ent as can be seen from the lowered rate in methanol and the comparatively negligible rate in acetonitrile (Table II). Sufficient aqueous perchloric acid was added to both these media to keep the carboxylic acid practically completely in the undissociated form, as was evidenced by the zero time spectra. Considerably more experimentation will be necessary to determine whether the changes in rate with solvent are due to the participation of solvent species in the rate-controlling step, a change in the ratio $f_{\text{reactants}}/f_{\text{transition}}$, or a change in a preliminary equilibrium (*e.g.*, ketonization to form III as an intermediate).

The activation energy in 10.7% perchloric acid for the decarboxylation, determined over a 40° range, is 19,600 calories (Fig. 4). The value of K, the acid ionization constant of 2,4,6-trihydroxybenzoic acid, was calculated for the several concentrations of perchloric acid for which the degree of ionization had been spectroscopically measured, with the assumption that the mean activity coefficient of RCO_2^- and H^+ is the same as that of hydrochloric acid at the same ionic strength (Table IV).[8] The average value obtained for K (omitting the value in 5.70% perchloric acid, in which the degree of ionization is small) was 2.8×10^{-2}. Ostwald[9] determined K to be 2.1×10^{-2} at 25° by the conductance method, but questioned the validity of the measurement since "the material disappears under one's hands." No doubt decarboxylation occurred during the measurement. Hammick and co-workers[2a] determined K to be $2.0 \pm 0.3 \times 10^{-2}$ by a pH meter method but regarded this value as approximate only.

Acknowledgment.—This work was performed as a joint undertaking of the University of Washington and the Office of Naval Research, U. S. Navy Department, under Contract N8onr-52006, Project NR 055187.

[8] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Ed. 2, Reinhold Publishing Corp., New York, N. Y., 1950, p. 547.

[9] W. Ostwald, *Z. physik. Chem.*, **3**, 253 (1889).

SEATTLE 5, WASHINGTON

[CONTRIBUTION FROM THE NICHOLS CHEMICAL LABORATORIES, NEW YORK UNIVERSITY, UNIVERSITY HEIGHTS]

The Action of Sulfuric Acid on Isocyanic Esters[1]

BY THEODORE I. BIEBER[2]

RECEIVED AUGUST 8, 1952

The action of sulfuric acid on ethyl isocyanate leads to ethylsulfamic acid and carbon dioxide. The reaction of alkyl socyanates with sulfuric acid appears to offer a convenient route to alkylsulfamic acids. Hexamethylenedisulfamic acid can be prepared from hexamethylenediisocyanate. A related reaction, that of 1,3-dimethylurea with oleum, produces methylsulfamic acid and carbon dioxide. The reaction of phenyl isocyanate with sulfuric acid yields sulfanilic acid and carbon dioxide.

It was shown by Linhard[3] that cyanic acid and 100% sulfuric acid react in ether solution at −60° to give an unstable addition compound, which decomposes into sulfamic acid[4] and carbon dioxide.

$$HNCO + H_2SO_4 \longrightarrow H_2N{-}SO_3H + CO_2$$

It seemed of interest to study the reaction of organic isocyanates with sulfuric acid, since by analogy monosubstituted sulfamic acids should be formed.

$$R{-}N{=}C{=}O + H_2SO_4 \longrightarrow RNH{-}SO_3H + CO_2$$

The Reaction of Aliphatic Isocyanates with Sulfuric Acid.—Ethyl isocyanate, a typical aliphatic isocyanate, was allowed to react with 20% oleum, 5% oleum and concentrated sulfuric acid. In each case carbon dioxide was readily evolved in the cold. The formation of a transitory white solid, which dissolved with gas evolution and which was probably an addition compound of the isocyanate with sulfuric acid, was observed in the course of these reactions. The experiments with 5% and 20% oleum afforded ethylsulfamic acid, which was isolated in about 85% yield. With concentrated sulfuric acid the major product was ethylamine acid sulfate. This was accompanied by a 13% yield of ethylsulfamic acid. The water content of the concentrated sulfuric acid was greater than that required for hydrolysis of all the isocyanate employed. The fact that some ethylsulfamic acid resulted even under these conditions demonstrates that oleum with its powerful sulfonating action is not required for the formation of ethylsulfamic acid. A high yield of ethylsulfamic acid can therefore be expected with 100% sulfuric acid. The proposed synthesis of monosubstituted sulfamic acids has thus been demonstrated with R = C_2H_5.

