FEATURE ARTICLE

Chemistry and physical properties of sulfamide and its derivatives: proton conducting materials

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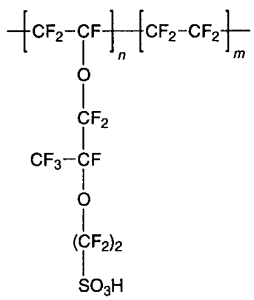
The state of the art in proton conducting polymers is described and the interest in the use of sulfonamide groups to prepare a series of such polymers is stressed. The most relevant aspects of the chemical and physical characteristics of sulfamide are reviewed. Its history is briefly presented. A detailed description of the structure and molecular environment of crystalline sulfamide is given. Our contribution to the interpretation of the Raman and IR spectra of sulfamide in the 4000–50 cm^{-1} range at melt temperature, 300 and 77 K is reported. The magnitude of the intra- and inter-molecular couplings existent in the NH stretching bands in sulfamide at room temperature and the geometry of the NH_2 groups in this compound are discussed. The existence of a phase transition is proposed and the participation of hydrogen bonds examined. The protonation and hydrolysis of sulfamide and related compounds are referred to. Reactions with amines, amine exchange and rearrangements of several sulfamide type compounds are analysed. Some data associated with the sublimation of sulfamide are indicated. The effect of ionizing radiation on sulfamide is mentioned. The interpretation of the thermochemistry and pyrolysis of sulfamide suggested in the literature is analysed. Several possible applications of sulfamide in polymer synthesis are pointed out. The results we present indicate that pristine sulfamide may be classified as the fourth known molecule to work as a solvent for acidic protons, in a way similar to water, phosphoric acid or imidazole. Our studies reveal that the electrochemical stability of crystalline sulfamide spans *ca.* 1 V. Future directions in the field of proton conducting materials based on sulfamide are suggested.

During the past two decades most of the activity in the field of proton conductivity has been undertaken by the materials science community whose major motivation has been to develop suitable proton conducting materials for application in all solid-state electrochemical devices, such as fuel cells, batteries, smart windows and sensors.

Organic/inorganic systems exhibiting moderate proton conductivity were first proposed by Takahashi *et al.*[1] as early as 1976. It was found that acids like sulfuric acid, H_2SO_4, or phosphoric acid, H_3PO_4, form compounds, in narrow composition ranges, with organic molecules containing basic groups. Compounds based on H_2SO_4 and triethylenediamine, $C_6H_{12}N_2$, or hexamethylenetetramine, $C_6H_{12}N_4$, have been reported.

An important contribution to the present state of the art is attributed to the American company E. I. Du Pont de Nemours which introduced, during the mid-1960s, a novel series of conducting perfluorosulfonate polymers. The discovery of these materials was seminal to the development of all future membranes. The polymers, named subsequently Nafion, were originally conceived as elastomers but it was quickly recognized they had potential technological applications as ion exchange membranes in cells for the production of chlorine and caustic soda.[2] Chemically, these materials are copolymers based on a Teflon backbone to which particularly stable perfluorosulfonate anions are grafted. The SO_3^- groups bond to acid protons (or alkaline cations).



From the standpoint of structure, these ionomers are formed by a hydrophobic matrix containing interconnected hydrophilic ionic aggregates. In the presence of water, Nafion becomes a conductor. The morphology of the aggregates has a remarkable influence on the transport properties of the membranes. The more the polymer absorbs water, the higher are the average size of the aggregates, the number of accessible exchange sites per aggregate and the number of water molecules per exchange site. Small aggregates favour high cationic selectivity. By adding a minimum amount of water, conductivities of *ca.* 10^{-3}–10^{-2} Ω^{-1} cm^{-1} are achieved at room temperature.[3] The use of Nafion as a protonic electrolyte in all solid-state electrolytes is however limited because: (1) it does not conduct when dry and (2) its performance strongly depends on the electroactivity domain of the solvent (water or other) added. Therefore the material closely resembles a conducting polyelectrolyte in liquid medium.

The strong demand aroused in the 1980s for thin proton conducting films led to the obvious concept of anhydrous proton conduction in polymer systems. It consists of mixing strong acids with polymers bearing oxygen or nitrogen donor centres, a strategy quite similar to the one successfully adopted in the area of polymer electrolytes through the complexation

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of inorganic salts by polyethers.[4] The acids used have been essentially H_2SO_4 and H_3PO_4. Due to extensive self-ionization and self-dehydration, these acids are themselves good proton conductors when pure.[5–8] At 25 °C, the conductivities observed for supercooled H_3PO_4 and for liquid H_2SO_4 reach 10^{-2} and $5\times10^{-2}\ \Omega^{-1}\ cm^{-1}$, respectively. A polymer is expected to induce the dissociation of the acids either by means of hydrogen bonds or by protonation of the basic sites. One of the main concerns is to prepare chemically stable blends. It is known that the C—O bond of ethers and alcohols is readily broken by strong acids. This degradation is especially fast in the presence of traces of water. Moreover, some polymers are easily hydrolysed in acidic solutions [poly(acrylamide), Paam], whereas others [poly(2-vinylpyridine), P_2VP, or poly(4-vinylpyridine), P_4VP] are oxidized by H_2SO_4. Fortunately, in spite of the fact that most of the polymers are water-soluble, it is possible to obtain blends by carrying out the synthesis by suppressing water or by eliminating it at the end. Blends of oxoacids with a great variety of polymers have recently been reviewed by Lassègues.[9] The nature of the basic polymers is illustrated in Table 1. Acid–polymer blends are generally classified according to the kind of interaction established between the acid, HX, and the polymer whose pK decreases when the degree of ionization, α, increases, as described in eqn. (1).[10]

$$pK = pK_0 + a_1\alpha + a_2\alpha^2 + \ldots \quad (1)$$

Weakly basic polymers, polymers with intermediate basicity and strongly basic polymers may thus be considered.

The prototype of a weak polybase is poly(oxyethylene), POE, which exhibits a pK_0 of -3. Well-defined complexes of POE–H_3PO_4 blends have been referred to.[11,12] Fig. 1 shows the phase diagram established for this system and the conductivity isotherms. A crystalline stoichiometric compound, $POE_{0.75}H_3PO_4$, associated with minimum conductivity, and two eutectics, one of them represented by the formula $POE_{0.48}H_3PO_4$, exist. The maximum conductivity at room temperature (*ca.* $4\times10^{-5}\ \Omega^{-1}\ cm^{-1}$) is attained with the latter composition. This result has been explained in terms of the diffusional segmental movements of the POE chains.

Polyamides, such as Paam and poly(vinylpyrrolidone), PVP, and polyamines, such as P_2VP and P_4VP, are polymers of intermediate basicity with pK_0 of 3–6. The corresponding acid mixtures have been extensively analysed by Lassègues' group at Bordeaux.[13–17] The specific conductivity of the complexes obtained with strong inorganic acids is extremely low at small acid concentration, but increases suddenly at $x = ca.$ 1 up to values as high as $6\times10^{-3}\ \Omega^{-1}\ cm^{-1}$ for Paam,1.5H_2SO_4, 10^{-4} for PVP,2H_2SO_4 and 4×10^{-3} for P_2VP_2,2H_2SO_4 at room temperature (Fig. 2).

Polyamides possess a basicity comparable to that of water or ethers and can be protonated at either oxygen or nitrogen. Due to their highly polar nature, they have strong interchain coupling. PVP is thus a glass, but the addition of the acid progressively plasticizes the macromolecule to an elastomer. The participation of hydrogen bonding between the amide group of Paam and H_3PO_4 has been demonstrated. In mixtures involving H_2SO_4, several techniques support the claim that the polymer is protonated by the first dissociation of the acid, while the second proton belongs to the anion HSO_4^-. However, the possibility of intrachain protonic exchange has not been excluded in order to account for the remarkable conductivity observed at room temperature ($10^{-2}\ \Omega^{-1}\ cm^{-1}$). A prototype of a smart window based on Paam,1.5H_3PO_4 and using tungsten and iridium oxides as electrochromic electrodes has been described.[17]

Alkyleneimine polymers, such as linear poly(ethyleneimine), LPEI,[18] and branched poly(ethyleneimine), BPEI,[13–16] have been thoroughly investigated. Due to their high basicity, these polymers are easily protonated. It has been concluded that conductivity depends strongly on acid concentration and three conduction regimes (regions **I**, **II** and **III**) can be distinguished (Fig. 3). At low protonation degrees ($x<0.15$, region **I**), the compounds are amorphous elastomers. Spectroscopic results support the hypothesis of conduction assured by proton exchange between protonated and non-protonated nitrogen sites. At higher acid contents, BPEI- and LPEI-based materials become glassy and crystalline, respectively. Above $x = ca.$ 0.35 (region **II**), the observed increase of conductivity is ascribed to proton migration along the mixed HSO_4^-/SO_4^{2-} or $H_2PO_4^-/HPO_4^{2-}$ anionic chains by successive proton transfer and anion reorientation steps. Above $x = ca.$ 0.7 (region **III**), conductivity reaches a plateau of the same order of magnitude as the conductivity of the pure acids.

A completely different new class of highly basic polymers was presented by Charbouillot[19,20] and later by Rousseau.[21–23] The structure of these ormolytes (organically modified silicate electrolytes), so-called aminosils, appears to be that of a non-crosslinked ladder polymer based on a silicate network supporting amino functions (*e.g.* aminopropyl, Fig. 4).

The continuous solid solutions formed with strong monoacids (perchloric acid, $HClO_4$, trifluoromethanesulfonic acid, HCF_3SO_3, hydrochloric acid, HCl, and nitric acid, HNO_3) exhibit remarkable conductivities which may reach *ca.* $3\times10^{-5}\ \Omega^{-1}\ cm^{-1}$ at room temperature (Fig. 3). Proton transport is believed to occur by hopping between protonated and non-protonated amine sites, probably induced by the movements of the neighbouring alkylamine chains. When the doping agent is H_3PO_4, the incorporation of a phosphate group in the silicate network is thought to occur. The network modifier alkylamine chain plays an important role in the transport properties, since as a base, it interacts with the acid, yielding transparent monolithic films. In addition, the dried products are non-porous, hard and thermally stable up to 180 °C. An electrochemical stability domain of 1.3 V has been reported for the aminosils doped with HCF_3SO_3. For all the reasons just mentioned and also because of the simplicity and versatility of the sol–gel chemistry, aminosils are considered excellent candidates for electrochemical devices such as smart windows.

