

SHORT
COMMUNICATIONS

Oxidation of Anthrone with Oxygen in DMSO

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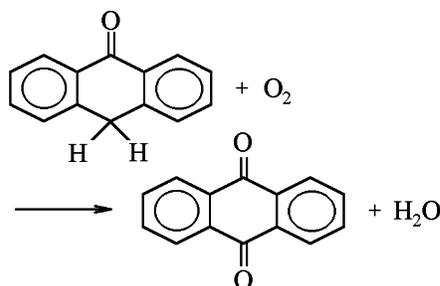
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Relatively weak CH-acids ($pK_a < 30$), as fluorenes, indenenes, dihydroanthracenes and other polycyclic compounds, were formerly shown [1, 2] to undergo oxidation with molecular oxygen in the presence of strong bases (benzyltrimethylammonium, potassium *tert*-butylate, complexes of alkali metal hydroxides with crown ethers) in aprotic solvents (DMSO and DMF).

We established that 10-hydro-9-ketoanthracene (anthrone) in DMSO solution was readily oxidized with molecular oxygen to anthraquinone in virtually quantitative yield in the absence of strong bases.

The oxidation kinetics was monitored by the volume of oxygen consumed on a device described in [3]. The reaction was studied in the temperature range 25–70°C, anthrone concentrations were varied within the limits 0.01–0.08 mol l⁻¹, partial pressure of oxygen in all runs was 760 mm Hg, solvent DMSO.

Under the reaction conditions used an intense consumption of molecular oxygen was observed. The kinetic curves attain stationary consumption rate. This fact permitted calculation of the maximum oxygen consumption from the value of the limiting consumption. The maximum consumption thus determined amounted approximately to 1 mole of oxygen per 1 mole of substrate. Thus the overall equation of the process is as follows.



Identification of reaction products was carried out by IR spectroscopy (from samples pelleted with KBr) and ¹H NMR spectroscopy in solutions in DMSO-*d*₆. The IR spectrum was in complete agreement with that of a sample of anthraquinone of the “chemically pure” grade and was distinguished from the IR spectrum of anthrone of the “chemically pure” grade by the presence of absorption bands at 1580, 1330 cm⁻¹ and by the absence of bands at 1480, 1460, 1450, 1400, 1150, 960 cm⁻¹. The ¹H NMR spectrum of the oxidation product was identical to that of anthraquinone sample, δ , ppm: 7.9 m, 8.2 m. whereas in the spectrum of anthrone appeared signals at δ , ppm: 4.3 s, 7.6 m, 8.2 d.

Analysis of the reaction mixture for hydroperoxide content performed by TLC procedure [4] showed the lack of peroxy compounds. The bright red color of the reaction mixture at the early stage of the reaction suggested carbanion formation. The addition of an initiator (azoisobutyronitrile) or an inhibitor (hydroquinone) did not affect the reaction course. These facts testify to the ionic character of the reaction.

It was shown experimentally that the reaction occurred also at lower temperature (10°C) in mixtures of DMSO with acetonitrile, thus in solvents of lower polarity than that of DMSO.

The ease of oxidation of a C–H bond in the compound under study under the chosen conditions may be due as we presume to two causes: relatively high acidity of anthrone as compared with the other alkylarenes facilitating carbanion formation, and high enthalpy of the reaction (–72 kcal mol⁻¹) (the calculation of reaction enthalpy was carried out by PMS procedure with the use of MOPAC software).

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