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Kinetic Study on The Base Catalysed α-Proton Elimination From 9-Halogenofluorene in Presence of Benzaldehyde And P-Nitrobenzaldehyde as Intercepting Agent.

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Kinetic Study on The Base Catalysed α-Proton Elimination From 9-Halogenofluorene in Presence of Benzaldehyde and P-Nitrobenzaldehyde as Intercepting Agent.

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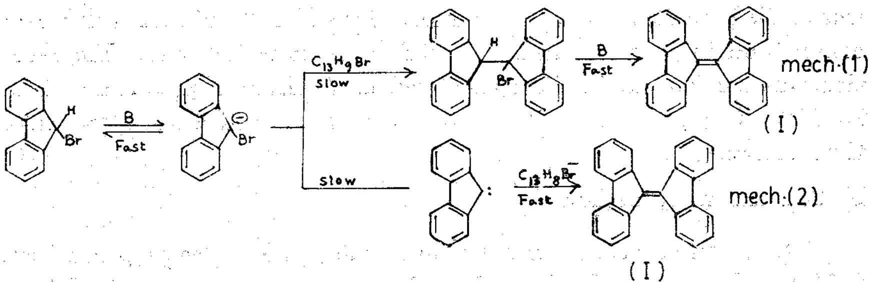
SUMMARY

Base catalysed C–C condensation reaction of intercepting carbonyl compound such as benzaldehyde and P– nitrobenzaldehyde with 9–chloro– and 9–bromo–fluorene was studied at different temperatures in aqueous dioxan solution. The reaction was followed up by a spectrophotometric method. The order of the reaction was found to be pseudo second order. FlHBr is faster than FlHCl by using the same aldehyde. The absorbance changes with the concentration of intercepting carbonyl compounds, indicating that the rate determining step involves the participation of aldehyde.

INTRODUCTION

The conversion of 9–bromofluorene (FlHBr) into bifluorenylidene by base in t–butanol has been kinetically studied by Bethel[1], who showed that the rate determining step involves nucleophilic attack by the 9–bromofluorenyl anion (cf. mechanism I). Bergman and Hervey[2] however, reported another mechanism involving a carbene formation (cf. mechanism 2).



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EXPERIMENTAL

Apparatus

Spectra were measured by using Pye Unicam Sp 1800 spectrophotometer provided with thermostated optical cell inwhich absorbance was automatically recorded.

Materials

Dioxan was purified according to the standard procedure[3].

9–Chlorofluorene (m.p. 90 °C) was prepared by reduction of fluorenone into hydroxyfluorene with KOH and Zn dust followed by chlorination with PCl_5 in dry benzene to give 9–chlorofluorene[4].

9–Bromofluorene (m.p. 104 °C) was prepared by bromination of fluorene with N–bromosuccinimide in carbon tetrachloride[5].

All aldehydes used were laboratory reagent grade (BDH) and recrystallized out from ethanol.

Kinetic technique and rate measurements:

The reaction of 9–halogenofluorene with aldehyde in presence of base were determined by two methods:

a) Dilute method:

Appropriate quantities of stock dioxan solutions of 9–halogenofluorene and aldeyhde in the same concentration (10^{-5}– 10^{-4} M) and aqueous sodium hydroxide (0.01–0.03 M) were prepared. The reaction was carried out in 70 % aqueous dioxan by adding 7 ml total volume of components in pure dioxan and 3 ml from sodium hydroxide. The reaction was carried out in the optical cell at different temperatures from 15–30 °C. The absorbance of solution was determined after appropriate time intervals.

b) Concentration method:

The reaction mixture of the molar ratio (1:1:10) was prepared from 0.01 M halide, 0.01 M aldehyde in 35 ml pure dioxan and 15 ml from 0.1 M sodium hydroxide. It was measured kinetically by withdrawal of

0.3 ml aliquots and quenching into 50 ml H_2O. Then 5 ml of this solution was transferred to 5 ml dioxan, in all aldehyde and halide. The reaction was carried out in conc. solution outer the reaction cell. The absorbed bands for 9-bromofluorene, p-nitrobenzaldehyde and final products are given in Fig. (1) The measurements were carried out at 259 nm without interference from the reactants.

