[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES, NORTHEASTERN UNIVERSITY]

The Preparation of Some Branched Chain Aliphatic Sulfonic Acids

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Introduction

Most of the work that has been done on the preparation of the anhydrous aliphatic sulfonic acids deals with the straight chain acids. Vivian and Reid[1] present data on the acids containing one to six carbon atoms in the chain, while Noller and Gordon[2] have prepared those containing nine to fourteen carbon atoms in the chain.

The present paper reports data on four branched chain aliphatic sulfonic acids: isopropyl, isobutyl, *t*-butyl and isoamyl. The method used for the preparation of these acids is different from any of those used by the above authors.

TABLE I

Alkyl halide	Used, g.	Satd. soln. of Na_2SO_3, cc.	Time of reflux, days	Yield of pure Na sulfonate, g.	% Eff.
Isopropyl bromide	118.0	250	2	129.1	92.2
Isobutyl bromide	75.6	250	4	65.8	74.6
Isoamyl bromide	36.6	250	1	40.4	95.7
t-Butyl bromide	54.9	250	7	36.4	56.8

TABLE II

	Na sulfonate used, g.	Decompn. time, hr.	Acid obtained, g.	Theo. yield, g.	% Eff.
Isopropyl	29.1	10	9.8	24.6	39.8
Isobutyl	18.7	7	9.2	16.1	57.2
Isoamyl	14.0	5	11.1	12.2	91.1
t-Butyl	20.24	14	7.2	17.5	40.1

Experimental

Preparation of the Sodium Salt of Isoamyl Sulfonic Acid.—36.6 grams of isoamyl bromide was refluxed with 250 cc. of a saturated water solution of C. P. sodium sulfite until the two layers disappeared (about one day). The resulting sodium isoamyl sulfonate was obtained from the solution by evaporating to dryness and purifying by repeated fractional crystallization from a 75% alcohol solution in water, until the salt obtained was practically free from bromide; yield 40.4 g. (95.7%).

Preparation of Anhydrous Isoamyl Sulfonic Acid.—14.01 grams of the dried (110°) and pulverized sodium salt was supended in approximately 250 cc. of absolute ether (distilled over sodium) and a current of dry hydrogen chloride introduced to decompose the sodium salt. The suspended salt changes in appearance from glossy flakes to a granular residue of sodium chloride that tends to settle quickly, thus affording a means of following the decomposition which, in this case, was complete in five hours. The residue was filtered off into a weighed sintered glass crucible and the weight of the dried residue indicated a practically quantitative decomposition. The filtrate was allowed to evaporate (at room temp.) in a vacuum desiccator, leaving a dark oily residue that was soluble in water. The last traces of hydrogen chloride and ether were removed in a drying pistol (under vacuum) using carbon tetrachloride vapors as a source of heat. The material was kept in the pistol for about four hours. In this manner the anhydrous isoamyl sulfonic acid was obtained (free from ether and chloride); yield 11.1 g. (91.0%).

Preparation of *m*-Toluidine Salts.—The *m*-toluidine salts were prepared by adding *m*-toluidine to an ether solution of the sulfonic acid. The precipitated salt was filtered off and purified by recrystallization from warm ether.

Determination of Melting Points.—The melting points of the sulfonic acids were determined by first freezing the acids in a bath of acetone and dry-ice and then allowing the bath to warm up to room temperature and noting the temperature of melting.

The tables summarize the data for the four acids reported.

The physical data obtained with these acids, together with the melting points of the *m*-toluidine salts are given in Table III.

TABLE III

IDENTIFICATION OF THE SULFONIC ACIDS

	B. p. °C.	B. p. Mm.	d^{25}_4	M. p., °C.	n^{20}_D	% Purity by titration	S, % Calcd.	S, % Found	*m*-Toluidine salts M. p., °C.
Isopropyl	159	1.4	1.1877	−37	1.4332	99.7	25.81	25.19	109
Isobutyl	171	1.2	1.1910	−61	1.4364	99.4	23.19	22.86	123
Isoamyl	177	1.5	1.1292	− 5	1.4400	99.8	21.05	20.84	115
t-Butyl	173	1.5	1.2180	−76	1.4315	99.7	23.19	22.40	131

Summary

1. Isopropyl, isobutyl, isoamyl and *t*-butyl sulfonic acids have been prepared in the anhydrous state.

2. The boiling points, melting points, densities, indices of refraction, *m*-toluidine salts and sulfur determinations have been used to characterize the above acids.

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[1] Vivian and Reid, THIS JOURNAL, **57**, 2559 (1935).

[2] Noller and Gordon, *ibid.*, **55**, 1090 (1933).