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Base-catalyzed Autoxidation of Fluorene in the Presence of Phase Transfer Catalysts[1)]

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Base-catalyzed autoxidation of fluorene to fluorenone has been carried out in an aqueous potassium hydroxide–benzene two-phase system in the presence of 18-crown-6 as a phase transfer catalyst. The initial rate of oxidation is proportional to the amount of fluorene. The addition of 18-crown-6 leads to the increased concentration of potassium hydroxide and water in the benzene phase, which is responsible for the increased rate of oxidation. Increasing the concentration of potassium hydroxide in the aqueous phase increases the concentration of 18-crown-6 and potassium hydroxide in benzene, resulting in a large increase in the rate of oxidation. The ease of oxidation with respect to the base is $KOH > NaOH > LiOH > Ba(OH)_2$. Less polar solvents such as cyclohexane used as an organic phase decrease the oxidation rate.

Fluorene, diarylmethanes, and other weak carbon acids that are unreactive toward oxygen in an aqueous or alcoholic solution can be oxidized in dimethyl sulfoxide or other dipolar aprotic solvents.[2)] For example, the oxidation of fluorene by molecular oxygen in the presence of potassium *t*-butoxide in *t*-butyl alcohol–dimethyl sulfoxide solution is known to proceed through fluorenide anion to yield fluorenone (Scheme 1).[2b)]

$$\begin{aligned}
&R_2CH_2 + B^- \longrightarrow R_2CH^- + BH\\
&R_2CH^- + O_2 \longrightarrow R_2CH\cdot + O_2^{\cdot -}\\
&R_2CH\cdot + O_2 \longrightarrow R_2CHOO\cdot\\
&R_2CHOO\cdot + R_2CH^- \longrightarrow R_2CHOO^- + R_2CH\cdot\\
&R_2CHOO\cdot + O_2^{\cdot -} \longrightarrow R_2CHOO^- + O_2\\
&R_2CHOO^- \longrightarrow R_2CO + OH^-
\end{aligned}$$

R_2CH: 9-Fluorenyl

Scheme 1.

Recently the oxidation of fluorene, xanthene, 9,10-dihydroanthracene, and other aromatic weak carbon acids was successfully carried out in an aqueous sodium hydroxide–benzene or –tolune two-phase system in the presence of phase transfer catalysts.[3)]

In the present paper we describe the reaction as regards the function of 18-crown-6 as a phase transfer catalysts.

Results and Discussion

Benzene was chosen as an organic phase containing fluorene and 18-crown-6. An aqueous phase contained a large amount of potassium hydroxide as a base. The two-phase system of water(10 ml) and benzene (40 ml) in a 100 ml flask was vigorously shaken under oxygen pressure(1 atm) at 40.0 °C and the rate of oxygen absorption was measured by the usual constant pressure oxygen absorption apparatus.[2b)] Despite the complexities of the two-phase system, the oxidation rates were reproducible within ±5%. The shaking speed between 150 and 200 strokes/min did not affect the rate of oxidation; therefore, that of 170—180 strokes/min was used in determination of the kinetic effects.

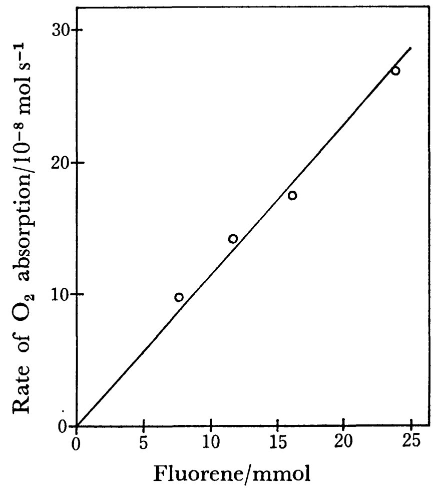


Fig. 1. Relation between fluorene used and the rate of O_2 absorption. Reaction conditions: benzene 40 ml, KOH 7.50 mol dm^{-3} in H_2O 10 ml, 18-crown-6 1.59 mmol, 40 °C.

TABLE 1. EFFECT OF TEMPERATURE[a)]

Temp °C	Fluorene mmol	KOH mol dm^{-3}	18-Crown-6 mmol	k[b)] $10^{-5}\ s^{-1}$
30	16.2	7.50	1.56	1.04
40	16.3	7.50	1.59	1.07
50	16.2	7.50	1.57	1.31

a) Benzene 40 ml, H_2O 10 ml. See Fig. 1 for other reaction conditions. b) k = [rate of O_2 absorption (mol s^{-1})]/[fluorene (mol)].

The initial rate of oxidation is proportional to the amount of fluorene (Fig. 1), which agrees with other base-catalyzed autoxidation.[2)] The effect of temperature on the rate of oxidation is not very great since the partial pressure of oxygen in the reaction flask decreases with rise in temperature (Table 1).

