X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF SULPHONAMIDES: CHARGE DISTRIBUTION AND TAUTOMERISM

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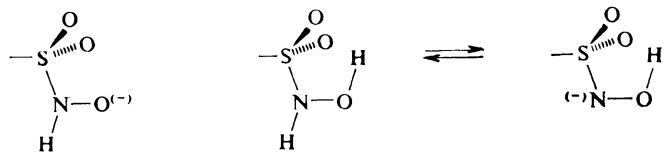
The X-ray photoelectron spectra of several sulphonamides, N-substituted sulphonamides, and their alkali salts were registered in the solid state. When comparing the salts with the corresponding acids, shifts of the N1*s*, S2*p*, and O1*s* core binding energies were observed which were discussed in terms of the charge distribution in the anion. In the case of N-hydroxybenzenesulphonamide (*III*) these shifts can also serve to confirm the tautomeric structure of the anion (*B*) as it has been inferred from other physical methods.

The experimental methods for studying structure of organic ions are more restricted than those for neutral molecules. This is true in particular if the salt is little stable in solution and single crystals cannot be prepared. Then it may be difficult to locate the charge and even the hydrogen atoms, so that questions may arise which hydrogen atom of a polybasic acid has dissociated, or which basic centre of a polyacid base is protonated. In addition, the actual charge distribution in the salt need not correspond to the simple ionization of the neutral molecule. The X-ray photoelectron spectroscopy[1] (ESCA) yields the values of core binding energies which are related to the atomic charges although not simply proportional to the charge on the given atom. For this reason the method was used several times to estimate the charge distribution in organic ions[2-8] and sometimes also the position of hydrogen atoms in ions[6] or in neutral molecules[8,9].

This paper is a continuation of the study[6] of hydroxamic acids and N-cyanoamides; it deals with the ionization of N-hydroxysulphonamides (sulphohydroxamic acids). Since their molecule has two acidic hydrogen atoms (*A*), the structure of the salt can be either *B* or *C*, where the charge need not be concentrated on a single atom, particularly in *B*. The results of the IR spectroscopy[10] of N-hydroxybenzenesulphonamide (*III*, Table I) and its lithium salt (not isolated in the pure state) were in favour of the structure *B*. The potentiometric titration of *III* and of its N-methyl derivative *IV* was in agreement with this structure, but the O-methyl derivative *V* is already a too weak acid to be titrated[11]. Due to the presence of several heteroatoms the problem appears suitable for X-ray photoelectron spectroscopy. The core electron spectra reported in this paper should corroborate the above finding and tell more about the charge localization in the anion. The interpretation is essentially empirical, making

use of model compounds like simple sulphonamides *I*, *II* and further compounds given in Table I.



C *A* *B*

EXPERIMENTAL AND RESULTS

Materials. Benzenesulphonamide (*I*) m.p. 155°C; potassium salt (*Ia*) prepared with potassium ethoxide and reprecipitated from ethanol–anhydrous ether, for $C_6H_6KNO_2S$ (195·3) calculated 20·02% K, found 19·85% K. 4-Methylbenzenesulphonamide (*II*) m.p. 153°C; sodium salt, for $C_7H_8NNaO_2S$ (193·2) calculated 11·90% Na, found 11·85% Na; potassium salt, for $C_7H_8.KNO_2S$ (209·3) calculated 18·68% K, found 18·42 K.

