Reaction of S-Cyanomethyl O,O-Diethyl Dithiophosphate with Hydrogen Sulfide.—S-Cyanomethyl O,O-diethyl dithiophosphate (50 g., 0.22 mole) was heated in an autoclave at 60° for 20 hours with hydrogen sulfide (7.6 g., 0.22 mole) and triethylamine (1 g., 0.01 mole) in toluene (100 ml.). The reaction mixture was then poured into a shallow dish and the toluene was allowed to evaporate, leaving a slurry of yellow crystalline solid in a brown oil. The crystals were separated by filtration; yield 26.3 g. (46%), m.p. 40–45°. An analytical sample was obtained by recrystallizing the yellow crystals first from toluene, then from 1:3 (by volume) toluene–hexane mixture, giving colorless crystals of the thioamide, m.p. 46–47°. *Anal.* Calcd. for $C_6H_{14}NO_2PS_3$: N, 5.41; S, 37.1. Found: N, 5.51; S, 37.2.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF WITTENBERG COLLEGE AND THE OHIO STATE UNIVERSITY]

Amine Salts of Imidodisulfuric Acid[1]

BY CLAUDE E. BOATMAN AND HARRY H. SISLER[2]

Sixteen amine salts of imidodisulfuric acid have been prepared and characterized. The effect of di-(cyclohexylammonium) imidodisulfate on the surface tension of water has been measured and it was found that there is insufficient lowering of the surface tension of water for the salt to have detergent properties. An explanation has been given for the failure of arylammonium imidodisulfates to be produced by the reaction of arylammonium chloride on trisilver imidodisulfate.

Because of the interesting properties of the metal salts of imidodisulfuric and other nitrogen-sulfur acids[3] and because it was believed that amine salts of this acid might possess detergent properties, it was decided to prepare and investigate a series of substituted ammonium imidodisulfates. No other investigation of these compounds has been reported.

Imidodisulfuric acid forms two series of salts: (a) the so-called "basic" salts with the formula $MN(SO_3M)_2$ and the so-called "neutral" salts with the formula $HN(SO_3)M_2$. Two general methods of preparation of the amine salts were tried in this study: (a) the displacement of ammonia from triammonium imidodisulfate by the amine in liquid ammonia, water or alcohol solution: and (b) the metathesis of the trisilver imidodisulfate with the amine hydrochloride.

$$NH_4N(SO_3NH_4)_2\cdot H_2O + 3RNH_2 \longrightarrow RNH_3N(SO_3H_3NR)_2 + 3NH_3 + H_2O \quad (a)$$

or

$$NH_4N(SO_3NH_4)_2\cdot H_2O + 2RNH_2 \longrightarrow HN(SO_3H_2NR)_2 + 3NH_3 + H_2O$$

$$\underline{AgN(SO_3Ag)_2} + 3RNH_3Cl \longrightarrow RNH_3N(SO_3H_3NR)_2 + \underline{3AgCl} \quad (b)$$

$$\underline{AgN(SO_3Ag)_2} + 3RNH_3Cl \longrightarrow HN(SO_3H_3NR)_2 + \underline{3AgCl} + RNH_2$$

Using method (a) the "neutral" salt was obtained with fifteen out of sixteen amines tried. Octadecylamine yielded the "basic" salt. It was not found possible to obtain a satisfactory preparation of the dimethylammonium or trimethylammonium imidodisulfates.

Dibenzylammonium imidodisulfate was prepared by method (b), but when it was attempted to prepare the *p*-toluidine or aniline salts, the corresponding sulfates were obtained.

Materials.—Triammonium imidodisulfate 1-hydrate was prepared by the method described by Sisler and Audrieth.[4] Trisilver imidodisulfate was prepared from triammonium imidodisulfate and silver nitrate by a modification of the method of Divers and Haga.[5]

Analytical Methods.—The analytical methods used in the characterization of the compounds are given: An ammoniacal solution of the alkylammonium imidodisulfate was treated with a few drops of a 5% barium chloride solution. The imidodisulfate ion produces a flocculent precipitate which is completely soluble in dilute hydrochloric acid. This test serves to distinguish among the sulfamate ion, the imidodisulfate ion and the sulfate ion; the sulfamate ion produces no precipitate, and the precipitate with the sulfate ion is, of course, insoluble in dilute hydrochloric acid.

