Kinetics of Solvolysis of Substituted ω-Bromo-2-acetonaphthones in Aqueous Ethanol

By **P. Ananthakrishna Nadar** * and **C. Gnanasekaran**, Postgraduate Department of Chemistry, V.H.N.S.N. College, Virudhunagar 626002, India

The kinetics of the solvolysis of ω-bromo-2-acetonaphthone in 70, 80, and 90% ethanol have been measured at several temperatures. The Grunwald–Winstein m value is 0.155 ±0.005 over the temperature range of 55—80°. The Hammett equation applies very well to the solvolysis of 6-substituted ω-bromo-2-acetonaphthones and the ρ value in 80% ethanol is 0.33 at 80°. The first-order rate constants are increased by electron-withdrawing groups and decreased by electron-donating groups. The products indicate that there is no rearrangement involving carbonyl oxygen and naphthyl group in the transition state. The reaction may be a simple nucleophilic displacement of bromide by solvent molecules.

AFTER a report of Slator and Twiss [1] that α-halogenoketones easily undergo S_N2 displacement, numerous aspects of such reactions have been actively studied.[2-5] Pasto and his co-workers [6] studied the solvolysis of substituted phenacyl bromides. However a similar study of the naphthalene system does not seem to have been made so far. We therefore thought it of interest to investigate the kinetics of solvolysis of 6-substituted ω-bromo-2-acetonaphthones in aqueous ethanol. The original intention of the present work was to study the kinetics of the reaction with alkoxides as nucleophilic reagents, but such reactions were found to be too fast for kinetic investigation by conventional methods.

EXPERIMENTAL

Preparation of Compounds.—Some of the 6-substituted ω-bromo-2-acetonaphthones were prepared from the corresponding acetonaphthones [7] by either method A or B.

Method A. To a solution of the ketone (0.06 mol) in glacial acetic acid (20 ml) a solution of bromine (0.06 mol) in glacial acetic acid (5 ml) was added dropwise with shaking. After the addition of the first drop, the solution was slightly warmed to initiate the reaction. Addition of bromine was complete within 15 min when evolution of HBr almost ceased and the solution was then poured immediately over crushed ice (100 g). The separated solid was filtered off, washed with water, dried, and recrystallized. By this method were prepared ω-*bromo*-6-*fluoro*-2-*acetonaphthone*, m.p. 84—85° (from methanol) (Found: C, 53.6; H, 3.25. $C_{12}H_8BrFO$ requires C, 53.95; H, 3.0%); ω-*bromo*-6-*chloro*-2-*acetonaphthone*, m.p. 138—139° (from light petroleum) (Found: C, 50.75; H, 2.95. $C_{12}H_8BrClO$ requires C, 50.8; H, 2.85%); and ω-bromo-6-methyl-2-acetonaphthone, m.p. 107—108° (from light petroleum) (lit.,[8a] 92°) (Found: C, 59.45; H, 4.35. Calc. for $C_{13}H_{11}BrO$: C, 59.35; H, 4.2%).

Method B. The ketone (0.03 mol) in chloroform (20 ml) was treated with liquid bromine (0.03 mol). After 10 min, dry air was passed through the solution to expel HBr gas. The solution was washed with water, dried, the solvent evaporated, and the product recrystallized. By this means were prepared ω-bromo-6-methylthio-2-acetonaphthone, m.p. 134—135° (from ethyl acetate) (lit.,[8b] 102°) (Found: C, 52.45; H, 3.9. Calc. for $C_{13}H_{11}BrOS$: C, 52.9; H, 3.75%) and ω-*bromo*-6-*methylsulphonyl*-2-*acetonaphthone*, m.p. 115—116° (from ethanol) (Found: C, 47.75; H, 3.35. $C_{13}H_{11}BrO_3S$ requires C, 47.7; H, 3.4%).

ω-Bromo-2-acetonaphthone and its 6-methoxy-derivative were prepared by known procedures.[9,10] Their m.p.s agreed with those in the literature.

Purification of Solvent.—Pure ethanol was prepared by Smith's method [11] with diethyl phthalate in place of diethyl succinate and had b.p. 78.0—78.5° at 760 mmHg. Karl Fischer titration [12] indicated a water content of <0.02%.

Rate Measurements.—Standard solutions (0.01—02M) of the substrate in the solvent systems were prepared. Aliquot portions of the solutions were sealed in ampoules which were placed in a constant temperature bath. At intervals, the ampoules were removed and chilled in ice. The contents were washed with water (10 ml) into a separatory funnel containing cold benzene (25 ml). Organic material was taken up in benzene. The acid (HBr) in the aqueous layer was estimated with standard baryta. The reactions were followed to 80% completion. Rate constants were calculated from the first-order rate equation.

Product Analysis.—Solutions of ω-bromo-2-acetonaphthone (0.5—1.0 g) in the solvent systems (10 ml) were sealed in ampoules and placed in a constant temperature bath at the kinetic temperature. After *ca*. 3 half-lives the contents were dissolved in ether. Ethereal solutions were washed with dilute sodium hydroxide solution and dried. The solvent was completely removed under reduced pressure. The product was a mixture of ω-ethoxy- and ω-hydroxy-2-acetonaphthone in the ratio *ca*. 75 : 25 (w/w). The percentage of ether and alcohol was obtained by direct estimation of ethoxy- and hydroxy-groups by the methods of Zeisel [13] and Ogg *et al*. [14] respectively. The product gave a

---

[1] A. Slator and D. F. Twiss, *J. Chem. Soc.*, 1909, 93.