TABLE I

Experimental core binding energies of substituted sulphonamides and their salts (eV)

	Compound	N1*s*	O1*s*	S2*p*
I	$C_6H_5SO_2NH_2$	400·0	532·4	168·6
Ia	$[C_6H_5SO_2NH]K$	398·1	531·6	168·1
II	$4\text{-}CH_3C_6H_4SO_2NH_2$	400·0	532·7	168·8
IIa	$[4\text{-}CH_3C_6H_4SO_2NH]Na$	398·0	531·6	168·1
IIb	$[4\text{-}CH_3C_6H_4SO_2NH]K$	398·2	531·6	168·0
III	$C_6H_5SO_2NHOH$	400·5	532·1[a]	168·9
IIIa	$[C_6H_5SO_2NOH]Na$	399·6	531·4[a,b]	167·1
IV	$C_6H_5SO_2N(CH_3)OH$	400·0	531·6[a,b]	168·2
IVa	$[C_6H_5SO_2N(CH_3)O]Na$	399·8 (decr.)	531·5; 529·4[d]	166·8[c]
V	$C_6H_5SO_2NHOCH_3$	400·4	531·9[a]	168·4
Va	$[C_6H_5SO_2NOCH_3]K$	399·1 (decr.)	[e]	168·2[c]
VI	$4\text{-}CH_3\text{-}3\text{-}NO_2C_6H_3SO_2NHNO_2$	401·7; 406·6[f]	533·1[a,b]	169·2
VIa	$[4\text{-}CH_3\text{-}3\text{-}NO_2C_6H_3SO_2NNO_2]NH_4$	399·9; 406·3[f] 402·1[g]	532·7[a,b]	168·8
VII	$C_6H_5SO_2Na$	—	531·7[b]	166·9

[a] Not resolved signals of non-equivalent oxygen atoms; [b] broad signal; [c] values possibly affected by decomposition of the sample; [d] assigned to the N—O^- oxygen; [e] very broad signal; [f] assigned to the NO_2 nitrogen atoms; [g] assigned to the ammonium nitrogen.

N-Hydroxybenzenesulphonamide[12] (*III*) m.p. 129°C. Pure samples of salts could not be prepared by a variety of procedures, *e.g.* with lithium diisopropylamide in tetrahydrofuran or with sodium hydride in the same solvent. Relatively most successful was the precipitation of concentrated ethanolic solution with sodium methoxide at −10°C, the salt was washed with methanol and ether, and used without further purification; for $C_6H_6NNaO_3S$ (195·2) calculated 7·18% N, 11·78% Na, found 6·39% N, 11·09% Na. The salt decomposes slowly in water or in methanol, its identity was checked by adding dilute acetic acid to yield *III*.

N-Hydroxy-N-methylbenzenesulphonamide[10] (*IV*) m.p. 75°C. In the preparation of salts the same difficulties were encountered as with *III*, the analyses were still less satisfactory; sodium salt, for $C_7H_8NNaO_3S$ (209·2) calculated 15·32% S, 10·99% Na, found 14·33% S, 11·52% Na

N-Methoxybenzenesulphonamide[13] (*V*) m.p. 79°C; potassium salt (*Va*) prepared with potassium hydroxide in water and reprecipitated from ethanol and anhydrous ether, for $C_7H_8KNO_3S$ (225·3) calculated 6·22% N, 17·35% K, found 6·03% N, 17·42% K.

4-Methyl-3,N-dinitrobenzenesulphonamide[14] (*VI*) m.p. 118–120°C; ammonium salt[14] (*VIa*), for $C_7H_{10}N_4O_6S$ (278·2) calculated 20·14% N, found 20·30% N.

Physical measurements. The X-ray photoelectron spectra were recorded on a VG ESCA 3 MKII spectrometer. The Al $K\alpha_{1,2}$ line was used as excitant radiation (source 10 kV, 20 mA). The base pressure during recording was less than 10^{-6} Pa. The samples were run in the solid state as powders applied to a stainless-steel holder from suspension in an inert solvent (cyclohexane, chloroform) to prevent hydrolysis. The N1*s*, O1*s*, and S2*p* peaks were calibrated against the composite C1*s* peak from the phenyl groups and from hydrocarbon residuals, which was attributed E_b = 285 eV as usual[6–8]; in this way the charging effects were mostly compensated for. The experimental binding energies are listed in Table I. Their error was estimated to 0·3 eV in the absolute values but the relative shifts are more accurate. Radiation damage was observed in the case of compounds IVa and Va, most striking was the progressive disappearance of the N1*s* signal.

