Calc. for $C_{10}H_{12}O_2Se$: C 49.38; H 4.98; Se 32.46; equiv. wt. 243.17).

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Some Properties of a Ternary Sulfide Mo-Sn-S

ARNE W. ESPELUND

Metallurgisk Institutt, Norges tekniske høgskole, Trondheim, Norway

Metallic tin has been suggested as a reducing agent for molybdenite, MoS_2.[1] The sulfur can be volatilized mainly as SnS, giving a metallic residue of molybdenum. In an attempt in our laboratory to measure the vapour pressures of the various univariant equilibria involved with subsequent examination of the products, the X-ray pattern of a new phase was obtained.

This compound could not be isolated by any conventional method from the other phases in the sample, and synthesis in quartz ampoules was resolved upon: Finely powdered molybdenum, sulfur, and tin were mixed together in certain proportions and sealed off under vacuum. When a certain temperature gradient was maintained along the ampoule — about 900 to 400°C — the highly exothermic reaction could take place without establishing an internal pressure causing destruction of the ampoule. The mixture was ground and given a second homogenizing treatment.

Upon microscopic examination black crystals with rectangular crystal faces were found.

Debye-Scherrer photographs showed the pattern of a single phase for a mixture with an atomic ratio Mo:Sn:S close to 6:1:7. It conjugated with the other substances MoS_2—Mo_2S_3—Mo—Sn, so that straight lines emerge from the ternary compound to each of these phases in a conventional ternary diagram. There was no variation in the θ-values from one three-phase combination to another, indicating a limited homogeneity range.

The pattern obtained, supplemented with electron diffraction suggests a unit cell of orthogonal symmetry. The observed lines are fairly well explained by assuming a pseudocubic unit cell with $a = 6.53$ Å, as shown in Table 1. Cubic unit cells with $a = 6.53\sqrt{2}$, 6.53×2 and $6.53\sqrt{3}$ were tried without complete resolution of all lines. Application of a Bunn chart for tetragonal crystals gives satisfactory indexing of the first lines with $a = b = 6.53$, $c = 9.23$ Å, *i.e.* $c \simeq a\sqrt{2}$, but some lines at high θ-values could not be resolved.

Several attempts to produce single crystals of a suitable size failed.

Measurement of the specific gravity by means of pycnometer gave as result 5.69 ± 0.03 g/cm³. The stoichiometric proportion referred to above (6 Mo:1 Sn:7 S) renders as formula weight 919. The calculated formula weight of the content of a pseudocubic unit cell with $a = 6.53$ Å is 950, — in reasonable agreement with the former value.

This new compound with a metal to sulfur ratio apparently 1:1 appears to be interesting because the presence of tin stabilizes a monosulfide, which has not been obtained in the binary system Mo—S. A further investigation of its

Table 1. Debye-Scherrer diagram of ternary sulfide Cu-radiation, Ni filter. Camera diam. 114.6 mm. Forbidden values for $h^2 + k^2 + l^2$ in brackets.

Intensity	$d_{obs.}$	λ	$\sin^2\theta_{obs} \times 10^1$	$a = b = c = 6.53$ Å	
				$h^2 + k^2 + l^2$	$\sin^2\theta_{calc} \times 10^4$
vs	6.56	$\bar{\alpha}_{1,2}$	138	1	139
vs	4.62	»	278	2	278
s	3.75	»	420	3	418
vs	2.895	»	708	5	697
vs	2.663	»	838	6	836
w	2.31	»	1114	8	1114
vw	2.237	»	1187	(8.5	1185)
vs	2.173	»	1259	9	1254
vw−	2.113	»	1331	(9.5	1324)
vs	2.058	»	1403	10	1394
vs	1.961	»	1545	11	1533
w	1.890	»	1664	12	1672
w	1.799	»	1837	13	1812
s	1.735	»	1974	14	1951
w	1.575	»	2395	17	2369
m	1.532	»	2530	18	2509
m	1.458	»	2797	20	2787
vw	1.418	»	2950	21	2927
m	1.324	»	3389	24?	3345
m	1.304	»	3496	25	3484
w	1.286	»	3593	(25.5	3554)
m−	1.275	»	3655	26	3624
vw	1.252	»	3790	27	3763
m	1.209	»	4068	29	4042
vw	1.191	»	4192	30	4181
vw	1.135	»	4616	33	4599
vw	1.124	»	4703	(33.5	4669)
vw	1.117	»	4765	34	4739
w	1.106	»	4860	35	4878
w	1.098	»	4930	(35.5	4948)
m	1.086	»	5039	36	5017
m	1.071	»	5183	37	5156
m	1.046−	»	5340−	38−	5296−
	1.055	»	5436	(39	5435)
m	1.007	»	5860	42	5853
vw	0.994	»	5997	43	5993
w	0.9748	α_1	6243	45	6237
w	0.9505	»	6567	(47	6539)
w	0.9414	»	6694	48	6679
w	0.9120	»	7134	51	7096
vw	0.8939	»	7424	(53.5	7443)
m	0.8876	»	7530	54	7513
m−	0.88025	»	7658	(55	7653)
m−	0.8719	»	7803	56	7793
m−	0.8581	»	8058	58	8070
w	0.8468	»	8274	(59.5	8279)
m	0.84315	»	8346	(60	8348)
m	0.8299	»	8615	62	8626
m	0.82644	»	8686	(62.5	8696)
vw	0.82260	»	8768	(63	8766)
w	0.8101	»	9140	(65.5	9113)
w +	0.7980	»	9318	67	9322
w +	0.7879	»	9557	(68.5	9560)
w +	0.78560	»	9613	69	9600
vw	0.78609	α_2	9649	69	9648