$$C_2H_5{-}N{=}C{=}O + H_2O + H_2SO_4 \longrightarrow C_2H_5NH_3HSO_4 + CO_2$$

This new preparation of ethylsulfamic acid seems superior to previous ones. The product is easily isolated by pouring the reaction mixture into ether, from which ethylsulfamic acid precipitates as a crystalline solid. Earlier methods involve the reaction of ethylamine with sulfur trioxide in the vapor phase,[5] the reaction of aqueous ethylamine

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[1] Presented before the Organic Division at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September 19, 1952.

[2] Address correspondence concerning this paper to the author at 80-40 Lefferts Blvd., Kew Gardens 15, New York.

[3] M. Linhard, *Ann.*, **535**, 267 (1938).

[4] Sulfamic acid has been shown to be a zwitterion molecule $H_3N^+{-}SO_3^-$, rather than $H_2N{-}SO_3H$, at least in the crystalline state [F. A. Kanda and A. J. King, THIS JOURNAL, **73**, 2315 (1951)]. The substituted sulfamic acids mentioned here and in the succeeding paper [T. I. Bieber, *ibid.*, **75**, 1409 (1953)] are no doubt more accurately represented by $RNH_2^+{-}SO_3^-$ than by $RNH{-}SO_3H$. For the sake of convenience the formulas showing the proton on the sulfonate group are employed.

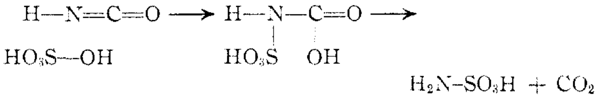
[5] F. Beilstein and E. Wiegand, *Ber.*, **16**, 1264 (1883).

with potassium fluorosulfonate[6] (both these reactions produce salts of ethylsulfamic acid and not the free acid), and the reaction of N-ethylhydroxylamine with sulfur dioxide.[7]

The reaction of alkyl isocyanates with sulfuric acid apparently offers a convenient route to alkylsulfamic acids. Hexamethylenedisulfamic acid, furthermore, has been prepared from hexamethylenediisocyanate.

$$O{=}C{=}N(CH_2)_6N{=}C{=}O + 2H_2SO_4 \longrightarrow HO_3SNH(CH_2)_6NHSO_3H + 2CO_2$$

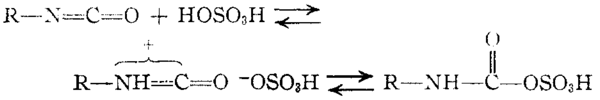
The following mechanism was suggested by Linhard[3] for the cyanic acid–sulfuric acid reaction.



$$\underset{HO_3S-OH}{H-N=C=O} \longrightarrow \underset{HO_3S\quad OH}{H-N-C=O} \longrightarrow H_2N-SO_3H + CO_2$$

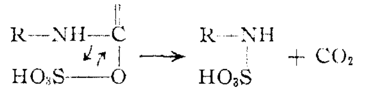
The proposed mode of addition of sulfuric acid to cyanic acid is at variance with the normal addition of active hydrogen compounds to cyanic acid, but it fundamentally represents a N-sulfonation. It is to be doubted, however, whether sulfuric acid is capable of acting as a sulfonating agent under the extremely mild conditions of the reaction, since the weakness of sulfuric acid as a sulfonating agent, especially in the cold, is well-known from studies of aromatic sulfonation.[8]

It is more reasonable to assume that sulfuric acid adds to R—N=C=O (R = H or alkyl) in a manner typical for active hydrogen compounds. Protonation of the isocyanate and combination of the resulting carbamyl ion with bisulfate ion produces a carbamylsulfuric acid.