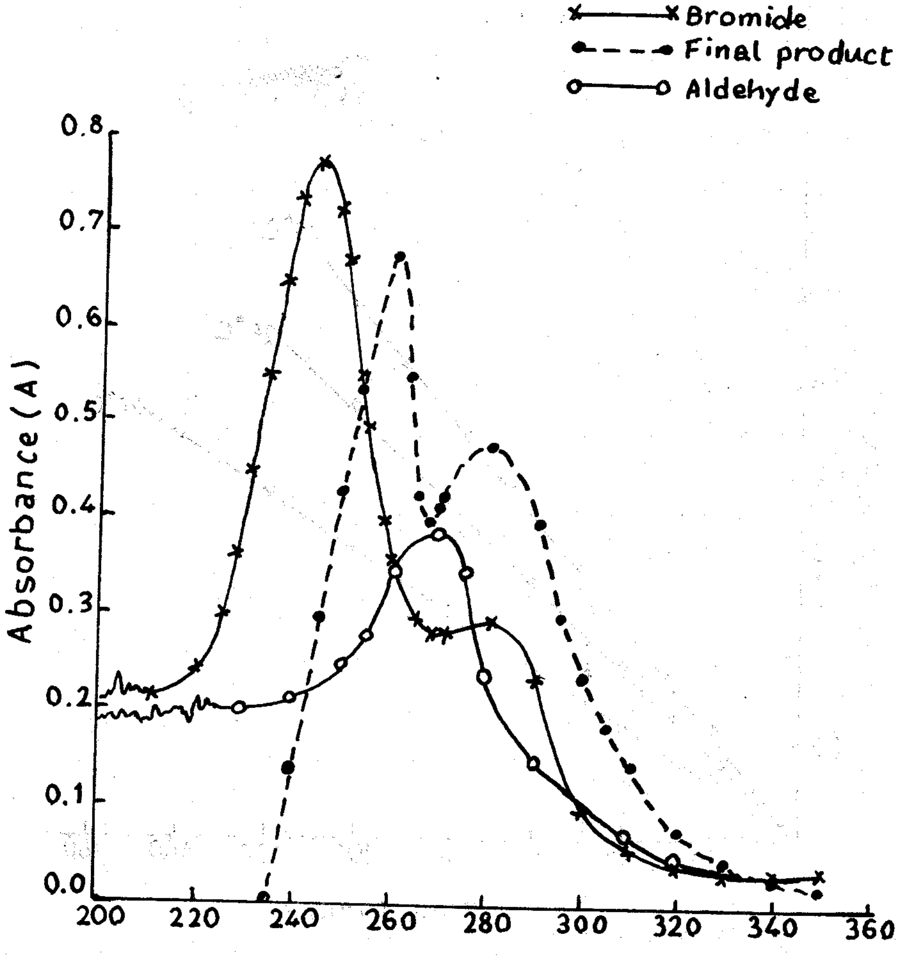
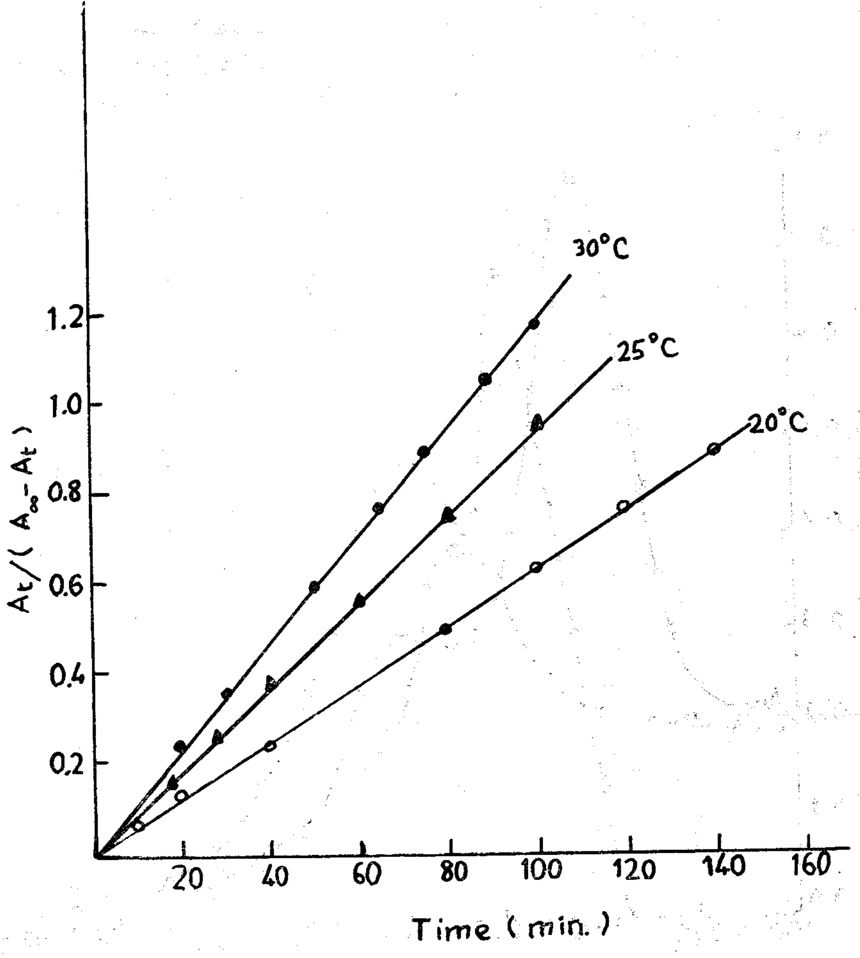