Mention must also be made of the protonic conductors investigated by Polak *et al.*[24] The materials, prepared with poly(vinyl alcohol), PVA, and H_3PO_4, contain water, since the presence of anhydrous acids is known to catalyse the dehydration of the polymer into polyacetylene. Though solid solutions are obtained apparently without protonation of the weakly basic oxygens of PVA, the exact nature of the interaction has not yet been established.

The interest in proton conducting polymers has not declined in the last decade. More recently, other protonic ormolytes which bear suitable characteristics for high requirement applications have been introduced.[25,26] The remarkable room temperature conductivity ($10^{-2}\ \Omega^{-1}\ cm^{-1}$) and good processability of these poly(benzylsulfonic acid)siloxane based materials makes it possible to foresee their use as membranes in direct methanol fuel cells.

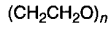
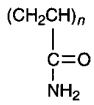
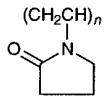
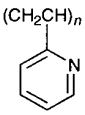
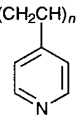
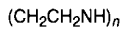
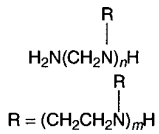
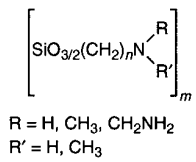
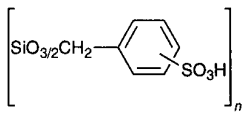
A series of benzylimidazole–H_3PO_4 complexes, characterized by an extraordinary mechanical strength and toughness, is currently being studied for application in fuel cell technology.[27–29]

In the hope of finding polymer electrolytes exhibiting good compatibility with electrode materials, whose stability lies in the 4–12 pH range (*e.g.* Ni, Ti, Mn or Ir oxides and hydroxides), we decided for the first time in 1990 to focus our efforts on the preparation of systems containing the sulfonamide function, RSO_2NH_2, since it is known that this group has a pK_a of *ca.* 11,[30] corresponding to the acid–base equilibrium shown in eqn. (2).

$$RSO_2NH_2 \rightleftharpoons H^+ + RSO_2NH^- \quad (2)$$

These preliminary studies induced us to introduce a novel family of basic to neutral protonic polymeric electrolytes based

Table 1 Polymers used in blends of strong acids (adapted from ref. 9)

polymer and abbreviation	chemical formula	acid	concentration range	ref.
poly(oxyethylene) (POE)		H_3PO_4	$0<x<2$	11, 12
poly(vinyl alcohol) (PVA)		H_3PO_4/H_2O		24
poly(acrylamide) (Paam)		H_3PO_4 H_2SO_4	$0.6<x<2$ $0.6<x<2$	14, 16, 17
poly(vinylpyrrolidone) (PVP)		H_3PO_4 H_2SO_4	$0.5<x<8$ $1<x<3$	11, 16
poly(2-vinylpiridine) (P_2VP)		H_3PO_4 H_2SO_4	$0.5<x<3$ $0.5<x<3$	16
poly(4-vinylpiridine) (P_4VP)		H_3PO_4	$0.5<x<3$	16
linear poly(ethyleneimine) (LPEI)		H_3PO_4 H_2SO_4	$0<x<1$ $0<x<1$	18
branched poly(ethyleneimine) (BPEI)		H_3PO_4 H_2SO_4 HCl	$0<x<3$ $0<x<3$ $0<x<0.8$	13–16
aminosils		$HClO_4$	$0<x<0.3$	19–23
poly(benzylsulfonic acid)silsesquioxane (PBSS)		CF_3SO_3H		25, 26

on sulfamide, $NH_2SO_2NH_2$. Unlike the systems described above, whose conductivity lies in an excess of protons, these materials are obtained by extracting protons from a sulfonamide function (RSO_2NH) present in the polymer, leading to the creation of defects or *proton-vacancies* in the latter. This process, which we have designated *proton-vacancy doping*, requires the addition of a minimum amount of an appropriate base (*doping* or *deprotonating agent*).

The remarkable solvating properties of POE *versus* cations explains the enormous amount of effort which has been devoted in the last few years to the study and development of polymer electrolytes based on this host polymer.[4] In terms of application at room temperature, the intrinsic crystallinity of high molecular mass POE represents a serious disadvantage, though, since it is responsible for the low conductivity exhibited by the corresponding POE–salt complexes. It is accepted that conduction in semi-crystalline electrolytes occurs exclusively in the amorphous phase. Nevertheless, these materials have been widely investigated and therefore are considerably better understood than proposed systems based on other host polymers. This is the reason why we initially introduced a family of basic proton conducting polymers synthesized by adding sulfamide to POE.[31]

In order to carry on these studies, a closer view of pristine sulfamide was demanded. Its complex and versatile chemistry will be analysed in this work. Some of the countless

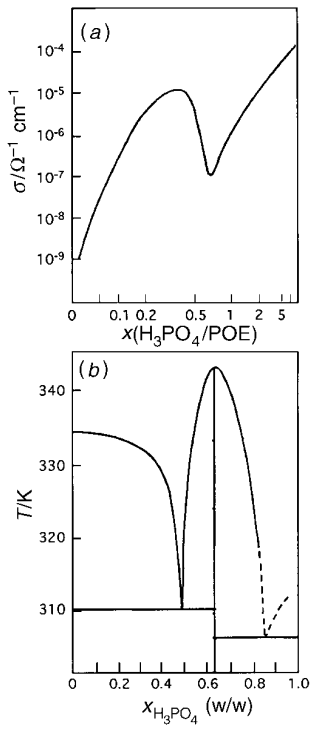


Fig. 1 (*a*) Conductivity isotherms and (*b*) phase diagram for the system POE–H_3PO_4 (ref. 11)

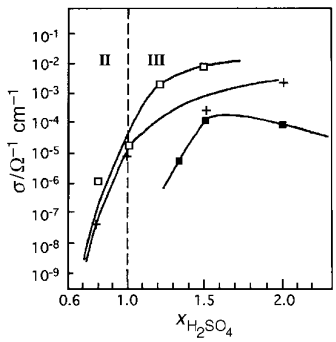


Fig. 2 Concentration dependence of the conductivity of several H_2SO_4 blends at room temperature; (■) H_2SO_4–PVP (refs. 11, 16), (□) H_2SO_4–Paam (refs. 14, 16, 17) and (+) H_2SO_4–P_2VP (ref. 16)

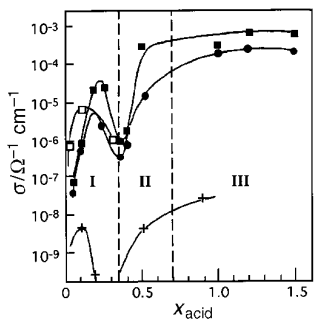


Fig. 3 Concentration dependence of the conductivity of several acid blends at room temperature; (■) BPEI–H_2SO_4 (refs. 13–16), (●) BPEI–H_3PO_4 (refs. 13–16), (+) LPEI–H_2SO_4 (ref. 18) and (□) Aminosil–$HClO_4$ (refs. 19–23)

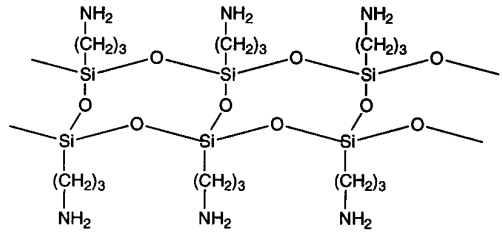


Fig. 4

possibilities of applications of this very simple molecule will be indicated. The thermal and electrochemical behaviour will be extensively examined and discussed as well. We have presented elsewhere[32] a detailed study dealing with the IR and Raman spectra of protonated and deuteriated sulfamide. The main conclusions of this spectroscopic study will be given in this article too.

Some Historical Facts

Sulfamides (or more precisely, sulfonamides) involve a family of products widely known mainly because of their pharmaceutical applications, in particular in several areas of antimicrobial chemotherapy. Sulfanilamide was discovered in 1908. Though sulfonamides first found application in the dye industry, they were used 25 years later as therapeutic drugs for the treatment of infectious diseases. Typically, these products are *p*-aminophenylsulfonamides. Because it is possible to introduce different substituents in the sulfonamide function, an unlimited number of substances may be obtained without any loss of activity.[33] The structure and the applications of some of the best known substituted derivatives are described in Table 2. It should be noted that nearly 5000 sulfanilamide substitutes have been mentioned by Northey.[35] Apart from being innocuous to human beings, sulfonamides are very efficient against pathogenic germs. They have also been used as oral antidiabetic agents. Their diuretic properties have limited use though.

The production of sulfonamide increased rapidly immediately after their introduction and especially during World War II. However, in 1944, with antibiotic commercialisation it suffered an abrupt decrease. The production level, at low price, has been practically stable ever since.

Crystal Structure

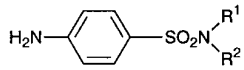
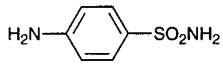
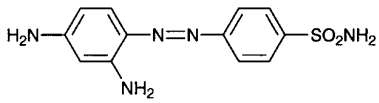
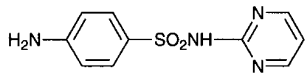
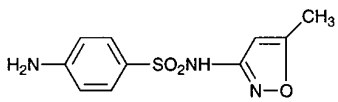
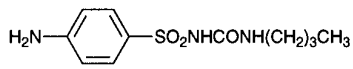
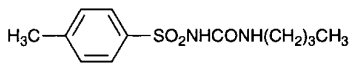
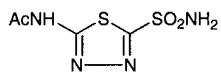
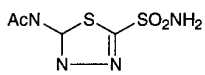
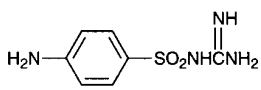
The only reported studies on the crystal structure of sulfamide date back to the 1950s and are attributed to Trueblood *et al.*[36] According to these authors, sulfamide forms orthorhombic crystals whose density was determined to be 1.807 g cm^{-3}. Its structure is represented by the space group $Fdd2$ (C_{2v}^{19}). The crystallographic parameters are $a=9.14$, $b=16.85$ and $c=4.58$ Å. The unit cell contains eight molecules and the primitive cell contains two molecules related by a glide plane.

Molecule

The sulfamide molecule is represented in Fig. 5. Its bond lengths and bond angles are shown in Table 3. Excluding hydrogen atoms, the molecule of sulfamide has *mm*2 symmetry implying that both the O—N and O—N′ distances are the same within experimental error and that the O—S—N and O—S—N′ angles are likewise not significantly different.

