Transfer of Sulphonic Acid Groups from *N*-Alkylsulphamic Acids: a New and Simple Sulphonation Procedure

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N-n-Butyl- and -cyclohexyl-sulphamic acids reacted (at temperatures of 150—195°) with aniline, *NN*-dimethylaniline, and anisole to yield the corresponding *p*-substituted benzenesulphonic acids (as either the n-butylammonium or cyclohexylammonium salts) in excellent (≥90%) yields. When the sulphamic acids were replaced by the corresponding ammonium sulphamates (including a secondary sulphamate salt, morpholinium morpholine-*N*-sulphonate), the salts proved substantially less reactive as sulphonating agents, and they failed, for example, to sulphonate anisole. These sulphamic acid reactions constitute the first use of such substituted sulphamic acids in sulphonation procedures.

WHILE sulphamic acid ($^+NH_3 \cdot SO_3^-$ or $NH_2 \cdot SO_3H$) and its fully *N*-alkylated derivatives, the tertiary amine sulphur trioxide complexes, $R_3N^+SO_3^-$, have been used [1] to sulphonate aromatic nuclei, there is no report on the use of either *N*-alkyl- or *N*-aryl-sulphamic acids in such reactions. The possible role of these latter materials in such aromatic electrophilic processes has received implicit support in a number of recent studies. Thus we [2] have observed sulphonations in the controlled (but limited) high temperature hydrolysis of diarylsulphamides in the presence of receptor aromatic nuclei which must arise *via* the corresponding *N*-arylsulphamic acids. Furthermore, in radiochemical studies [3] on the rearrangement of 1-naphthylsulphamic acid in sulphuric acid–dioxan the radiochemical balance implied not only that the 1-naphthylsulphamic acid could *trans*-sulphonate but also that it did so to a substantial extent without exchange of the sulphonic acid function with the sulphuric acid in the medium. In a similar way Shilov [4] has found that the sodium salt of 1-naphthylsulphamic acid can sulphonate both 1-naphthylamine and 1-naphthol (in naphthalene at 186°).

We were anxious to examine such *trans*-sulphonations further. Inasmuch as the *N*-arylsulphamic acids are unknown in the free state,[5] we prepared a number of *N*-alkylsulphamic acids (and their ammonium salts) to use as substrates and we have probed their reactions with a number of receptor aromatic compounds.

EXPERIMENTAL

M.p.s were determined with an Electrothermal apparatus. Microanalyses were carried out by Drs Weiler and Strauss (Oxford). n-Butylamine, cyclohexylamine, and morpholine were redistilled before use. Aniline and *NN*-dimethylaniline were redistilled over potassium hydroxide pellets and the latter was stored over sodium wire. The alkylsulphamic acids and their alkylammonium salts were dried *in vacuo* (20 mmHg) at 100° for 24 h over phosphorus pentoxide. The sulphamic acids and their salts, the aromatic amines, and anisole were titrated against Karl Fischer reagent (to dead-stop end point on a Radiometer pH meter type PHM 23d) using Vogel's technique,[6] and were found to contain negligible quantities of water (not more than 0·05 mg ml^{-1}). Sulphanilic acid was commercially available.

n-Butylammonium N-*n-Butylsulphamate*.—(a) *By the aminolysis of chlorosulphonic acid.* n-Butylamine (21·9 g, 0·3 mol) was maintained at −5° and vigorously stirred while chlorosulphonic acid (11·65 g, 0·1 mol) in chloroform (60 ml) was added slowly. When the reaction had ceased, the chloroform was removed under reduced pressure to leave a viscous oil which was dissolved in boiling water (*ca.* 300 ml). The solution was concentrated to *ca.* 100 ml by boiling and in this process chloroform and some unchanged n-butylamine were driven off. On cooling, the product separated out (9 g, 36%) as a white crystalline solid, m.p. 125—127° (from water) (lit.,[7] 128°) (Found: C, 42·2; H, 9·7; N, 13·0; S, 14·8. Calc. for $C_8H_{22}N_2O_3S$: C, 45·5; H, 9·7; N, 12·4; S, 14·2%); picrate, m.p. 151° (lit.,[8] 151°); *S*-benzylthiouronium derivative, m.p. 131—132° (lit.,[9] 130° (Found: C, 44·6; H, 6·9; N, 13·4; S, 19·7. Calc. for $C_{12}H_{21}N_3O_3S_2$: C, 45·1; H, 6·6; N, 13·2; S, 20·1%).

