Oxidative polycondensation of 8-oxyquinoline alcoholate

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Oxidative polycondensation of 8-oxyquinoline alcoholate by molecular oxygen has been accomplished at 323–371 K. Product compositions, structures and molecular weights were determined by elemental and chemical analyses, by gel permeation chromatography, and infra-red and ultra-violet spectroscopy. The process was found to yield oligomers comprising 8-oxyquinoline units. Optimum conditions for oxidative polycondensation and the main kinetic parameters of the process were established. It was shown that the process was autocatalytic and proceeded with an induction period. A mechanism for oligo(oxyquinoline) formation is proposed. It was found that the oligo(oxyquinoline) was thermally stable up to 573 K and its paramagnetic and semiconductor properties were studied.

(Keywords: oxidative polycondensation; 8-oxyquinoline; kinetics; thermal stability; paramagnetic and semiconductor behaviour)

INTRODUCTION

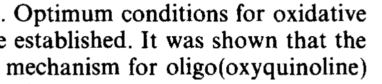
The specific interactions of the hydroxyl group and tertiary nitrogen of 8-oxyquinoline (OQ) and its derivatives are responsible for their high efficiency as physiologically active agents[1] and as selective analytical reagents[2]. Despite these useful properties, to the best of our knowledge no synthesis has been attempted to obtain conjugated polymers or oligomers with oxyquinoline units in the main chain. In addition to the types of applications indicated above, such high-molecular-weight compounds may be of interest as organic semiconductors with controlled electrophysical properties[3,4] and for the preparation of heat-resistant and thermally stable polymeric compositions[5,6].

We have studied the kinetics and reaction products of the oxidative polycondensation of 8-oxyquinoline alcoholate by molecular oxygen in ethanol. This particular route to polymeric 8-oxyquinoline was chosen because of its relative simplicity and the well established knowledge of oxidation of numerous phenols[7,8].

EXPERIMENTAL

The oxidative polycondensation of OQ was carried out in a three-necked flask fitted with a stirrer, thermometer and air bubbler. The flask was charged with 3.64 g (0.025 mol) of OQ, 1.4 g (0.025 mol) KOH and 25 ml H_2O and heated. After reaching the prescribed temperature, CO_2-free air was bubbled through the reaction medium at the rate of $6.0\,l\,h^{-1}$. After a certain lapse of time the reaction mixture was treated with cationite and fractionated on a glass column to trap potassium ions. The unreacted monomer was removed by steam distillation. The products of OQ polycondensation were recovered by filtration, and dried to constant weight under reduced pressure (13.6 Pa) at 373 K.

The kinetics of 8-oxyquinoline oxidative polycondensation were studied in a closed system comprising a 50 ml glass reactor with a magnetic stirrer connected to a DAGV-70-2M volumeter under constant oxygen pressure (9.8×10^4 Pa). Freshly distilled ethanol was used as solvent. The volumeter and the reactor were thermostatted. Then 8-oxyquinoline and the solvent were charged into the reactor. The system was purged and filled with oxygen. After reaching the prescribed temperature the required amount of 10% ethanolic KOH was added to the OQ mixture without affecting the tightness of the reaction system. The amount of the reacted OQ was derived from the actual volume of oxygen consumed from the reaction equation:



The molecular-weight distributions of OQ polycondensation products were determined by gel permeation chromatography at 298 K using a Waters apparatus with a refractometer as detector, three styragel columns with porosities of 200, 500 and 1000 Å, and tetrahydrofuran ($1.0–1.1\,ml\,min^{-1}$) as eluent. The sample was introduced as a 0.2% solution in dimethylformamide (DMF). The molecular weights were estimated as previously described[9].

The number of hydroxyl groups in the products of OQ oxidative polycondensation was determined by acylation[10]. The i.r. spectra were recorded for pellets made out of powdered reaction products and KBr. The thermooxidative destruction of the resulting oligomers was studied on a MOM derivatograph under dynamic conditions with a 0.100 g sample at heating rate of $5°C\,min^{-1}$.