The S—O lengths in sulfamide are unusually short. Comparable dimensions of related molecules are listed in Table 4. It is apparent that the S—O and S—N lengths are appreciably shorter than the single-bond distances deduced on the basis of the Pauling radii (equal to 1.69 and 1.73 Å, respectively). In the great majority of these molecules the S—O

Table 2 General structure and applications of some sulfamides[34]

common designation	chemical formula	applications
sulfamide (general formula)		
sulfanilamide		antibacterial
sulfamidochrysoidine		hydrochloride as antibacterial
sulfadiazine		antibacterial
sulfamethoxazole		antibacterial
carbutamide		hypoglycaemic
tolbutamide		antidiabetic
acetazolamide		carbonic anhydrase inhibitor, diuretic; treatment of glaucoma
methazolamide		carbonic anhydrase inhibitor
sulfaguanidine		antibacterial

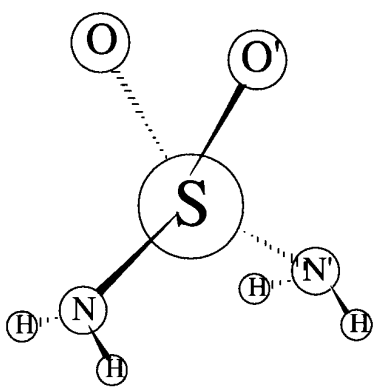


Fig. 5 Sulfamide molecule (ref. 53)

Table 3 Bond lengths and bond angles in the molecule of sulfamide[36]

atoms	distance/Å	atoms	angle (°)
S—O	1.391	O—S—O′	119.4
S—N	1.600	N—S—N′	112.1
O—O′	2.402	O—S—N	106.6
N—N′	2.654	O—S—N′	106.2
O—N	2.401		
O—N′	2.394		

Table 4 Bond lengths and bong angles in sulfamide and analogous molecules[36]

	distance/Å		angle (°)	
	S—O	S—N	O—S—O	O—S—N
$NH_2SO_2NH_2$	1.39	1.60	119	106, 107
KO_3SNH_2	1.44	1.57	110, 114	106, 107
$K_2(O_3S)_2NH$	1.44–1.45	1.66	112–114	103–107
$KO_3SN_2O_2$	1.43	1.63	108, 116	106, 108
O_3SNH_3	1.47–1.49	1.73	114–119	92–102
$(CH_3SO_2)_2CCNCH_3$	1.43		118	
$KOSO_2OC_2H_5$	1.44–1.49[a]		110–116[a]	
	1.60[b]		101–109[b]	
SO_2	1.432		119	
	1.43		119	
	1.43		120	
SO_3	1.43		120	
SOF_2	1.412		—	
SO_2F_2	1.37		129.6	
	1.43		130	
$SOCl_2$	1.45		—	
SO_2Cl_2	1.43		120	
$C_5H_8SO_2$	1.44		114	
S_4N_4		1.62		106
		1.60		102

[a]Not including esterified oxygen. [b]Including esterified oxygen.

distance is comparable or even shorter than that predicted for a conventional covalent double bond, while the distance to the second atom corresponds to a bond order of 1.5 or greater. According to Cruickshank,[37] the contraction of the X—O bond in XO_4^{n-} tetrahedral ions (where X = Si, P, S or Cl) is due to the formation of two strong π-bonding molecular orbitals between the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of X and the appropriate $2p\pi$ and $2p\pi'$ orbitals of each oxygen atom. In these XO_4^{n-} ions, each of the two 3d orbitals of the central atom is π-bonded to four oxygen atoms, meaning that, in terms of valence bond theory, each X—O bond has a bond order of $1/2 = 1/4 + 1/4$. In sulfamide the situation is slightly different since two nitrogen atoms replace two oxygen atoms leading to a N_2XO_2 tetrahedron. Since each nitrogen atom only possesses one available p orbital for the participation in the π-system, the problem is to know whether one of the molecular orbitals embraces the two oxygen atoms and both nitrogens and the other just the oxygens or whether both molecular orbitals embrace the nitrogen atoms separately. The relative orientation of the SNH_2 allows the conclusion to be drawn that the p orbitals of both nitrogen atoms hybridise with the same d orbital. Therefore, the S—N bonds are of order 1/4 and the S—O bonds are of the order $3/4 = 1/4 + 1/2$.

The knowledge of the H—N—H angle in sulfamide is of great importance. A nitrogen atom forming three bonds can be found in two extreme configurations: either trigonal pyramidal ($\alpha = 109.5°$) or trigonal planar ($\alpha = 120°$). The NH_2 group is generally assumed to be pyramidal in amines and planar in amides.[37] However, Pedersen[38] concluded that the amine groups of sulfamide may be regarded as pyramidal. Assuming an N—H distance equal to 1.03 Å, he found a HNH angle of 110° and a corresponding H—H bond length of 1.693 Å.

Molecular environment

In the crystal, sulfamide molecules are packed in an approximately hexagonal array (Fig. 6) in layers parallel to (010) (Fig. 7).[36] Four equivalent N—H···O hydrogen bonds bond each sulfamide molecule to four other close neighbours in the layer, ensuring the molecular cohesion (dashed lines in Fig. 6).

The intermolecular lengths shorter than 3.6 Å are listed in Table 5. These values clearly indicate that several contacts of different nature are present in the structure of sulfamide.[32]

In-layer contacts. Each oxygen atom makes one short contact (*A*, 3.02 Å) and four longer contacts (*B*, *C*, *D* and *D*, of *ca.* 3.5 Å) in the *xz* plane.

The distance 3.02 Å is appreciably shorter than that of any other contact and may be properly described as a weak N—H···O bond. The fact that the S—N···O angle is 111° (practically tetrahedral) supports this interpretation. However, an associated N···O—S angle equal to 156° suggests that the localized unshared pairs of electrons in the oxygen atom are very unfavourably placed for interaction with the proton, thus explaining the weakness of the bond.

Contrary to what could be expected, the oxygen atoms are not located in the *xz* plane (otherwise the site symmetry would be C_{2v} instead of C_2), but deviate from it by approximately 0.55 Å. Consistent with this, the nitrogen atoms are also tilted out of *yz* plane of about 0.63 Å.

Out-of-layer contacts. Although the shortest out-of-layer contact corresponds to a distance of 3.14 Å, the presence of a strong hydrogen bond is highly improbable. However, the other short distance equal to 3.18 Å might be associated with a very weak N—H···N hydrogen bond taking place between adjacent layers.

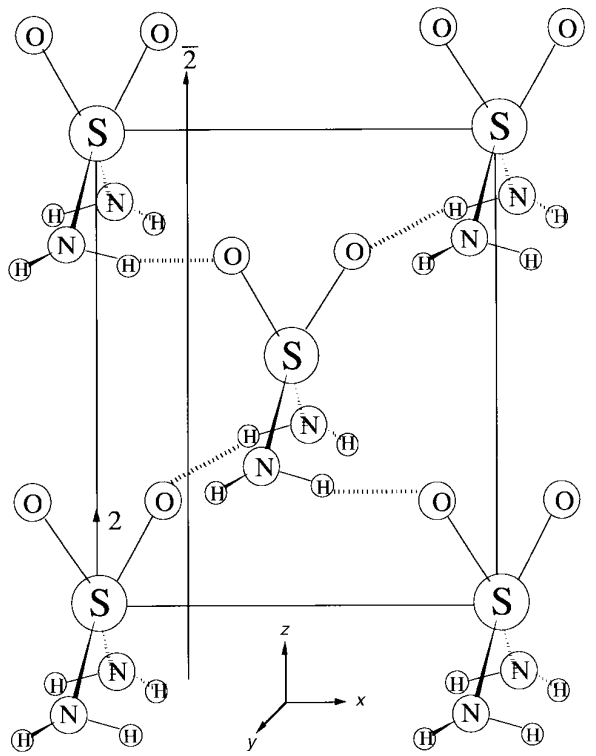


Fig. 6 Molecular environment of sulfamide in the layer (ref. 32). Reprinted from *J. Mol. Struct.*, **297**, V. de Zea Bermudez, G. Lucazeau, L. Abello and C. Poinsignon, 'Vibrational spectra, structure and phase transition in crystalline sulfamide', 185–206, 1993 with kind permission of Elsevier Science, NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

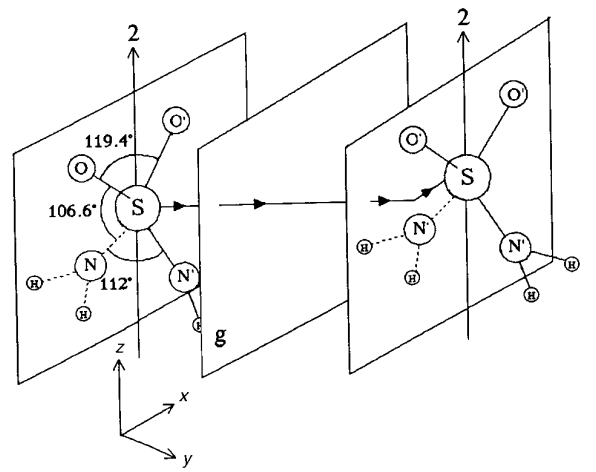


Fig. 7 Molecular environment of sulfamide in the primitive cell (g = glide plane) (ref. 32). Reprinted from *J. Mol. Struct.*, **297**, V. de Zea Bermudez, G. Lucazeau, L. Abello and C. Poinsignon, 'Vibrational spectra, structure and phase transition in crystalline sulfamide', 185–206, 1993 with kind permission of Elsevier Science, NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

Spectroscopy

While Hoffman *et al.*[39] were the first to obtain in 1956 the Raman spectrum of sulfamide in aqueous solutions, it was not until 1965 that Herrick *et al.*[40] recorded the IR spectra of thin sublimed films of sulfamide and deuteriosulfamide in the range 5000–300 cm^{-1} at room temperature and 197 K (−76 °C) and 83 K (−190 °C). The observed spectra were satisfactorily interpreted on the basis of the structure of $NH_2SO_2NH_2$ with

Table 5 Intermolecular distances in crystalline sulfamide[36 a]

atoms	contact	distance/Å
primarily parallel to (010)		
0 to N_{202}	A	3.02
0 to N_{004}	B	3.48
0 to $N_{0\prime04}$	C	3.48
0 to $O_{\bar{2}02}$	D	3.55
primarily out of the plane parallel to (010)		
0 to $N_{\bar{1}13}$	E	3.14
N to N_{111}	F	3.18
0 to $N_{\bar{1}1\bar{1}}$	G	3.74

[a]Subscripts refer to the position of the sulfur atom of the molecule in quarter-translations; thus 0_{111} is attached to the sulfur atom at (1/4, 1/4, 1/4) and $N_{00\bar{4}}$ is attached to the sulfur atom at (0, 0, $\bar{1}$). Atoms without subscript are attached to the sulfur at the origin.

site symmetry C_2, almost C_{2v}. The assignments seemed to be consistent with the normal coordinate treatment based on a single valence force potential function. Partial double bonding of the S—N bonds was indicated, but no indications of the ionic, $NH_3{}^+(NH{=})SO_2{}^-$, or isodiamidic, $NH_2(NH{=})S(O)OH$, forms were observed. Participation of all the hydrogen atoms in a moderate hydrogen bond was suggested.