Fig-1

The order of the reaction was determined kinetically by graphical method where (A_t) is the observed absorbance at time (t) and (A_∞) is the infinity of the absorbance and the rate constants K_2 were determined by plotting $A_t / A_\infty - A_t$ vs t (min.) A straight line was obtained passing through the origin indicating typical second order reaction (of. Fig. 2)



Fig·2

Reaction product:

The reaction mixture of concentration solution ,without aldehyde, was left overnight at room temperature. A yellow crystalline precipitate separated out, filtered off, acidified, extracted with ether and recrystallized out from ethanol to give compound (I) (cf. page 167) with the yield of 64 % . It was proved to be bifluorenylidene by m.p. and mixed m.p. with authentic sample. The UV spectrum shows λ_{max} at 270 nm, ε_{max} 44.28×10^3. The same product (I) was formed in the case of 9–bromo and 9–chlorofluorene.

Base-catalysed condensation of 9–bromofluorene with intercepting carbonyls:

To the previous mixture containing 0.01 M of the halide and 0.1 M of sodium hydroxide, add 0.01 M aldehyde at the same reaction condition. A crude product was separated after acidification and extracted with ether to give crystalline products II and III (cf. page 174) frombenzaldehyde and p-nitrobenzaldehyde, respectively. The final product was proved to be epoxide as shown by two splitted epoxide bands at 1100–1090 and at 850[6] cm^{-1}. λ_{max} at 256 nm $\varepsilon = 15.24 \times 10^3$ for benzaldehyde, λ_{max} 259, $\varepsilon = 20.24 \times 10^3$ for p-nitrobenzaldehyde. Table I contains the analysis and properties of the reaction products.

Table 1. Proparties and Analysis of the reaction products.

Compound	m.p. °C	Colour	Mol. Formula		Analysis	
					Found	Calc.
I	188	red	$C_{26}H_{16}$	C	95.00	95.30
				H	4.70	4.87
II	131–2	yellow	$C_{20}H_{14}O$	C	88.40	88.90
				H	5.40	5.20
III	150–3	yellow	$C_{20}H_{13}NO_3$	C	76.80	76.19
				H	4.30	4.16
				N	3.83	4.44

RESULT and DISCUSSION

The spectrophotometric method was used at low concentration as well as high concentration by dilution followed by measurement at certain concentration as mentoined before 2–2.4 × 10^{-5}. The absorbance of reaction mixture after completion of the reaction usually agreed closely with the products. Quantitative conversion of the 9–halogenofluorene being assumed.

Rate constants were evaluated graphically by the use of appropriate integrated kinetic equation.