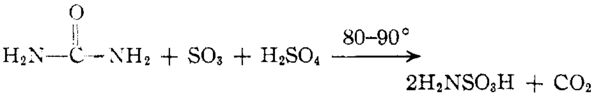
$$R-N=C=O + HOSO_3H \rightleftarrows \overset{+}{R-NH=C=O}\ {}^-OSO_3H \rightleftarrows R-NH-\overset{O}{\overset{\|}{C}}-OSO_3H$$

Such a substance, being a mixed anhydride of sulfuric acid and the carbamic acid RNHCOOH, can be expected to be a much more effective sulfonating agent than sulfuric acid, since anhydrides of sulfuric acid, simple or mixed, are generally good sulfonating agents. Intramolecular N-sulfonation by way of a cyclic quasi-4-membered transition state with simultaneous elimination of carbon dioxide is the most likely path for conclusion of the reaction. Such a transition state, incidentally, is subject to considerably less strain than a true 4-membered ring, since bonds are formed and broken simultaneously.



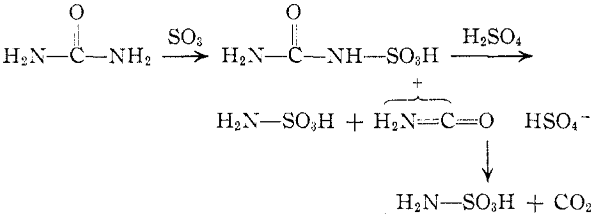
$$\begin{matrix} R-NH-\overset{O}{\overset{\|}{C}} \\ HO_3S-O \end{matrix} \longrightarrow \begin{matrix} R-NH \\ HO_3S \end{matrix} + CO_2$$

The Reaction of 1,3-Dimethylurea with Oleum.—The action of oleum on urea is the basis for the large-scale synthesis of sulfamic acid.[9]



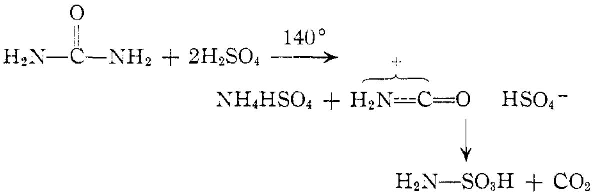
$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 + SO_3 + H_2SO_4 \xrightarrow{80-90^\circ} 2H_2NSO_3H + CO_2$$

Ureasulfonic acid is known to be an intermediate.[9,10] This undergoes a urea cleavage, and the subsequent course of the reaction is clearly related to the cyanic acid–sulfuric acid reaction.



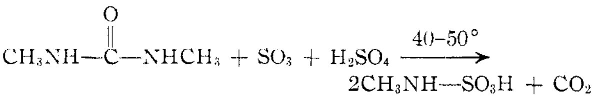
$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{SO_3} H_2N-\overset{O}{\overset{\|}{C}}-NH-SO_3H \xrightarrow{H_2SO_4} H_2N-SO_3H + \overset{+}{H_2N=C=O}\ HSO_4^- \longrightarrow H_2N-SO_3H + CO_2$$

Decomposition of urea in the presence of sulfuric acid (without prior conversion to ureasulfonic acid) leads to ammonium bisulfate along with sulfamic acid.[9]



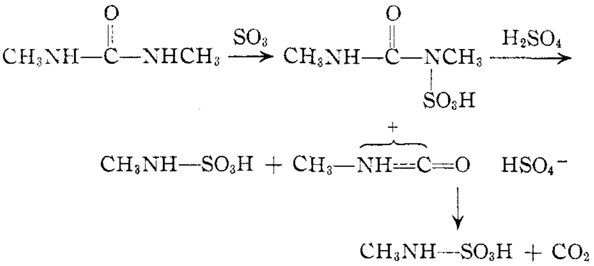
$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 + 2H_2SO_4 \xrightarrow{140^\circ} NH_4HSO_4 + \overset{+}{H_2N=C=O}\ HSO_4^- \longrightarrow H_2N-SO_3H + CO_2$$

A symmetrically substituted dialkylurea, 1,3-dimethylurea, has now been subjected to the action of oleum, and methylsulfamic acid has been obtained in 91% yield.



$$CH_3NH-\overset{O}{\overset{\|}{C}}-NHCH_3 + SO_3 + H_2SO_4 \xrightarrow{40-50^\circ} 2CH_3NH-SO_3H + CO_2$$

The following mechanism accounts for this reaction



$$CH_3NH-\overset{O}{\overset{\|}{C}}-NHCH_3 \xrightarrow{SO_3} CH_3NH-\overset{O}{\overset{\|}{C}}-\underset{SO_3H}{NCH_3} \xrightarrow{H_2SO_4} CH_3NH-SO_3H + CH_3-\overset{+}{NH=C=O}\ HSO_4^- \longrightarrow CH_3NH-SO_3H + CO_2$$

In order to avoid cleaving the urea before sulfonation has occurred, the reaction must be carried out under rather mild conditions. In the absence of prior sulfonation a molecule of 1,3-dimethylurea gives rise to only one molecule of methylsulfamic acid, together with methylamine acid sulfate.

