Concerning the ability of oligooxyquinoline to accumulate reversibly bound oxygen

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A study was performed to find and then to optimize the conditions under which alkaline solutions of H_2O_2 convert 8-oxyquinoline into an oligomeric oxide. According to infra-red and ultra-violet spectroscopy and gel permeation chromatography data, the oligomer consists mostly of oxyquinoline *N*-oxide repeat units. A kinetic study of the decomposition of this oligomeric oxide under the action of sulphuric acid in the temperature range 313–343 K showed that up to 6.8 litres of free oxygen were liberated per 100 g of the oligomer. The first-order rate constant at 333 K and activation energy for decomposition were $6.05 \times 10^{-4} s^{-1}$ and 99.2 kJ mol^{-1} respectively.

(Keywords: oligooxyquinoline *N*-oxide; reversibly bound oxygen; kinetics; decomposition of *N*-oxides)

INTRODUCTION

We have recently found[1] that oligooxyquinoline (OQ) synthesized via oxidative polycondensation of 8-oxyquinoline under the action of H_2O_2 contains 1.9 to 2.8% of reversibly bound oxygen. Routes to new types of polymers and oligomers containing reversibly bound oxygen are of current interest[2,3] because of their potential use as unconventional sources of oxygen, electron exchangers, highly efficient oxidants for the synthesis of cumene hydroperoxide[4] and crosslinked polymers[5], as well as in various redox processes.

EXPERIMENTAL

Oligooxyquinoline (OQ) ($\bar{M}_n = 330$, $\bar{M}_w = 440$, $T_{soft} = 343$ K) was synthesized through oxidative polycondensation of 8-oxyquinoline with air in an aqueous alkaline medium and purified according to ref. 6.

To oxidize OQ, it was treated with H_2O_2 in aqueous alkali. Oxyquinoline (0.021 mol repeat unit) was dissolved in a 10% aqueous solution of KOH (9 ml) placed in a thermostatted flask, which was fitted with a reflux condenser, a thermometer and a mechanical stirrer. Then a 30% solution of H_2O_2 (3 ml, 0.026 mol of H_2O_2) was added dropwise. The reaction mixture was permanently stirred and kept at 353 K during the course of the reaction. Then it was evaporated on a steam bath, and the residue was dried at 343 K under vacuum (13.3 Pa).

To determine oxygen incorporated in this product (OQ→O) and to follow the kinetics of its release, a gas-tight glass device was used consisting of a reaction flask fitted with a magnetic stirrer and carrying a bent tube connected to the flask via a ground-glass joint; the flask was also connected to a Soviet volumometer DAGV-70-2M. After heating the flask to the required temperature, sulphuric acid contained in the tube was added to the reaction flask by rotation of the joint carrying the bent tube. The volume of O_2 evolved was periodically measured until the reaction was complete and then referred to the standard state.

RESULTS AND DISCUSSION

Oligooxyquinoline, which was initially brown, turns black after reaction with alkaline H_2O_2. Simultaneously, its molecular mass and temperature of softening increase to some extent (viz. to the new values of $\bar{M}_n = 360$, $\bar{M}_w$480 and $T_{soft} = 348$ K). Thus oxidized OQ is soluble in aqueous alkalis and acids, dimethylformamide (DMF) and dimethylsulphoxide. The u.v. spectrum of OQ→O (*Figure 1*) exhibits absorption bands, which occur at the same wavelengths as bands characteristic of both oxidized oxyquinoline (at 259 and 264 nm) and oxyquinoline (at 240 nm), which is consistent with the hypothesis that OQ→O contains links of both types. The i.r. spectrum of the oxidized oxyquinoline includes an absorption band at 1350 cm^{-1}, which is characteristic of the $\geqslant N \rightarrow O$ group[7].

OQ→O was shown to liberate iodine from KI in neutral and acidic media. Hydroquinone is converted into coloured semiquinone under similar conditions. Both the facts suggest that OQ→O contains the *N*-oxide structure. This is consistent with the literature[8], which establishes that interaction of pyridine and quinoline derivatives with hydrogen peroxide results in the formation of *N*-oxides.

