

## Reversible Solid State Redox Reactions of the Layered Carbide $Ta_2S_2C$

ROBERT SCHÖLLHORN and WOLFGANG SCHMUCKER  
Anorganisch-chemisches Institut  
der Universität Münster

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Tantalum sulfide carbide  $Ta_2S_2C$  is shown to present a novel type of electronically conducting layer structure which undergoes reversible topotactic redox reactions in aqueous and nonaqueous electrolyte solutions.

Among the members of the group of complex carbides  $M_xM'_yC$  ( $M$  = transition metal,  $M'$  = transition or main group metal) the sulfide carbide  $Ta_2S_2C$  shows an outstanding anisotropy in terms of structure and bonding<sup>1</sup>. This carbide is built up from sandwich type layers (Fig. 1); within the

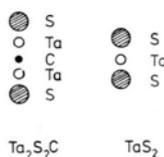


Fig. 1. Scheme of two-dimensional layer units in tantalum sulfide carbide and tantalum disulfide.

layers atoms are held together by strong forces of essentially covalent character. In the crystal lattice these two-dimensional units are separated by a VAN DER WAALS gap, *i.e.* interlayer bonding forces are relatively weak. As was pointed out by BECKMANN *et al.*<sup>1</sup>, there is an interesting structural relationship between  $Ta_2S_2C$  and the transition metal dichalcogenides  $MX_2$ . We were able to demonstrate in previous reports that the latter phases may undergo reversible topotactic redox reactions<sup>2-4</sup>. This phenomenon must be attributed to the structural anisotropy of the dichalcogenides and to the ability to take up electrons reversibly into the conduction band of the two-dimensional layer units. In this communication we present experimental evidence for similar reactions of tantalum sulfide carbide.

$1s-Ta_2S_2C$  was prepared according to the literature<sup>1</sup>; hexagonal lattice constants were  $a = 3.25 \text{ \AA}$  and  $c = 8.54 \text{ \AA}$ . Reduction was observed when suspensions of  $Ta_2S_2C$  were treated with strong

Requests for reprints should be sent to Prof. Dr. R. SCHÖLLHORN, Anorganisch-chemisches Institut der Universität Münster, D-4400 Münster, Gievenbecker Weg 9, FRG.

reducing agents in aqueous electrolyte solutions at room temperature. Reaction rates were found to increase considerably at  $pH > 7$ . As in the case of dichalcogenides, sodium dithionite  $Na_2S_2O_4$  turned out to be a most convenient reagent for this type of reaction; after 24 h the samples had reacted quantitatively. On reduction the basal spacing (distance between neighbouring layers perpendicular to the layer planes) of the sulfide carbide is increasing; electrons are transferred from the  $S_2O_4^{2-}$  ions to the layers which become negatively charged and a complementary amount of hydrated sodium ions is taken up into the VAN DER WAALS gap (Fig. 2). Layers are now held together by ionic and



Fig. 2. Scheme of reversible redox reactions of  $Ta_2S_2C$ .

VAN DER WAALS forces. Samples are susceptible to oxidation (*cf.* below) and to protolysis and have to be handled under inert gas atmosphere. The analytical value found for  $Na^+$  corresponds to a negative charge density of  $0.2 e^-/\text{unit cell}$ . This contrasts with  $TaS_2$  which may exhibit layer charge densities of  $0.3 e^-/\text{unit cell}$  and higher in aqueous medium. Differences in electronic band structure of the two compounds are supposed to be responsible for this divergence; no data have been published on  $Ta_2S_2C$  in this respect.

The activation energy for the movement of  $Na^+$  atoms in  $Na_{0.2}^+(H_2O)_y[Ta_2S_2C]^{0.2-}$  within the solvent phase is obviously very low. The interlayer cations equilibrate rapidly with positive ions in ambient electrolyte solutions, *i.e.* the reduced compounds are polyelectrolytes. Table I shows basal spacings

Table I. Basal spacings  $d$  and interlayer spacings  $\Delta d$  of reduced phases  $A_{0.2/n}^{+n}(H_2O)_y[Ta_2S_2C]^{0.2-}$  obtained by cation exchange.