A previous preparation of methylsulfamic acid involves the sulfonation of aqueous methylamine by means of potassium fluorosulfonate.[6]

The Reaction of Phenyl Isocyanate with Sulfuric Acid.—Phenyl isocyanate was allowed to react near 0° with (A) 20% oleum, (B) 5% oleum, (C) highly concentrated sulfuric acid containing a quantity of water insufficient for hydrolysis of all the isocyanate to aniline acid sulfate, and (D)

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(6) W. Traube and E. Brehmer, *Ber.*, **52**, 1284 (1919).

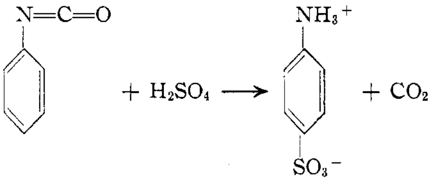
(7) A. I. Ryer and G. B. L. Smith, This Journal, **73**, 5675 (1951).

(8) The mechanism of Linhard is patterned after an erroneous one for the C-sulfonation that occurs in the ethylene–oleum reaction [H. Wieland and E. Sakellarios, *Ber.*, **53**, 204 (1920)]. This C-sulfonation is really due to the action of oleum and is not observed when 100% sulfuric acid is used; with the latter ethylsulfuric acid is the sole product [A. Michael and N. Weiner, This Journal, **58**, 294 (1936)].

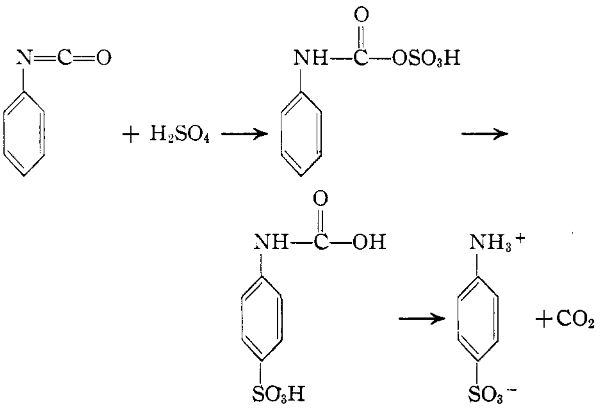
(9) P. Baumgarten, *Ber.*, **69**, 1929 (1936).

(10) D. P. Hill and G. A. Peirce, U. S. Patent 2,390,648 (1945); *C. A.*, **40**, 1289[9] (1946).

concentrated sulfuric acid containing more than sufficient water for hydrolysis of all the isocyanate. Carbon dioxide was rapidly evolved from each of these reaction mixtures, which were subsequently poured on ice. This led to the precipitation of solid product in experiments A, B and C. The solid was shown to be sulfanilic acid in each case by conversion to *p*-chlorobenzenesulfonamide. The acidic aqueous solutions were found to contain aniline in experiments C and D. Thus both aniline acid sulfate and sulfanilic acid are obtained when the sulfuric acid contains insufficient water for hydrolysis of all the isocyanate.[11] The equation for sulfanilic acid formation is

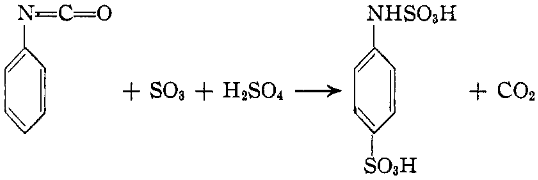


In view of the fact that oleum is not required for this sulfonation and that sulfuric acid is a very poor sulfonating agent in the cold, the facile formation of sulfanilic acid is somewhat surprising. The addition of sulfuric acid to the isocyanate group can be expected, however, to generate an effective sulfonating agent, inasmuch as phenylcarbamylsulfuric acid is a mixed anhydride involving sulfuric acid. Sulfanilic acid will then result by an inter- or intramolecular sulfonation.