In all cases the absorbance, increased by time at different temperatures was used to determine the order, mechanism and reactivity of 9–chloro and 9–bromofluorene. Condensation with benzaldehyde and p-nitrobenzaldehyde as intercepting agent with excess alkali 1 × 10^{-2} or 2 × 10^{-2} M were studied to show the effect of concentration of base upon reactivity. The reactant bands were at 244 and 280 nm for 9–bromofluorene and 266 nm for p-nitrobenzaldehyde. New bands at 255, 259 nm for the product with benzaldehyde or p-nitrobenzaldehyde respectively. However, the spectrum of the reaction mixture with base was completely different from that of 9–halogenofluorene in pure dioxan i. e .the band of the product is not interfering with bands of reactants as shown in Fig. 1. Blank experiment was measured and substracted from all runs ($A_0 = 0.4$).

The reaction was carried out in nitrogen atmosphere in a closed system as shown by Bethell[1] and Bethell and Cockerill[7].

The kinetic data of the reaction. 2.4 × 10^{-5} M of 9–bromo or 9– chlorofluorene in 70 % aqueous dioxan at 30°C in the presence of excess sodium hydroxide 1 × 10^{-2} M is shown in Table 2.

Table 2.- Kinetic Data for the Reaction of 9–halofluorene with Sodium Hydroxide in 70 % Aqueous dioxan at 30°C.

10^5 (FlHCl) M	10^2 (NaOH) M	$K_1 \times 10^4 sec^{-1}$
a) 2.4	1.0	0.03
b) 2.0	1.0	0.015
10^5(FlHBr) M		
c) 2.4	1.0	9.60
d) 2.0	1.0	5.20
e) 2.0	2.0	11.04

Pseudo first order kinetics of reaction was indicated by the linear plot of log $A_t / (A_\infty - A_t)$ vs t $A_\infty = 1.3$ for various runs (in the absence of aldehyde) which gave a straight line passing through the origin. By increasing the concentration of the base from 0.01 M to 0.02 M the reactivity of the reaction increased nearly to double (cf. Table 2 d&e).

This result supported that the reaction is pseudo first order depending on the halide and the base concentration (present in excess), and kinetic equation $\nu = K_2$ [FlHBr] [Base] is attributable to the base concentration.

In case of the reaction of 9–chloro or 9–bromofluorene with sodium hydroxide in 70% equeous dioxan, the same product (bifluorenylidene m.p. 188°C) was obtained. From the data given the reactivity decreases in the order 9–bromofluorene > 9–chloro-fluorene (cf. Table 2 a&c). The calculation of entropy change ($\triangle S^{\neq}$) for FlHBr = –30.8 and FlHCl = –39.5 eu at 30°C proved that it is decreased in the same order.

On the other hand, the kinetic data for the condensation of 9–chloro or bromofluorene with benzaldehyde (R″) or p–nitrobenzaldehyde (R′) are given in Table 3. The results were obtained By linear plot of $A_\infty / (A_\infty - A_t)$ vs t.

Order of Reaction:

The order of the reaction was evaluated graphically by the use of appropriate integrate kinetic equation. By plotting $A_\infty / (A_\infty - A_t)$ vs t (min.). A straight lines for all cases were obtained passing through the origin indicating that the reaction proceeds by pseudo second order. By doubling the concentration of the carbonyl compound from 2.4×10^{-5} (M) to 4.8×10^{-5} and plotting log $\frac{A_a - A_t}{A_b - A_t} \times \frac{A_b}{A_a}$ vs t a straight line was obtained with K_2 at 25° C equal to 6.5 L. mol^{-1}. sec^{-1}. The observed second order velocity constant (K_2) was found to be nearly the same value (cf. Table 3 c & d). The tate constand K_2 increases in case of FlHBr than FlHCl in the same aldehyde (a & i). The reactivity increases in p-nitrobenzaldehyde more than benzaldehyde Table 3 (a & k)

Table 3. Kinetic Data for the Reaction of 9–Halofluorene with Aldehyde in Precence of NaOH in 70 % Aqueous Dioxan.