A year later, Uno *et al.*[41] recorded the IR spectra of sulfamide and [$^2H_4$]sulfamide under ordinary and polarized radiations. Their vibrational assignment was made by referring to the IR dichroism as well as the isotopic effect. Normal coordinate analysis of sulfamide was carried out by assuming C_{2v} molecular symmetry and is essentially consistent with that of Herrick *et al.*[40] except for differences in the assignment of the skeletal frequencies in the deuteriated compound.

Preliminary results obtained with the sulfamide-based electrolytes indicated the need for a full understanding of the spectral signals of the NH groups in crystalline sulfamide. Mainly because many contradictory questions arose when we compared our results with those reported by the authors mentioned above, we were led to the conclusion that some details needed further reexamination. Especially, the lack of Raman data for crystalline sulfamide, in particular the low-frequency region, stimulated our work. It was also clear from the available literature that the important NH stretching region was far from being fully interpreted, thus deserving a closer look. Moreover, the studies of Trueblood *et al.*,[36] on crystalline sulfamide are incomplete as the position of the protons in the structure was not determined. We have therefore undertaken a deeper IR and Raman analysis on both protio- and deuteriosulfamide, especially by recording polarized Raman spectra.[32]

We have studied the Raman spectra of powdered sulfamide and deuteriosulfamide at 300 and 77 K in the 4000–50 cm^{-1} range. Polarised Raman spectra of orientated microcrystals and orientated films have also been obtained. New bands have been detected and some framework modes have been reassigned. Special attention has been given to the low-frequency region for which no data existed in the literature. The main results of this study are collected in Table 6.

The presence of non-equivalent protons within the same amine group of the sulfamide molecule was confirmed by the presence of two bands in the high frequency Raman spectrum recorded for the 95% deuteriated compound [Fig. 8(*a*)]. The high frequency narrow band at 3310 cm^{-1} corresponds to a practically free proton H_f (where f stands for free) having a negligible participation in an interlayer hydrogen bond and completely decoupled from other protons (in the same NH_2 group, in the same molecule or in the cell). In contrast, the low frequency broad band at 3256 cm^{-1} has been associated with a NH vibrator involved in a moderately strong intralayer hydrogen bond. Considering the different nature of the protons in each amine group, the NH stretching modes were thus designated νNH_b (where b stands for bonded) and νNH_f, respectively.

The frequencies observed in the Raman spectrum of the deuteriated sulfamide and the frequency components found in the polarized spectra of the fully protio compound were used to derive the intra- and inter-molecular couplings existent in the NH stretching bands in sulfamide at room temperature. Intramolecular coupling will take place between NH_f and NH_b groups within the same molecule. Two sorts of intramolecular coupling were considered: one between different NH groups in the same amine group (N_1H_f–N_1H_b) and the other between identical NH groups belonging to different amine groups in the same molecule (N_1H_f–N_2H_f') and (N_1H_b–N_2H_b'). The intermolecular coupling will involve identical amine groups belonging to two different neighbouring molecules or layers (N_1H_f–$N_1'H_f''$) and (N_1H_b–$N_1'H_b''$). The frequencies of the uncoupled amine groups are 3310 and 3256 cm^{-1} [Fig. 8(*a*)]. They belong to the NH vibrators of NHD groups dispersed in ND_2 groups, the corresponding ND frequencies being 2452 cm^{-1} and probably the shoulder at 2391 cm^{-1} [Fig. 8(*c*)]. The difference in the chemical bonding of the H_f and H_b protons leads to a $\Delta\bar{\nu}$ of 54 (=3310–3256) cm^{-1}. The interaction between H_f and H_b protons within the same amine group generates a shift of approximately 22 (3332–3310) cm^{-1} for H_f and 21 (=3256–3235) cm^{-1} for H_b. Values of 1 and 28 cm^{-1} were found for the intramolecular coupling resulting from the interaction between identical amine groups in the same molecule, respectively, for the H_f and for the H_b protons. The polarized components of the crystal vibrations derived from the νNH_f mode present extremely close frequencies, indicating that the coupling in the crystal at room temperature is very weak. In the case of the νNH_b modes, a much more important coupling is present: while the difference between the highest and lowest frequency component is 3 cm^{-1} for the νNH_f vibration, the value obtained for νNH_b is 38 cm^{-1}.

The strong polarization effects observed in the IR spectra of sulfamide in the form of powder and orientated film (deposited on a silicon plate) allowed us to deduce the geometry of the NH_2 groups of sulfamide. Taking into account the minimization of energy of the strong intralayer hydrogen bonds and symmetry considerations, both planar and pyramidal geometries were acceptable. A trigonal planar bonding situation would result in the presence of a relatively linear, parallel to the *xz* plane, short N—H···O contact. According to this model, the N—H···O angle should be close to 160° and the hydrogen bond would form an angle of 45° with the *x* direction, instead of being primarily directed along the *x* direction, as proposed by Trueblood *et al.*[36] Nevertheless, in this model none of the NH bonds of each amine group is strictly parallel to the *xy* plane or perpendicular to it and cannot account for the IR results. Thus, a model of trigonal pyramidal NH_2 groups, in which the NH_f bond is strictly parallel to the *xy* plane, seems to be more acceptable. In such a model the N—H···O angle is approximately 150°, a value which is still admissible for hydrogen bonding. Since the NH_f band appears in both spectra, whereas the NH_b band is polarized, it was concluded that the hydrogen atoms H_b, involved in the moderately strong intralayer hydrogen bonds, lie approximately in the *xz* plane, whereas the H_f atoms are directed perpendicularly to the same plane, so being more suited for the weak, long interlayer hydrogen bonding situation.

We have also analysed the melting transition of sulfamide by Raman spectroscopy. Fig. 9 shows the spectral evolution of sulfamide with the increase of temperature in the NH stretching region. Between 80 and 90−ε °C, the bands associated with the τNH_2 and νNH modes become broader. In reaching the liquid state, at temperatures higher than 90+ε °C, the torsion modes are no longer present, whereas the NH stretching bands are dramatically modified. An increase of the frequency of the

Table 6 Room temperature spectra of crystalline sulfamide[32] [a]

$NH_2SO_2NH_2$									$ND_2SO_2ND_2$
IR 300 K		Raman 300 K							Raman 300 K
powder	orientated film (pol)	powder	orientated microcrystals			isotopic ratio	assignments		powder
			xx *zz* (A1)	*xz* (B1)	*xx, yy* *yz* [A1 + A2 + B2(?)]				
		3332	3330			1.33	νNH_f ip	A1	2499
					3333			A2	
3334 S	3330 (σ)			3332			νNH_f op	B1	
								B2	
									2452 vw
		3256 ep		3241			νNH_b op	B1	
								B2	
3238 S	3238 (π)	3222			3226	1.36		A2	2373
			3216				νNH_b ip	A1	
			3099				$2\delta NH_2$		2313
					1559		δNH_2 op	A2	
					1560		op	B2	
1560 m	1560 w(σ,π)	1557 w	1556			1.34	ip	A1	1167
				1553			ip	B1	
		1375 sh			1367	0.99	$\nu_a SO_2$	B2	1358
1356 S	1356 (σ)	1358 w		1356				B1	1339
		1181 sh			1179		$\nu_s SO_2$	A2	
1165	(π)	1150 S	1150			1.02		A1	1140 S
	1128 S	1130 sh		1127		1.12	ωNH_2 op	B1	1000 vw
1122 sh								B2	
					980		ωNH_2 ip	A2	
								A1	
		1078					2*528	A1	
933	931 (σ,π)			932		1.02	$\nu_a SN_2$	B1	910 vw
								B2	870
					909		$\nu_s SN_2$	A2	831 vw
906	904 (π)	908 S	901			1.09		A1	811
729 sh	729 S (σ)						rNH_2 op	B1	
								B2	
722 S	(π)	724 m	724		724	1.15	rNH_2 ip	A1	629
								A2	
570 w	568 (σ)	571		569		1.01	rSO_2	B1	564
								B2	
535 m	(π)		527			1.02	δOSO	A1	516
		528 m			526			A2	
	544 (σ)	542 sh			538	1.17	rSN_2	B1	469
504 w	505 (σ)							B2	
		435 sh		420	420	1.00	tO_2SN_2	A2	438
417 m	420 (π)	420				1.00		A1	423
356		360 S	360			1.10	δNSN	A1	325
					360			A2	
		326 w				1.21	τNH_2 op	B1	259
					331			B2	
		320 w	320			1.27	τNH_2 ip	A1	251
					320			A2	
		140			138	1.03	T'_x	B2	136
121 m		121		123		1.06		B1	116
							R'_x	B2	
		116				1.07	and	B1	108
							R'_y	B2	
		88	88			1.06	R'_z	A1	83
								A2	
		72				1.01	T'_z	A2	71
								A1	
49 m		48		49		1.00	T'_y	B1	48
								B2	

[a] ip and op = in-phase and out-of-phase vibration relatively to the C_2 axis of the molecule, respectively; A1, A2, B1, B2 = crystalline components (in-phase and out-of-phase A and B type vibrators relatively to the glide plane). S = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

NH_b band is observed as the temperature is increased, reflecting weaker intermolecular interactions. Moreover, this frequency appears to approach that of the NH_f band. The frequency of this latter band is approximately constant, confirming the proton's free character. In the liquid state, the two protons become equivalent and couple. Modes belonging to the framework spectral region undergo similar changes. As expected, the external modes disappear at this stage and are replaced by an important Rayleigh scattering.