An alternative mechanism, in which phenylcarbamylsulfuric acid is converted by N-sulfonation and decarboxylation to phenylsulfamic acid, followed by rearrangement of the latter to sulfanilic acid, is unlikely, since phenylsulfamic acid is known to rearrange in the cold to orthanilic acid, and not to sulfanilic acid.[12]

If the reaction is carried out in oleum, direct sulfonation of the benzene ring by the oleum may be expected to occur to some extent.



The resulting N-sulfosulfanilic acid would undergo rapid hydrolysis to sulfanilic acid and sulfuric acid after dilution of the reaction mixture with water, since sulfamic acids derived from aromatic amines are readily hydrolyzed in acidic solution.[13]

Phenyl isocyanate was also subjected to the action of chlorosulfonic acid in the cold. Sulfanilic acid, identified by conversion to *p*-chlorobenzenesulfonamide, was obtained on pouring the reaction mixture on ice.

Experimental

Ethylsulfamic Acid from Ethyl Isocyanate.—To 70 g. of ice-cooled and mechanically stirred 20% oleum was added dropwise 6.0 g. of ethyl isocyanate. Reaction proceeded with evolution of carbon dioxide. A white solid, which dissolved with bubbling, was observed during the reaction. The ice-bath was removed when about half of the isocyanate had been added; the reaction mixture was slightly lukewarm at completion of the addition. The chilled reaction mixture was poured slowly into 450 ml. of anhydrous ether, which was ice-cooled and shaken. The precipitated ethylsulfamic acid was collected on a sintered-glass funnel and washed with ether. It weighed 8.8 g. (83%) and gave only a very faint test for sulfate ion. The product could be purified by dissolving it in methanol and reprecipitating it by the addition of a relatively large quantity of ether.

The following more complicated purification method was used in an initial experiment but should be resorted to only in cases of heavy sulfate contamination: The product was dissolved in water and more than an equivalent of lead monoxide was added. Excess lead hydroxide and lead sulfate were removed by filtration, and the filtrate, which contained lead ethylsulfamate, was treated with hydrogen sulfide. After removal of the precipitated lead sulfide the solution was distilled at reduced pressure (the bath temperature did not exceed 55°). The residual solid was taken up in methanol, and, on slow evaporation of the solvent, large crystals of ethylsulfamic acid were obtained, m.p. 170–171°.

Anal. Calcd. for $C_2H_7NO_3S$: C, 19.19; H, 5.64; N, 11.19; S, 25.62. Found: C, 19.21; H, 5.58; N, 10.93; S, 25.74.

The use of 5% oleum in the reaction with ethyl isocyanate gave very similar results.

Reaction of Ethyl Isocyanate with Concentrated Sulfuric Acid.—Reaction of 55.2 g. of 95.5–97.0% sulfuric acid with 3.6 g. of ethyl isocyanate occurred readily in the cold with evolution of carbon dioxide and the transitory appearance of a white solid. Complete hydrolysis of the isocyanate to ethylamine acid sulfate requires 0.91 g. of water, but at least 1.65 g. was present in the acid. When the reaction mixture was poured into ether, an oil separated, which consisted chiefly of ethylamine acid sulfate, known to be extremely hygroscopic. The oil was dissolved in water and the ethylsulfamic acid content of the solution was determined by the method described below. The result showed that 13% of the ethyl isocyanate had been converted to ethylsulfamic acid.

Determination of Sulfamic Acid and Alkylsulfamic Acids.—For the determination of sulfamic acid or alkylsulfamic acids in aqueous solution a method was used whose principle is decomposition of the sulfamic acid by means of sodium nitrite and precipitation of the resulting sulfate as barium sulfate, which was weighed.

$$RNH—SO_3H + NaNO_2 \longrightarrow ROH + NaHSO_4 + N_2$$

$$(R = H \text{ or alkyl})$$

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[11] A. W. Hoffmann [*Ann.*, **74**, 13 (1850)] reported the formation of sulfanilic acid by reaction of phenyl isocyanate with concentrated sulfuric acid. This reaction may have been carried out at elevated temperatures, where conversion of aniline acid sulfate to sulfanilic acid occurs, but it is, of course, also possible that the water content was insufficient for hydrolysis of all the isocyanate, in which case, as we have shown, some sulfanilic acid results even in the cold. M. S. Newman and H. L. Gildenhorn [THIS JOURNAL, **70**, 318 (1948)] obtained aniline from a reaction that appears to correspond to our experiment D.