Treatment of OQ→O with aqueous sulphuric acid at 323–343 K leads to evolution of oxygen. On the other hand, the oxygen content of OQ→O is not diminished by protracted exposure to a dilute solution of a ferrous salt (number of links of the oligomer per Fe^{2+} ion was ~50). Hence the liberation of oxygen does not result from the decomposition of hydroperoxide groups, which might have been formed through the interaction of OQ and H_2O_2. Such groups could also not be detected in an OQ analogue, namely oxidized oligo-α-naphthol.

Table 1 summarizes conditions found for the formation of OQ→O through the interaction of oxyquinoline with H_2O_2. One can see that in an alkaline medium the yield of bound oxygen increases with duration of the reaction, so that after 10 h at 353 K it reaches 61.6% of the theoretical value. Efficiency of the oxidation of OQ

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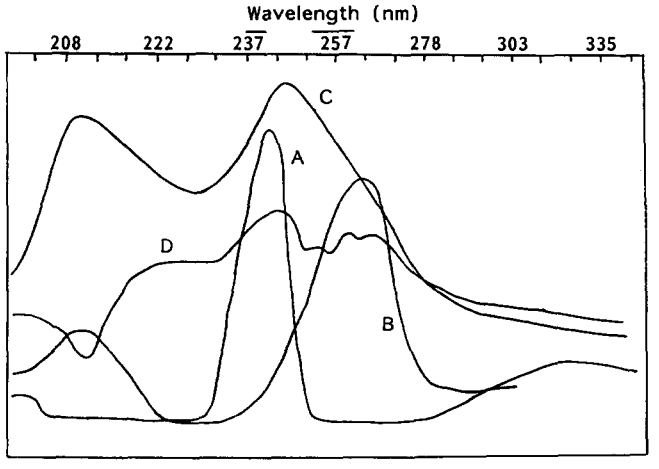


Figure 1 U.v. spectra of 8-oxyquinoline (A), 8-oxyquinoline *N*-oxide (B), oligooxyquinoline (C) and oxidized oligooxyquinoline (D) in ethanol

Table 1 Oxidation of OQ with hydrogen peroxide at 353 K: yield of reversibly bound oxygen as a function of conditions used

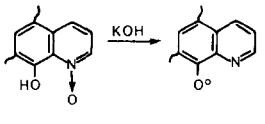
$[OQ]_0$ (mol repeat unit/l)	$[H_2O_2]_0$ (mol l^{-1})	Medium	Duration (h)	Bound O_2 (l/100 g oligomer)
0.42	0.58	Aqueous alkali	1	1.63
0.42	0.58	same	2	1.84
0.42	0.58	same	3	1.77
0.42	0.58	same	4	2.90
0.42	0.58	same	10	4.30
0.14	0.88	same	5	2.75
0.84	1.32	same	10	6.80
0.13	0.65	AcOH	5	0.18
0.13	0.65	DMF	5	0.62

strongly depends on pH. For example, the products obtained from 0.5 g of OQ and 2 ml of H_2O_2 (concentration 30%) in 25 ml of aqueous alkali, or DMF, or acetic acid after 5 h at 353 K contain 21.1, 0.9 or 3.1 ml of bound oxygen, respectively.

Thus, we could produce OQ→O containing as much as 6.8 litres of bound oxygen per 100 g of the oligomer. This result opens the way for wide use of OQ as an accumulator of active oxygen.

It should be noted that OQ is also formed through the action of air or sodium hypochlorite on OQ alkoxide solution. However, these oxidants are less effective by far. Thus, after 0.5 g of OQ had been treated with 2 ml of a 14% solution of NaOCl for 5 h or exposed to air for 16 h, in both cases at 353 K, the yield of bound oxygen was only 6.4 or 6.7% respectively of the theoretical value.

Heating OQ→O in aqueous alkali at 333 K for 5 h results in decreasing content of reversibly bound oxygen by 24%. This is evidently due to the intramolecular electron exchange process:



On the other hand, OQ→O is highly stable in neutral media. Thus, heating at 373 K for 2 h does not change the initial oxygen content.

OQ→O is capable of regeneration; for example, a sample that had initially contained 6.02% of oxygen, after a cycle of decomposition and repeated oxidation, was even enriched slightly (by 0.05%) in oxygen.

