Kinetics of Solvolysis of Substituted ω-Bromo-1-acetonaphthones in Aqueous Ethanol

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The kinetics of solvolysis of ω-bromo-1-acetonaphthone in 70, 80, and 90% ethanol have been measured at several temperatures. The Grunwald–Winstein *m* value is 0.112 ± 0.005 over the temperature range 55—80 °C. The Hammett equation applies well to the solvolysis of 4-substituted ω-bromo-1-acetonaphthones and the ρ value in 80% ethanol is 0.41 at 80°. The first-order rate constants are increased by electron-withdrawing groups and decreased by electron-donating groups. The nature of the products indicates that there is no rearrangement involving the carbonyl oxygen and the naphthyl group in the transition state. The reaction may be a simple nucleophilic displacement of bromide by solvent molecules.

We have previously described a study of the kinetics of solvolysis of 6-substituted ω-bromo-2-acetonaphthones.[1] We now report a similar investigation of 4-substituted ω-bromo-1-acetonaphthones, with a view to ascertaining the mechanism and also to test the applicability of the Hammett equation [2] to this solvolysis reaction.

EXPERIMENTAL

Preparation of Compounds.—All the 4-substituted ω-bromo-1-acetonaphthones were prepared from the corresponding acetonaphthones [3] by treatment with bromine. Their purity was ascertained by microanalysis and t.l.c. ω-Bromo-1-acetonaphthone had b.p. 197° at 12 mmHg (lit.,[4] 83—84°) (Found: C, 57.7; H, 3.8. Calc. for $C_{12}H_9BrO$: C, 57.8; H, 3.6%); *ω-bromo-4-methyl-*1-*acetonaphthone* had b.p. 209° at 12 mmHg (Found: C, 58.9; H, 4.3. $C_{13}H_{11}BrO$ requires C, 59.3; H, 4.2%).

Purification of Solvent.—Pure ethanol was prepared by Smith's method [5] with diethyl phthalate in place of diethyl succinate and had b.p. 78.0—78.5° at 760 mmHg. Karl Fischer titration [6] indicated a water content of $<0.2\%$.

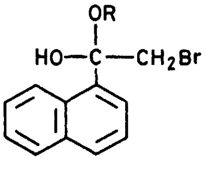
Rate Measurements.—The kinetic procedure was essentially that employed previously.[1] The reactions were followed to 80% completion. Rate constants were calculated from the first-order rate equation.

Product Analysis.—The procedure described previously [1] was followed. The product from the ethereal solutions was a mixture of ω-ethoxy- and ω-hydroxy-1-acetonaphthones in the ratio *ca.* 70 : 30 (w/w). The proportions of ether and alcohol were obtained by direct estimation of ethoxy- and hydroxy-groups by the methods of Zeisel [7] and Ogg *et al.*,[8] respectively. The product gave a negative result in a test for esters. T.l.c. on silica gel [benzene–light petroleum (b.p. 60—80 °C) (3 : 1)] gave only two spots, corresponding to those from authentic samples of ether and alcohol.

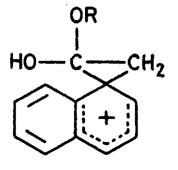
The sodium hydroxide extract gave $<3\%$ w/w of an acidic compound whose m.p. did not agree with that of 1-naphthylacetic acid. The total recovery of product was 95—98%.

RESULTS AND DISCUSSION

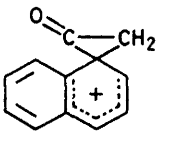
The solvolysis of 6-substituted ω-bromo-2-acetonaphthones [1] in aqueous ethanol is a simple nucleophilic displacement of bromide by solvent molecules. We therefore considered it of interest to see whether the solvolysis of 4-substituted ω-bromo-1-acetonaphthones is also a simple nucleophilic displacement process or whether it proceeds through any of the possible intermediates (1)—(4) that could result either from the addition of solvent to the carbonyl group followed by rearrangement or by participation of carbonyl oxygen and naphthyl group. However, the products formed under the conditions of our kinetic study were mostly ether and alcohol; we did not detect any rearrangement products. This appears to rule out the possibility of the reaction proceeding through the intermediate ions (2)—(4) and also the participation of the naphthyl group and the carbonyl oxygen in the transition state. The ρ value observed is 0.41 at 80 °C. This low value rules out the intermediate (1), for its formation would require a high value such as is found in the carbonyl-addition



(1)



(2)