(b) *By sulphamation of n-butylamine with pyridine–2-sulphur trioxide.** n-Butylamine (14·6 g, 0·2 mol) and water (30 ml) were maintained at 0° with constant stirring. Pyridine–2-sulphur trioxide (12 g, 0·05 mol) was added slowly. When the mixture had been stirred for 2 h, it was boiled until all the pyridine had been driven off. The solution was evaporated to *ca.* 20 ml and cooled. The required n-butylammonium *N*-n-butylsulphamate separated out (11 g, 50%), m.p. 125—127° (from water). This material did not depress the m.p. of the sample prepared in (a).

Barium N-*n-Butylsulphamate*.—Barium hydroxide (3·5 g, 11 mmol) dissolved in hot water (20 ml) was added to a solution of n-butylammonium *N*-n-butylsulphamate (5 g, 0·02 mol) in hot water (20 ml). The mixture was boiled until all the n-butylamine was driven off and it was then cooled to 60°. Carbon dioxide gas was passed through

* There are two pyridine–sulphur trioxide complexes available of types, $Py \cdot SO_3$ and $Py(SO_3)_2$. The latter, designated herein (and elsewhere [1]) as pyridine–2-sulphur trioxide, was the reagent used in this present work.

[1] E. E. Gilbert, 'Sulfonation and Related Reactions,' Interscience, 1965, ch. 1 and 2.
[2] F. L. Scott and O. J. J. Broderick, *Chem. and Ind.*, 1962, 1058; F. L. Scott, J. A. Barry, and W. J. Spillane, unpublished data.
[3] W. J. Spillane, F. L. Scott, and C. B. Goggin, *J. Chem. Soc.* (*B*), 1971, 2409.
[4] E. A. Shilov, M. N. Bogdanov, and A. E. Shilov, *Doklady Akad. Nauk S.S.S.R.*, 1953, **92**, 93.
[5] L. F. Audrieth and M. Sveda, *J. Org. Chem.*, 1944, **9**, 89.
[6] A. I. Vogel, 'Quantitative Inorganic Analysis,' 3rd edn., Longmans, 1962, p. 948.
[7] G. E. McCasland and R. B. Hadgraft, *J. Amer. Chem. Soc.*, 1951, **73**, 5507.
[8] See, 'Organic Reagents for Organic Analysis,' Hopkin and Williams, Chadwell Heath, Essex, 1956.
[9] W. J. Spillane, F. L. Scott, and C. B. Goggin, *Internat. J. Sulphur Chem.*, *A*, 1971, **1**, 223.

until all the excess of barium hydroxide was precipitated out. The solution was filtered. Concentration of the filtrate to a small bulk gave a quantitative yield (4·88 g) of the barium salt of n-butylsulphamic acid. Its *S*-benzylthiouronium derivative, m.p. 131—132°, did not depress the m.p. of the *S*-benzylthiouronium derivative of the material prepared in (a) above.

N-*n-Butylsulphamic Acid.*—Barium *N*-n-butylsulphamate (6 g, 13·6 mmol) was dissolved in water (30 ml) and the solution was heated to 90°. 0·5N-Sulphuric acid was added slowly until the barium present was completely precipitated as barium sulphate. Filtration through a layer of Celite gave a clear solution, which on concentration gave a quantitative yield (4·1 g) of *N*-n-butylsulphamic acid, m.p. 192—194° (lit.,[10] 183°) (Found: C, 32·0; H, 7·3; N, 9·0; S, 20·8. Calc. for $C_4H_{11}NO_3S$: C, 31·4; H, 7·2; N, 9·2; S, 20·9%).