[12] E. Bamberger and J. Kunz, *Ber.*, **30**, 2274 (1897).

[13] C. D. Hurd and N. Kharasch, THIS JOURNAL, **69**, 2113 (1947), and references 15–23 contained therein; W. M. Lauer, M. M. Sprung and C. M. Langkammerer, *ibid.*, **58**, 225 (1936).

For removal of initially present sulfate (the solutions generally contained much sulfuric acid, also ammonium bisulfate or amine acid sulfates), 0.4 *M* barium chloride was added in excess. The precipitation of barium sulfate was carried out at room temperature and the digestion was omitted to avoid any hydrolysis of sulfamic acids; as a result, the filtration proved very difficult, and it was more convenient to siphon off a measured volume of clear supernatant solution, after having allowed the precipitate to settle, and to proceed with that volume. Traces of sulfur dioxide, which were sometimes present as a result of the oxidative effect of oleum or sulfuric acid on organic compounds, were converted to sulfate, prior to the sulfate removal, by the dropwise addition of 3% hydrogen peroxide until a positive test for hydrogen peroxide was obtained (starch–iodide–ammonium molybdate spot test). This treatment was necessary since barium sulfite does not precipitate in a strongly acidic solution and sulfur dioxide would later be oxidized by nitrite,[14] giving rise to sulfate and thus interfering with the sulfamic acid determination.

After the removal of sulfate (and sulfite) the sulfamic acids were decomposed by the addition of 3 *M* sodium nitrite. In the case of the alkylsulfamic acids 6 *N* hydrochloric acid was also added, as this was found to accelerate the decomposition. The precipitated barium sulfate was filtered and weighed. Any heat treatment was again dispensed with to prevent hydrolysis of organic sulfates, if any should be present.

Hexamethylenedisulfamic Acid from Hexamethylenediisocyanate.—To 22.4 g. of 5% oleum was slowly added 5.3 g. of hexamethylenediisocyanate with mechanical stirring and ice-cooling. A white solid formed and carbon dioxide was evolved. After the addition, gas evolution continued sluggishly in the cold, and, in order to carry the reaction to completion, the mixture was gradually heated to 95°, when no more gas was given off. It is possible that reaction of the second isocyanate group requires a higher temperature than that of the first because of the low solubility of the substance formed in the intermediate stage. The reaction mixture, which contained a finely divided solid, was chilled to 0° whereupon considerably more solid precipitated, and was then poured into 300 ml. of ice-cooled ether. The solid, after being filtered by suction on a sintered-glass funnel and washed with ether, weighed 8.6 g.; the theoretical yield is 8.7 g. It contained a little sulfate, probably as sulfuric acid. Solution in methanol and reprecipitation by the addition of ether did not achieve complete removal of sulfate, even when repeated, and the lead oxide method, as described for the purification of ethylsulfamic acid, was therefore used. The white sulfate-free solid which remained after evaporation of the water solution at reduced pressure (the bath temperature never exceeded 45°) melted unsharply at 154–159° after being dried *in vacuo*.

Anal. Calcd. for $C_6H_{16}N_2O_6S_2$: N, 10.14; S, 23.20. Found: N, 9.96; S, 22.95.

Methylsulfamic Acid from 1,3-Dimethylurea.—To 39.0 g. of ice-cooled and mechanically stirred 30% oleum was gradually added 5.0 g. of 1,3-dimethylurea. Evolution of carbon dioxide commenced after removal of the ice-bath and became increasingly vigorous. The temperature rose to about 45° and then fell again as gas evolution slackened. The clear reaction mixture was allowed to stand overnight, chilled and poured slowly into 350 ml. of ether, which was well shaken and ice-cooled. The resulting white solid was filtered by suction on a sintered-glass funnel and washed with ether, until the sulfate test for the washings became very weak. The crude product still contained sulfate, of which it was readily freed by dissolving it in methanol and then reprecipitating it by the addition of a much larger quantity of ether. The purified material weighed 11.5 g. (91%), m.p. 179°.

