Dramatic Effects Caused by Alkali Metal Salts on Hydrolytic Reaction Rates of Diaryl Ethers in Aqueous Solutions at High Temperatures (250 and 315 °C)

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Variations in hydrolysis rates indicate that alkali metal halides and sodium sulfate behave as salts of strong bases and weak acids at high temperatures.

Our extensive work on 'aquathermolysis' (reactions of organic compounds in hot water) has shown[1,2] that ionic reactions of many classes of organic compounds are favoured in liquid water at 250–350 °C. We now report that low concentrations of alkali metal halides and other salts can dramatically slow the acid catalysed cleavage reaction of diaryl ethers under these conditions. The results demonstrate that alkali metal halides and sodium sulfate behave at these temperatures as the salts of strong bases and weak acids, and that this raises the effective pH.

The possible hydrolysis of NaCl by water at high temperatures has previously been considered in reference to the solubility of NaCl in steam, and hence to the question of the transportation of NaCl in engineering systems. The previous evidence is not clear cut: thus Galobardes *et al.*[3] found that the condensate from steam was acidic (pH ~ 5.4) and that the ratio of [Cl^-] to [Na^+] was *ca.* 1.2 and concluded that some hydrolysis had occurred. Bischoff *et. al.*,[4] found using 'pH test paper' that the pH was essentially neutral in all condensate samples, and concluded that 'such hydrolysis was not important at least up to 500 °C at pressures high enough for liquid to be present'. Pitzer and Pabalan[5] concluded that 'the hydrolysis was certainly no larger than the other experimental uncertainties'.

We have now examined the effect of various salts on the aqueous hydrolysis of ether linkages of 1-phenoxynaphthalene and 9-phenoxyphenanthrene using 1 g of substrate in 7 ml of solution kept in 11 ml T316SS reaction bombs.

Our previous work[6] showed that hydrolysis of 1-phenoxynaphthalene in water at 315 °C for 72 h, gave 94.6% conversion mainly to phenol and naphthol. Using in place of pure water 0.1, 0.5, 1 and 5% aqueous solutions of NaCl, 46, 29, 7.4 and 0% conversion, respectively, into the same products was observed. Previously[6] 9-phenoxyphenanthrene had shown high reactivity (92.6% conversion, 1 h) at 315 °C in hot water alone. We have now found that heating in water at a lower temperature (at 250 °C) gave 80% conversion after 72 h and the main products were phenol and 9-hydroxyphenan-

Table 1

			Conversion(%)				
Compound	T/°C	t/h	Water	1% LiCl	1% KCl	1% KBr	1% Na_2SO_4
1-Phenoxynaphthalene	315	72	94.6	4.8	8.1	3.8	0
9-Phenoxyphenanthrene	250	72	80.0	10.5	10.2	7.9	3.5

threne. The rate of hydrolysis was significantly reduced by the presence of dissolved NaCl in the water and this reduction in the rate became intensified with increase in concentration of NaCl: *i.e.* 24, 10.9 and 0% conversions over 72 h at 250 °C for 0.1, 1.0 and 5% NaCl, respectively. The products remained the same.

Additional experiments were carried out in sealed tubes of Vycor glass. The hydrolysis of 9-phenoxyphenanthrene at 250 °C for 24 h increased from 35% in hot water alone to 100% in 1.1% phosphoric acid. However, in aqueous sodium chloride the rate of hydrolysis was reduced: in 1% NaCl, a 10% conversion was achieved and in 5% NaCl there was no change over 24 h at 250 °C.

We have demonstrated that these Ar–O bond cleavage reactions are strongly catalysed by 15% phosphoric acid (almost 100% conversion at 315 °C over 30 min). They are completely inhibited in basic media: *i.e.* 1% pyridine or 1% Na_2CO_3 over 72 h at 315 °C.

Further runs with other salts present showed similar suppressing effects on the hydrolysis of these ethers; the % conversions are summarized in Table 1.

These results strongly suggest that at high temperature, but well below 500 °C, alkali metal halides and sodium sulfate behaved as salts of strong bases and weak acids, somewhat similar to the behaviour of sodium acetate at normal temperatures. We have not been able to locate any previous report on the hydrolysis of such salts affecting reaction rates.

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