RESULTS AND DISCUSSION

The 8-oxyquinoline in the solid state or dissolved in

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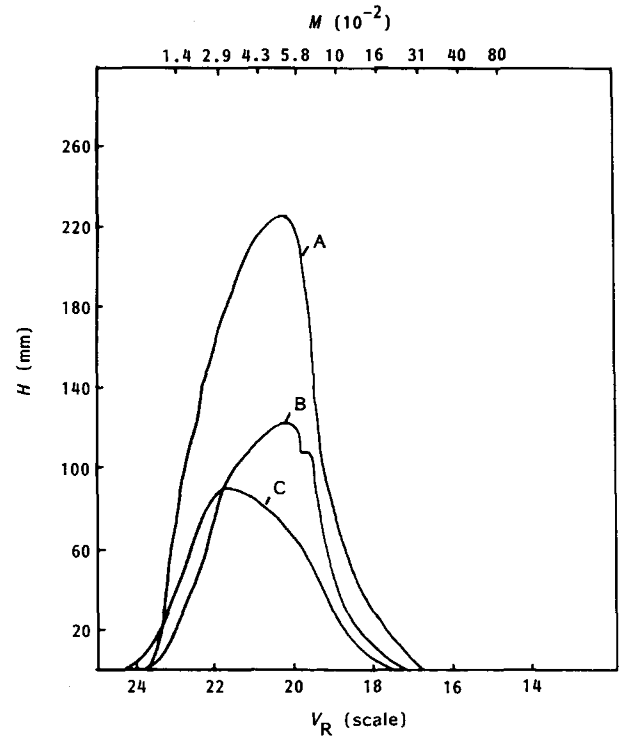


Figure 1 Molecular-weight distribution curves of OOQ obtained at $T=363$ K, $\tau=7$ h. $[OQ]_0$ (mol l^{-1}): 1 (A), 2 (B), 0.5 (C). $[KOH]_0$ (mol l^{-1}): 1 (A), 2 (B), 0.5 (C)

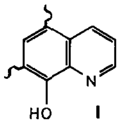
neutral and acidic media does not interact with molecular oxygen, while its potassium alcoholate in alcohol at 313–373 K consumes oxygen and gradually becomes deep brown. When air or pure oxygen is bubbled through the reaction mixture, the coloration is accelerated.

The g.p.c. analysis of the OQ oxidative polycondensation products shows (*Figure 1*) that they consist mainly of oligomers with $\bar{M}_w = 360$–400, $\bar{M}_n = 320$–370 and low polydispersity values (1.0–1.13). The major part of the product is that with $\bar{M}_n = 300$–600, while a relatively high-molecular-weight part ($\bar{M}_n = 4000$–8000) was also present. The proportion of the high-molecular-weight material increases with temperature and duration of OQ oxidative polycondensation. However, the oligo(oxyquinoline) (OOQ) becomes infusible and its solubility decreases. The OOQ samples obtained at 343–371 K after 4–14 h soften under load (1.59 kg cm^{-2}) at 353–393 K. They are soluble in DMF, quinoline, acetic acid, aqueous alkalis and acids. The latter fact is due to hydroxyl groups and tertiary nitrogen available in the OOQ structure. The results of elemental analysis (found C 75.3%, H 4.7%, N 9.5%; calculated C 75.5%, H 3.5%, N 9.18%) and the percentage of hydroxyl groups (found 10.5–11.2%; calculated 11.2%) are in good agreement with calculated data for 8-oxyquinoline units.

The i.r. spectra of oligomers show absorption bands in the region of 720, 730, 790, 835 and 890 cm^{-1} corresponding to out-of-plane deformation vibrations of aromatic C–H bonds, those at 790 and 835 cm^{-1} being most intense and characteristic of three and two neighbouring unsaturated C–H groups of the aromatic ring[11]. The relatively weak band at 890 cm^{-1} is due to isolated C–H groups.

The broad band at 3320–3600 cm^{-1} with a maximum at 3380 cm^{-1} is due to stretching modes associated with hydroxyl groups, and their bending modes are responsible for the absorption bands near 1200 cm^{-1}. Absorption bands due to C=C and C=N bonds of the aromatic nucleus appear at 1380, 1410, 1475, 1510 and 1600 cm^{-1}.

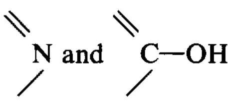
Thus the spectral, structural and chemical evidence is consistent with the hypothesis that 8-oxyquinoline consists mainly of units *I*:



I

that is, the polycombination in OQ oxidative polycondensation takes place in positions 5 and 7 of the quinoline ring.