Anal. Calcd. for CH_5NO_3S: N, 12.61; S, 28.85. Found: N, 12.99; S, 29.20.

If the reaction is performed with too rapid addition of 1,3-dimethylurea and inadequate cooling, methylamine acid sulfate is formed in appreciable amount. This not only decreases the yield of methylsulfamic acid but also complicates its purification, since it then becomes necessary to purify it by the lead oxide method.

Qualitative tests showed that both methylsulfamic acid and ethylsulfamic acid are hydrolyzed considerably more slowly by boiling water than is sulfamic acid.

Reaction of Phenyl Isocyanate with Oleum and Sulfuric Acid. A.—When 22.0 g. of phenyl isocyanate was slowly added to 191 g. of 20% oleum with mechanical stirring and ice-cooling, reaction occurred with carbon dioxide evolution. The reaction mixture was poured on 300 g. of cracked ice, and the resulting white solid was collected by filtration. The filtrate was made alkaline and extracted with ether; the ether extract contained no aniline. The solid, which weighed 23.5 g., was identified as sulfanilic acid by conversion to *p*-chlorobenzenesulfonamide. Analysis showed it to be anhydrous sulfanilic acid; the anhydrous form is known to precipitate from strongly acidic solution.

Anal. Calcd. for $C_6H_7NO_3S$ (anhydrous form): N, 8.09. Calcd. for $C_6H_9NO_4S$ (monohydrate): N, 7.33. Found: N, 8.21, 8.01.

The conversion to *p*-chlorobenzenesulfonamide was accomplished by a modification of the method of Allen and Frame.[15] Diazotized sulfanilic acid was collected by filtration and treated with concentrated hydrochloric acid in the absence of cuprous chloride. Evaporation of the solution led to crude *p*-chlorobenzenesulfonic acid, which was transformed into the acid chloride by excess chlorosulfonic acid in chloroform, the reaction being carried out with cooling. The reaction mixture was allowed to stand several hours at room temperature and was then poured on ice. The chloroform layer was dried over magnesium sulfate and evaporated, leaving *p*-chlorobenzenesulfonyl chloride as a liquid residue. When this was treated with concentrated aqueous ammonia, *p*-chlorobenzenesulfonamide resulted. After recrystallization from xylene, the product melted at 143–144°. Admixture with an authentic sample caused no depression of the melting point.

Application of the same procedure to known orthanilic acid produced *o*-chlorobenzenesulfonamide, m.p. 185–186°.

B.—Practically identical results were obtained when 5% oleum was used in place of 20% oleum.

C.—To an ice-cooled mixture of 73.6 g. of 95.8% sulfuric acid and 76.0 g. of 15% oleum was slowly added 31.1 g. of phenyl isocyanate. Hydrolysis of all the phenyl isocyanate to aniline acid sulfate requires 4.7 g. of water; only 0.5 g. was present. Carbon dioxide was vigorously evolved in the cold. When the reaction mixture was poured on ice, 23.0 g. of sulfanilic acid, identified by conversion to *p*-chlorobenzenesulfonamide, precipitated. The aqueous solution was made alkaline and extracted with ether; distillation of the ether extract yielded 1.2 g. of aniline.

D.—When 100 g. of 95.5–97.0% sulfuric acid was allowed to react with 16.9 g. of phenyl isocyanate in the usual fashion, carbon dioxide was vigorously evolved, but no sulfanilic acid precipitated after the reaction mixture was poured on ice. Small amounts may, however, have been present in solution. Even if the concentration of the sulfuric acid was as high as 97.0%, more than sufficient water was present for hydrolysis of all the isocyanate. Aniline was isolated from the aqueous solution that had been made alkaline.

Acknowledgment.—The author wishes to express his sincere appreciation to Professor H. G. Lindwall for his well-wishing interest in this investigation.

NEW YORK, N. Y.

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[14] *Cf.* J. W. Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. X, Longmans, Green and Co., New York, N. Y., 1930, p. 219.

[15] C. F. H. Allen and G. F. Frame, *J. Org. Chem.*, **7**, 15 (1942); see also R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 217.