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An X-Ray Emission Spectroscopic Investigation of the Chemical Bond of Sulfur. II. The Number of Valence Electrons of the Sulfur Atom in Organic Compounds

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We have calculated the number of valence electrons, N, of the sulfur atom in fifty compounds (or samples)[1] on the basis of this theoretical correlation; $\delta E = n(n+3)/8$,[2] where δE is the energy shift of the S$K\alpha$ line and where n is $N-6$. We also checked the reliability of the relation by using the dipole moment and structural data of several sulfur compounds.

Recently improved theoretical calculations have

TABLE 1. WAVELENGTH OF S$K\alpha$ LINE AND MEAN NUMBER OF VALENCE ELECTRONNS OF SULFUR ATOM IN COMPOUNDS

Compound	Wavelength (Å)	Energy (eV)	ΔE (eV)	Mean number of valence electrons[a]
Rhombic sulfur, S_8[b]	5.37270	2307.55	0.00	6.00
$(NH_2)_2CS$[b]	7287	7.48	−0.07	6.21±0.14
$[(CH_3)_2N]_2CS$	7283	7.49	−0.06	6.18±0.12
NH_2CSCH_3	7275	7.53	−0.02	6.06±0.12
$(NH_2CS)_2$	7262	7.58	0.03	5.92±0.12
$Et_2NCSSNa$	7210	7.81	0.26	5.42±0.08
$(p\text{-}O_2NPhO)PS(OEt)_2$	7257	7.61	0.06	5.85±0.11
2-Mercaptobenzimidazole	7302	7.41	−0.14	6.44±0.16
2-Mercaptobenzoxazole	7308	7.38	−0.17	6.50±0.23
2-Thiobarbituric acid	7298	7.43	−0.12	6.36±0.15
Thiouracil	7301	7.42	−0.13	6.40±0.16
2-Methylthiobenzimidazole	7283	7.49	−0.06	6.18±0.12
Phenothiazine[b]	7275	7.53	−0.02	6.06±0.12
Methylene blue	7255	7.61	0.06	5.85±0.11
Na_2SO_3[b]	7100	8.29	0.74	4.65±0.06
$NaHSO_3$	7120	8.20	0.65	4.78±0.07
$(EtO)_2SO$	7127	8.16	0.61	4.83±0.07
$PhSO_2Na$	7107	8.25	0.70	4.70±0.06
$HOCH_2SO_2Na$[b]	7157	8.04	0.49	5.03±0.08
PhNSO	7164	8.01	0.46	5.07±0.08
$(CH_2)_4SO$	7161	8.02	0.47	5.05±0.08
$(CH_3)_2SO$[b]	7193	7.88	0.33	5.30±0.08
Cl_2SO	712	8.20	0.65	4.78±0.14
HCHO+ $NaHSO_3$[c]	708	8.37	0.82	4.54±0.12
CH_3CHO+ $NaHSO_3$[c]	709	8.33	0.78	4.59±0.12
$(CHO)_2\cdot 2NaHSO_3$	7053	8.48	0.93	4.39±0.06
$PhCHO\cdot NaHSO_3$	7049	8.50	0.95	4.36±0.06
$CaSO_4$[b]	6992	8.74	1.19	4.07±0.05
Na_2SO_4[b]	7002	8.70	1.15	4.12±0.05
$NaHSO_4$	6999	8.71	1.16	4.10±0.05
$PhNH_2\cdot \frac{1}{2}H_2SO_4$	7010	8.67	1.12	4.15±0.05
$(EtO)_2SO_2$	7000	8.71	1.16	4.10±0.05
$PhOSO_3K$	7012	8.66	1.11	4.16±0.05
$C_{12}H_{25}OSO_3Na$	7025	8.60	1.05	4.23±0.05
NH_2SO_3H[b]	7030	8.59	1.04	4.24±0.06
$PhSO_3H$	7047	8.51	0.96	4.34±0.06
$HOCH_2SO_3Na$	7049	8.50	0.95	4.36±0.06
$PhSO_2F$	7052	8.49	0.94	4.37±0.06
$p\text{-}EtPhSO_2Cl$[b]	7072	8.40	0.85	4.50±0.06
$PhSO_2NH_2$[b]	7070	8.41	0.86	4.48±0.06
$PhSO_2NHBu$	7054	8.48	0.93	4.38±0.06
$p\text{-}EtPhSO_2NEt_2$[d]	705	8.50	0.95	4.36±0.12
$(CH_3)_2SO_2$[b]	7095	8.30	0.75	4.64±0.06
Cl_2SO_2	704	8.54	0.99	4.30±0.12

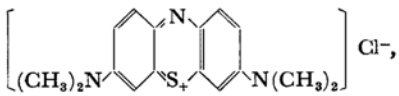
a) Calculated by the formula, $\delta E = n(n+3)/8$.[2]
b) Refined data on previous reported compounds.[1]
c) Aqueous solution, 50%, estimated in adduct, keeping aldehyde excess.
d) Benzene solution, 50%.

1) T. Sato, Y. Takahashi and K. Yabe, This Bulletin, **40**, 298 (1967).
2) C. A. Coulson and C. Zauli, *Mol. Phys.*, **6**, 525 (1963).

been made on this problem[3,4] on the same fundametal assumption that $\delta E=f(N)$; these calculations gave results a little different from the old one. Therefore, from the experimental point of view, it is important to obtain more accurate data on δE as a basis for discussion.

In this note, we will give new data on about thirty compounds and will give refined data on some compounds previously reported on. The measurements were carried out on the same apparatus and in the same manner as in a previous work.[1] Table 1 shows the mean value of at least three measurements; the precision of the wavelength measurements was thereby improved to an extent of $\pm 0.5'$ (2θ) (± 0.0001Å). On the measurements of the liquid samples, a sample holder with a Mylar film (10 μ thick) window was used. In the cases of sulfuryl chloride and thionyl chloride, the Mylar film was replaced by polyethylene film (30 μ thick), the precision being to the extent of $\pm 1.0'$ (2θ) (± 0.0002 Å).

The structure of the methylene blue molecule has thus far been given as follows:



of which the sulfur atom has a plus charge. However, our measurements led to the finding that the number of valence electrons of its sulfur atom is similar to those of rhombic sulfur and phenothiazine. Consequently, the above formula for the methylene blue molecule is not proper.

The molecular structures of aldehide-bisulfite adducts and 2-mercaptobenzimidazole, *etc.*, will be discussed on the basis of the wavelength value of the S$K\alpha$ line and the shape of the S$K\beta$ band in our next paper.[5]

3) F. A. Gianturco and C. A. Coulson, *Mol. Phys.*, **14**, 223 (1968).

4) A. T. Shuvaev, *Izv. Akad. Nauk S.S.S.R., Ser. Fiz.*, **28**, 758 (1964).

5) Y. Takahashi and K. Yabe, This Bulletin, **42**, No. 11 (1969), in press.