BENZENESTEAROSULPHONIC ACID AND OTHER SULPHONIC ACIDS CONTAINING THE STEARIC RADICAL.[1]

BY E. TWITCHELL.

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IN connection with some experiments on the action of sulphuric acid on the higher fatty acids I prepared a mixture of benzene and oleic acid and treated this with an excess of concentrated sulphuric acid. I found that a union took place between the benzene and the oleic acid, and at the same time a sulphonic acid was formed.

$$C_6H_6 + C_{18}H_{34}O_2 + H_2SO_4 = C_6H_4 (SO_3H) C_{18}H_{35}O_2 + H_2O.$$

To prepare this benzenestearosulphonic acid, a mixture of oleic acid and benzene is treated with a large excess of concentrated sulphuric acid, avoiding any excessive rise in temperature by cooling the mixture and by adding the acid slowly. After several hours the greater part of the oleic acid will have combined as expressed by the above equation, and the benzenestearosulphonic acid can be separated and freed from the excess of the original components of the mixture and from the results of secondary reactions which have occurred.

A consideration of the action of sulphuric acid on oleic acid will make it plain that these impurities can only be the following:

1. Unacted-on oleic acid;
2. Other fatty matters, such as oxystearic acid and fatty anhydrides, produced by the action of the sulphuric acid and subsequent decomposition of the sulpho compounds;
3. Unacted-on benzene;
4. Stearosulphuric acid, $C_{18}H_{35}O_2.HSO_4$;
5. Benzenesulphonic acid;
6. Sulphuric acid in large excess.

From its mixture with these substances the pure benzenestearosulphonic acid can be separated by virtue of the following properties it possesses, to which I will again refer: It is soluble

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[1] Read before the meeting of the Cincinnati Section, November 15, 1899.

in water, but can be rendered completely insoluble (salted out) by the presence in the water of a little hydrochloric acid or sulphuric acid. It is very stable, not decomposed by boiling with acid solutions. It is insoluble in petroleum ether.

The reaction mixture is treated with water and heated to boiling, whereby the excess of sulphuric acid is diluted and the mass separates into two layers; the lower, a clear aqueous liquid, contains the excess of sulphuric acid and whatever benzenesulphonic acid may have been produced. The upper layer, a viscous oil, contains the benzenestearosulphonic acid with the remaining impurities insoluble in dilute sulphuric acid. If any stearosulphuric acid was present, this will have been decomposed by the heating into sulphuric acid and oxystearic acid and anhydrides. The lower layer is removed and the upper is washed with water containing hydrochloric acid until free from sulphuric acid. By this operation the benzenesulphonic acid is also washed out. The oily layer is now washed a number of times with petroleum ether, which dissolves the oleic acid, the benzene, and the other fatty matters before mentioned, leaving the compound pure except for small quantities of water and hydrochloric acid, and these can easily be removed by drying at 100° C.

The washing with petroleum ether is a tedious process, as some of the decomposition products of oleic acid are rather difficultly soluble in this liquid. For this reason, when quantitative results are not required, it is better to dissolve the partially purified product in ether and shake with water. The aqueous extract, containing most of the benzenestearosulphonic acid, is treated with a little hydrochloric acid, taken up with ether and again extracted with water. On evaporating the aqueous solution the compound is obtained in a pure state.

The composition of the compound was determined by the estimation of the sulphur and carbon and by its acid equivalent, it being a dibasic acid containing an acid hydrogen of the sulphonic radical, which can be exactly titrated by using methyl orange as indicator, and an acid hydrogen of the fatty radical which can be titrated with phenolphthalein as indicator.

The several analyses represent samples prepared at different times.

	Sulphur.	Carbon.	Ratio of sulphur to carbon.	$n/10$ alkali required to combine with SO_3 H group in 1 gram of substance. Methyl orange as indicator. cc.	Additional $n/10$ alkali required to combine with the fatty group. Phenol-phthalein as indicator. cc.
Calculated for $C_{10}H_6.SO_3H.C_{18}H_{35}O_2$.	7.2727	65.45	9.00	22.727	22.727
Found 1				21.56	22.41
" 2	7.12			22.49	22.44
" 3	7.22	64.70	8.96	22.66	23.19

The composition was further fixed by the determination of the weight of benzenestearosulphonic acid obtained from the oleic acid which entered into the reaction. From the molecular weights of the two compounds, 282 parts of oleic acid would yield 440 parts of benzenestearosulphonic acid, or the yield on 100 parts of oleic acid would be 156.03.

