

On Catalyser in Electrolytic Oxidation of Benzene. (Part 1)

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Concerning the study on electrolytic oxidation of benzene several reports have already been presented. Referring to these reports the following investigation was carried out. The variation of the current efficiency and the kinds of the reaction products have been found when benzene has been electrolytically oxidized in presence of a small quantity of the heavy metallic compounds as the catalyser on anode solution. In addition, the influence of the various catalysers upon the electrolytic oxidation of a series of polycyclic aromatic hydrocarbons, such as benzene, naphthalene and anthracene etc., and their mechanism in the catalytic oxidation were studied.

The apparatus used in our experiment was the reformed one which has generally been used in such an experiment. The gas evolved at anode was gathered in gas buret through a condenser and alkali bottle, its volume being measured. It was a remaining oxygen which was not exhausted in the electrolytic oxidation and it did not contain carbon dioxide (CO_2), and unsaturated hydrocarbons (C_nH_{2n} and $\text{C}_n\text{H}_{2n-2}$), as the decomposition products under the conditions of electrolysis written below. Since hydrogen which contained a very small quantity of sulphurous anhydride (SO_2), evolved at cathode, it was suctioned by aspirator so that the excitation might be avoided.

Of course the anode electrolyte was been emulsifying by motor all the time. As anode the porous lead dioxide (PbO_2), was used. (Lead anode was coated with PbO_2 by electrolysis in H_2SO_4 solution of sp. gr. 1.6 before the present experiment)

As anode solution about 130 c.c. of 4% sodium sulphate solution dissolving 20 g. of purified benzene (C_6H_6), and mixed with a small quantity of catalyser for

inspecting its effect shown in Table 1, was used and it was electrolyzed with D_A . 3 amperes at 4~6 volts keeping the temperature below 15°C . This condition was the best one among the various method adopted by the above investigators concerning the electrolytic preparation of benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$) from benzene, and it was most appropriate

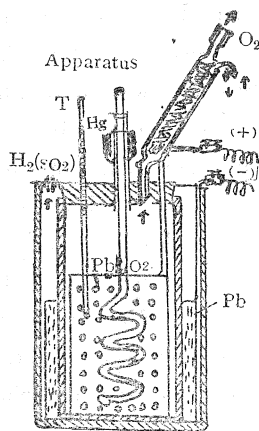


Fig. 1

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Table 1 Catalystser

| | Compound | Conc. % | A. H. | Current efficiency % |
|----|--|------------|-------|-------------------------|
| As | $\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ | 0.1 | 21.0 | 9.98 |
| Cd | $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$ | ∕ | ∕ | 80.8 |
| Ce | $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ | ∕ | ∕ | 57.9 |
| Co | $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ | ∕ | ∕ | 22.0 |
| Cr | $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ | ∕ | ∕ | 28.5 |
| Fe | $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | ∕ | ∕ | 20.0 |
| Mn | $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ | ∕ | ∕ | 18.5 |
| Mo | $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ | ∕ | ∕ | 43.7 |
| S | H_2SO_4 | ∕ | ∕ | 21.6 |
| Se | H_2SeO_3 | ∕ | ∕ | 82.8 |
| Te | H_2TeO_3 | ∕ | ∕ | 75.7 |
| Ti | $\text{Ti}_2(\text{SO}_4)_3$ | ∕ | ∕ | 17.1 |
| V | VCl_4 | ∕ | ∕ | 31.0 |
| W | Na_2WO_4 | ∕ | ∕ | 76.5 |
| Zn | $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ | ∕ | ∕ | 55.0 |
| — | — | — | ∕ | 21.6 |

for our standard condition.

In the electrolytic oxidation of benzene, the first product formed is probably phenol ($\text{C}_6\text{H}_5\text{OH}$), but this cannot be isolated, because it is a better depolarizer than benzene, due to its greater solubility in the electrolyte. By further oxidation quinol forms the relatively stable p-benzoquinone ($\text{O}=\text{C}_6\text{H}_4=\text{O}$), which is the main product of the reaction together with some maleic acid ($\text{HOOC H C}=\text{C H COOH}$), when a diaphragm is used. Mr. Kempf oxidized a solution of benzene in 10% sulphuric acid with a current of 4~5 amperes. The by-products were maleic, formic, racemic and tartaric acid, carbon oxide and carbon dioxide with sometimes maleglycidic acid. However, we cannot

find those compounds in our experiments of conditions mentioned above.