DISCUSSION

The core binding energies given in Table I are of differing reliability and of differing relevance for structural discussion. The limiting factor is the instability of the salts, particularly of *IIIa* and *IVa* during the preparation and of *IVa* and *Va* on irradiation. The radiation damage affects mostly the S2*p* binding energies. These are shifted to lower values, approaching the value for sodium benzenesulphinate which is one of the decomposition products in water solution. On the other hand, N1*s* signals are only weakened by decomposition and can finally disappear, but their position is not changed. The greatest relevance of N1*s* binding energies follows also from their greatest sensitivity to structural changes, *i.e.* from the range of values in Table I (3·7 eV for the sulphonamide nitrogen only). The O1*s* binding energies except the charged oxygen in *IVa* differ by 1·7 eV at most, and S2*p* by 1·2 eV – disregarding the decomposition products and the unexplained low value for *IIIa*. More important, the significance of O1*s* binding energies is impaired by the fact that only undeconvoluted signals of several non-equivalent oxygen atoms were obtained for the most compounds. Therefore, further discussion is focussed on N1*s* energies. Our values for sulphonamides *I* and *II* compare favourably with the measure-

ments on three substituted benzenesulphonamides[15]. The values for further neutral molecules (*III*, *IV*, *V*) can be compared with those calulated by the group additivity scheme[16] but the agreement is rather poor. For instance the substitution of H by OH would require a shift of 1·3 eV according to this scheme (found +0·5), the substitution by CH_3 +0·1 eV (found −0·5). It follows that the additivity of substituent effects[16] is fulfilled only very roughly and does not work for small structural changes. The N1*s* binding energies of the NO_2 and NH_4^+ nitrogens in *VI* and *VIa* are reasonably close to expectation[16].

The main object of our study were the changes due to ionization. To this purpose we have arranged the respective binding energy shifts in Table II. Of several theories[17] describing the dependence of binding energies E_b on atomic charges q, the charge potential model is the most popular[2-5,18]:

$$E_{b(A)} = k_A q_A + 1\,439{\cdot}9 \sum_{B \neq A} q_B / r_{AB} + E_A^0 .$$

The second term of the equation (the Madelung potential) represents a correction for the charges (q_B) on the other atoms of the molecule according to their distance r_{AB}. The constant 1 439·9 arises from converting atomic units to pm (r_{AB}), eV (E_b), and unit charges (q). In these units the empirical constant k_N (intraatomic coefficient) for nitrogen has the value[2,5,18] approximately 17, the constant E^0 is irrevelant as far as only binding energy shifts are considered. In crystals the Madelung potential is to be extended to all atoms of the lattice[19] and can be formally separated into the intramolecular and intermolecular (or lattice) potentials[2,4]. Since many unknown

TABLE II

Binding energy shifts with ionization (eV) and calculated charges Δq (in unit charges)

Compound	ΔE_b		
	N1*s* (Δq)	O1*s*	S2*p* (Δq)
I, *II* } N-acids	−1·9[a] (−0·39)	−1·0[a]	−0·7[a] (−0·14)
V } N-acids	−1·3 (−0·25)	—	−0·2 (−0·04)
VI } N-acids	−1·8 (−0·32)	−0·4	−0·4 (−0·08)
III	−0·9 (−0·17)	−0·7	−1·8
IV O-acid	−0·2 (−0·04)	−0·1	−1·4[c]
		−2·2[b]	

[a] Average values for the compounds *I* → *Ia*, *II* → *IIa*, *II* → *IIb*; [b] assigned to the charged oxygen atom; [c] sample decomposition.