As sulfamide is a non-centrosymmetric crystal at room temperature, a phase transition may be expected, probably leading to a more symmetric structure including a centre of inversion. Due to the dynamic disorder which accompanies the rise in temperature, sulfamide may suffer an evolution from a non-

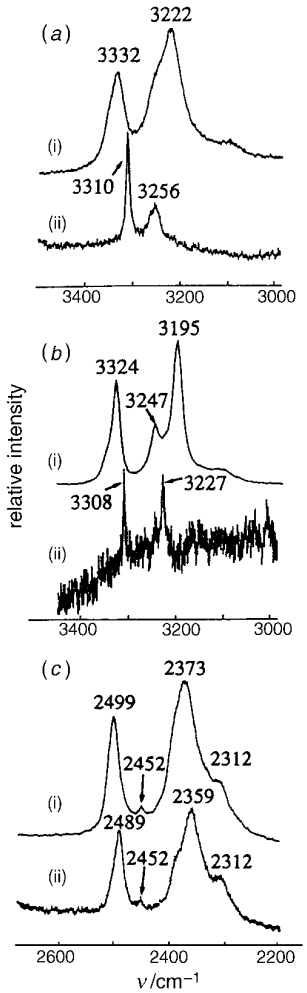


Fig. 8 High frequency Raman spectra of the fully protonated and 95% deuteriated sulfamide at (*a*) 300 and (*b*) 77 K [(i) corresponds to $NH_2SO_2NH_2$ and (ii) corresponds to 5% of H among 95% of D)]; (*c*) high frequency Raman spectra at (i) 300 and (ii) 77 K for $ND_2SO_2ND_2$ (ref. 32). Reprinted from *J. Mol. Struct*., **297**, V. de Zea Bermudez, G. Lucazeau, L. Abello and C. Poinsignon, 'Vibrational spectra, structure and phase transition in crystalline sulfamide', 185–206, 1993 with kind permission of Elsevier Science—NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

centrosymmetric (and possibly ferroelectric) phase to a centrosymmetric (and possibly paraelectric) phase. The DSC thermogram of crystalline sulfamide, represented in Fig. 10, suggests that a phase transition could take place some degrees before melting. In the hope of finding spectroscopic evidence for this phenomenon, we analysed the Raman spectra for this compound at increasing temperatures, from room temperature up to the melting temperature (Fig. 9). A systematic anomaly in terms of a positive ($+\Delta\bar{\nu}$) or negative ($-\Delta\bar{\nu}$) wavenumber deviation with respect to the general trend (for instance, $\Delta\nu_aSO_2 = -5\ cm^{-1}$, $\Delta rNH_2 = +3\ cm^{-1}$ and $\Delta\nu NH_f$ *ca.* $+4\ cm^{-1}$) is present in the 80 to $90-\varepsilon$ °C temperature range. Naturally, this very subtle anomaly would not be recognised without support from the DSC result.

Reactions

Protonation

The NMR studies of Birchall *et al.*,[42] provide conclusive evidence that the protonation of sulfamide occurs preferentially on the nitrogen atom. In a previous paper, the same authors established unambiguously that in the case of amides, which

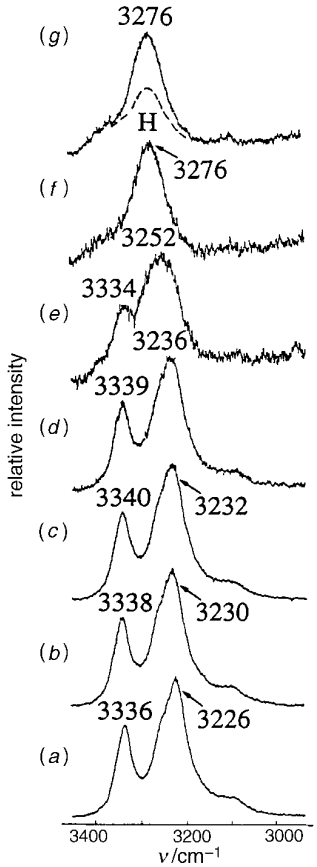


Fig. 9 Spectral evolution of the N–H stretching region of sulfamide when temperature is raised from 35 °C to melting (ref. 32); (*a*) 35, (*b*) 70, (*c*) 80, (*d*) $90-\varepsilon$, (*e*) $90+\varepsilon$, (*f*) 100 and (*g*) 110 °C. Reprinted from *J. Mol. Struct*., **297**, V. de Zea Bermudez, G. Lucazeau, L. Abello and C. Poinsignon, 'Vibrational spectra, structure and phase transition in crystalline sulfamide', 185–206, 1993 with kind permission of Elsevier Science, NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

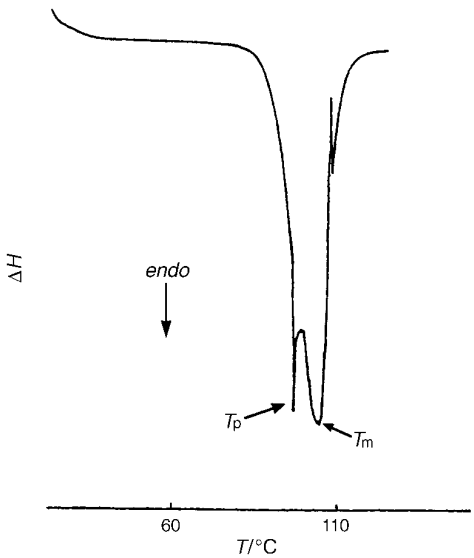


Fig. 10 DSC thermogram of crystalline sulfamide (T_p = phase transition temperature; T_m = melting temperature) (ref. 32). Reprinted from *J. Mol. Struct*., **297**, V. de Zea Bermudez, G. Lucazeau, L. Abello and C. Poinsignon, 'Vibrational spectra, structure and phase transition in crystalline sulfamide', 185–206, 1993 with kind permission of Elsevier Science, NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

are analogous weak bases, protonation occurs on the carbonyl oxygen atom and not on the nitrogen.[43]

The protonation and deprotonation mechanisms in sulfamide were also studied by Garrett *et al.*[44] A dependence of the width of the NMR signal of water in aqueous solutions of sulfamide with pH was observed. The evolution of linewidth at half height of the water signal $\Delta\nu_{1/2}$ with pH exhibits two maxima (at pH 4.1 and 5.7) and one minimum (at pH 5.1), which are interpreted in terms of the following two reactions involving proton exchange between water and sulfamide [eqn. (3) and (4)],

$$NH_2SO_2NH_2 + H^+ \xrightarrow{k_1} NH_2SO_2NH_3^+ \quad (3)$$

$$NH_2SO_2NH_2 + OH^- \xrightarrow{k_2} NH_2SO_2NH^- + H_2O \quad (4)$$

where k_1 and k_2 are sulfamide protonation and deprotonation rate constants, respectively.

The sum of the rates of the acid- and the base-catalysed exchange reactions is represented by eqn. (5).

$$R = k_1(H^+)(NH_2SO_2NH_2) + k_2(OH^-)(NH_2SO_2NH_2) \quad (5)$$

Relying on experimental data, $k_1 = 3 \times 10^7$ and $k_2 = 2 \times 10^{11}$ dm^3 mol^{-1} s^{-1} have been proposed. The magnitude of sulfamide protonation rate constant k_1 is similar to that of weak bases, such as hydrogen peroxide, H_2O_2 (2×10^7 dm^3 mol^{-1} s^{-1}) and methanol, CH_3OH (10^8 dm^3 mol^{-1} s^{-1}). However, the protonation rate constant of *N*-methylacetamide (NMA), $CH_3CONH(CH_3)$, which might be expected to be comparable to that of sulfamide, is considerably lower (400 dm^3 mol^{-1} s^{-1}). This result, attributable to the presence of partial double bonding of the type O^--$(CH_3)=N^+H(CH_3)$, indicates either the absence of a partial double bond S=N in sulfamide or a considerably less important contribution than in NMA. The rate constant k_2 is in good agreement with the rate constants for the deprotonation of acids stronger than water (*K ca.* 10^{10} to 10^{11} dm^3 mol^{-1} s^{-1}).

The deprotonation equilibrium of sulfamide is indicated by a pK_a constant of *ca.* 11,[30] whereas the corresponding *aquoacid* (water molecule having a proton replaced by a group R), sulfamic acid, NH_2SO_2OH, has a p$K_a = 1$. Other sulfamides [phenylsulfonamide, $C_6H_5SO_2NH_2$, and sulfanilamide, $(NH_2)C_6H_4SO_2NH_2$] exhibit pK_a close to 10.[30]

Hydrolysis

At the end of the last century, Traube[45] demonstrated that when sulfamide is heated to boiling under reflux in a sodium hydroxide solution, ammonia rapidly evolves. Aminosulfonic acid (NH_2SO_3H, also called sulfamic acid), which is very resistant to alkaline hydrolysis, is produced simultaneously [eqn. (6)].

$$NH_2SO_2NH_2 + H_2O \xrightarrow{NaOH} NH_2SO_3H + NH_4OH \quad (6)$$

If diluted hydrochloric acid is used instead, aminosulfonic acid is rapidly formed too, but the reaction continues with slow hydrolysis of the sulfamic acid, yielding ammonia and sulfuric acid [eqn. (7)].

$$NH_2SO_2NH_2 + H_2O \xrightarrow{HCl} NH_2SO_3H + NH_4OH \quad (7)$$
$$\downarrow H_2O$$
$$H_2SO_4 + NH_4OH$$

The studies of Yamaguchi *et al.*[46] focused on the hydrolysis of *N*-monosubstituted and *N*,*N*- and *N*,*N*′-disubstituted sulfamides in water and in alkaline solution, and show that the major products formed are the corresponding ammonium sulfamates.

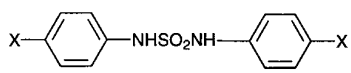
An example is the hydrolysis of a *N*-monosubstituted sulfamide [eqn. (8)].

$$RNHSO_2NH_2 + H_2O \rightarrow (RNHSO_3^-)(NH_4^+) \quad (8)$$

In contrast, in aqueous sodium hydroxide, a hydrolytic cleavage reaction is responsible for the formation of sodium sulfamate and ammonia [eqn. (9)].