Cyclohexylammonium N-*Cyclohexylsulphamate and* N-*Cyclohexylsulphamic Acid.*—The cyclohexylammonium compound was prepared by the method of Audrieth and Sveda,[5] namely, the reaction of cyclohexylamine and chlorosulphonic acid in chloroform solution. The pure material (69%) had m.p. 198—199° (lit.,[5] 198—200°) (Found: C, 51·6; H, 9·4; N, 9·5; S, 11·5. Calc. for $C_{12}H_{25}N_2O_3S$: C, 51·8; H, 9·4; N, 10·0; S, 11·5%). The free acid was obtained from the cyclohexylammonium salt by the process described for the preparation of *N*-n-butylsulphamic acid. *N*-Cyclohexylsulphamic acid was thus obtained in 97% yield, m.p. 172—173° (lit.,[5] 169—170°). Both the cyclohexylammonium salt and the free sulphamic acid formed *S*-benzylthiouronium derivatives, m.p. and mixed m.p. 178° (lit.,[9] 178°) (Found: C, 49·2; H, 6·8; N, 12·6; S, 19·3. Calc. for $C_{14}H_{23}N_3O_3S_2$: C, 48·7; H, 6·7; N, 12·2; S, 18·6%).

Morpholinium Morpholine-4-sulphonate.—(a) *By the aminolysis of chlorosulphonic acid.* This method was analogous to method (a) used above in the preparation of n-butylammonium *N*-n-butylsulphamate. Recrystallization (from aqueous ethanol) of the crude product gave morpholinium morpholine-4-sulphonate (39·4 g, 48%), m.p. 161—162° (Found: C, 38·9; H, 6·7; N, 10·7; S, 12·1. Calc. for $C_8H_{18}N_2O_5S$: C, 37·8; H, 7·1; N, 11·0; S, 12·6%); *S*-benzylthiouronium derivative, m.p. 168—169° (Found: C, 43·2; H, 5·7; N, 12·6; S, 18·8. Calc. for $C_{12}H_{19}N_3O_4S_2$: C, 43·2; H, 5·7; N, 12·6; S, 19·2%).

(b) *By sulphonation of morpholine with pyridine–2-sulphur trioxide.* This method was similar to method (b) for the preparation of n-butylammonium *N*-n-butylsulphamate above. A 38% yield was obtained.

n-Butylammonium Sulphate.—98% Sulphuric acid (1·0 g, 0·01 mol) was diluted with water (10 ml) and the solution was cooled to 0°. This solution was added to n-butylamine (3 ml, 0·02 mol) and concentrated by boiling. On cooling, n-butylammonium sulphate separated out, m.p. >300° (from aqueous ethanol) (Found: C, 39·0; H, 10·2. Calc. for $C_8H_{24}N_2O_4S$: C, 39·3; H, 9·9%).

p-*Methoxybenzenesulphonate Salts.*—(a) *Ammonium salt.* Anisole (10 g, 0·09 mol) and sulphamic acid (5 g, 0·05 mol) were heated under reflux at 155° for 4 h. The cooled solution was left at ambient temperatures for 24 h, when ammonium *p*-methoxybenzenesulphonate (7·83 g, 83%), m.p. 283—285° (lit.,[11] 283—285°), separated out; *S*-benzylthiouronium derivative, m.p. 158—160° (Found: C, 50·4; H, 5·7; N, 8·1; S, 18·1. Calc. for $C_{15}H_{18}N_2O_4S$: C, 50·9; H, 5·1; N, 7·9; S, 18·1%).

(b) *n-Butylammonium salt.* This compound was formed by boiling a solution of the ammonium salt (0·5 g, 2·4 mmol) in n-butylamine (5 ml) for 5 min. The n-butylamine salt precipitated out on addition of ether (20 ml). Recrystallization from ethanol gave a near quantitative yield (0·6 g); m.p. 134—135° (Found: C, 50·5; H, 7·8; N, 5·2; S, 12·2. Calc. for $C_{11}H_{19}NO_4S$: C, 50·6; H, 7·3; N, 5·4; S, 12·3%).