The quantitative determination of carbon, hydrogen and nitrogen were carried out by micro combustion methods. Many of the nitrogen determinations were checked by the Kjeldahl method.

Sulfur was determined by first hydrolyzing an aqueous solution of the salt with nitrous acid and precipitating the resulting sulfate ion as barium sulfate.

Results.—The preparations and some of the properties of the salts prepared are summarized in Table I.

The failure to obtain arylammonium imidodisulfates by the reaction of trisilver imidodisulfate with the arylammonium chlorides (p-$CH_3C_6H_4NH_3)Cl$ and $(C_6H_5NH_3)Cl$ is worthy of note. Let us presume that the initial reaction is to form silver chloride in accordance with the equation

$$\underline{AgN(SO_3Ag)_2} + 3Cl^- \longrightarrow N(SO_3)_2^{\equiv} + \underline{3AgCl}$$

The third ionization constant of imidodisulfuric acid as determined by Doyle and Davidson[6] is such as to cause immediate reaction in accordance with the equation

$$N(SO_3)_2^{\equiv} + ArNH_3^+ \longrightarrow HN(SO_3)_2^= + ArNH_2$$

We know further that $HN(SO_3)_2^=$ ion is susceptible to acid-catalyzed hydrolysis[2] and so, since sulfate rather than imidodisulfate is found in the solution,

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(3) Audrieth, Sveda, Sisler and Butler, *Chem. Rev.*, **26**, 49 (1940).

(4) Sisler and Audrieth, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., p. 179.

(5) Divers and Haga, *J. Chem. Soc.*, **61**, 974 (1892).

(6) Doyle and Davidson, THIS JOURNAL, **71**, 3491 (1949).

TABLE 1

Ammonium compound	T, g.[a]	Method amine	Solvent ml.	Appearance	Solubility in H₂O	EtOH	Me₂CO	Et₂O
Dimethyl-	5	$MeNH_2$ bubbled into liq. NH_3 2 hrs.		White powder	Sol.	Sl. sol.	...	Insol.
Dicyclohexyl-	10	24 g.	H_2O 20 reflux	White needles	Sol.	Sl. sol.	...	Insol.
Dibenzyl-	Eq. amts. S[b] + Am:HCl in H_2O			White flakes	Sol.	Sl. sol.	...	Insol.
Trioctadecyl-	3.5	Excess	EtOH[e] 100 reflux	White flakes[d]	Insol.	Sl. sol.	Insol.	Insol.
Didibutyl-	5	45 ml.	EtOH 30 reflux	White, hygroscopic	Sol.	Sl. sol.	Sl. sol.	Insol.
Diisopropyl-	5	Excess	EtOH 30 reflux	White needles	Sol.	Sl. sol.	Insol.	Insol.
Dipiperidonium	7.8	10 g.	EtOH 30 reflux	Hygroscopic white flakes	Sol.	Sol.	Insol.	Insol.
Didiethyl-	5	20 ml.	EtOH 30 reflux	White needles	Sol.	Sol.	Insol.	Insol.
Dicyclohexyl-	5	40 ml.	EtOH 110 reflux	White needles	Sol.	Sl. sol.	...	Insol.
Diisobutyl-	5	20 ml.	EtOH 28 reflux	White needles	Sol.	Sl. sol.	Insol.	Insol.
Di-*n*-butyl-	5	25 ml.	EtOH 31 reflux	White	Sol.	Sol.	Insol.	Insol.
Di-*s*-butyl-	5	25 ml.	EtOH 31 reflux	White	Sol.	Sl. sol.	Insol.	Insol.
Diisoamyl-	5	25 ml.	EtOH 30 reflux H_2O 4	White flakes	Sol.	Sl. sol.	Insol.	Insol.
Didodecyl-	2	5 g.	EtOH 200 reflux H_2O 20	White flakes[d]	Insol.	Sl. sol.	Insol.	Insol.
Diethyl-	5	Excess $EtNH_2$ cond. in liq. NH_3		White solid	Sol.	Sl. sol.	...	Insol.