$A^{n+}$	$d$ [Å]	$\Delta d$ [Å]	$A^{n+}$	$d$ [Å]	$\Delta d$ [Å]
$Li^+$	14.63	6.09	$Ba^{2+}$	14.94	6.40
$Na^+$	14.39	5.85	$NH_4^+$	11.78	3.24
$K^+$	11.77	3.23	$C_4H_9NH_3^+$	12.19	3.65
$Rb^+$	11.78	3.24	$C_6H_{13}NH_3^+$	12.27	3.73
$Cs^+$	11.94	3.40	$C_8H_{17}NH_3^+$	12.18	3.64
$Mg^{2+}$	15.42	6.88	$C_{12}H_{25}NH_3^+$	24.99	16.45
$Ca^{2+}$	14.63	6.09	$C_{16}H_{33}NH_3^+$	52.02	43.48
$Sr^{2+}$	14.66	6.12			

of derivatives  $A_{0.2/n}^{+n}(H_2O)_y[Ta_2S_2C]^{0.2-}$  obtained from the  $Na^+$ -form by cation exchange with 1 M aqueous solutions of the ions indicated. Taking the length of the  $c$ -axis ( $8.54 \text{ \AA}$ ) in  $Ta_2S_2C$  as the layer thickness of the sulfide carbide sandwich units we find two groups of values for the height of the interlayer space  $\Delta d$  ranging between  $5.85\text{--}6.88 \text{ \AA}$

resp. 3.23–3.40 Å in the alkali and alkaline earth series. Similar values for  $\Delta d$  of 5.98–6.09 Å resp. 3.07–3.14 Å are found for the analogous series  $A_{0.3/n}^{+n}(\text{H}_2\text{O})_y[\text{TaS}_2]^{0.3-}$ . These values correspond to monomolecular resp. bimolecular layers of water in the interlayer space<sup>2-4</sup>. As discussed earlier, differences in hydration energies of the cations under consideration are responsible for this effect. Only cations with a charge/radius ratio  $> 1$  may stabilize bimolecular  $\text{H}_2\text{O}$  layers. Fig. 3 gives a comparison of

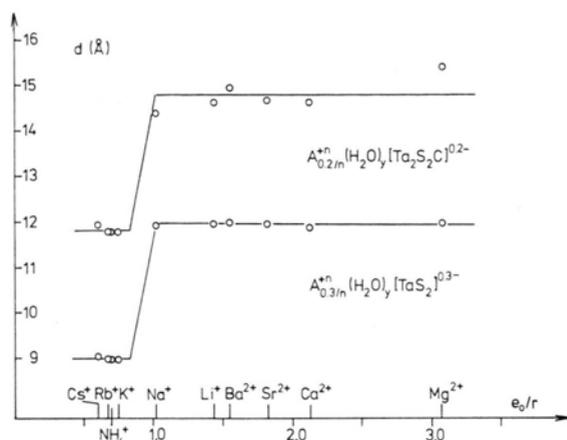
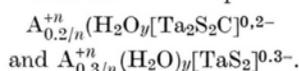


Fig. 3. Dependence of basal spacings  $d$  on charge/radius ratio for reduced phases

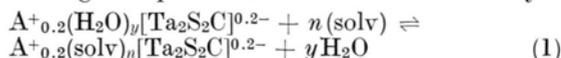


basal spacings for  $A_{0.3/n}^{+n}(\text{H}_2\text{O})_y[\text{TaS}_2]^{0.3-}$  and  $A_{0.2/n}^{+n}(\text{H}_2\text{O})_y[\text{Ta}_2\text{S}_2\text{C}]^{0.2-}$  in dependence of the charge/radius ratio of the interlayer ions. The average difference in  $d$ -values between the two series agrees reasonably well with the difference in height of the matrix layers which amounts to 8.54 Å–6.05 Å = 2.49 Å.