The u.v. spectrum of the low-molecular-weight fraction of OOQ (dimer–trimer) in ethanol shows three peaks at 210, 244 (intense) and 333–335 nm (very weak) (*Figure 2*). The first and second are E and B bands, respectively, caused by $\pi \rightarrow \pi^*$ transitions of the C=C and C=N bonds. The peak at 333–335 nm seems to account for the $n \rightarrow \pi^*$ transition of the lone-pair electrons of



fragments in the OOQ structure. The u.v. spectrum of OOQ potassium salt shows a bathochromic shift of the E (217 nm) and B (256 nm) bands due to OH-group ionization[12]. This spectrum is identical to that of 8-oxyquinoline potassium salt (peaks at 215, 253 and 335 nm), which again supports the proposed structure of OOQ. The slight bathochromic shift of these maxima in passing from OQ to its oligomer seems to be due to the effect of a polyconjugated bond system in the oligomer. The u.v. spectrum of the HCl salt of OOQ shows a hypsochromic shift of the E band (200 nm) and the B band appears at 255 nm. The absorption band of neutral OOQ molecule at 335 nm disappears.

A study of OOQ synthesis using air in an aqueous medium revealed a low rate of oligomer formation at 373 K. As can be seen from *Table 1* after 7 h with

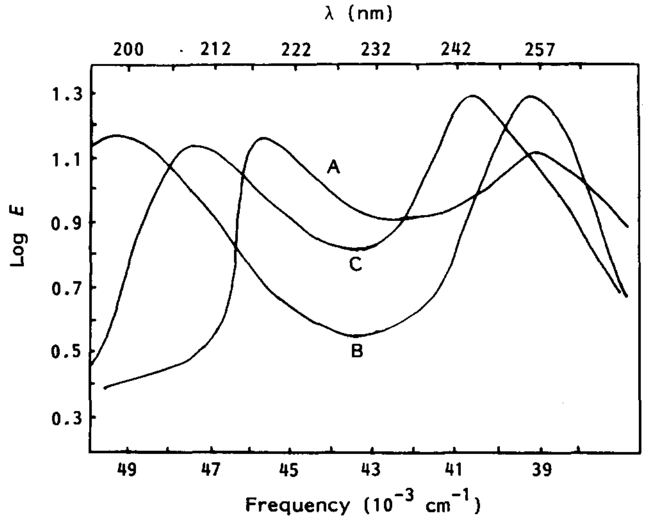


Figure 2 Electronic spectra of potassium (A) and hydrochloric acid (B) salts of OOQ in water and of OOQ in ethanol (C)

$[OQ]_0 = 1.0\,mol\,l^{-1}$ and $[KOH]_0 = 1.5\,mol\,l^{-1}$ the yield of OOQ was as low as 27.7%. The oligomer yield is favoured by increasing monomer concentration, reaction temperature, duration and air flow rate. Thus, a 28 K increase in temperature causes a 31.6% increase of OOQ yield. However, for monomer and alkali concentrations up to $1.5\,mol\,l^{-1}$ or higher, reaction duration more than 7 h, and air flow rates greater than $6.0\,l\,h^{-1}$, no significant increase in oligomer yield was observed. The maximum yield of OOQ after 7 h is reached at $[OQ]_0 = [KOH]_0 = 1.5\,mol\,l^{-1}$, $T = 371$ K, air flow rate $6.0\,l\,h^{-1}$.

A kinetic study of molecular oxygen consumption in the oxidative polycondensation of OQ alcoholate in alcohol shows that at 323–343 K the reaction proceeds with a large induction period (80–140 min) and low rate (*Figure 3*, *Table 2*). The autocatalytic nature of 8-oxyquinoline oxidation may be accounted for by the increasing reactivity of the forming oligomeric phenols[8], as well as by OQ molecule activation as a result of complexing with intermediate aroxyl radicals[13].

At constant oxygen pressure a first-order increase in the reaction rate with OQ and alkali concentrations is observed. The plots of maximum oxygen consumption against the initial monomer and KOH concentrations are straight lines passing through the origin (*Figure 4*). Increased reagent concentrations and higher temperatures significantly reduce the induction period of the reaction. The latter is likely to correspond to the accumulation of reaction centres (*Table 2*).

At constant oxygen pressure (9.8×10^4 Pa) and excess of alkali the reaction rate obeys the pseudo-first-order equation

$$W = k[OQ]$$

where k is the approximate reaction rate constant. Using this equation the reaction rate constant was estimated to be $(0.48\text{–}3.7) \times 10^{-5}\,s^{-1}$ at 323–343 K. The activation energy E of the reaction derived from the Arrhenius plot amounted to $98.5\,kJ\,mol^{-1}$.

