[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

OXIDATIONS IN THE BENZENE SERIES BY GASEOUS OXYGEN

I. OXIDATION OF METHYLBENZENES

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The fact that methylbenzenes are oxidized by gaseous oxygen in the presence of moisture and in direct sunlight has been reported by Ciamician and Silber[1] who obtained under these conditions benzoic acid from toluene, the three toluic acids from the corresponding xylenes and cumic acid from cymene. In each case traces of aldehydes were obtained but the quantities were too small for identification. Suida[2] found later that these hydrocarbons, in the presence of water, when exposed to actinic or ultraviolet rays, were oxidized to acids and that part of the oxygen absorbed was activated.

A series of investigations carried out by the writer shows that oxidation of the methylbenzenes by gaseous oxygen also occurs under quite different conditions from those employed by the above-mentioned investigators. The results obtained throw much more light on the course of these reactions. In these experiments dry hydrocarbons were used and oxygen was bubbled through them at elevated temperatures. All oxidations were carried out in dim, diffused light. The hydrocarbons were placed in bulbs sealed to the ends of tall air condensers and into these were inserted small tubes which delivered the oxygen. The temperatures employed were chiefly in the neighborhood of 100°.

In each case the main identifiable product was an aldehyde, and the product occurring in smaller quantity the corresponding acid. This is rather a remarkable fact in view of the reputed ease with which aromatic aldehydes are oxidized. In addition to these two identifiable products there always occurred an appreciable amount of reddish-brown gum, or solid resin, presumably from condensations of the aldehydes.

Although the possibility of alcohol formation as an intermediate stage has not been excluded, in no case examined has the presence of an alcohol been detected in the products. The question of their formation is one which is being further investigated.

Apparently, then, the first recognizable stage in these oxidations results in the formation of aldehydes, and these are later oxidized to the corresponding acids. The "activated" oxygen in Suida's investigations[2] might well be accounted for by the auto-oxidation of the aldehydes[3] although this does not preclude the possibility of intermediate peroxides being formed in earlier stages.

[1] Ciamician and Silber, *Ber.*, **45**, 38 (1912).

[2] Suida, *Monatsh.*, **33**, 1255 (1912).

[3] Jorissen, *Chem. Centr.*, **67**, II, 964 (1896).

The proportions of aldehyde and acid in the products will be governed by the speeds of the two reactions.

$$RCH_3 + O_2 \longrightarrow RCHO + H_2O \qquad (1)$$

and

$$2RCHO + O_2 \longrightarrow 2RCOOH \qquad (2)$$

The great difference in concentrations of hydrocarbon and aldehyde in the early stages of oxidation will, of course, favor the first reaction but the fact that Ciamician and Silber[1] obtained acids almost exclusively, seems to indicate that an increase of temperature also favors Reaction 1.

Ease of oxidation increases with increasing number of methyl groups, toluene being scarcely affected at 100° and durene being oxidized relatively rapidly. In no case was any product found that would indicate oxidation of more than one methyl group.

The Inhibitory Action of Water.—In carrying out oxidations of this type under water condensers, whereby the water formed by the reaction was caused to accumulate, it was noticed that the speed of reaction diminished. To test further the effect of water on the reactions, mixtures of hydrocarbon and water were treated, at the boiling point, with oxygen. In the cases of *m*-xylene and mesitylene it was found that oxidation was almost entirely inhibited, no aldehyde or acid being detected in either case. This remarkable effect seems to find its simplest explanation in the assumption that, somewhere in the series of reactions that take place, the elements of water are eliminated, and that this reaction is reversible. The study of the action of water is being continued in this Laboratory.

Experimental Part

For the purpose of purification, the hydrocarbons were shaken several times with small amounts of concd. sulfuric acid, washed with sodium hydroxide solution and water and finally fractionated over sodium. Except where specified no attempt was made to dry the oxygen.

The general method of isolating aldehyde and acid was the following. The crude reaction product was distilled under reduced pressure until the boiling point began to rise noticeably, and then the last fraction was distilled into a fresh receiver. This fraction usually contained some acid as well as the aldehyde. Removal of the aldehyde was effected by shaking the mixture with a saturated solution of sodium bisulfite and allowing it to stand for 12 hours or more, when the addition compound was filtered dry and washed several times with ether. The residue of the liquid from which the aldehyde was removed was then washed with water, combined with non-volatile residue from the distillation and treated with sodium bicarbonate solution. Addition of dil. sulfuric acid to this solution yielded the crude acid. Sodium bicarbonate was found to be more satisfactory than sodium carbonate as the latter dissolved or peptized a considerable amount of gummy material. The amount of aldehyde was calculated from the weight of sodium bisulfite compound while the crude acid was weighed directly.

Toluene.—Oxygen bubbled through 100 g. of toluene for 48 days at 100° gave a trace of material which reduced Tollens' reagent, presumably indicating the presence of aldehyde, no acid and a slight residue of gum.

***m*-Xylene.**—Ninety g. of *m*-xylene when treated with oxygen for 30 days at 100° gave 1.9 g. of toluic aldehyde, identified as the phenylhydrazone, m. p. 88–9°,[4] and 0.98 g. of toluic acid, m. p. 110–110.5°.[5]

Action of Water.—One hundred g. of *m*-xylene and 25 cc. of water treated with oxygen for 60 days at the boiling point gave no aldehyde, no acid and only a trace of non-volatile residue.

Mesitylene.—Twenty g. of mesitylene when treated with oxygen for 24 days at 100° gave 0.55 g. of 1,3-dimethyl-benzaldehyde (5), identified as semicarbazone, m. p. 201.5°,[6] and 0.27 g. of mesitylenic acid, m. p. 165.5–166°.[7]

Action of Water.—Fifteen g. of mesitylene and 20 g. of water treated with oxygen for 21 days gave no aldehyde, no acid and a trace of residue.

Durene.—Seventeen g. at 100° when treated with oxygen for nine days gave 0.99 g. of durylic aldehyde identified as semicarbazone, m. p. 241.5°,[8] and 0.84 g. of durylic acid, m. p. 148–149°.[8]

Cymene.—One hundred g. at 85° for 14 days gave 1.23 g. of cumic aldehyde, identified as the semicarbazone, m. p. 201.5°,[9] and 0.81 g. of cumic acid, m. p. 116–116.5°.[10,11]

Summary

1. The oxidation of methylbenzenes by gaseous oxygen has been studied and it has been found that the oxidation proceeds in two recognizable stages, (1) oxidation of hydrocarbon to aldehyde and (2) oxidation of aldehyde to acid.

2. Aldehydes have been identified for the first time in the oxidation of these hydrocarbons by gaseous oxygen.

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[4] Rudolph, *Ann.*, **248,** 100 (1888); m. p., 87–88.5°.

[5] Jacobsen, *Ber.*, **14,** 2349 (1881); m. p., 110.5°.

[6] Law and Perkin, *Trans. Faraday Soc.*, I Reprint, **1–11** (1904); m. p., 201.5°.

[7] Geuther and Frölich, *Ann.*, **202,** 310 (1880); m. p., 166°.

[8] Auwers and Köckritz, *Ann.*, **352,** 310 (1907); m. p., 243–4°.

[9] Walbaum and Hüthig, *J. prakt. chem.*, [2] **66,** 55 (1902); m. p., 201–2°.

[10] Jacobsen, *Ber.*, **12,** 1516 (1879); m. p., 116–7°.

[11] There was also obtained from cymene a quantity of *p*-tolylmethyl ketone, the production of which will be discussed in a later paper.