structure can only be carried out, however, when single crystals are provided.

1. U.S.Pat. 2834671, May 13th 1958.

Studies on Sulfinic Acids

V.* Correlation of the IR-Frequencies of the Sulfur-Oxygen Bonds in Substituted Aromatic Sulfinates and Sulfonates with Hammett Substituent Constants

BERNT J. LINDBERG

Research Division, Pharmacia AB, Uppsala, Sweden

This communication forms part of a series which has hitherto been mainly concerned with the reactivity and conjugation of the ionic aromatic sulfinate group, using the linear free energy relationship approach.[1] Good correlations with the Hammett equation were obtained.

In 1948 Flett suggested that if a relationship could be established between IR-frequencies and reaction rates, it would be possible to use IR-frequencies to gain the same kind of information as is obtained from the correlation of reaction rates with substituent constants and illustrated this with some series of substituted aromatic compounds.[2] Since then interest in the linear relationships between non reactivity data and substituent constants has grown, and IR-frequencies have attracted much attention from this point of view.

The Hammett equation and it's modifications have been applied to various group

frequencies as well as to intensities with good results,[3,4] and Rao and Venkataraghavan have evaluated the correlations of IR group frequencies and intensities in organic molecules with substituent constants, statistically.[5]

The correlations mentioned were obtained with, for instance, various aromatic carbonyl groups, aromatic isothiocyanates, nitrobenzenes, benzonitriles, phenols and anilines. In connection with the work reported in part III of this series,[6] the SO-frequencies of the aromatic sodium sulfinates under study were therefore recorded in order to investigate whether similar correlations could be demonstrated with these compounds. In aqueous solution, fairly good correlations with the Hammett equation were obtained for the frequencies assigned to the SO symmetric and SO asymmetric stretching vibrations. There was, however, at that time insufficient material to confirm the assignments or interpret the results. Since then ex-
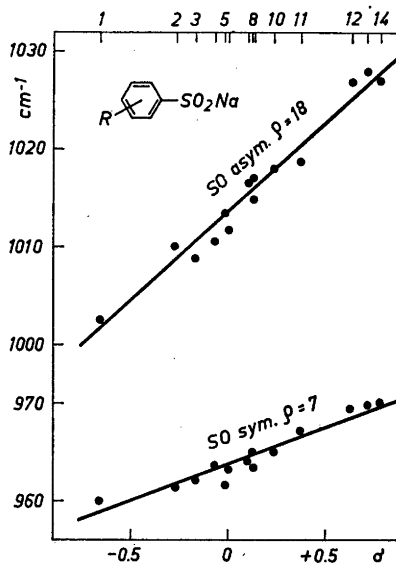

Fig. 1. Asymmetric and symmetric SO-stretching vibrations for substituted aromatic sodium sulfinates in 15 % aqueous solution. Substituents: 1, *p*-NH$_2$; 2, *p*-CH$_3$O; 3, *p*-CH$_3$; 4, *m*-CH$_3$; 5, *p*-CH$_3$CONH; 6, none; 7, *m*-COO⁻; 8, *m*-CH$_3$O; 9, *p*-COO⁻; 10, *p*-Cl; 11, *m*-Cl; 12, *p*-CN; 13, *m*-NO$_2$; 14, *p*-NO$_2$. Substituent constants from Jaffé.[11]