BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (9), 2741—2742 (1979)

Kinetics of Reaction of 4-Substituted ω-Bromo-1-acetonaphthones with Aniline in Methanol

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(Received September 25, 1978)

Synopsis. Rate constants have been measured for the reactions of 4-substituted ω-bromo-1-acetonaphthones with aniline in methanol at three temperatures. Arrhenius parameters, the enthalpies and the entropies of activation have been evaluated. The Hammett ρ value of 0.90 obtained at 40 °C indicates that a triangular transition state is more likely in this reaction.

In a previous paper[1)] we reported a study of the reaction of 4-substituted ω-bromo-1-acetonaphthones with benzoate ion. The reaction between 4-substituted ω-bromo-1-acetonaphthones and aniline is now investigated with a view to examine the applicability of the Hammett equation.

Experimental

Materials. All the 4-substituted ω-bromo-1-acetonaphthones were prepared from the corresponding acetonaphthones by treatment with bromine. Their purities were ascertained by microanalysis and TLC.[2)]

Methanol was dried and purified by the method of Lund and Bjerrum.[3)]

Rate Measurement. The kinetic procedure was similar to that employed previously[4)] and the rate constants were calculated using the suitable second-order rate equation when two moles of aniline are consumed per mole of the ω-bromoacetonaphthones.

Products. Standard solutions of the appropriate ω-bromo-1-acetonaphthone and aniline in methanol were mixed in the molar ratio 1:4 and maintained at the kinetic temperature until completion. After concentration of the solution to small volume under reduced pressure, the products precipitated were collected, and recrystallized. In all cases only the ω-anilinoacetonaphthone was formed. No other product was detected. Table 1 lists the compounds isolated, their mp and elemental analyses.

Results and Discussion

The reaction is found to be first order in each of the reactants. This was established by usual procedure with ω-bromo-1-acetonaphthone. Hence we assume that the reaction follows a two-stage mechanism, with the bimolecular rate-determining first stage.

$$RCOCH_2Br + PhNH_2 = RCOCH_2NHPh + HBr \qquad (1)$$

$$HBr + PhNH_2 = PhNH_3^+Br^- \qquad (2)$$

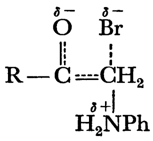
where R is 4-substituted 1-naphthyl group.

The kinetic data are presented in Table 2. The entropies of activation are found to be negative as expected for bimolecular reactions.[5)] But they are more negative than those observed in reactions with benzoate ion.[4)] This may be due to the fact that charge is dispersed in the transition state in the case of reactions with benzoate ion, while in the present case the charge is newly produced in the transition state.

A linear relationship between the enthalpies and the entropies of activation has been realised. As explained by Exner,[6,7)] the isokinetic relationship has also been examined through a plot of $\log k_1$ *versus* $\log k_2$ where k_1 and k_2 refer to the rate constants at temperatures T_1 and T_2 respectively with $T_1 > T_2$. From the slope ($b=0.854$) of the linear plot, the isokinetic temperature (β) is calculated to be 508 K, when $T_1=323$ and $T_2=303$ K.

The plot of $\log k/k_0$ at 40 °C against σ constants[8)] of the 4-substituents in 1-naphthyl system is linear. The ρ value is 0.90 at 40 °C (excluding the result for 4-OCH_3). The correlation coefficient is 0.998 showing excellent Hammett fit.

Depending upon the mode of attack of aniline, one may consider transition states I and II in this reaction.



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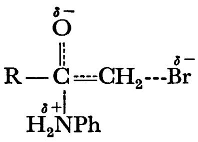
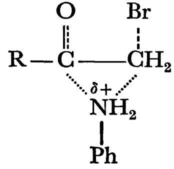


II

The formation of II may require very high ρ value in view of the ρ values of 3.2 and 2.76(2.24) found for the addition reactions of methoxide, and hydroxide ion, respectively, to substituted benzaldehydes.[9,10)] The low ρ value observed in the reaction of 6-substituted ω-bromo-2-acetonaphthones[4)] with aniline was ascribed to S_N2 attack of aniline at the methylene carbon. The ρ value of 0.90 calculated in the present case is significantly higher than the ρ values obtained in S_N2 displacement of substituted ω-bromoacetonaphtones at methylene carbon by different nucleophiles.[11)] This may, therefore, point out that a triangular transition state III which is a hybrid between I and II is more likely in the present case.



III

The cause for the difference in the nature of the transition state in the present case compared to that in the case of 6-substituted ω-bromo-2-acetonaphthones may possibly be due to the partial inhibition of resonance between >C=O group and the ring as a result of the

Table 1. 4-Substituted ω-anilino-1-acetonaphthones

Substituent	Mp °C	Formula	Calcd, %		Found, %	
			C	H	C	H
H	150—151a)	$C_{18}H_{15}NO$	82.8	5.8	82.5	5.9
F	123—124b)	$C_{18}H_{14}FNO$	77.4	5.0	77.3	5.1
Cl	139—140a)	$C_{18}H_{14}ClNO$	73.1	4.7	73.0	4.6
Br	120—121a)	$C_{18}H_{14}BrNO$	63.5	4.1	63.6	3.8
CH_3	100—101a)	$C_{19}H_{17}NO$	82.9	6.2	82.6	6.0
OCH_3	144—145a)	$C_{18}H_{17}NO_2$	78.3	5.8	78.1	5.4

Compounds crystallized from a) benzene-light petroleum (bp 40—60 °C) and b) light petroleum (bp 40—60 °C).

Table 2. Rate constants and activation parameters for the reaction between 4-substituted ω-bromo-1-acetonaphthones and aniline

Substituent	Rate constant $k/10^{-4}$ l mol^{-1} s^{-1}			E_a kcal mol^{-1}	ΔH^{*} kcal mol^{-1} (40 °C)	ΔS^{*} e. u. (40 °C)	log PZ
	30 °C	40 °C	50 °C				
H	3.77	7.65	15.9	14.8	14.2	−27.6	7.2
F	4.46	8.83	18.2	14.5	13.9	−28·0	7.1
Cl	6.11	12.5	25.3	14.1	13.5	−28.8	7.0
Br	6.24	12.6	25.5	14.1	13.5	−28.9	7.0
CH_3	2.78	5.79	12.2	15.1	14.5	−27.3	7.3
OCH_3	2.38	4.80	10.3	15.2	14.6	−27.2	7.5

ω-bromoacetyl group going out of coplanar configuration in the presence of *peri*-H interaction.[12] Such inhibition of resonance is absent in the 2-series. The inhibition of resonance helps the carbonyl carbon to acquire more positive charge in 1-series than 2-series. Presumably this may be responsible for the operation of the transition state III in 1-series as compared to its counterpart in 2-series, thereby making the ρ value larger in the former case than in the latter case.[4]

The authors dedicate this paper to Professor V. Baliah, Vice-Chancellor, Nagarjuna University, India on the occasion of his 60 th birthday and thank the managing board of V.H.N.S.N. College, Virudhunagar for the research facilities.

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