On the mechanism of electrolytic oxidation and the catalysis, Mr. Kempf has led to the conclusion that in all electrochemical oxidation process, the actual oxidizing agent is a metallic oxide formed by the action of nascent oxygen on the electrode. But this is hardly in accordance with the work of Mr. Fichter and Mr. Stocker, who were able to obtain the small products using either platinum, lead or graphite electrodes in a dilute sulphuric acid which is emulsified with benzene. The results show that the use of a lead electrode increases the amount of quinol and quinone formed, but qualitatively the results are the small with all the electrodes. It may be that the lead dioxide formed changes the equilibrium in favor of the quinol and quinone, as the primary oxidation products of benzene. Above reports are concerning the catalytic action of electrode itself. In the case of the added catalystser in solution, peroxide or peracid which formed intermediately may be supposable as the actual catalystser. Mr. Elbs, Mr. Inoue and Mr. Shikata considered that the electrochemical oxidation is due to the intermediate peracid, therefore we will explain the mechanism of catalytic oxidation based on our experiment in the next report.

The following data show the current efficiency and the catalytic action of those compounds, and are discussed in relation to the periodic system of elements. Since benzene is almost oxidized to p-quinone only and not to the fatty acids such as maleic and oxalic acid under the above electrolytic condition, it is adequate to regard the oxidation efficiency as the current efficiency. It is known that, as Mr. Fujioka and Mr. Kamio have pointed

out, the impurities, especially thiophene in benzene, make the yield of quinone to decrease.

The volume of oxygen which was evolved at the electrolysis of anode solution mixed with 0.1% catalyser were reduced to the values at 0°C and under 1 atmosphere.

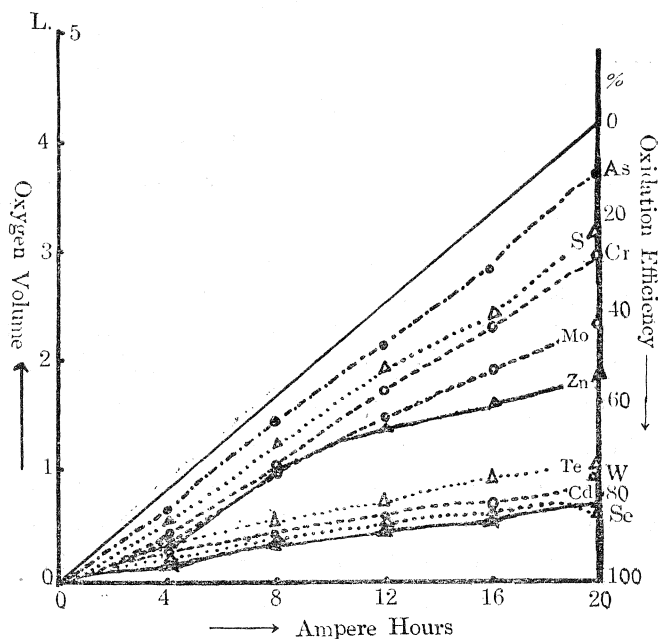


Fig. 2

Fig. 2 is a plot of the oxidation efficiency calculated from these values versus the electric quantity, where 1 F equals 26.8 amp. hours. From this graph it is found that the addition of catalyser to the electrolyte changes the oxidation efficiency remarkably. The thick line indicates the volumes of oxygen evolved by each electric quantities. The dotted line gives the corresponding volumes of oxygen when 4% Na_2SO_4 solution is electrolyzed without any catalyser under the same condition as described above. The concentration of catalyser may be given as $X = \frac{na}{mv} \cdot 100\%$, where n expresses the weight of compound used as catalyser; a , the atomic weight of the element in it; v , the total volume of the anode solution and m , the molecular weight of the compound. For example, when 0.46g. of sulphuric acid is added in 150 c.c. of the anode solution, it is called as 0.1% solution of S. As catalyser the acids and sulphates are generally used in order to avoid the influence of other ions as well as possible. The dotted line shows the result concerning the elements belonged to the B of group VI in periodic table, which is so called that of oxygen. And lines show ones concerning those of the A of group VI, and of the B of group II respectively. However, the A of group II which is so called alkali earth elements, can not be used as catalyser owing to the little solubility of its sulphate against water.