At water vapor pressures below 10 Torr, the bimolecular  $\text{H}_2\text{O}$  layers collapse reversibly to monomolecular layers. In aqueous medium layer distances decrease slightly with increasing electrolyte concentration. Derivatives of transition metal ions, *e.g.*  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  *etc.*, exhibit interlayer spacings corresponding to bimolecular water layers. Ion exchange with less polar organic cations leads to derivatives in which the geometry of the cations and cation-cation interactions are dominating the structural arrangement of species between the layers. Thus for  $n$ -alkylammonium-ions  $\text{C}_n\text{H}_{2n+1}\text{NH}_3^+$  with  $n < 10$  ( $n$  = number of carbon atoms per cation) cations are lying with the plane of the carbon atoms parallel to the sulfide carbide layers. For  $n > 10$  we find either monomolecular or bimolecular paraffin type arrangement of the organic cations with the axis of the extended carbon chains tilted at an angle  $\alpha < 90^\circ$  against the sulfide surfaces.

Replacement of water in the reduced phases by

polar solvents proceeds rapidly at room temperature according to Eq. 1. Values observed for interlayer



spacings are comparable to those found for the corresponding dichalcogenide compounds and for intercalation compounds of  $\text{Ta}_2\text{S}_2\text{C}$  with neutral molecules<sup>5</sup>. Whereas water seems to interact preferably with the interlayer cations, solvation of the layers must play an important role in the case of "soft" solvate molecules.

Table II. Basal spacings  $d$  of solvated phases  $N_{0.2}^{+n}(\text{solvent})_n[\text{Ta}_2\text{S}_2\text{C}]^{0.2-}$ .

Solvate	$d$ [Å]	Solvate	$d$ [Å]
Formamide	18.99	Dimethylsulfoxide	21.20
N-Methylformamide	20.15	$(\text{C}_4\text{H}_9)_3\text{PO}$	24.37
N,N-Dimethylformamide	20.08	$(\text{CH}_3\text{O})_3\text{PO}$	20.85
Diglycoldimethylether	17.17	$[(\text{CH}_3)_2\text{N}]_3\text{PO}$	21.43

The reduced phases can be oxidized quantitatively by electron acceptors such as dioxygen, transition metal ions in higher valence states *e.g.*  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ , anionic species such as  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\text{MnO}_4^-$  *etc.* On oxidation the exchangeable cations leave the interlayer space; the water molecules which themselves are not able to solvate the layers because of the low energy of  $\text{O-H}\cdots\text{S}$  hydrogen bonds are expelled simultaneously. In the oxidation product  $\text{Ta}_2\text{S}_2\text{C}$  the negative layer charge density is zero and the layers are held together by VAN DER WAALS bonding only (Fig. 2). Reaction rates for reduction and oxidation of the system  $\text{Ta}_2\text{S}_2\text{C}/[\text{Ta}_2\text{S}_2\text{C}]^{x-}$  are – under comparable conditions – considerably lower than those found for the  $\text{TaS}_2/[\text{TaS}_2]^{x-}$  system. Since the topochemical reactions in both phases are associated with mechanochemical processes *i.e.* reversible elastic deformation of the layers, this observation may be explained in terms of a higher activation energy for deformation of the structurally more complex sulfide carbide layer units.

In strongly alkaline solutions (aqueous  $\text{NH}_3$ , alkali hydroxides *etc.*) the layers of  $\text{Ta}_2\text{S}_2\text{C}$  are partially hydrolyzed under release of  $\text{S}^{2-}$  which acts as an electron donor being itself oxidized to sulfur and/or polysulfide resp.; the resulting phases  $A_{0.2}^{+n}(\text{H}_2\text{O})_y[\text{Ta}_2\text{S}_{2-x}\text{O}_x\text{C}]^{x-}$  ( $A = \text{NH}_4^+$ , alkali cation *etc.*) are sulfur deficient, the S-atoms having been replaced partially by oxygen. Similar observations were made in the dichalcogenide series<sup>4</sup>.

Electrons may also be transferred to the electrically conducting  $\text{Ta}_2\text{S}_2\text{C}$  layers by cathodic reduction in electrolyte solutions. Results of cyclic voltammetric and galvanostatic studies in aqueous and nonaqueous media will be the subject of a forthcoming article<sup>6</sup>.

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