Effects of various bases on the rate of oxidation are given in Table 2. As expected, potassium hydroxide is the most active, the order of activity being consistent with that of the stability of the corresponding metal complexes of 18-crown-6.[4)]

The solvent effects on the oxidation rate (Table 3)

Table 2. Effects of bases[a)]

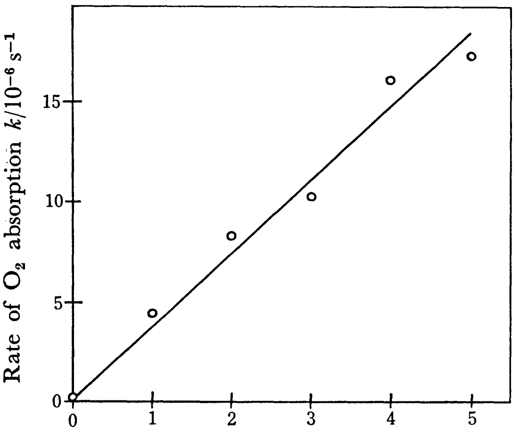
	Base mmol	Fluorene mmol	k s^{-1}
LiOH	34.4	3.06	5.1×10^{-6}
NaOH	59.9	3.04	7.8×10^{-4}
KOH	75.2	2.67	1.9×10^{-3}
$Ba(OH)_2$	46.5	3.01	small

a) Benzene 40 ml, 18-crown-6 5.0×10^{-5} mol. See Fig. 1 for other reaction conditions.

Table 3. Effects of solvents[a)]

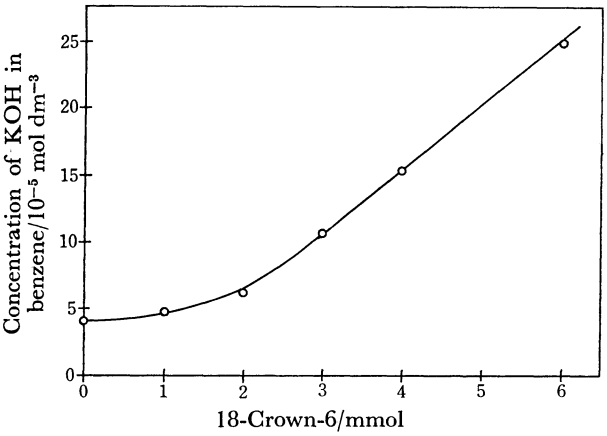
Solvent	18-Crown-6 mmol	k 10^{-5} s^{-1}
Benzene	1.59	1.19
t-Butylbenzene	1.59	1.14
Cyclohexane	1.54	0.283

a) Fluorene 16.2 mmol, solvent 40 ml, KOH 7.50 mol dm^{-3} in H_2O 10 ml, 40 °C. See Fig. 1 for other reaction conditions.



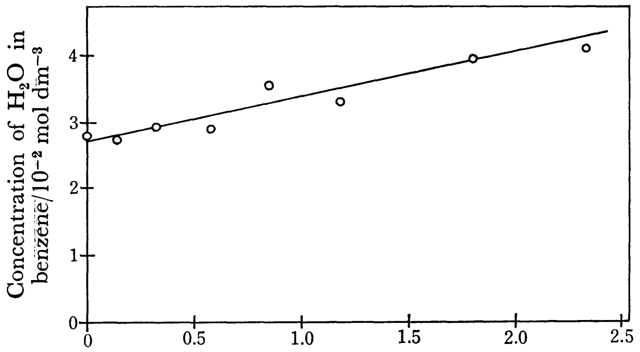
18-Crown-6/mmol

Fig. 2. Effect of 18-crown-6. Reaction conditions: fluorene 16.2 mmol, KOH 7.98 mol dm^{-3}, 40 °C. See Fig. 1 for other reaction conditions.



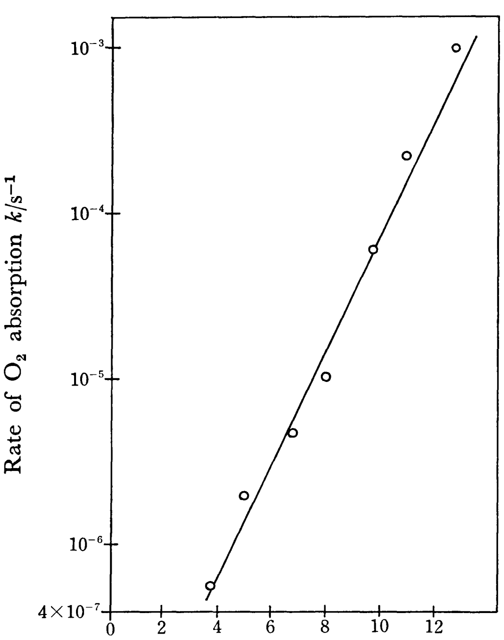
18-Crown-6/mmol

Fig. 3. The effect of 18-crown-6 on the concentration of KOH in benzene. Reaction conditions: See Fig. 1.