Ammonium compound	M. p., °C.	Yield, %	Analyses, % Carbon Calcd.	Found	Found	Hydrogen Calcd.	Found	Found	Nitrogen Calcd.	Found	Found	Sulfur Calcd.	Found
Dimethyl-	157	80.6	10.03	10.03	10.06	5.45	5.30	5.25	17.60	17.75		26.80	26.84
Dicyclohexyl-	239.2	74.2	38.37	38.09	38.06	7.80	7.38	7.49	11.19	11.65	11.67	16.56	16.80
Dibenzyl-	198.8	32	42.95	42.97	43.28	5.44	5.03	5.17	10.74	10.52	10.77	16.41	16.41
Trioctadecyl-	101.5	95.2	65.82	65.44	65.10	12.26	11.85	11.83	5.45	5.46	5.50	...	...
Dibutyl-	121.5	63.7	44.12	44.20	43.94	9.49	9.26	9.24	9.65	9.36	9.51	14.72	14.72
Diisopropyl-	179–180	64	24.40	24.79	24.56	7.15	7.05	6.83	14.22	14.16	14.41	21.60	21.20
Dipiperidonium	166	93.9	34.70	35.96	35.92	7.20	6.91	6.91	12.19	12.14	12.17	18.39	18.06 18.46
Didiethyl-	144.5	68.9	29.70	29.84	29.73	7.79	7.95	7.77	12.99	13.61	13.27	19.84	19.77
Dicyclohexyl-	201	46	53.60	52.45	52.69	8.97	8.64	8.89	7.82	7.89	7.84	11.90	11.56
Diisobutyl-	225	58.3	29.70	30.25	30.14	7.79	7.71	7.76	12.99	14.09	13.65	19.84	19.71
Di-*n*-butyl	204.5	80	29.70	30.20	29.95	7.79	7.34	7.76	12.99	12.69	12.64	19.84	19.90
Di-*s*-butyl-	163	81.2	29.70	30.07	29.87	7.79	7.65	7.42	12.99	12.66	12.73	19.84	20.02
Diisoamyl-	200 d.	95.6	34.39	34.33	34.11	7.70	8.22	7.96	...	...		18.23	18.24
Didodecyl-	197–199[c]	50	52.61	52.62	52.84	10.38	10.09	10.26	7.67	7.55	7.46	...	...
Diethyl-	199.5	70	17.97	18.14	18.01	6.41	6.07	6.28	15.17	15.34	15.50	24.00	23.99

[a] T = Triammonium imidodisulfate. [b] S = trisilver imidodisulfate. [c] There was an initial softening at about 118–120° indicating a possible transition. [d] Feel like graphite, resistant to acid hydrolysis. [e] EtOH refers to 95% EtOH.

we must conclude that the arylammonium ions used are sufficiently strong acids to catalyze this hydrolysis as

$$HN(SO_3)_2^- + H_2O \xrightarrow{ArNH_3^+} H_2NSO_3^- + HSO_4^-$$

No explanation is, at present, available for the very low solubility of the octadecylamine and dodecylamine salts nor for their resistance to hydrolysis.

Measurement of Surface Tension of Solutions of Di-(cyclohexylammonium) Imidodisulfate.—It was originally thought that some of these salts of high mol. wt. amines might have detergent properties. In order to test this hypothesis the surface tension of several solutions of di-(cyclohexylammonium) imidodisulfate were measured with a du Nöuy tensimeter. The results are shown in Table II.

TABLE II

Molality	Surface tension, dynes/cm.
0.1	60.5
.05	58.0
.025	64.9
.0125	69.2
.00625	68.2
.003125	71.3

Whereas the surface tension of the water is somewhat lowered for the higher concentrations of di-(cyclohexylammonium) imidodisulfate, the effect is insufficient to indicate detergent properties. No qualitative evidence of detergent qualities was observed in aqueous solutions of the salts.

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