CLXXXIX.—*The Catalytic Oxidation of Nitro- and Halogen Derivatives of Toluene by Means of Air.*

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BY the oxidation of aromatic hydrocarbons containing a side chain, by means of air in the presence of vanadium compounds, carboxylic acids are obtained as in the wet oxidation with chromic acid or permanganate. For instance, Walter (*J. pr. Chem.*, 1895, **51**, 107) found that benzoic acid, together with benzaldehyde, could be

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* It has been previously shown that a compound containing the $Si{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$ group may be decomposed by alkalis, giving toluenesulphonic acid (Kipping, J., 1908, **93**, 472).

obtained by passing a mixture of toluene vapour and air over heated vanadium pentoxide; and the reaction has more recently received renewed attention with a view to its technical application. The oxidation of alcohols and aldehydes in a similar way is also well known; for instance, Naumann, Moeser, and Lindenbaum (*ibid.*, 1907, **75**, 149) prepared acetic acid and acetaldehyde by leading a mixture of ethyl alcohol vapour and air over vanadium pentoxide in a combustion tube.

It was considered of interest to ascertain whether the method could be extended to substances other than oxy-compounds and hydrocarbons, and, in the work here described, the reaction has been applied to aromatic derivatives containing, in addition to a methyl group, a halogen atom or a nitro-group attached to the nucleus. It was found that the side chain could be oxidised to carboxyl, as in the wet oxidation method, without the splitting off of the halogen or the nitro-group, a fair yield of the corresponding acid being obtained.

EXPERIMENTAL.

The catalyst employed consisted of granular tin vanadate, which was contained in a glass U-tube immersed in a bath of fused sodium and potassium nitrates, the volume of the catalyst space being 10 c.c. in each case. Air, from a reservoir under pressure, was led, at a rate measured by a velocity meter of the constricted tube type, through a small wash-bottle, which contained the substance to be oxidised and acted as a carburettor, and thence through the catalyst tube. The products of oxidation passed into a small tubular receiver, which could be detached for weighing before and after each experiment. The rate of passage of the substance undergoing oxidation was regulated by maintaining the carburettor at a suitable temperature, which was determined by means of preliminary experiments for each substance tested.

Oxidation of p-*Nitrotoluene.*—For the 10 c.c. of catalyst used, a suitable rate of passage of air through the small bubbling tube containing the *p*-nitrotoluene was found to be 10 litres per hour, the carburettor temperature being 80—100°. The product consisted of *p*-nitrobenzoic acid, unchanged *p*-nitrotoluene, and some *p*-nitrobenzaldehyde, and it was sufficiently free from acidic decomposition products—for instance, oxides or oxy-acids of nitrogen—to render possible the determination of the *p*-nitrobenzoic acid content by simple titration. From a filtered alkaline solution of the product, by acidification with hydrochloric acid, pure *p*-nitrobenzoic acid (m. p. 237°; *M*, 167) was obtained.

In order to determine the most suitable catalyst temperature, a series of experiments with a uniform carburettor temperature of

93° was carried out. Under these conditions, with the air at a rate of 10 litres per hour, about 0·3 g. of nitrotoluene passed the 10 c.c. of catalyst per hour. The percentage yields (*a*) of *p*-nitrobenzoic acid are in Table I, *t* denoting the temperature of the catalyst.

TABLE I.

t	260°	270°	275°	280°	285°	290°	310°
a	8·4	14·0	15·0	14·0	16·0	15·6	11·2

It will be seen that the reaction begins below 260°, and that for catalyst temperatures from 270° to 300° the yield remained fairly constant at 14—16%.

The oxidation of *o*-nitrotoluene was also examined; but much decomposition occurred at catalyst temperatures sufficient to cause oxidation, and little or none of the corresponding acid could be isolated.

Oxidation of o-*Bromotoluene.*—Under similar conditions to those used for *p*-nitrotoluene, the following results were obtained with a carburettor temperature of 60°.

TABLE II.

t	255°	265°	275°	285°	290°	295°	300°	305°
a	7·4	12·1	13·7	21·0	24·3	14·0	7·8	6·3

Some hydrogen bromide was also formed by decomposition; but, since *o*-bromobenzoic acid is not very soluble in cold water, it was found possible to correct for this mineral acid by titrating the mixture with standard alkali first in the cold and then boiling, the difference between the two end-points representing bromobenzoic acid. The acid was also isolated in a pure condition and identified. Some *p*-bromobenzoic acid was apparently also present, due probably to *p*-bromotoluene in the material taken for oxidation.

Oxidation of o-*Chlorotoluene.*—*o*-Chlorobenzoic acid was in some experiments obtained in a pure condition, free from water, hydrochloric acid, and unchanged chlorotoluene, by adjusting the temperature of the receiver, the crude reaction product having m. p. 135° and a titration value of approximately 156; but in most cases unchanged chlorotoluene was also condensed.

The percentage yields (*a*) of chlorobenzoic acid obtained in a series of tests, with the carburettor temperature maintained at 60°, are tabulated below.

TABLE III.

t	260°	275°	285°	287°	293°
a	4·9	7·4	13·0	13·8	12·6

In cases in which the product in the receiver was not free from unchanged raw material, the pure chloro-acid could readily be isolated by solution in sodium hydroxide and precipitation with hydrochloric acid.

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