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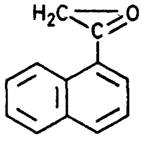

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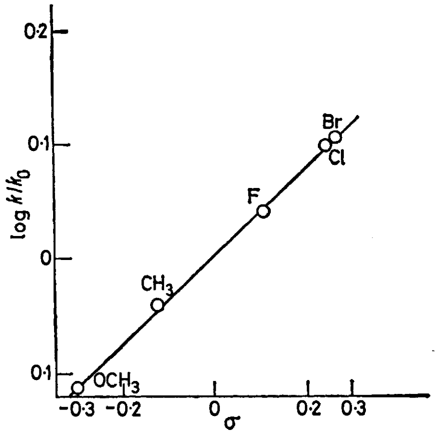
reactions of substituted benzaldehydes.[9-11] All these results suggest that the reaction proceeds by direct displacement of bromide by solvent molecules.

Linear Free Energy Relationship.—The applicability of the Hammett equation[2] to the solvolysis in 80% ethanol was tested. The reaction conforms at the three temperatures studied. The correlation coefficient is 0.970 at 80 °C (Figure).



Hammett plot of σ-values evaluated for the 4-substituents from the hydrolysis of 4-substituted methyl 1-naphthoates (values taken from V. Baliah and P. Ananthakrishna Nadar, *Indian J. Chem.*, 1971, **9**, 1241.)

Activation Parameters.—The activation parameters are given in Table 1. Activation enthalpies show a regular variation with substituents in the naphthalene ring; electron-withdrawing groups increase the rate and decrease $\Delta H^{\ddagger}$ while the reverse is the case for electron-donating groups.

TABLE 1

First-order rate constants and activation parameters for 4-substituted ω-bromo-1-acetonaphthones in 80% ethanol

Substituent	10^6k/s^{-1}			$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal mol^{-1} K^{-1}
	55 °C	70 °C	80 °C		
H	2.0	7.7	21.5	20.5	−22.4
F	2.5	8.8	23.7	19.5	−25.2
Cl	3.5	10.7	27.1	17.6	−30.2
Br	3.6	10.8	27.4	17.4	−30.8
CH_3	1.5	6.7	19.6	21.9	−18.7
OCH_3	1.1	5.4	16.6	24.1	−12.8

Grunwald–Winstein Relationship.—Application of the Grunwald–Winstein relationship[12] to the data in Table 2 for the solvolysis of ω-bromo-1-acetonaphthone in 70, 80, and 90% ethanol yields *m* values of 0.120, 0.112, and 0.104 at 55, 70, and 80 °C, respectively. For comparison the *m* values for ω-bromo-2-acetonaphthone are included in Table 3. These values indicate that the carbocationic character of the transition state for the solvolysis of ω-bromo-1-acetonaphthone is less than that for the solvolysis of ω-bromo-2-acetonaphthone.

TABLE 2

Solvolysis of ω-bromo-1-acetonaphthone

Solvent	10^6k/s^{-1}		
	55 °C	70 °C	80 °C
70% EtOH	2.4	9.0	25.0
80% EtOH	2.0	7.7	21.5
90% EtOH	1.6	6.5	18.1

TABLE 3

Grunwald–Winstein *m* values in aqueous ethanol

Compound	Temp. (°C)	*m*
ω-Bromo-1-acetonaphthone [a]	55	0.120 [b]
ω-Bromo-1-acetonaphthone [a]	70	0.112 [b]
ω-Bromo-1-acetonaphthone [a]	80	0.104 [b]
ω-Bromo-2-acetonaphthone	55	0.155 [c]
ω-Bromo-2-acetonaphthone	70	0.150 [c]
ω-Bromo-2-acetonaphthone	80	0.160 [c]

[a] Present investigation. [b] Accurate to within ±0.005. [c] Ref. 1.

Isokinetic Relationship.—As outlined by Exner,[13,14] the isokinetic relationship in the solvolysis of 4-substituted ω-bromo-1-acetonaphthones has 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 $T_1 > T_2$. If we have $T_1 = 353$ and $T_2 = 328$ K in this series, the plot is linear and is of slope $b = 0.393$ (by least squares). This gives a value of 373 K for the isokinetic temperature, which agrees closely with the value calculated from a linear plot of enthalpy of activation ($\Delta H^{\ddagger}$) against entropy of activation ($\Delta S^{\ddagger}$). The linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ shown by all the substituents is indicative of a single mechanism.[15]

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