While the oxidation of amines leading to formation of the $\geqslant N \rightarrow O$ group is well known[8], we could not find any information on routes and general rules of releasing free oxygen by the *N*-oxides in chemical literature available to us. In this connection we studied the kinetics of the liberation of oxygen by reaction of OQ→O with excess aqueous sulphuric acid at temperatures ranging from 313 to 343 K. Even at the lower end of the range (313 K), the rate of oxygen evolution proved to be as high as 0.11×10^{-5} mol l^{-1} s^{-1} (*Table 2* and *Figure 2*). Increasing the temperature by 30 K increases the rate by a factor of 13. The rate of oxygen evolution calculated according to the first-order rate law increases from 0.35×10^{-4} to 15.9×10^{-4} s^{-1} in that temperature interval. The corresponding $\lg k$ vs. $1/T$ relationship follows

Table 2 Conditions for decomposition of OQ→O and some kinetic parameters of the reaction

$10^2[OQ \rightarrow O]_0$ (mol repeat unit/l)	$[H_2SO_4]$ (mol l^{-1})	T (K)	$10^5 W$ (mol l^{-1} s^{-1})	$10^4 k$ (s^{-1})
3.14	0.602	313	0.11	0.35
3.14	0.602	323	0.19	0.61
3.14	0.602	328	0.66	2.1
3.14	0.602	333	1.9	6.05
3.14	0.602	343	5.0	15.9
2.20	0.602	333	1.41	
1.57	0.602	333	0.98	
0.94	0.602	333	0.44	
3.14	0.299	333	1.8	
3.14	0.201	333	0.66	
3.14	0.150	333	0.35	
3.14	0.099	333	0.15	

$E = 23.7$ kcal mol^{-1} $= 99.2$ kJ mol^{-1}

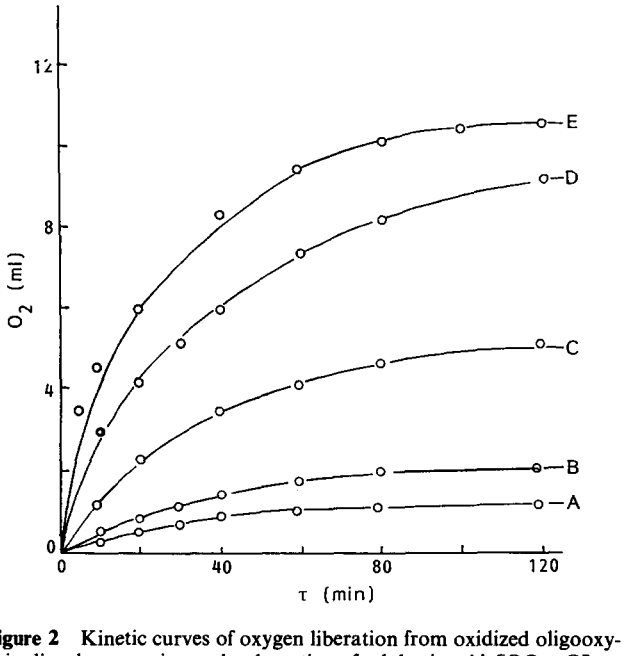


Figure 2 Kinetic curves of oxygen liberation from oxidized oligooxyquinoline decomposing under the action of sulphuric acid. $[OQ \rightarrow O]_0 = 0.0314$ mol repeat unit/l; $[H_2SO_4]_0 = 0.602$ mol l^{-1}; volume of reaction mixture, 30 ml. Temperature (K): 313 (A), 323 (B), 328 (C), 333 (D), 343 (E)

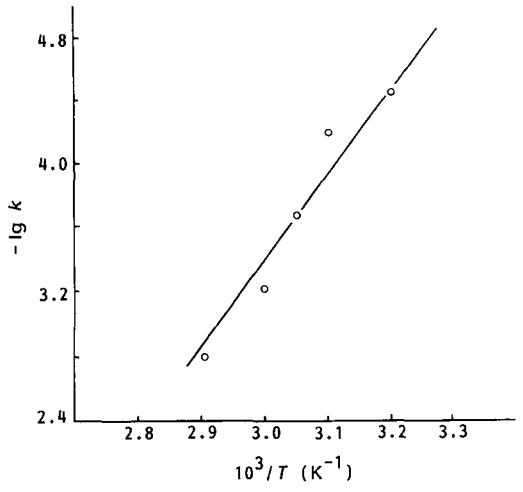


Figure 3 The Arrhenius plot for the decomposition of OQ→O. $[OQ \rightarrow O]_0 = 0.0314$ mol repeat unit/l; $[H_2SO_4]_0 = 0.602\,mol\,l^{-1}$