Table 1 Oligomer yields as a function of conditions of OQ oxidative polycondensation by oxygen in the air in an aqueous alkaline medium

Item no.	$[OQ]_0$ ($mol\,l^{-1}$)	$[KOH]_0$ ($mol\,l^{-1}$)	T (K)	τ (h)	Air flow rate ($l\,h^{-1}$)	Yield (%)
1	1.0	1.0	363	7	6.0	37.0
2	1.0	1.25	363	7	6.0	41.1
3	1.0	1.5	363	7	6.0	46.0
4	1.0	2.0	363	7	6.0	44.2
5	0.5	0.5	363	7	6.0	26.5
6	1.5	1.5	363	7	6.0	70.6
7	2.0	2.0	363	7	6.0	71.5
8	1.0	1.5	343	7	6.0	27.7
9	1.0	1.5	353	7	6.0	34.8
10	1.0	1.0	371	7	6.0	59.3
11	1.0	1.5	363	14	6.0	68.8
12	1.0	1.5	363	4	6.0	27.1
13	1.0	1.5	363	6	6.0	38.7
14	1.0	1.5	363	8	6.0	48.5
15	1.0	1.5	363	10	6.0	52.7
16	1.0	1.5	363	7	3.0	26.7
17	1.0	1.5	363	7	5.0	33.2
18	1.0	1.5	363	7	8.0	48.3

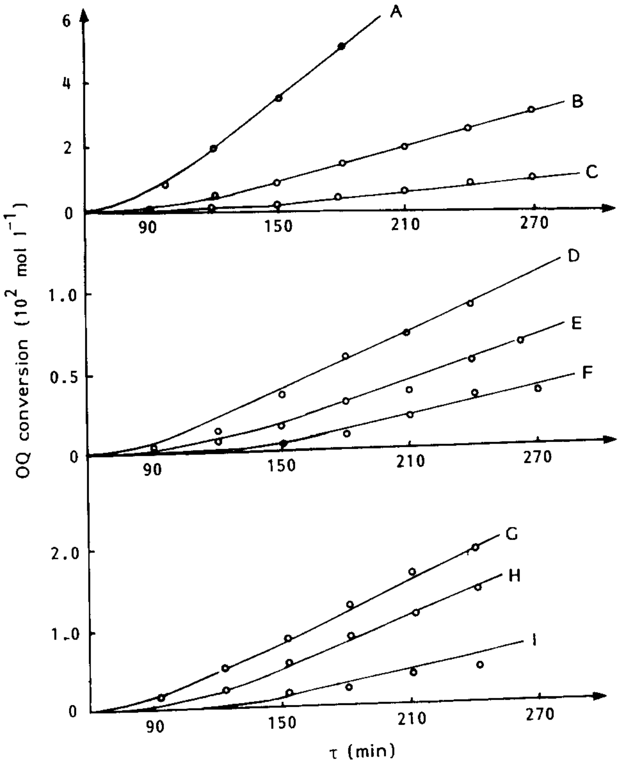


Figure 3 Kinetic curves of OQ oxidative polycondensation by oxygen in alcoholic alkaline medium. $[OQ]_0$ ($mol\,l^{-1}$): 0.230 (A–C, G–I), 0.172 (D), 0.115 (E) and 0.057 (F). $[KOH]_0$ ($mol\,l^{-1}$): 0.357 (A–F), 0.238 (G), 0.179 (H) and 0.089 (I). T(K): 343 (A), 333 (B, D–I) and 323 (C)

Table 2 Kinetics of interaction between 8-oxyquinoline alcoholate and oxygen in alcohol

Item no.	$[OQ]_0$ ($mol\,l^{-1}$)	$[KOH]_0$ ($mol\,l^{-1}$)	T (K)	τ_{ind} (min)	$W_{max} \times 10^6$ ($mol\,l^{-1}\,s^{-1}$)	$k_{ef} \times 10^5$ (s^{-1})
1	0.230	0.357	323	80	1.1	0.48
2	0.230	0.357	333	90	3.1	1.4
3	0.230	0.357	343	115	8.6	3.70
4	0.172	0.357	333	85	2.1	
5	0.115	0.357	333	110	1.3	
6	0.057	0.357	333	140	0.70	
7	0.230	0.238	333	90	2.0	
8	0.230	0.179	333	105	1.7	
9	0.230	0.089	333	135	0.80	