In any groups described above, the catalytic action increases with the period numbers, but Se in the fourth period and Cd in the fifth period show the maximum value above all. The B of group V, especially As, greatly decreases the oxidation efficiency. It is thought that the above phenomena are revealed owing to the formation of coating by As_2O_3 or As_2O_5 on the electrode which has the high electric resistance.

Fig. 3 shows the catalytic oxidation power of transition elements. It is found in this graph that the higher the atomic number and period number grow, the greater the action of catalytic oxidation becomes. Such a tendency is shown a little in the fourth period which starts from 21 Sc. But Cr does not distinctly agree with this principle, because it belongs to the group VI. In the fifth period, Mo and in the sixth period, 58 Ce and 74 W, became the object as catalyser in our experiment. According to the result, the catalytic action increases by the turn of Mo, Ce and W.

Fig. 4 shows the relation between the concentration of catalyser and the current efficiency. In general, raising the concentration brings the increase of oxidation efficiency, but when concentration becomes too high, it is unfavourable for the catalytic oxidation. Because the catalyser has its own solubility against the electrolyte and the oxidation of the catalyser itself consumes the large amount of oxygen.

As described above, the promoting action of oxidation by catalyser is classified into two forms: one is that peracid is produced by the oxidation of catalyser as the intermediate product and another is that higher oxide is formed. The action of elements in the group VI belongs to the former, and that of Ce and Cd belongs to the latter.

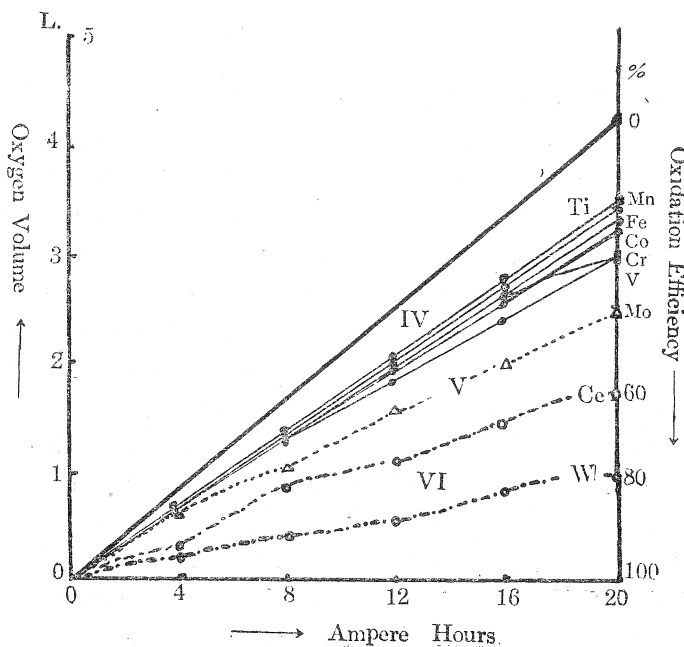


Fig. 3

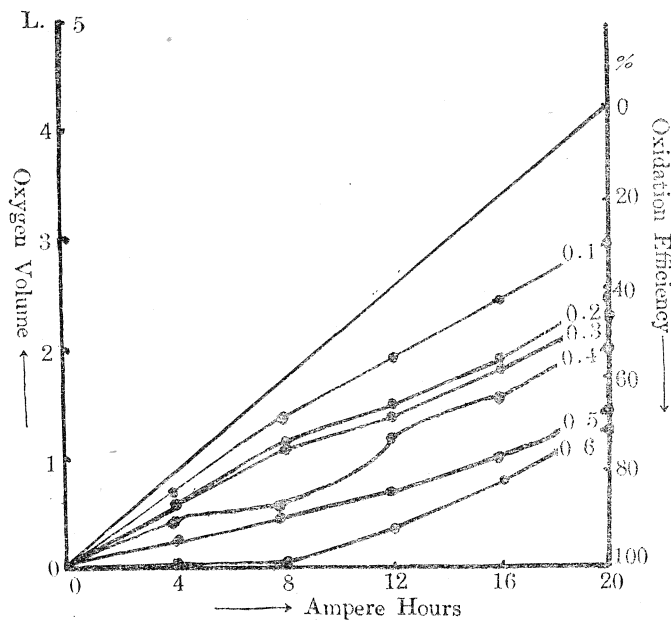


Fig. 4

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