silver and arsenious trisulphide (c).

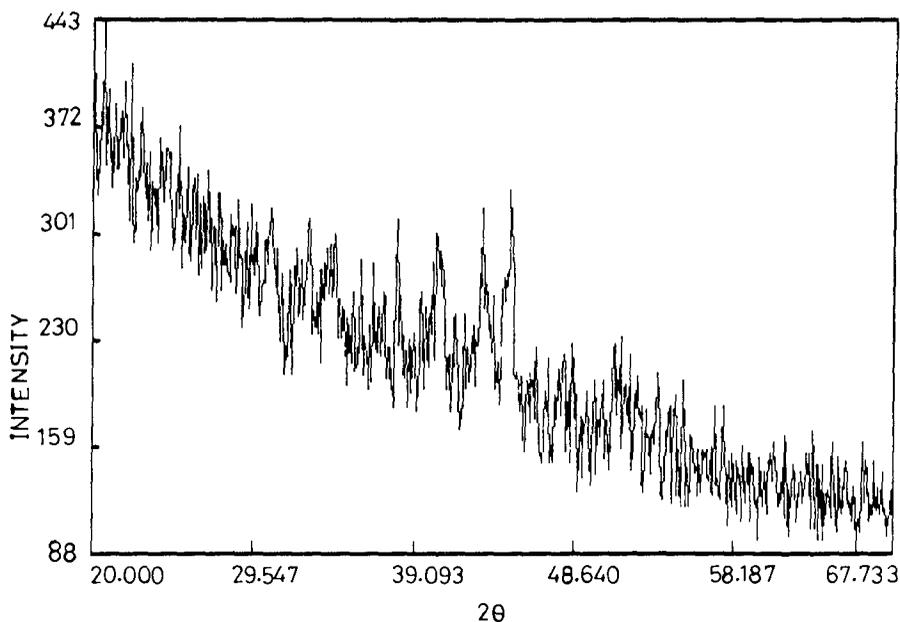


Figure 2. X-ray diffraction pattern of the product of interaction between clusters of silver and arsenious trisulphide.

Table 1. EDAX results.

Elements	Atomic (%)	Weight (%)
Ag	58.910	74.783
S	21.699	8.136
As	19.391	17.081

instead of surface adsorbate bonds as in the case of chemisorptive reactions. The study of formation of the Pd-C phase through the interaction of palladium black with ethylene, acetylene or carbon monoxide has revealed that the reaction process involves the deposition of a carbonaceous overlayer on Pd followed by activated diffusion of carbon atoms through the metal lattice (Ziemecki *et al* 1985). Also reaction studies of Fe clusters with excess hydrogen to yield fully hydrogenated products have shown that the Fe clusters probably have a specific configuration having least free energy, and that the iron substructure, because of the diffuse nature of metal-metal bonding, rearranges during hydrogenation so that in the hydride it differs from that in the bare metal clusters (Parks *et al* 1985). The possibility of interaction between Ag and As₂S₃ clusters along the conceived lines may be considered to be consistent with the above results.

The electron-diffraction pattern of the product of interaction exhibits a strong broadening of the diffraction rings, which are also diffused. A similar strong broadening of the diffraction lines of carbon-supported palladium was reported by Anton and Poppa (1982). This broadening indicates a higher degree of disorder within the particle lattice (Lamber *et al* 1990). The X-ray diffraction pattern of the product

of interaction substantiates the results obtained from electron diffraction. The microdiffraction pattern observed for chemisorptive metal support interactions in the case of chemisorption of carbon on crystalline Pd particles reveals that the crystalline nature of the Pd particles remains undistorted even after chemisorptive reactions (Lamber *et al* 1990). The appearance of diffused and broadened ring patterns as shown by the reaction products of Ag and As₂S₃, in sharp contrast with the electron diffraction pattern shown by Ag and As₂S₃, indicates that the reaction may not be purely chemisorptive. A few diffraction spots are present in the electron-diffraction pattern of the product of interaction, indicating the presence of some unreacted Ag clusters. The EDAX results of different samples of the product of interaction show that the percentages of various elements in the reaction product are not consistent with a stoichiometric compound. Thus it appears that bulk reaction between Ag and As₂S₃ may not be stoichiometric and the possibility of formation of complexes between Ag and As₂S₃ cannot be discarded.

4. Conclusion

The electron diffraction and EDAX results indicate that the interaction between clusters of silver and arsenious trisulphide may be classified as the bulk reaction. The formation of complexes between the clusters is also probable.

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