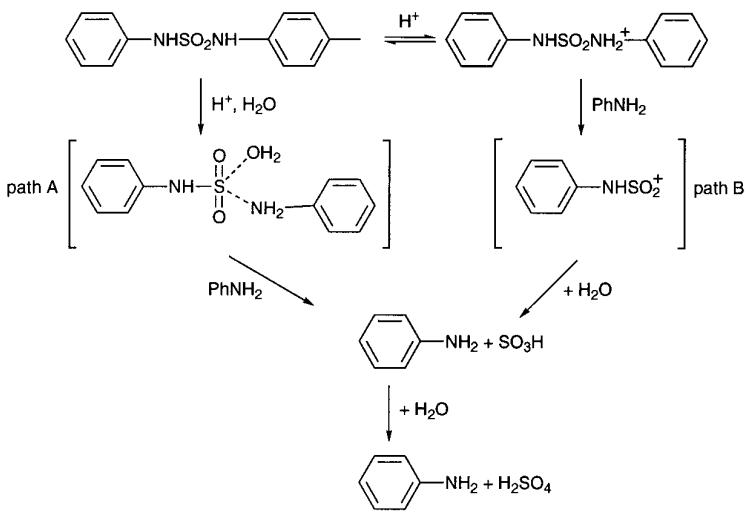
$$RNHSO_2NH_2 + H_2O \xrightarrow{NaOH} RNHSO_3Na + NH_3 \quad (9)$$

The hydrolysis kinetics of a series of *N*,*N*′-diarylsulfamides



X = H, CH_3, OCH_3, Cl or NO_2

were analysed by Spillane *et al.*[47] who claimed that several mechanisms may be envisaged for the hydrolysis reaction. The



Scheme 1 Hydrolysis catalysed by *N*,*N*′-diphenylsulfamide (ref. 47)

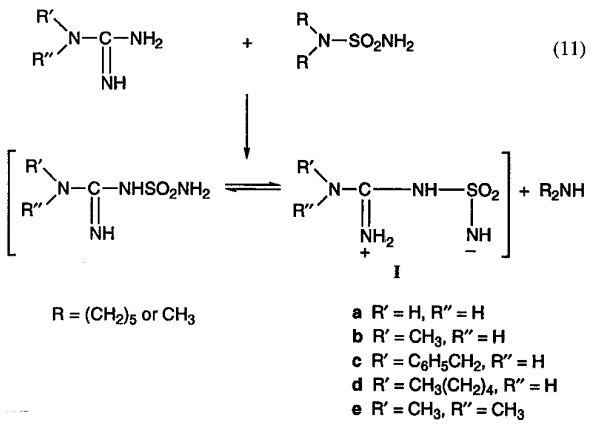
hydrolysis of the *N*,*N*′-diphenylsulfamide is exemplified in Schemes 1 and 2. Irrespective of whether the first step is an acid-catalysed displacement at the sulfur atom (path A, Scheme 1), an acid-catalysed heterolysis yielding substituted sulfamoylium ions (path B, Scheme 1) or a spontaneous bimolecular hydrolysis of unprotonated sulfamide (Scheme 2), phenylsulfamic acid is a likely intermediate. It was proved that: (1) the rate determining step is the formation of phenylsulfamic acid; (2) the participation of the sulfamoylium ions is not consistent with the results revealed by the substitution effect. It was also concluded that the major hydrolytic pathway involves bimolecular water attack on the unprotonated diarylsulfamide.

Reactions with amines

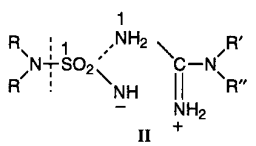
Reaction with primary and secondary amines. The reactions of sulfamide or monosubstituted sulfamides (*i.e.* sulfamylamines) and primary or secondary amines to displace ammonia are well known[48,49] [eqn. (10)].

$$RNHSO_2NH_2 + R'NH_2 \rightarrow RNHSO_2NHR' + NH_3 \quad (10)$$

Though ordinarily *N*,*N*-disubstituted sulfamylamines are unreactive, an unexpected reaction which provides a facile method for preparing new sulfamylguanidines was reported by Lombardino.[50] He observed that treating substituted guanidines with *N*,*N*-disubstituted sulfamylamines, at temperatures close to 100 °C, did not result in the displacement of ammonia; instead sulfamylguanidine **I** was detected. Moreover evidence indicated that this reaction appeared to be of general application when guanidines, monosubstituted guanidines or *N*,*N*-disubstituted guanidines were reacted with *N*,*N*-disubstituted sulfamylamines.

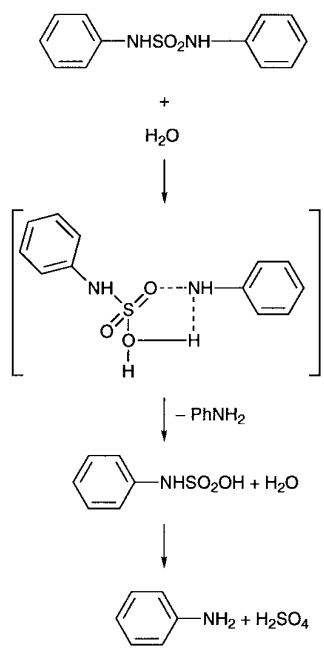


The reaction in eqn. (11) could be initiated by the proton transfer from the slightly acidic sulfamylamine to the very basic guanidine. In its anionic form, sulfamylamine, unable to lose ammonia, forms a cyclic ion pair **II** with the guanidinium cation.



The five-centred cyclic intermediate facilitates bond formation between the guanidine nitrogen and the sulfamylamine sulfur, with concomitant elimination of R_2NH and formation of **I**. The abnormal reactivity of *N*,*N*-disubstituted sulfamylamines is encouraged both by the high basicity of guanidines and the ability to form a cyclic intermediate **II**.

The inertness of sulfamylguanidines towards a variety of amines under various experimental conditions, even at temperatures up to 150 °C, supports the claim that sulfamylguanidines are best represented by a zwitterionic structure. The increase of the thermal stability of the zwitterionic form over the neutral one arises from the resonance energy of guanidinium and the proximity of the opposite charges arranged in a five-membered ring.



Scheme 2 Non-catalysed hydrolysis of the *N*,*N*′-diphenylsulfamide (ref. 47)

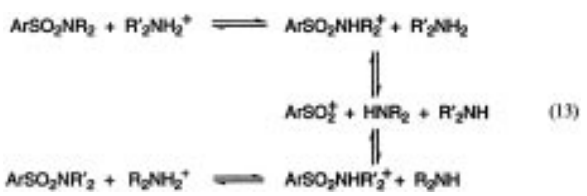
Rearrangements

Amine exchange. The *amine exchange* reactions undergone by sulfonamides, leading to the cleavage of the sulfur–nitrogen bond, are essentially *aminolyses* [eqn. (12)]. Such reactions are generally carried out by heating a sulfonamide with a primary or secondary amine, in the presence of the hydrochloride of the latter.[51] If an aliphatic amine is used, acid catalysis is not required.

$$ArSO_2NRR' + R''R'''NH \rightleftharpoons ArSO_2NR''R''' + RR'NH \quad (12)$$

The susceptibility of sulfonamides in amine exchange depends largely on their basicity, alkyl substituents increasing it and aryl ones decreasing it. On a kinetic basis, the ease of breaking of the sulfur–nitrogen bond in sulfonamides increases in the following series: *N*-phenylsulfonanilide < *N*-ethylsulfonanilide < sulfamide < *N*-ethylsulfonamide < *N*,*N*-diethylsulfonamide.

The reaction of amine exchange occurs by a dissociative mechanism involving the conjugated acid of the sulfonamide. In the absence of catalyst, a displacement reaction takes place [eqn. (13)].



Amine exchange of sulfonamides has been widely utilized for synthetic purposes. The synthesis of sulfanilylguanidine from sulfanilamide and guanidine,[52] which has been patented, is an example.

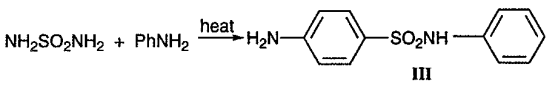
We have recently reported the preparation of low mass polymers exhibiting a conductivity of $3 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$

at room temperature by reacting a Jeffamine difunctional amine, α,ω-diaminepoly(oxyethylene-co-oxypropylene), with $NH_2SO_2NH_2$.[53]

Trans-sulfamoylation. At the beginning of the 1960s, Scott *et al.*[54,55] reported a new aromatic rearrangement, mechanistically very interesting, based on an intermolecular transfer of a sulfamoyl function ($RNHSO_2$) from *N*,*N*-diarylsulfamides. This rearrangement, designated trans-sulfamoylation, is best interpreted in terms of direct nucleophilic attack on sulfur in the protonated sulfamide, most probably by the *p*-aryl carbon site in the aromatic nucleophilic substrate.[56] Hence, the presence or absence of trans-sulfamoylation and amine exchange results from the competition of the reactive N and C centres of the nucleophile, the attack occurs *via* carbon atom in the first case and *via* nitrogen atom in the second.

Trans-sulfamoylation and amine exchange are probably the most characteristic reactions of sulfamides.

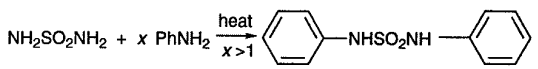
Sulfamide, $NH_2SO_2NH_2$. By reacting sulfamide and aniline at 150 °C, Scott *et al.*[55] observed the production of sulfanilanilide **III** [eqn. (14)].



(14)

III

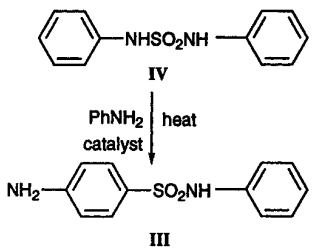
At the same temperature and using an excess of aniline, 1,3-diphenylsulfamide **IV** is the major product, though small amounts of **III** are also obtained [eqn. (15)].



(15)

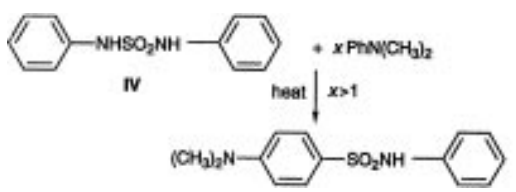
IV

By further heating **IV** with aniline in the presence of catalysts such as ammonium, anilinium or triethylammonium hydrochlorides, it can be converted to **III** [eqn. (16)].



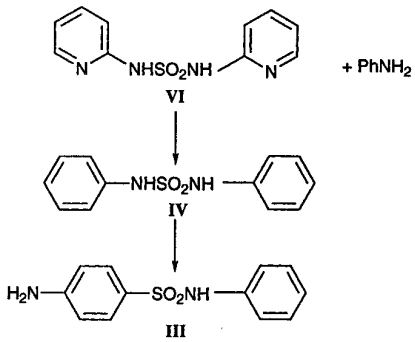
(16)

Moreover, when **IV** is heated to 150 °C, with an excess of *N*,*N*-dimethylaniline, 4-dimethylaminobenzenesulfonanilide **V** is formed. The reaction mechanism implies the transfer of a phenylsulfamoyl group of **IV** to the amine and suggests that the rearrangements undergone by the 1,3-diphenylsulfamide **IV** are intermolecular [eqn. (17)].



(17)

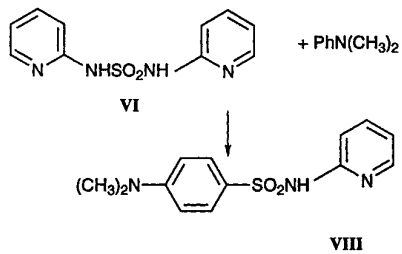
Disubstituted sulfamides, $NHRSO_2NHR$ or $NRR'SO_2NH_2$. Scott *et al.*[55–57] showed that *N*,*N*′-di(-2-pyridyl)sulfamide **VI** readily undergoes an amide exchange with aniline to give **IV**, which further rearranges to **III** [eqn. (18)].



