sary to heat the tube very gradually in order to keep an excess of oxygen in the tube to oxidize all the sulphurous acid. As the sulphuric anhydride does not condense readily, a slow current of gas is requisite, and a combustion requires about two hours and a half.

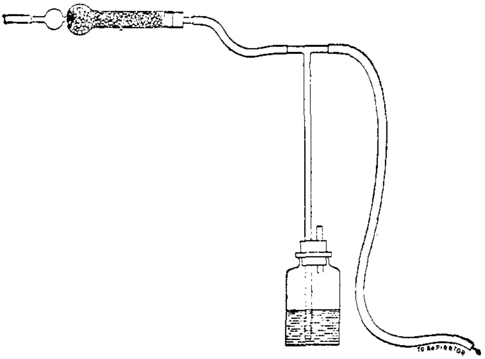

Fig. 4.

At the end of the operation the tube is opened and the plugs and boats removed. The fused mass is readily removed from the boats which, with the cover, are washed and ignited, ready for another combustion. About three determinations can be made in a day. Duplicate determinations agree within 0.01 per cent.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 51.]

THE ELECTROLYTIC OXIDATION OF TOLUENE.

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THE oxidation of toluene by electrolytic oxygen has been tried by Jos. H. James.[1] The products were a minute quantity of liquid, with an ester-like odor, and a resin, together with unaltered toluene.

Our attention has been attracted to this interesting subject and we have repeated the experiments, varying the conditions, of course, with the hope of finally changing the methyl side-chain to carboxyl.

The apparatus used in the electrolysis was similar to that

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[1] This Journal, 21, 890.

generally employed in electrolytic oxidations: a large beaker glass in which stood a porous cup containing the anode liquor, and separating it from the cathode liquor. The porous cup was provided with a rubber stopper, carrying a condenser. The cathode liquor was either a 15 per cent. acid or alkali solution Ordinary alcohol served as solvent for the toluene.

Experiment 1.—The conditions were as follows:

Toluene	10 grams.
Concentrated sulphuric acid	5 cc.
Water	50 cc.
Alcohol	150 cc.
$N.D._{100}$	1.1 A.
Volts	3.7
Temperature	40° C.
Time	7 hours.

As the action progressed the liquor assumed a dark yellow color. Upon examination, at the expiration of the oxidation period, unaltered toluene and a little resin were found present.

Experiment 2.—Acetone was substituted for the alcohol and the conditions were:

Toluene	10 grams.
Concentrated sulphuric acid	5 cc.
Water	75 cc.
Acetone	175 cc.
$N.D._{100}$	1.1 A.
Volts	3.5
Temperature	35°
Time	6 hours.

The anode liquor was carefully searched for new products: toluene and a little resin represented all that could be discovered.

Experiment 3.—An alkaline liquor was substituted for the acid of the two preceding experiments. The conditions were:

Toluene	10 grams.
Alcohol	110 cc.
Water	50 cc.
Sodium carbonate	5 grams.
$N.D._{100}$	0.54 A.
Volts	14
Temperature	40° C.
Time	3 hours.

Carbon dioxide was conducted through the cathode liquor during the experiment. Very little of the toluene was changed. Resin was formed but nothing definite could be extracted from it.

Experiment 4.—A return to an acid solution will be observed in this experiment. Larger quantities of material were also used. The conditions were:

Toluene	55 grams.
Alcohol	190 cc.
Concentrated sulphuric acid	15 cc.
Water	15 cc.
$N.D._{100}$	1.1–1.6 A.
Volts	5–26
Temperature	20°–33° C.
Time	12 hours.

The anode liquor had the odor of benzaldehyde, and apparently that of ethyl benzoate. Three grams of resin were obtained. The fraction, boiling at about 213° C., was saponified with caustic potash, and the solution acidified with hydrochloric acid. The product, which separated, was recrystallized from ether. It melted at 121° C., and showed the characteristic tests of benzoic acid. The oxidation of toluene to benzoic acid had, therefore, really taken place, but in the presence of sulphuric acid and alcohol, ethyl benzoate (b. p. 213°) was formed. The quantity of the latter was not very great. The oxidation was far from being quantitative.

Another fraction, obtained from the anode liquor, boiled at 110°–190°. Phenylhydrazine was added to it. The hydrazone, which separated, was purified, when it melted at 150°, the melting-point of the hydrazone of benzaldehyde.

Additional experiments were made; the products were *resin*, *benzaldehyde*, and *ethyl benzoate*. The tests for the last two bodies were unmistakable. The gases evolved in these oxidations were carbon dioxide and oxygen.

The oxidation of ethyl benzene, under conditions similar to those last mentioned for toluene, gave some resin, ethyl benzoate, benzaldehyde, and a small fraction containing an aldehyde other than the latter, but in such slight amount that it could not be definitely identified.

It is proposed to attempt the electrolytic oxidation of the xylenes and of mesitylene.

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