Note: $E_{ef} = 98.5\,kJ\,mol^{-1}$

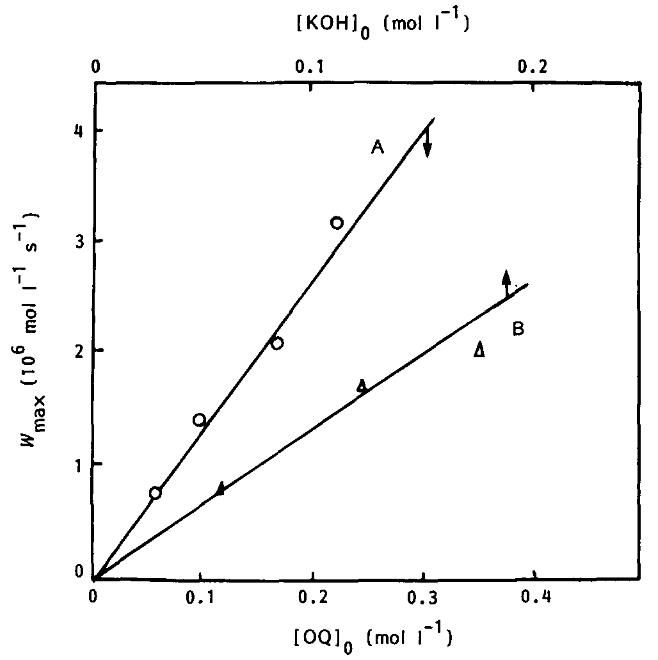


Figure 4 W_{max} vs. initial concentrations of 8-oxyquinoline (A) and alkali (B), at T=333 K. $[OQ]_0$=0.230 mol l^{-1} (B). $[KOH]_0$=0.357 mol l^{-1} (A)

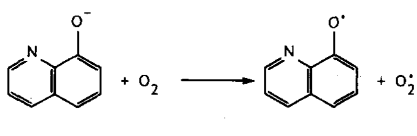
The comparison of k and E values for this oxidative polycondensation reaction shows the lower reactivity of OQ as compared to α-naphthol[14]. This is accounted for by the strong electron-acceptor effect of the

fragment, which increases the energy of homolytic breaking of the O–H bond[15]. This is the reason for the increased induction period and activation energy of OQ oxidative polycondensation compared to that of α-naphthol.

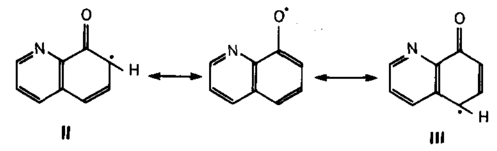
Nevertheless, the similarity of the kinetic curves and the identical reaction orders for the monomer and alkali are evidence that the oxidative polycondensations of 8-oxyquinoline and α-naphthol proceed via the same route.

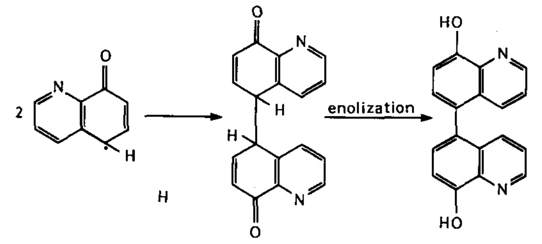
As was suggested earlier, one of the probable causes of the autocatalytic character of the kinetic curves of oxygen consumption by 8-oxyquinoline alcoholate is the accumulation of more reactive di-, tri- and oligomers in the reaction medium. To check this concept we attempted a kinetic study of OOQ oxidation in alcoholic alkaline medium. It was found that OOQ oxidizes without an induction period (*Figure 5*) with a greater k value (0.64×10^{-4} to 5.8×10^{-4} s^{-1} at 313–333 K) and lower activation energy (91.2 kJ mol^{-1}).

These studies of oligomer structure and the kinetics of the process together with literature data[16] suggest the following mechanism of 8-oxyquinoline oxidative polycondensation by oxygen in alkaline medium:

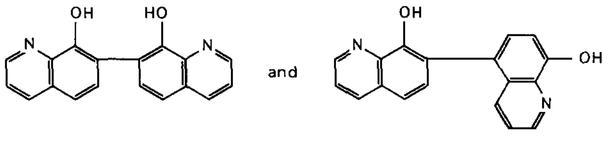


The resonance forms of the intermediate radicals obtained undergo recombination followed by enolization of dimers:





The recombination of radicals **II** and **II** and of **II** and **III** similarly yields dimers of the following structures:



Then the dimers, trimers, etc., are likewise oxidized. The process-limiting stage is electron transfer from oxyquinoline anion to oxygen.