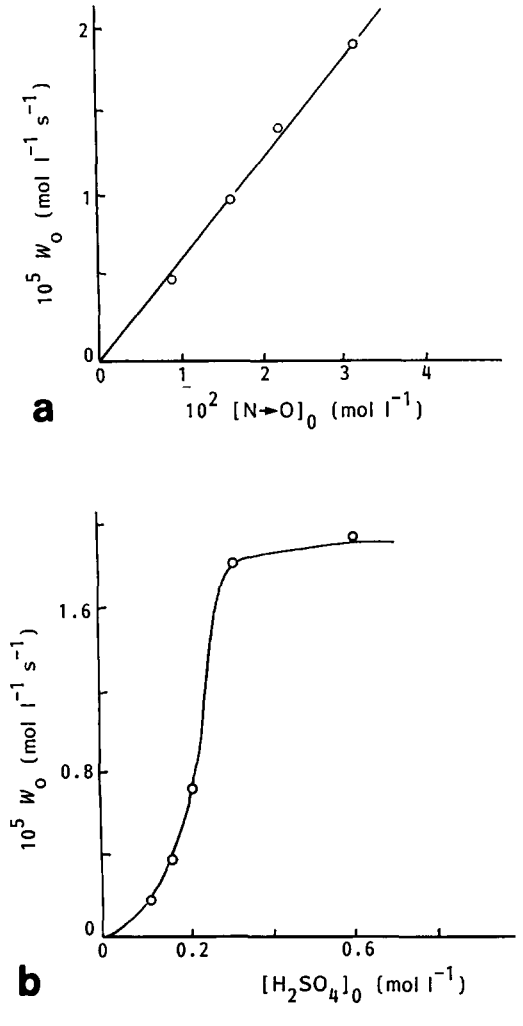
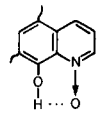


Figure 4 Decomposition of OQ→O: dependence of the initial rate on (a) initial substrate and (b) reagent concentrations. $T = 333$ K. (a) $[H_2SO_4]_0 = 0.602\,mol\,l^{-1}$, and (b) $[OQ \rightarrow O]_0 = 0.0314$ mol repeat unit/l

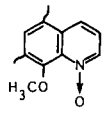
the Arrhenius equation (*Figure 3*), giving an activation energy for the release of oxygen from OQ→O by the action of aqueous H_2SO_4 of 99.2 kJ mol^{-1}.

The rate of oxygen evolution measured at 333 K increases linearly with initial concentration of oxyquinoline oxide from 0.94×10^{-2} to 3.14×10^{-2} mol repeat unit/l (*Figure 4a*), while the effect of $[H_2SO_4]_0$ is rather complex. As can be seen from *Figure 4b*, there is a moderate increase of the rate with $[H_2SO_4]_0$ in the concentration range 0.10–0.20 mol l^{-1} and then a much stronger dependence at concentrations up to ~0.30, while at higher concentrations it becomes insignificant. Such a complex relationship between $[H_2SO_4]_0$ and the rate of decomposition reflects its complicated mechanism, consisting of several parallel and consecutive steps: neutralization of the alcoholate by the acid, formation of salts $\geqslant N \cdot H_2SO_4$, decomposition of the $\geqslant N \rightarrow O$ bond, solvation of macromolecules, etc.

In our view, the most interesting point is the ability of $\geqslant N \rightarrow O$ groups in OQ oxide to liberate oxygen under the action of H_2SO_4. Our studies have shown that other compounds, both low-molecular-weight ones and polymers, containing $\geqslant N \rightarrow O$ bonds lack this property. Thus, neither pyridine *N*-oxide nor oligopyridine *N*-oxide evolve oxygen under similar conditions. The ability of oligooxyquinoline to bind oxygen reversibly is probably due to weakening of the $\geqslant N \rightarrow O$ bond caused by hydrogen bonding with the adjacent OH group:



This suggestion was supported by the following experiment. The (oligo) methyl ether of oligooxyquinoline oxide:



prepared via reaction of the potassium salt of OQ with dimethyl sulphate, when treated with H_2SO_4 under conventional conditions releases only a small amount of oxygen, viz. 0.18% by weight. Probably, it originates from the decomposition of $\geqslant N \rightarrow O$ groups in the few non-methylated links still present in the oligomeric ether.

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