(c) *Cyclohexylammonium salt.* This compound was prepared from the ammonium salt and cyclohexylamine. The procedure followed was similar to that in (b). A near quantitative yield of the cyclohexylammonium salt of *p*-methoxybenzenesulphonate, m.p. 164—165°, was obtained (Found: C, 54·0; H, 7·7; N, 5·0; S, 11·2. Calc. for $C_{13}H_{21}NO_4S$: C, 54·3; H, 7·4; N, 4·9; S, 11·2%).

n-Butylammonium Sulphanilate.—Sulphanilic acid (1 g, 5·8 mmol) was stirred for 5 min in n-butylamine (5 ml). Ether (30 ml) was added to the solution and n-butylammonium sulphanilate (quantitative yield), m.p. 170—173°, separated out. Recrystallization (from aqueous ethanol) raised the m.p. to 174—175° (Found: C, 48·9; H, 7·5; N, 11·5; S, 12·6. Calc. for $C_{10}H_{18}N_2O_3S$: C, 48·9; H, 7·3; N, 11·4; S, 13·0%). The cyclohexylammonium salt was similarly prepared from sulphanilic acid and cyclohexylamine. Recrystallization (from water) gave a solid, m.p. 256—257° (Found: C, 53·1; H, 7·5; N, 10·5; S, 11·3. Calc. for $C_{12}H_{20}N_2O_3S$: C, 53·0; H, 7·3; N, 10·3; S, 11·8%).

p-*Dimethylaminobenzenesulphonic Acid.*—This acid was prepared by a modified Vilsmeier–Haack reaction as we have described elsewhere.[12] The morpholine salt of this acid was prepared by heating a solution of the ammonium *p*-dimethylaminobenzenesulphonate (1 g, 4·6 mmol) in morpholine (5 ml) at 70—80° for 5 min; m.p. 185—186° (Found: C, 49·7; H, 6·7; N, 9·3; S, 11·0. Calc. for $C_{12}H_{20}N_2O_4S$: C, 50·0; H, 7·0; N, 9·7; S, 11·1%). The cyclohexylammonium salt, m.p. 247—248° (Found: C, 56·2; H, 8·2; N, 9·3; S, 10·6. Calc. for $C_{14}H_{24}N_2O_3S$: C, 56·0; H, 8·0; N, 9·4; S, 10·7%), and n-butylammonium salt, m.p. 115—116° (Found: C, 52·8; H, 8·1; N, 10·3; S, 11·2. Calc. for $C_{12}H_{22}N_2O_3S$: C, 52·6; H, 8·0; N, 10·2; S, 11·7%), were similarly prepared.

Sulphonation Runs.—All runs were carried out in sealed glass ampoules which contained the aromatic amine or anisole (10 ml), and the appropriate sulphamic acid or its salt. The amount of sulphonating agent, the temperature of the reaction, the reaction time, and the products of each reaction are shown in the Table. The work-up was standardized as far as possible and the following (for run 1) also applies to runs 2, 4, 5, 7, 9, 11, 14, and 17: n-butylammonium *N*-n-butylsulphamate (0·5 g, 2·2 mmol) in aniline (10 ml) was maintained at 185° for 6 h in a sealed glass ampoule immersed in an oil-bath at the appropriate temperature. The mixture was kept for 24 h at ambient temperatures. The contents of the ampoule were doused with ether (10 ml), whereupon a white solid separated out. This material was recrystallized (from ethanol) to give n-butylammonium sulphanilate (0·42 g, 78%), m.p. 174—175°. Identification was based on comparison with an unambiguously prepared sample of the n-butylammonium salt of sulphanilic acid.

Runs 8 and 10 were worked-up by an identical procedure.

[10] H. Yamaguchi, *Nippon Kagaku Zasshi*, 1961, **82**, 483 (*Chem. Abs.*, 1962, **56**, 9926).