18-Crown-6/mmol

Fig. 4. The effect of 18-crown-6 on the concentration of H_2O in benzene. Reaction conditions: See Fig. 1.



Concentration of KOH in H_2O/mol dm^{-3}

Fig. 5. Effect of the concentration of KOH. Fluorene 16.2 mmol, 18-crown-6 1.50 mmol, 40 °C. See Fig. 1 for other reaction conditions.

may be consistent with Scheme 1, since the less polar solvent or cyclohexane is presumed to involve the less amount of potassium hydroxide responsible for the formation of the fluorenide anion.

The Effect of Concentration of 18-Crown-6. The rate of oxidation is proportional to the amount of 18-crown-6 used, *ca.* 97% of which is distributed into the benzene phase (Fig. 2). The result can be predicted from Fig. 3 which shows the proportional relationship between the concentration of potassium hydroxide in benzene and that of 18-crown-6, since the rate of base-catalyzed autoxidation is known to be proportional to the concentration of bases.[2)] The extremely low concentration of potassium hydroxide in benzene as compared with that in the aqueous phase indicates that 18-crown-6 is not very effective in complexing and solubilizing potassium hydroxide into benzene.

The amount of water involved in benzene increases linearly with the concentration of 18-crown-6 (Fig. 4).

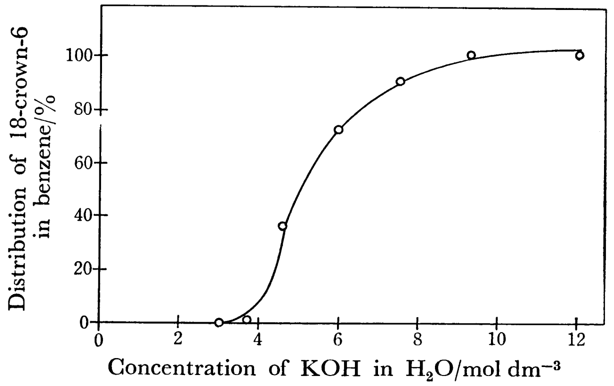


Fig. 6. Relation between the concentration of KOH in water and 18-crown-6 in benzene. Reaction conditions: See Fig. 5.

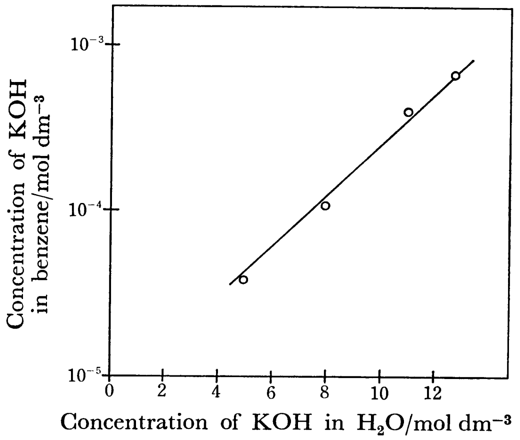


Fig. 7. Relation between the concentration of KOH in water and in benzene. Reaction conditions: See Fig. 5.

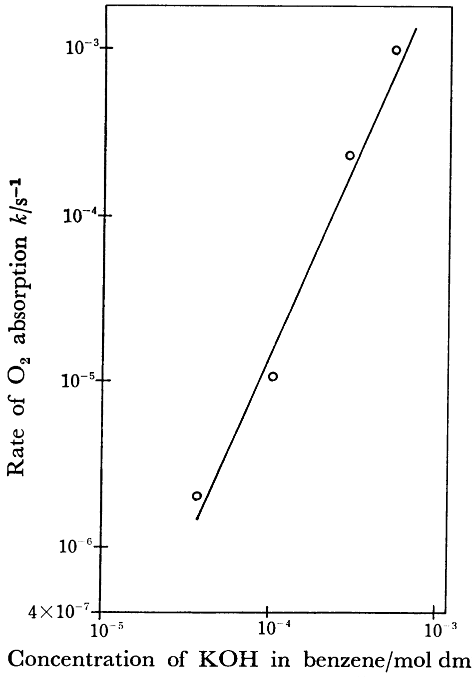


Fig. 8. Relation between KOH in benzene and the rate of oxidation. Reaction conditions: See Fig. 5.