(18)

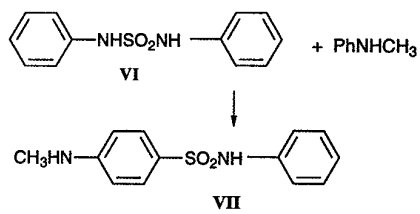
Pyridyl substituted rearrangement products could not be isolated, presumably because the cleavage reaction to give a 2-pyridylsulfamoylonium ion is not competitive with the facile amide exchange.

In excess of *N*,*N*-dimethylaniline, the *N*-(2-pyridyl)-4-dimethylaminobenzenesulfonamide **VIII** forms[56] [eqn. (19)].



(19)

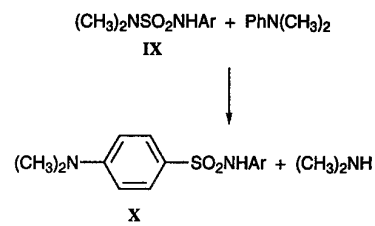
However, by refluxing **IV** in *N*-methylaniline, 4-*N*-methylaminobenzenesulfonanilide **VII** results.[55] The possible exchange product does not rearrange [eqn. (20)].



(20)

Both reactions demonstrate the fundamental role played by steric factors, apparently favouring transfer reactions, before exchange reactions.

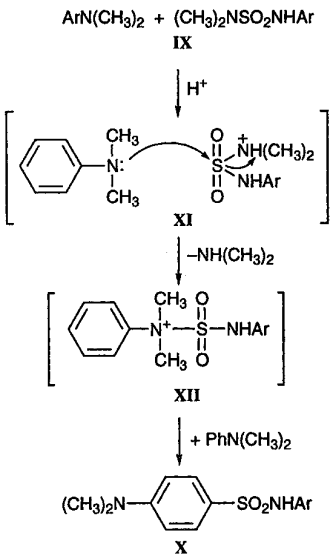
Trisubstituted sulfamides, $NRR'SO_2NHR''$. Scott *et al.*[54] reported that a trans-sulfamoylation reaction occurs when trisubstituted sulfamides **IX** react with excess *N*,*N*-dimethylaniline to yield 4-dimethylaminobenzenesulfonanilides **X** [eqn. (21)].



(21)

The most probable mechanism involves a displacement process at the sulfonyl sulfur [eqn. (22)]. This reaction sequence explains why rearrangements may be catalysed by acid (protonation facilitates bond scission in **XII**) and why the greatest yields of **XI** are obtained with Ar groups containing electron attracting groups that increase the acidity of the sulfur atom, facilitating the formation of **XII**. The lack of reaction of tetrasubstituted sulfamides is consistent with the proposed

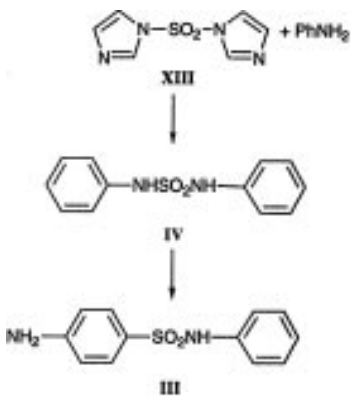
mechanism since these sulfamides offer steric hindrance to the approach of the base in the process forming **XII**.



(22)

Tetrasubstituted sulfamides, NRR′SO$_2$NR″R‴. In general tetrasubstituted sulfamides, RR′NSO$_2$NR″R‴, are extremely unreactive and do not undergo hydrolysis, amide exchange or trans-sulfamoylation reactions. The great stability of the tetrasubstituted sulfamides contrasts strongly with the behaviour of mono- and di-substituted sulfamides for which these processes take place easily.

In contrast Scott *et al.*[56] have found that *N,N′*-sulfuryldiimidazole **XIII** undergoes hydrolysis and on refluxing with aniline gives sulfanilanilidine **III**, possibly *via* amide exchange, followed by rearrangement [eqn. (23)].



(23)

Sublimation

According to Tagaki *et al.*[58] the experimental values of the vapour pressures of crystalline sulfamide, listed in Table 7, are well reproduced by eqn. (24).

$$\log_{10}P = 11.047 - 5300.4/T \qquad (24)$$

The heat, entropy and free energy of sublimation of sulfamide were found to be 101.46 ± 1.00 kJ mol^{-1}, 155.89 ± 2.84 J K^{-1} mol^{-1} and 54.85 kJ mol^{-1}, respectively. A value of 19.7 kJ mol^{-1} was obtained for the intralayer N—H···O hydrogen bond of sulfamide by subtracting from the observed heat of sublimation the contribution of both the dispersion energy and the electrostatic interaction energy.

Table 7 Vapour pressures of crystalline sulfamide[58]

T/K	$p/10^{-5}$ mmHg
347.8	6.370
348.7	7.017
349.7	7.960
350.7	8.671
352.7	10.430
354.7	12.810
357.7	17.040

Effect of Ionizing Radiation

Mishra *et al.*[59] have shown that exposure of sulfamide to ^{60}Co γ rays at 77 K gave results summarized in eqn. (25)–(27).

$$NH_2SO_2NH_2 \rightarrow H_2^+ \dot{N}SO_2NH_2 + e^- \qquad (25)$$

$$H_2^+ \dot{N}SO_2NH_2 + NH_2SO_2NH_2 \rightarrow H\dot{N}SO_2NH_2 + H_3^+ NSO_2NH_2 \qquad (26)$$

$$NH_2SO_2NH_2 + e^- \rightarrow NH_2^- + NH_2\dot{S}O_2 \qquad (27)$$

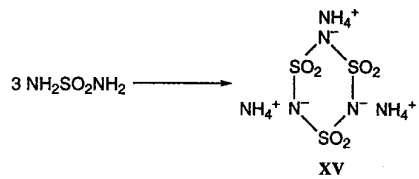
Thermochemistry and Pyrolysis

It is stated in Traube's work[60] that the thermal decomposition of sulfamide starts at 100 °C and that at *ca.* 200 °C *sulfimide* **XIV** forms. Owing to the instability of monomeric sulfimide, only the trimeric form has been isolated [eqn. (28)].

$$NH_2SO_2NH_2 \xrightarrow{\text{heat}} SO_2{=}NH + NH_3\uparrow \qquad (28)$$

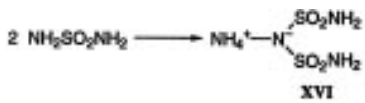
XIV

Heinze *et al.*[61] prepared the ammonium salt of *trisulfimide* **XV** by heating sulfamide to 200 °C [eqn. (29)]. Decomposition of **XV** occurred above 210 °C.



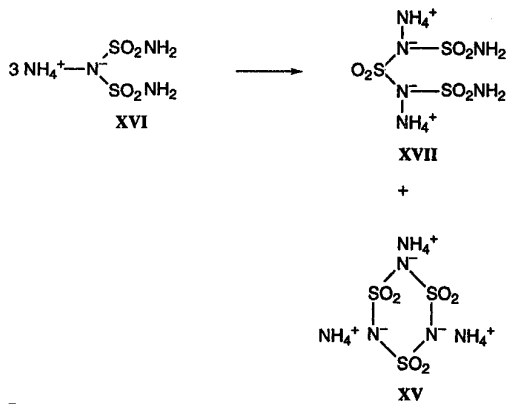
(29)

The thermal decomposition of sulfamide between its melting temperature (*ca.* 92 °C) and 200 °C was later examined by Ito.[62] This author proposed that below 170 °C the ammonium salt of *imidodisulfamide* **XVI** is obtained [eqn. (30)].

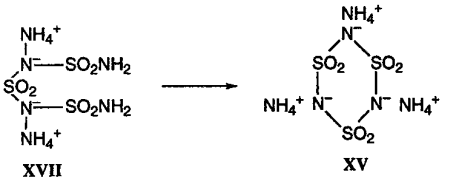


(30)

Above this temperature sulfamide would be transformed first into the ammonium salt of *sulfuryldisulfamide* **XVII** and then into the ammonium salt of *trisulfimide* **XV** [eqn. (31) and (32)].



(31)

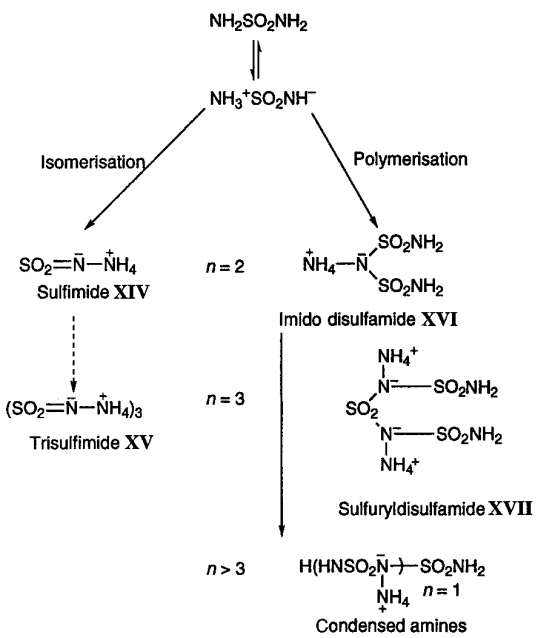


(32)

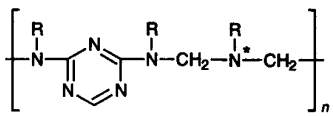
The study carried out by Cuilleron *et al.*[63] at 92–300 °C suggests that sulfamide undergoes appreciable changes as it decomposes (Scheme 3) in a way far more complex than proposed by the authors mentioned above. Cuilleron *et al.* demonstrated that sulfamide is thermally stable up to 140 °C. Above this temperature, isomerisation and polymerisation of sulfamide are found to occur simultaneously. Isomerisation, favoured by slow heating, results in the formation of the ammonium salt of trisulfimide **XV** whose decomposition starts at *ca.* 220 °C. Polymerization takes place below 180 °C. It is facilitated by rapid heating and gives rise above 150 °C to the ammonium salts of imidodisulfamide **XVI** and sulfuryldisulfamide **XVII**, together with linear amides of formula $H(HN{-}SO_2)_nNH_2$ (with $n>3$). At temperatures higher than 180 °C, sulfamide and imidodisulfamide **XVI** are no longer detected, but sulfuryldiamide, monosulfonic sulfamide and more condensed amides, stable up to 250 °C, remain. Above 280 °C, the only stable product which has been isolated is ammonium sulfate, $(NH_4)_2SO_4$. Monteil[64] obtained mass spectrometric evidence for the ion $SO_2NH_2^+$ and proposed that this cation may be responsible for the polymerization of sulfamide.