[11] A. Quilico, *Gazzetta*, 1927, **57**, 793.

[12] F. L. Scott and J. A. Barry, *Tetrahedron Letters*, 1968, 2457.

For example, in run 8, cyclohexylammonium sulphate (0·06 g, 12%) separated out when the mixture was left overnight at room temperature. On addition of ether to the filtered mixture, cyclohexylammonium sulphanilate (0·37 g, 76%) was obtained; m.p. 256—257°. Cyclohexylammonium *p*-dimethylaminobenzenesulphonate (0·43 g, 86%), m.p. 247—248° was formed in run 10 together with cyclohexylammonium sulphate (0·05 g, 9%). Run 10 was repeated and worked-up in a different way by treating the crude sulphonate product with 5N-hydrochloric acid to give *p*-dimethylaminobenzenesulphonic acid (0·165 g, 32%).

Run 15 was worked-up as follows: the mixture was cooled and kept at room temperature for 24 h, but no solid material separated out. Ether (50 ml) was added slowly to the solution at 0° and a brown oil separated out. The oil dissolved on addition of water (5 ml). The aqueous solution was extracted with ether (3 × 5 ml) to remove the last traces of aniline. 5N-Hydrochloric acid (5 ml) was added to the aqueous solution which was then boiled for 15 min, evaporated to half bulk, and then cooled. Sulphanilic acid precipitated from solution in 33% yield (0·11 g); *S*-benzylthiouronium derivative, m.p. 182° (lit.,[8] 182°).

RESULTS

The reactions summarized in the Table show clear patterns of behaviour. For example, comparing the reactivity of n-butylammonium sulphamate (1) with that of the corresponding free sulphamic acid, (2), we find that the ammonium salt of the sulphamic acid is a much milder sulphonating agent than the free acid. Thus reactions of

$RNH{\cdot}SO_3^-\ NH_3R^+$	$RNH{\cdot}SO_3H\ (RNH_2^+SO_3^-)$
(1) R = Bu^n	(2) R = Bu^n
(4) R = C_6H_{11}	(5) R = C_6H_{11}
p-$MeO{\cdot}C_6H_4{\cdot}SO_3^-\ NH_3R^+$	$RN{\cdot}SO_3^-\ H_2NR^+$
(3) R = Bu^n	(6) RN = morpholino

the salt (1) with either aniline or *NN*-dimethylaniline take longer and occur to lesser extents than the corresponding reactions with the acid (2), which are almost quantitative under our conditions. Nowhere is the difference more clearly indicated than in their reactions with anisole. Attempted reaction of the salt (1) with anisole (6 h, 155°) resulted in no sulphonation, the salt (1) being recovered in 97% yield. Reaction of the acid (2) with anisole (4 h, 155°) formed the corresponding sulphonic acid [as the n-butylammonium salt (3)] in 98% yield.

Exactly similar patterns were revealed with cyclohexylammonium *N*-cyclohexylsulphamate (4) and the corresponding acid (5), except that when the ammonium salt was used, appreciable (*ca.* 10%) hydrolysis (to cyclohexylammonium sulphate) accompanied the sulphonation process. With the salt (4), longer reaction (12 h) still failed to effect sulphonation with anisole. With the sole secondary sulphamic acid which we prepared, handling difficulties restricted our study to those of the corresponding ammonium salt (6). Here again the trends encountered (runs 15—17) were entirely consistent with those already observed in the monoalkyl cases.

DISCUSSION

The reactions we have described all show that *N*-substituted sulphamic acids can effectively sulphonate aromatic nuclei, the main reaction being (1). Presumably in this regard they are midway in reactivity

$$R_2N{\cdot}SO_3H + ArH \longrightarrow ArSO_3^-HNR_2^+ \qquad (1)$$

between the unsubstituted $^+NH_3{\cdot}SO_3^-$ and fully substituted $R_3\overset{+}{N}SO_3^-$ complexes of sulphur trioxide. It is accepted that the efficiencies of such amine complexes as sulphonating species are inversely related to the base strengths of the parent amines.[13] The precise mechanism(s) whereby *trans*-sulphonation occurs is still