10^5(FlHBr) M	10^5(R′) M	10^2(NaOH) M	T°C	K_2 L mol^{-1} sec^{-1}
a) 2.4	2.4	1.0	30	7.65
b) 2.4	2.4	2.0	30	4.40
c) 2.4	2.4	1.0	25	6.25
d) 2.4	4.8	1.0	25	6.50
e) 2.4	2.4	1.0	20	4.40
f) 2.0	2.0	1.0	30	4.10
g) 2.0	2.0	1.0	22	3.27
h) 2.0	2.0	1.0	15	2.50
10^5(FlHCl) M				
i) 2.4	2.4	1.0	30	1.16
j) 2.4	2.4	1.0	15	0.31
10^5(FlHBr) M	10^5(R″) M			
k) 2.4	2.4	1.0	30	2.82

Effect of cencentration of base upon absorbitivity:

In the same molar ratio of 9–bromofluorene and p–nitrobenzaldehyde (R′) but different concentrations of the base, the value of K_2 changed into nearly double by doubling the concentration of the base from 1×10^{-2} M into 2×10^{-2} M at 30°C but the order remained the same as shown in Table 3 (a &b). This indicates that the reaction is a pseudo second order and the rate of reaction may be given by the expression $\nu = K_3[\mathrm{FlHBr}][R'][\mathrm{Base}]$. The rate is dependent upon first power of halide, first power of aldehyde with respect to the base (present in excess).

Activation parameters:

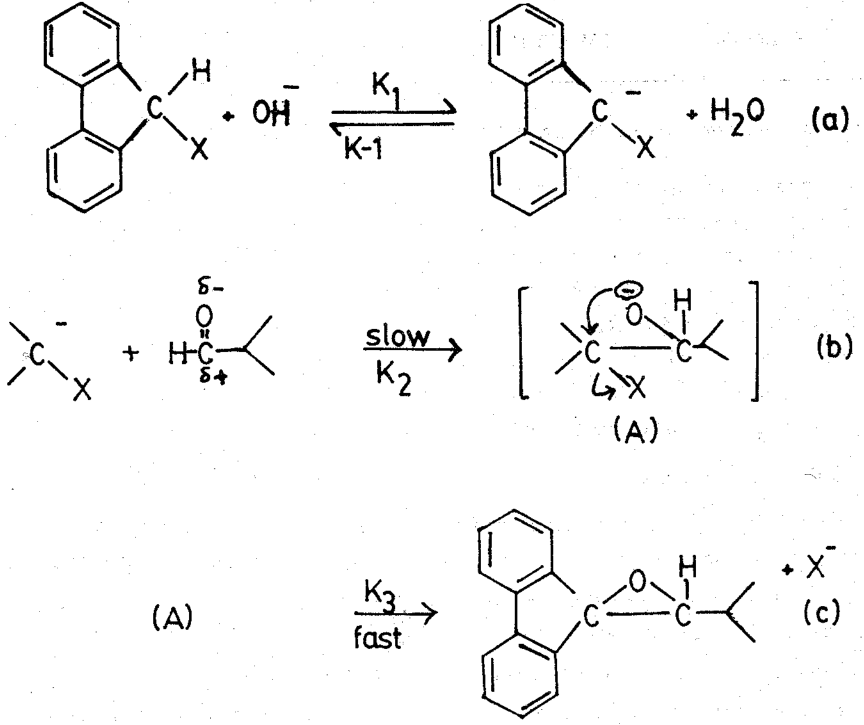
From Table 3 E_a was calculated from the slope of the corresponding linear plot of log K_2 vs $1/T$ and by application of arrhenius equation. From E_a and the corresponding K_2 value at 30°C, the $\triangle S^{\neq}$ was also calculated. At the concentration of 2.4×10^{-5} M, $\triangle$ E was equal to 1.005 Kcal, $\triangle S^{\neq} = -31.33$ eu and at the concentration of 2.0×10^{-5} M $\triangle$ E was equal to 0.617 Kcal, and $\triangle S^{\neq} = -53.73$ eu. This indicates that the reaction acquires higher order as the concentration decrease.

Ractivity change with change halogenofluorene:

The reaction of 9–chlorlo or 9–bromofluorene with p–nitrobenzaldehyde under the same conditions of Table 3 (a &i) show that the bromide is greater seven times than chloride.

Mechanism of the reaction

The absorbance schanges with the change of carbonyl compound concentration in presence of excess alkali is shown in Table 3 (c &d) This means that the rate determining step involves the participation of aldehyde as follows:



X= Cl , Br

epoxide product
II or III

carbonyl = benzaldehyde (II), p-nitrobenzaldehyde (III)

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