quantities are involved in the whole theory, attempts were made at its simplifying. So the lattice potential was neglected or assumed to be constant[4], the intramolecular potential was confined to adjacent atoms, or – in the case of a salt – to the counterion[2], finally the distance dependent Madelung potential was replaced by topological calculations[20–22]. Our attempt to apply such simplified calculations failed completely. If the charge in sulphonamide anion were concentrated completely on N and the distance of the counterion was only 230 pm, the N1*s* energy shift of −10·2 eV with ionization would be calculated. For S2*p* the shift would be −4·7 eV when using $k_S = 8{\cdot}9$ (see[5]). These values are approximately 6× higher than experimental (Table II). If a considerable charge delocalization is assumed, *e.g.* the fractional charges −0·5 on N, −0·3 on H, and −0·2 on S, the above values are shifted to −8·0 and −4·0, respectively. Qualitatively similar results were in fact obtained for pyrazinium iodide and 4-(4′-nitrobenzyl)pyridinium iodide[2] but they were interpreted by charge delocalization: in the former between the two nitrogen atoms, in the latter to an arbitrary point within the pyridine ring. In piperazinium fluoroborate an effective charge delocalization is not possible, yet the N1*s* shift is quite similar[7]. If the constants *k* are not overestimated, the only explanation is in considerable lattice potentials of the salts, which are not found in crystals of neutral molecules.

A more empirical approach[2,4–8,20,23] compares only binding energies of similar molecules, in particular a salt with the corresponding neutral compound. This is justified by small effects of the counterion on the binding energies[2,20] – or at least on the relative shifts within one molecule[2] – and by small effects of other individual atoms[23]. Finally, the charge on a given atom can be roughly estimated from its mere core binding energy, using an empirical calibration curve[1]. In this latter procedure the influence of adjacent atoms is neglected completely while that of the counterion may be partly involved in the calibration. The results of Table I confirm that the effect of the cation is negligible even in our compounds.FromTable II one can deduce that the charge in sulphonamide cations is concentrated on nitrogen as expected. In Table II are also given the charges on nitrogen and on sulphur arising by ionization as read from the calibration graphs[1]. For simple sulphonamides they would suggest that considerable charges are also situated on hydrogen and the two oxygens, probably the delocalization is somewhat overestimated. In compounds *V* and *VI* the charge on N is reduced since a part of it is shifted to the methoxy and nitro group, respectively. In compound *IV*, the only O-acid investigated, the shift on nitrogen is negligible but an additional oxygen signal is observed in the salt, attributed to the charged O^- atom. The shift cannot be quantitatively evaluated due to the lack of calibration graph for O1*s* energies and to the composite character of the O1*s* signal in the neutral molecule. Nevertheless, the qualitative interpretation is evident. As regards the problem of ionization of benzenesulphohydroxamic acid (*III*), our results give two proofs for regarding it as an N-acid. Fistly the N1*s* shift with ionization is considerable and resembles much more the O-methyl derivative *V*

than the N-methyl derivative *IV*. Secondly and more important, no splitting of the O1*s* signal was observed in the spectrum of *III* which was evident with the N-methyl derivative *IV*. It is true that O1*s* signals of *IIIa* and *Va* are broadened, indicating some charge delocalization to oxygen, too. However, the shift of 2·1 eV in *IVa* proves that the dominant part of the charge is situated on oxygen. Interestingly enough, a similar trend can be seen already with the parent acids: *IV* displays broader O1*s* signal than *III* or *V*, suggesting higher degree of bond polarization. In all observable facts the sulphohydroxamic acid *III* resembles its O-methyl derivative *V* and differs from N-methyl derivative *IV*. Only the S2*p* shifts cannot be fully interpreted, although the irregularities are partly due to the decomposition of sample.

Our findings are thus in agreement with previous evidence from infrared spectroscopy[10] and from dissociation constants[11]. We conclude that X-ray photoelectron spectroscopy may serve as a complementary method for attacking problems of tautomerism, particularly the structure of salts, in spite of the difficulties connected with the investigation in the solid state and decomposition of samples. For determining the exact position of the charge a simple and reliable theory is still lacking.

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