Use in Polymer Synthesis

Scott *et al.*[65,66] have pointed out the efficient cross-linking properties of sulfamide by preparing a series of copolymers of sulfamide–formaldehyde and sulfamide–formaldehyde–melamine. The products are hard resins, insoluble in water and most organic solvents, and form cohesive plaques by applying heat and pressure. The presence of melamine allows a workable material to be obtained. In spite of being extremely resistant to chemical attack, their lack of thermal stability (decomposition occurs in the range 220–270 °C) limits the usefulness of these materials for high temperature applications. Based on the relative thermal stability of the acid- and base-catalysed compounds, of both the ternary polymers and those from condensations of sulfamide and HCHO, Florentine *et al.*[67] have concluded that acid catalysis favours asymmetric polymerization about the sulfamide fragment and proposed that the thermal decomposition of the product at 225 °C may provide a novel polymerization route to C—N—C type polymer chains, where N* was originally part of the sulfamide.



Scheme 3 Thermal decomposition of sulfamide (ref. 63). Reproduced by permission from *Bull. Soc. Chim. Fr.*, J. Cuilleron and Y. Monteil, 'Préparation et décomposition thermique du sulfamide-nø 143-III', 892, 1966.



Basic catalysis favours symmetric polymerization around SO_2 but can produce di- and tetra-functional fragments of sulfamide in the polymerization.

The reaction of sulfamide–formaldehyde compounds (molar ratio 1:4) with melamine suggests that basic catalysis can lead to the inclusion of reactive hydroxymethyl groups (CH_2OH) as side groups in the polymer. Thermal copolymerization of melamine with these CH_2OH groups appears to occur at 225 °C. Linear sulfamide–formaldehyde–melamine polymers containing tetrasubstituted sulfamide fragments are proposed as those S—N—C polymers likely to possess maximal thermal stability, suitable solubility and desirable plastic properties.

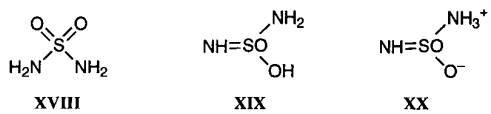
Conductivity and Electrochemical Stability

It was stated in the introduction that the anomalous proton conductance observed in several non-aqueous media, such as anhydrous H_3PO_4 and anhydrous H_2SO_4, is the result of extensive self-ionisation and self-dehydration. Sulfamide might be expected to exhibit proton conductivity as well considering its *amphoteric* nature which allows us to foresee the self-protonation equilibrium in eqn. (33).

$$2NH_2SO_2NH_2 \rightleftharpoons NH_2SO_2NH_3^+ + NH_2SO_2NH^- \quad (33)$$

Surprisingly, only one reference, the work of Monteil,[64] has dealt with its conducting properties. In his conductimetric study, aimed at finding the intermediate responsible for the thermal transformations of sulfamide, he reported a maximum conductivity of $10^{-2}\ \Omega^{-1}\,cm^{-1}$ at approximately 166 °C. This temperature would correspond to the maximum rate of transformation of sulfamide into more condensed products. Above it, conductivity dropped reaching $6\times10^{-3}\ \Omega\,cm^{-1}$ at 200 °C. Mass spectrometry has provided conclusive evidence of the presence of the ion $SO_2NH_2^+$.[64]

Solid sulfamide and solutions of sulfamide in water and dioxane had been closely examined by Devoto in the early 1930s. Magnetic susceptibility measurements supported the claim that in the solid state sulfamide must be described by an *amidic* form **XVIII**.[68] The fact that solutions of sulfamide in dioxane exhibited a dipole moment of 3.9 D indicated that sulfamide is best represented by an *isoamidic* or semi-polar form **XIX** in solvents of low relative permittivity.[69] In solvents of high relative permittivity, such as water, sulfamide is present in its *polar* form **XX**.[70]



Sulfamide is certainly an interesting compound. Kreuer *et al.*[71] recently stated that only three compounds may act as solvents for acidic protons in polymers and liquids: water, phosphoric acid and imidazole (pyrazole). All these systems allow for the formation of protonic defects and provide strongly

fluctuating proton donor and acceptor functions in an otherwise unpolar environment. Our results suggest that sulfamide might be the fourth system.[53] Fig. 11 represents the behaviour of solid state sulfamide in the undoped and doped states. While at room temperature sulfamide exhibits a conductivity of $10^{-6}\ \Omega^{-1}\ cm^{-1}$, at 60 °C proton doping, achieved by the addition of sulfamic acid, enhances that value tenfold. We have also concluded that the electrochemical stability region of crystalline sulfamide spans *ca.* 1 V (Fig. 12).[53]

The interest in the use of sulfamide for providing new basic proton conducting polymers was intensified after the recognition that the materials we had initially introduced, based on POE, did exhibit good electrochemical performance.[31]

It was found that the $POE_nNH_2SO_2NH_2$ system (where $n=$ O/S indicates the ratio of monomer units per sulfamide molecule) presents a phase diagram with three eutectics at compositions $n=2$, 4 and 30 and three stoichiometric compounds at compositions $n=2.5$, 5 and 20.[53] The electroactivity domain of the electrolytes is approximately 1.7 V.[72] By doping the eutectics with the guanidinium cation acting as a proton-vacancy inducer, introduced as guanidine carbonate, $[H_2NC(=NH)NH_2]_2{\cdot}H_2CO_3$, a remarkable enhancement of the conductivity results. For all the compositions analysed the optimum doping level is N/H = 5% (where N/H indicates the ratio of guanidine molecules added per proton extracted) and the best room temperature conductivity ($6\times10^{-5}\ \Omega^{-1}\ cm^{-1}$) is observed for the most concentrated sample considered ($n=$ 2). Complementary investigations have been recently performed by ^1H PFG NMR spectroscopy.[73] Cyclic voltammetry studies indicate however that the use of the guanidinium cation

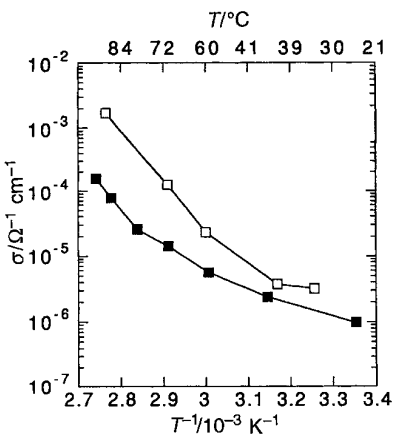


Fig. 11 Arrhenius conductivity plot of (□) doped (10% sulfamic acid) and (■) undoped crystalline sulfamide (ref. 53)

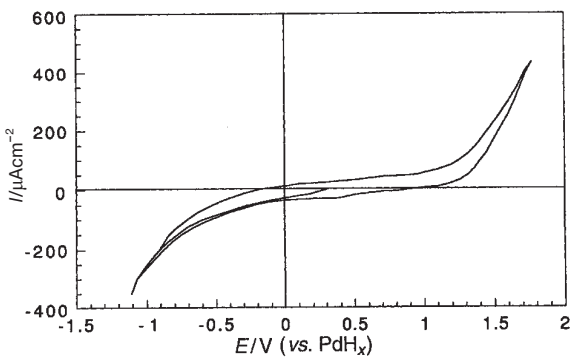


Fig. 12 Cyclic voltammogram of crystalline sulfamide (working electrode = vitreous carbon, counter electrode = stainless steel, reference electrode = ring-shaped palladium laden with hydrogen on the $\alpha\beta$ plateau, scanning rate = 500 mV min^{-1}, number of cycles = 50, $T=$ 90 °C) (ref. 53)

should be avoided as it is presumably responsible for an oxidation reaction which limits the electrochemical stability region anodically.[72] The Raman and IR spectra of POE and POE-based complexes of sulfamide with compositions of $n=2$, 2.5, 4, 5, 20 and 30 have been recorded at 300 K in the 4000–100 cm^{-1} range.[74] The evolution of sulfamide–polymer interactions with sulfamide concentration was studied on the basis of the changes in the spectral feature of the NH stretching region. For the more concentrated samples a situation similar to that found in crystalline sulfamide is observed (non-equivalence of the protons). For the more dilute samples, the spectroscopic behaviour of sulfamide supports the absence of specific interactions and the complete orientational disorder accounts for the weak character of the hydrogen bonds, a situation also encountered in molten sulfamide. The Raman spectra of compositions 2, 4 and 5 show that doping induces disorder in the materials. The degree of crystallinity of the compounds was observed to depend on the nature of the substrate, as well as on the thickness of the films. We concluded that *in situ* micro Raman techniques provide a good tool to assess the level of heterogeneity of the samples.

This series of new materials has been enlarged by the use of other polyethers, such as tetraethylene glycol dimethyl ether, TEGDME,[75] and polymethoxy[poly(ethylene glycol monomethacrylate)], PMPEGMM.[76] The polymer electrolytes based on the latter host polyether are particularly interesting. They comprise a comb polymer with a poly(methyl methacrylate) backbone and side oligo(oxyethylene) chains of variable length, sulfamide and a doping agent (guanidinium cation). Sulfamide compositions with n ratios of 2, 4 and 30 and N/H doping levels of 0, 1, 5, 10 and 20% have been studied. Copolymers with shorter side chains lead to entirely amorphous systems, regardless of sulfamide concentration or doping level. Best conductivities at 25 °C ($3\times10^{-5}\ \Omega^{-1}\ cm^{-1}$) have been reported for the copolymer based on short side chains, high concentration in sulfamide ($n=2$) and a doping level of 5%. Considering their mechanical, thermal and transport properties, these materials constitute a good alternative to sulfamide complexes of POE.

Two families of very attractive proton-vacancy conducting polymers have also been synthesized *via* the sol–gel method by copolymerization of trialkoxysilanes which, through the hydrolysis-condensation process, leads to a silica-based backbone: the *sulfonamidosils*, which include a methanesulfonamide group (CH_3SO_2NH) or a benzenesulfonamide group ($C_6H_5SO_2NH$) grafted to the inorganic network, and the *free sulfamoyl ormolytes*, in which the sulfamoyl group (NH_2SO_2) belongs to free sulfamide.[77] The products are entirely amorphous, non-porous, hard and obtained as transparent monolithic films. Methanesulfonamidosils are thermally stable up to 220 °C and benzenesulfonamidosils up to 350 °C. The electrochemical stability range of the most conducting methanesulfonamidosil is close to 2 V. Free sulfamoyl ormolytes constitute a viable alternative to sulfonamidosils, as they lead to higher conductivities ($2\times10^{-7}\ \Omega^{-1}\ cm^{-1}$ at room temperature).

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