As might be expected, the oligo(oxyquinoline) shows marked thermal stability and paramagnetic and semiconductor properties.

The OOQ undergoes thermo-oxidative destruction starting from 473–483 K, and weight losses at 573 K reach 10–13%. Above 563–583 K the destruction processes are intensified and reach 40–43% and 52–68% at 773 and 873 K, respectively. They depend a great deal on the composition of OOQ, an increase in the proportion of high-molecular-weight fraction in OOQ enhancing its thermal stability. An exothermic process is observed in

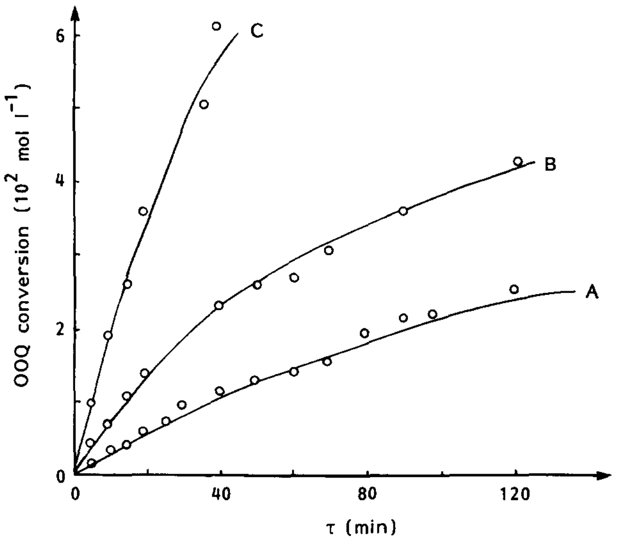


Figure 5 Kinetic curves of OOQ oxidation by oxygen in alcoholic alkaline medium. $[OOQ]_0$=0.070 mol l^{-1}. $[KOH]_0$=0.179 mol l^{-1}. T(K): 313 (A), 323 (B) and 333 (C)

d.t.a. curves in the range 473–593 K with a maximum at 568–573 K, and starting from 583 K the rate of heat evolution is increased. The maximum of the observed exotherm occurs in the temperature range 743–763 K.

The concentration of paramagnetic centres in OOQ is within the range 10^{20}–10^{21} spin/kg depending on the synthesis conditions. The e.s.r. spectra of OOQ powder consist of a singlet 0.60 mT broad with g-factor equal to 2.0032.

The oligo(oxyquinoline) is a semiconductor with high resistance; its specific d.c. conductance at 293 K is $1.6 \times 10^{-8}\ \Omega^{-1}\,\mathrm{m}^{-1}$ and it increases exponentially with temperature. The a.c. conductivity of OOQ (σ) at room temperature increases exponentially with frequency according to $\sigma = af^n$, where $n = 0.8$–0.9 and a is a proportionality factor. At 10 MHz σ reaches $5 \times 10^{-6}\ \Omega^{-1}\,\mathrm{m}^{-1}$. By oxidizing OOQ with oxygen in an alkaline medium to stable aroxy radical forms, the concentration of paramagnetic centres may be increased 2–3 times. This is accompanied by the rise of oligomer conductivity (for oxidized OOQ at 10 MHz $\sigma = 2 \times 10^{-4}\,\Omega^{-1}\,\mathrm{m}^{-1}$).

CONCLUSIONS

It was shown that oxidative polycondensation of 8-oxyquinoline alcoholate by oxygen at 323–371 K leads to oligomers comprising 8-oxyquinoline units combining in the positions 5 and 7. It is established that OQ oxidation by oxygen in an alcoholic alkaline medium proceeds with a relatively large induction period and is autocatalytic. Process rate constants k and activation energies E are found and it is demonstrated that, in passing from OQ to its oligomer, k is increased and E of oxidation is decreased. Oligo(oxyquinoline) formation supposedly proceeds via electron transfer from OQ anion to oxygen molecule, followed by combination of the intermediate radicals and then by enolization. The OOQ is found to be thermally stable up to 573 K and to show paramagnetic (10^{20}–10^{21} spin/kg) and semiconductor behaviour.

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