Sulphonation of aniline, *NN*-dimethylaniline, and anisole with alkylsulphamic acids and their ammonium salts

Run no.	Sulphonating agent [a]	Substrate	Temp (°C)	Time (h)	Sulphonation product	Yield (%)	Other material recovered	Yield (%)
1	$Bu^nNH{\cdot}SO_3^-\ \overset{+}{N}H_3Bu^n$	$PhNH_2$	185	6	p-$NH_2{\cdot}C_6H_4{\cdot}SO_3^-\ \overset{+}{N}H_3Bu^n$	78		
2	$Bu^nNH{\cdot}SO_3H$	$PhNH_2$	185	4	p-$NH_2{\cdot}C_6H_4{\cdot}SO_3^-\ \overset{+}{N}H_3Bu^n$	94		
3	$(Bu^nNH{\cdot}SO_3)_2Ba$	$PhNH_2$	185	6			Starting material	98
4	$Bu^nNH{\cdot}SO_3^-\ \overset{+}{N}H_3Bu^n$	$PhNMe_2$	195	6	p-$Me_2N{\cdot}C_6H_4{\cdot}SO_3^-\ \overset{+}{N}H_3Bu^n$	87		
5	$Bu^nNH{\cdot}SO_3H$	$PhNMe_2$	195	4	p-$Me_2N{\cdot}C_6H_4{\cdot}SO_3^-\ \overset{+}{N}H_3Bu^n$	94		
6	$Bu^nNH{\cdot}SO_3^-\ \overset{+}{N}H_3Bu^n$	PhOMe	155	6			Starting material	97
7	$Bu^nNH{\cdot}SO_3H$	PhOMe	155	4	p-$MeO{\cdot}C_6H_4{\cdot}SO_3^-\ \overset{+}{N}H_3Bu^n$	98		
8	$C_6H_{11}{\cdot}NH{\cdot}SO_3^-\ \overset{+}{N}H_3{\cdot}C_6H_{11}$ [b]	$PhNH_2$	185	6	p-$NH_2{\cdot}C_6H_4{\cdot}SO_3^-\ \overset{+}{N}H_3{\cdot}C_6H_{11}$ [b]	76	$(C_6H_{11}{\cdot}NH_2)_2{\cdot}H_2SO_4$ [b]	6
9	$C_6H_{11}{\cdot}NH{\cdot}SO_3H$ [b]	$PhNH_2$	185	4	p-$NH_2{\cdot}C_6H_4{\cdot}SO_3^-\ \overset{+}{N}H_3{\cdot}C_6H_{11}$ [b]	90		
10	$C_6H_{11}{\cdot}NH{\cdot}SO_3^-\ \overset{+}{N}H_3{\cdot}C_6H_{11}$ [b]	$PhNMe_2$	195	6	p-$Me_2N{\cdot}C_6H_4{\cdot}SO_3^-\ \overset{+}{N}H_3{\cdot}C_6H_{11}$ [b]	86	$(C_6H_{11}{\cdot}NH_2)_2{\cdot}H_2SO_4$ [b]	9
11	$C_6H_{11}{\cdot}NH{\cdot}SO_3H$ [b]	$PhNMe_2$	195	4	p-$Me_2N{\cdot}C_6H_4{\cdot}SO_3^-\ \overset{+}{N}H_3C_6H_{11}$ [b]	97		
12	$C_6H_{11}{\cdot}NH{\cdot}SO_3^-\ \overset{+}{N}H_3{\cdot}C_6H_{11}$ [b]	PhOMe	185	6			Starting material	96
13	$C_6H_{11}{\cdot}NH{\cdot}SO_3^-\ \overset{+}{N}H_3{\cdot}C_6H_{11}$ [b]	PhOMe	155	12			Starting material	98
14	$C_6H_{11}{\cdot}NH{\cdot}SO_3H$	PhOMe	155	6	p-$MeO{\cdot}C_6H_4{\cdot}SO_3^-\ \overset{+}{N}H_3{\cdot}C_6H_{11}$ [b]	99		
15	$RN{\cdot}SO_3^-\ H_2\overset{+}{N}R$ [c]	$PhNH_2$	185	6	p-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$	33		
16	$RN{\cdot}SO_3^-\ H_2\overset{+}{N}H$ [c]	$PhNH_2$	150	6			Starting material	95
17	$RN{\cdot}SO_3^-\ H_2\overset{+}{N}R$ [c]	$PhNMe_2$	195	6	p-$Me_2N{\cdot}C_6H_4{\cdot}SO_3{-}H_2NR^+$ [c]	70		

