Notes

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Hiroya Tanabe: Studies on the Periodic Acid Oxidation of N-Glycosides. XV. Studies on the Periodic Acid Oxidation of Anilines. (8). A Consideration on the Mechanism of Periodic Acid Oxidation of α -Glycols.

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In the preceding paper¹⁾ of this series, it was shown that methyl methacrylate was polymerized and benzoic acid was oxidized to salicylic acid in the oxidation reaction solution of aniline with periodic acid, proving completely that this oxidation of aniline proceeded as a free radical reaction.

In the present work, examinations were made on one of the hypotheses for the reaction mechanism of α -glycol split with periodic acid, mainly for this reaction periodic acid is applied in organic chemistry, and this mechanism was compared with that of aniline oxidation with the same oxidant.

As the mechanism of periodic acid oxidation of α -glycol, four hypotheses have been suggested up to the present by Price, et al., Duke, Waters, Among these, the hypotheses of Price and Duke are characteristic in the formation of intermediate cyclic compounds containing iodine and they presumed the reaction to be ionic, but according to Waters and Dewar this oxidation reaction is considered to consist of radical reaction, and Waters presumed the mechanism to be typical of radical reaction, free radicals being produced as intermediates, but Dewar presumed it to be a bimolecular reaction, no free radical being produced.

Of late, Duke's hypothesis has generally been accepted and its kinetics are being studied in detail, 60 but suggestions of Waters and Dewar are completely neglected and no studies on these hypotheses have been reported up to the present.

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¹⁾ Part XIV: H. Tanabe: This Bulletin, 7, 316(1959).

²⁾ C. C. Price, et al.: J. Am. Chem. Soc., 60, 2726(1938); 64, 552(1942).

³⁾ F. R. Duke: *Ibid.*, **69**, 3054(1947); **76**, 3803(1954).

⁴⁾ W. A. Waters: Trans. Faraday Soc., 42, 185(1946).

⁵⁾ M. J. S. Dewar: "The Electronic Theory of Organic Chemistry," 276. Clarendon Press.

⁶⁾ J. E. Taylor: J. Am. Chem. Soc., 75, 3912(1953); 77, 2656(1955); G. J. Buist, et al.: J. Chem. Soc., 1954, 1406.

Among these four hypotheses, it seems to be most simple to ascertain the theory of Waters, because, if the periodic acid oxidation reaction of α -glycol proceeds according to his theory, methyl methacrylate should be polymerized in this oxidation reaction solution just as in that of aniline with the same oxidant.

In the present series of experiments, methyl methacrylate was added to the periodic acid oxidation solution of α -glycol, varying the concentration of oxidation systems over a wide range and observing the reaction mixtures for one week. Deposition of polymethyl methacrylate) was not observed in spite of strict exclusion of inhibitors, proving that Waters' hypothesis was consequently not reasonable.

Thus it was shown that the mechanisms of the periodic acid oxidation reactions of aniline and of α -glycol are different from each other.

Experimental

Reaction of Methyl Methacrylate in the Reaction Solution of Periodic Acid Oxidation of α -Glycol—Purification of methyl methacrylate, water, and NaIO₄, and cleaning of the apparatus were carried out as reported in the preceding paper¹⁾ of this series.

In the main tube of a Thumberg tube, $0.5\,\mathrm{g}$. NaIO₄ was dissolved in 10 cc. of water and to this solution, $0.1\,\mathrm{cc}$. of methyl methacrylate was added. In the side tube, a solution of $0.1\,\mathrm{cc}$. of ethylene glycol and $0.1\,\mathrm{cc}$. of methyl methacrylate dissolved in 10 cc. of water was placed. Both tubes were connected and evacuated under cooling until vigorous boiling set in and then O_2 -free N_2 gas was introduced. This procedure was repeated three times and the tube wss finally evacuated and left in the dark at room temperature.

Other than the concentration of the reaction solution mentioned above (about $10^{-1}M$), examinations were also made over the range of concentrations of 10^{-2} to $10^{-5}M$ solutions of the oxidation systems and reaction solutions were observed over 1 week but the polymer did not appear at all in every case.

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Summary

The hypothesis suggested by Waters on the mechanism of the decomposition of α -gly-col with periodic acid was examined and from the fact that in the periodic acid oxidation solutions of α -glycol the formation of a free radical was not observed, this hypothesis was proved not to be reasonable and consequently it was shown that the periodic acid oxidation mechanisms of aniline and of α -glycol were different from each other.

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