A Note on the Accelerating Action of Biacetyl and Benzil on the Autoxidation of Cyclohexene.

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In view of the recent report by T. Kubota

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and Y. Shimazu[2] that ergosterol reacts with oxygen in the presence of biacetyl in xylene at 30°, we wish to place on record our findings obtained in the course of an investigation of the autoxidation of cyclohexene which was carried out in 1948 to 1949 and the results of which have remained unpublished.

It has frequently been observed that biacetyl accelerates the deterioration of butter and margarine[3] to which it has been added as a flavouring, and promotes the peroxide formation[4] in fat. There seemed to be no doubt that biacetyl played the role of an autoxidation catalyst. The following experiments demonstrated that biacetyl and benzil, probably 1, 2-diketones as a class, act as a catalyst in the autoxidation of cyclohexene. Purified cyclohexene freshly distilled before use was shaken in an atmosphere of 760 to 780 mm. Hg of oxygen in a Warburg manometer in the dark at 27°. After the lapse of an induction period ranging from 8 to 10 hours the oxygen uptake became gradually noticeable (about 0.1 cc. of oxygen per cc. of cyclohexene in the course of 20 hours). When 7.0 mg. of biacetyl per cc. of cyclohexene was present, no induction period was observed and the oxygen uptake began immediately with a rate of 0.12 cc. per hour per cc. of cyclohexene, a further absorption ensuing with a characteristic behaviour of autocatalysis. Biacetyl itself absorbed oxygen at a rate of about 0.0025 cc. per hour per cc. of biacetyl after an induction period of 9 hours. Benzil (20.9 mg. per cc. of cyclohexene) also was found to exert a similar, though somewhat weaker, accelerating effect, the initial rate of oxygen uptake being 0.04 cc. per hour per cc. of cyclohexene. The cyclohexene used in the above experiments could not be considered as quite free from any traces of the peroxide; for, though a freshly distilled sample gave hardly perceptible coloration with ferrous ammonium sulfate and ammonium thiocyanate solutions, 1 cc. of it, added to 5 cc. of acetic acid, 1 g. of potassium iodide and 50 cc. of water and, after 20 minutes, the liberated iodine titrated, consumed 0.08 to 0.15 cc. of N/20 sodium thiosulfate solution.

Incidentally, the addition of 43.2 mg. of bromanil per cc. of cyclohexene inhibited the absorption of oxygen by cyclohexene, the induction period being prolonged to more than 60 hours. This observation may be of interest in view of the action of chloranil as an effective chain transfer agent in the polymerization of styrene.[5]

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(2) T. Kubota and Y. Shimazu, *Proc. Japan Acad.*, **28**, 80 (1952).

(3) N. King, *Chem. Abstr.*, **25**, 4943 (1931). T. Tapernaux, ibid., **27**, 785 (1933). B. W. Hammer, ibid., **29**, 6658 (1935). H. Schmallfuss and U. Stadie, ibid., **39**, 3370 (1945).

(4) W. Ritter and T. Nussbaumer, ibid., **33**, 9467 (1939). Recently A. Reinart (ibid., **44**, 2664 (1950)) reported that biacetyl also has a deleterious effect on the carotene and bixin.

(5) J. W. Breitenbach and V. Taglieber, *Ber.*, **76**, 272 (1943).