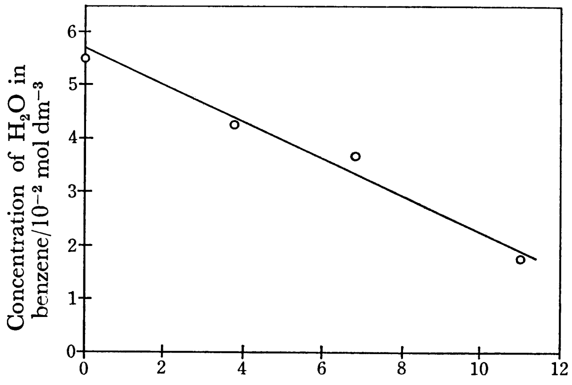


Fig. 9. Relation between the concentration of KOH in water and H_2O in benzene. Reaction conditions: See Fig. 5.

This might cause the decreased basicity of potassium hydroxide in benzene leading to a decrease in the rate of oxidation. The results shown in Figs. 2 and 4 indicate that the basicity of potassium hydroxide in benzene is almost constant at a high molar ratio of water to potassium hydroxide in benzene, calculated to be *ca.* 160—700 from Figs. 3 and 4.

Effect of the Concentration of Potassium Hydroxide in an Aqueous Phase. The concentration of potassium hydroxide in an aqueous phase has a large effect on the rate of oxidation (Fig. 5). The concentration of 18-crown-6 and potassium hydroxide in benzene increases rapidly with rise in that of potassium hydroxide in the aqueous phase. The large increase of the oxidation rate with the increasing concentration of potassium hydroxide in benzene (Fig. 9) suggests the increased basicity in the benzene phase. From Figs. 7 and 9, the molar ratios of water to potassium hydroxide in benzene are calculated to be *ca.* 1700 and 20, where the concentration of potassium hydroxide in the aqueous phase are 4.0 and 12.5 mol dm^{-3}, respectively. This indicates that the molar ratio decreases by a factor of 1/85 at the higher concentration of potassium hydroxide in the aqueous phase, which may be responsible for the increased basicity.[5] Thus, the increase of potassium hydroxide in the aqueous phase is doubly reflected on the rate of oxidation by increasing both the amount and base strength of potassium hydroxide in the benzene phase.

Experimental

Materials. Reagent grade fluorene was recrystallized twice from ethanol and dried *in vacuo.* 18-Crown-6 was prepared according to the reported procedure: mp 34.5—35.5 °C (lit, 36.5—38.0 °C).[6] Found: C, 54.61; H, 8.85; O, 36.54%. Calcd for $C_{12}H_{24}O_6$: C, 54.53; H, 9.15; O, 36.32%. Reagent grade benzene, *t*-butylbenzene and cyclohexane were shaken with sulfuric acid, washed, dried with sodium, and distilled. Hydroxides of lithium, sodium, potassium, and barium were of guaranteed grade.

Standard Oxidation Procedure. A 100 ml flask with a side arm containing 40.0 ml benzene solution of fluorene 2.71 g (16.3 mmol) and 18-crown-6 0.396 g (1.50 mmol) and 10.0 ml aqueous solution of potassium hydroxide (7.50 mol dm^{-3}) was connected by rubber tubing to a gas buret, evacuated, and filled with oxygen a number of times. The flask was then shaken at a rate of 170—180 strokes/min with a movement of 10 cm in a thermostated water bath. The oxygen absorption was measured at 1 atm by the gas buret with an automatic pressure control apparatus.[2b] After 3 h, the reaction mixture was extracted with benzene and the extracts were used for analysis. The rate of oxygen absorption was not appreciable in the absence of fluorene or 18-crown-6.

Analysis. *Fluorenone*: The yield of fluorenone was determined on a Hitachi 163 type gas chromatograph using a 25 m Chemi-column coated with Silicone SF 96. The oxidation of 1 mol of fluorene to fluorenone under the reaction conditions mentioned above consumed *ca.* 1 mol of oxygen. No appreciable amount of other oxidation products of fluorene was detected.

Water in Benzene: The reaction mixture containing 40 ml of benzene phase and 10 ml of aqueous phase was shaken at 40.0 °C for 20 min and then left to stand for 10 min. A 10 ml sample pipetted from the benzene phase was used for the determination of water content by the Karl-Fischer method.

Potassium Hydroxide in Benzene: A 10 ml sample pipetted from the benzene phase was distilled off benzene *in vacuo* and then added with 10 ml of 0.035 mol dm^{-3} hydrochloric acid solution for measuring potassium ion on a Hitachi 207 type atomic absorption spectrometer.

18-Crown-6 in Benzene: A 5 ml sample pipetted from the benzene phase was diluted with 3 ml of benzene containing 1.44×10^{-2} g ml^{-1} of fluorenone and was determined at 180 °C on a Hitachi 163 type gas chromatograph using a 25 m Chemi-column coated with Silicone SF 96.

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