An accurately weighed, quantity of oleic acid was mixed with benzene and then treated with an excess of sulphuric acid. After removing the impurities soluble in acidified water, the product was extracted with petroleum ether, the extract weighed and deducted from the amount of oleic acid taken. The difference was that which had combined with benzene and sulphuric acid. The residue insoluble in petroleum ether was also dried and weighed, giving the yield of benzenestearosulphonic acid.

In two experiments 100 parts of oleic acid were found to yield 151.0 and 156.7 parts of benzenestearosulphonic acid.

In this calculation there is an error, in that the petroleum extract does not consist wholly of unaltered oleic acid, but also contains oxystearic acid and anhydrides; but this error is very small considering the small quantity of oleic acid deducted as a correction, and the fact, established by an experiment, that the weight of the fatty matter is only slightly altered on treating oleic acid alone with sulphuric acid and then decomposing by boiling with water.

Benzenestearosulphonic acid resembles in its physical characteristics, and also in many of its chemical ones, the stearosulphuric acid obtained by acting on oleic acid in the cold with concentrated sulphuric acid. At 100° C. the dry compound is a very viscous oil, while at ordinary temperatures it is a sticky, semisolid mass. It, as well as its mono- and di-alkaline salts, is soluble in water in all proportions, yielding colloidal solutions which, on agitating, form a strong lather and are precipitated (salted out) by any strong acid, base or salt. The free acid is perfectly stable in boiling water, even in the presence of mineral acids, differing in this from stearosulphuric acid. On heating to high temperatures with hydrochloric acid it decomposes only very slowly. A small quantity heated in a sealed tube to 170° C. for three and a half hours, had decomposed only to the extent of 15 per cent.

Benzenestearosulphonic acid when fused with caustic potash gives potassium sulphite. Here again it differs from stearosulphuric acid, which when similarly treated yields potassium sulphate.

As shown by the formula, benzenestearosulphonic acid is dibasic, the two acid hydrogens having very different strengths, so that, as has been already pointed out, they can be independently titrated with caustic soda solution, using different indicators.

NAPHTHALENESTEAROSULPHONIC ACID,

$C_{10}H_6\,(SO_3H)\,C_{18}H_{35}O_2$.

This compound is prepared and purified in a manner precisely similar to that used in the preparation of the benzene compound, which it closely resembles, being, however, rather less fluid in its character.

The analysis gives the following results:

	n/10 alkali required to combine with the SO_3H group in one gram of substance. Methyl orange as indicator. cc.	Additional *n*/10 alkali required to combine with the fatty group in 1 gram of substance. Phenolphthalein as indicator. cc.
Calculated for $C_{10}H_6.SO_3H.C_{18}H_{35}O_2$	20.408	20.408
Found 1	20.07	19.97
“ 2	20.28	20.17
“ 3	20.35	20.41

PHENOLSTEAROSULPHONIC ACID,

$C_6H_3OH\,(SO_3H)\,C_{18}H_{35}O_2$.

This compound is prepared like the others and closely resembles them in its character. The following analytical results show that the compound had not been obtained pure.

	n/10 alkali required to combine with the SO_3H group in 1 gram of substance. Methyl orange as indicator. cc.	Additional *n*/10 alkali required to combine with the fatty group in 1 gram of substance. Phenolphthalein as indicator. cc.
Calculated for		
$C_6H_3OH.SO_3H.C_{18}H_{35}O_2$.	21.929	21.929
Found 1	24.47	20.39
" 2	29.75	20.77

These results clearly indicate the presence of a disulphonic acid. This I have not yet attempted to separate, but its quantity can be calculated and allowed for, and if this is done it will be seen that the figures will agree closely with those required by the formula.

In much of the analytical work described in this paper and also in the preparation of some of the compounds, I was kindly assisted by Mr. Wm. Simonson.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 12.]

A NEW INTERRUPTER FOR THE KOHLRAUSCH-OSTWALD CONDUCTIVITY METHOD.

BY J. LIVINGSTON R. MORGAN.

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IN a recent paper[1] I described three useful additions to the Kohlrausch-Ostwald conductivity method. Since then an improvement has been made in the interrupter, the first of the three described, which simplifies it to such an extent that a description of it is deemed advisable. In the apparatus as first proposed, the primary current (2–5 volts from the electric light circuit or from storage cells) was used to charge the vibrating wire as well as to excite the electromagnet. The current from the cell used in the conductivity apparatus was then connected, through the vibrating wire and an extra mercury cup, to a small induction coil (without the breaker), the secondary of the coil being connected to the bridge arrangement in the usual way. The intermittent current produced by the vibrating wire and the mercury cup becomes a rapidly alternating one, such as is desired, in passing through the induction coil.

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[1] This Journal, **22**, 1 (1900).