[a] The quantity of sulphonating agent used was generally 0·5 or 1·0 g. [b] Cyclohexyl compound. [c] RN is morpholino.

[13] Ref. 1, p. 7 *et seq.*

not clear. If we write the sulphamic species in the zwitterionic form (7) then the possibility exists that a dissociative mechanism of the type (2) takes place, with

$$\underset{(7)}{R_2\overset{+}{N}HSO_3^-} \longrightarrow R_2NH + SO_3 \qquad (2)$$

the aromatic nuclei acting as traps for the sulphur trioxide released. Our experiments are in one sense thermolyses of such sulphamic acids (at between 155—195°), and such a mechanism is not unlikely under these conditions. The lower reactivity of the ammonium salts which exist not as internal zwitterions but as the true salts $RNH{\cdot}SO_3^-\overset{+}{N}H_3R$ may then be explained by the greater difficulty of generating sulphur trioxide from such species. A cognate observation is the failure to generate any sulphonating species when barium *N*-n-butylsulphamate was used. Such dissociative mechanisms have been suggested in the reactions between alcohols and sulphamic acids [14] and in amine-catalysed decompositions of *N*-alkylsulphamic acids,[15] without any clear-cut evidence however. Our studies on the acid-catalysed hydrolyses of such *N*-alkylsulphamic acids lead us to conclude also that dissociative processes [9] were not primarily involved.

A second mechanism which may be postulated involves direct sulphonation of the amine by the sulphamic acid (or sulphamic acid zwitterion). Relevant to this are our studies of the rearrangement of 1-naphthylsulphamic acid,[3] where we have suggested that such a bimolecular mechanism operates. A mechanism involving free SO_3 or an amine–SO_3 adduct, both of which would exchange fully with the [^{35}S]sulphuric acid of the medium, can be excluded under the conditions which we used for the naphthylsulphamic acid rearrangement since we obtained a high proportion of non-labelled product. Koptyug [16] considers that bimolecular sulphonation mechanisms are quite common. They have been reported,[17] and in some cases supported by [^{35}S]-tracer work.[4] The importance of bimolecular mechanisms in the Fischer–Hepp rearrangement has been noted recently, when it was found that the nitroso-amine substrate can transfer the NO group to a suitable acceptor without its becoming kinetically free.[18]

Whatever the precise mechanisms involved we conclude that substituted sulphamic acids constitute ready reagents for sulphonation of aromatic nuclei. Hitherto sulphamic acids have been rarely used for sulphonation but, they have been employed extensively in sulphation (formation of oxygen–sulphur bonds) and in sulphamation (formation of nitrogen–sulphur bonds).

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[14] K. Nakano and H. Yamaguchi, *Kogyo Kagaku Zasshi*, 1964, **67**, 2055 (*Chem. Abs.*, 1966, **65**, 583).
[15] K. Nagasawa and H. Yoshidome, *Chem. and Pharm. Bull.* (*Japan*), 1969, **17**, 1316; 1970, **18**, 2023.
[16] V. A. Koptyug, 'Isomerization of Aromatic Compounds,' ed. N. N. Vorozhtsov, jun., Oldbourne Press, London, 1965.
[17] G.P. 75,319 and 77,118; E. Koop, *Ber.*, 1871, **4**, 978.
[18] T. D. B. Morgan and D. L. H. Williams, *J.C.S. Perkin II*, 1972, 74.