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Antioxidants and the Autoxidation of Fats v. Mode of Action of Anti- and Pro-Oxidants

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BASIC STRENGTH OF KETIMINES BY THE USE OF
THE GLASS ELECTRODE

J. B. CULBERTSON AND DEWALT YOUNG

The relative strengths of the ketimines as organic nitrogen bases has been considered one of the prime factors affecting the stability of the ketimine salts toward hydrolysis to ketones. A measurement of the hydrogen (hydronium) ion concentration of ketimine salts (hydrochlorides) furnishes the information necessary for the calculation of these basic strengths.

Four years ago a report ¹ was made on a portion of these measurements by the use of the quinhydrone electrode. Other results had been obtained with the hydrogen electrode and by colorimetric methods. Due no doubt to catalytic hydrogenation in the case of the hydrogen electrodes and to reactions with quinhydrone and with indicators, these previous figures on ketimine basic strengths have been considered open to some doubt as to accuracy, and were so reported.

The advent of the glass electrode has suggested a tool for these determinations free from the above sources of error. With it measurements have been made upon phenolic ketimines, which caused the greatest trouble in the previous work, and stable potentials quite commensurate with the hydrolytic stability of their ketimine salts have been obtained. The results on a number of other ketimines, not previously described, are also given in this report.

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ANTIOXIDANTS AND THE AUTOXIDATION OF FATS
V. MODE OF ACTION OF ANTI- AND
PRO-OXIDANTS

L. A. HAMILTON AND H. S. OLCOTT

Experiments on the oxidation of purified methyl oleate support the view that its induction period, and probably that of natural oils, is due to the presence of inhibitors and that purified unsaturated compounds have no induction period, other than the time required for gaseous oxygen to diffuse into the liquid.

Experiments with antioxidants indicate that phenolic inhibitors

¹ Culbertson, Bieber and Zavodsky. Iowa Acad. Science, 39:177.

and inhibitols cause no change subsequent to the end of the induction period, that they exert their effect solely by inhibiting the formation of the initial active moloxide, and that they are entirely destroyed before the start of rapid oxidation which characterizes the end of the induction period.

The mode of action of several different pro-oxidants is analyzed. Perbenzoic acid, and presumably other peracids, and Cu oleate decrease the induction period by virtue of their destruction of natural inhibitors.

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ORIENTATION STUDIES IN THE DIBENZOFURAN SERIES

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2-Hydroxydibenzofuran on bromination gives 1-bromo-2-hydroxydibenzofuran (m.p., 123.5°) and 2-hydroxy-3-bromo-dibenzofuran (m.p., 143-144°). The corresponding products but in a different ratio are obtained by the bromination of 2-methoxydibenzofuran. The allyl ether of 2-hydroxydibenzofuran rearranges to 1-allyl-2-hydroxydibenzofuran (m.p., 82.5°-83°), the methyl ether of which melts at 68°. Also, 2-hydroxydibenzofuran and benzenediazonium chloride couple to give 1-phenylazo-2-hydroxydibenzofuran. The 3-hydroxydibenzofuran couples to give 2-phenylazo-3-hydroxydibenzofuran (m.p., 166°), the structure of which was established by conversion to 2-bromo-3-hydroxydibenzofuran (m.p., 166°), the structure of which was established by conversion to 2-bromo-3-hydroxydibenzofuran (m.p., 115°-116°).

In bromination of the 4-hydroxy-, 4-methoxy- and 4-acetaminodibenzofuran bromine goes to the 1-position; and in coupling of the 4-hydroxy compound with benzenediazonium chloride the phenylazo group also goes to the 1-position (m.p., 175°). The Grignard reagent of 1-bromodibenzofuran (m.p., 67°-67.5°) (obtained by deamination of the 1-bromo-4-amino compound, m.p., 119°-120°) gives on oxidation 1-hydroxydibenzofuran (m.p., 140.5°) and on carbonation the dibenzofuran-1-carboxylic acid (m.p., 232°). Methyl dibenzofuran-1-carboxylate (m.p., 63°) on nitration gives methyl 7-nitro-dibenzofuran-1-carboxylate (m.p., 216°).