[2] E. D. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.

[3] J. W. Baker, *J. Chem. Soc.*, 1938, 445; *Trans. Faraday Soc.*, 1941, **37**, 643.

[4] R. G. Pearson, S. H. Langer, F. V. Williams, and W. J. McGuire, *J. Amer. Chem. Soc.*, 1952, **74**, 5130.

[5] P. D. Bartlett and E. N. Trachtenberg, *J. Amer. Chem. Soc.*, 1958, **80**, 5808.

[6] D. J. Pasto, K. Garves, and M. P. Serve, *J. Org. Chem.*, 1967, **32**, 774.

[7] P. Ananthakrishna Nadar and C. Gnanasekaran, *Indian J. Chem.*, 1975, **13**, 1238.

[8] (*a*) A. F. Gowther, R. Howe, and L. Harold, Belg. P., 626,434/1963 (*Chem. Abs.*, 1964, **60**, 7968); (*b*) Ng. Buu-Höi, Ng. Hoan, and D. Lavit, *J. Chem. Soc.*, 1953, 485.

[9] T. Immediata and A. R. Day, *J. Org. Chem.*, 1940, **5**, 512.

[10] L. Novak and M. Protiva, *Chem. Listy*, 1956, **50**, 1610 (*Chem. Abs.*, 1957, **51**, 3533).

[11] E. L. Smith, *J. Chem. Soc.*, 1927, 1288.

[12] W. Seaman, W. H. McComas, and G. A. Allen, *Analyt. Chem.*, 1949, **21**, 510.

[13] A. Elek in ' Organic Analysis,' Interscience, New York, 1955, vol. 1, p. 68.

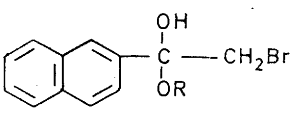
[14] C. L. Ogg, W. L. Porter, and C. O. Willits, *Ind. and Eng. Chem., Analyt. Edn.*, 1945, **17**, 394.

negative test for ester. T.l.c. analysis on silica gel [benzene–light petroleum (b.p. 60—80°) (3 : 1)] gave only two spots which corresponded with those of authentic samples of ether and alcohol.

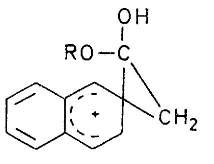
The sodium hydroxide extract gave <4% w/w of acidic compound whose m.p. did not agree with that of 2-naphthylacetic acid. Total recovery of product was 95—98%.

RESULTS AND DISCUSSION

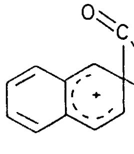
The mechanism suggested by Cope [15] for the reaction of bicyclic bromo-ketones with silver ion in aqueous ethanol involved the addition of solvent to the carbonyl group followed by rearrangement and expulsion of bromide. On this basis several mechanistic pathways are potentially possible in the solvolysis of ω-bromo-2-acetonaphthones. One such to be considered is simple nucleophilic displacement of bromide by solvent. Others may lead to the formation of any of the intermediates (1)—(4). We, therefore, considered it worthwhile to see whether the solvolysis of 6-substituted ω-bromo-2-acetonaphthones is a simple nucleophilic displacement process or if it proceeds through any of the intermediates (1)—(4). The products formed under the conditions of our kinetic study are mostly ether and alcohol and there was no detectable trace of rearranged products. This shows that there is little sign of the reaction proceeding through the intermediate ions (2)—(4) and hence no participation of naphthyl group and carbonyl oxygen in the transition state. The ρ value observed by us is 0.33 at 80°. This low value is very similar to those obtained by others [16,17] in direct S_N2 displacement reactions of phenacyl bromide with nucleophiles. The low ρ value rules out intermediate (1), for its formation would require a high ρ value in view of the values of 2.0, 3.2, and 2.76 (2.24) found for the addition reactions of methanol, methoxide ion, and hydroxide ion, respectively, to substituted benzaldehydes.[18-20] All these seem to suggest that the reaction may be direct displacement of bromide by solvent molecules. Similar conclusion has been reached by Pasto and his co-workers [6] in the solvolysis of phenacyl bromides.



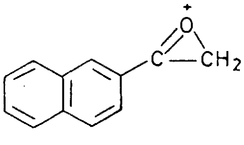
(1)



(2)



(3)



(4)

Linear Free Energy Relationship.—The validity of the Hammett equation [21] was examined in the solvolysis of 6-substituted ω-bromo-2-acetonaphthones in 80% ethanol. The reaction conforms very well with the Hammett equation at three temperatures. The correlation coefficient is 0.996 at 80°.

Activation Parameters.—Activation parameters are noted in Table 1. The values of the 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 true for electron-donating groups.

TABLE 1

First-order rate constant and activation parameters for 6-substituted ω-bromo-2-acetonaphthones in 80% ethanol

Substituent	$10^6k/s^{-1}$ 55°	70°	80°	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
H	3.0	11.3	28.6	20.3	−22.2
F	3.3	12.1	30.2	19.3	−25.0
Cl	3.8	13.6	31.8	18.7	−26.4
CH_3	2.3	10.2	26.5	21.8	−17.9
OCH_3	2.1	9.6	25.4	22.4	−16.3
SCH_3	3.1	11.7	29.3	19.8	−23.6
SO_2CH_3	6.4	17.6	38.8	16.2	−33.3

Grunwald–Winstein Relationship.—Application of the Grunwald–Winstein relationship [22] to the data in Table 2 for the solvolysis of ω-bromo-2-acetonaphthone in 70, 80, and 90% ethanol yields *m* values of 0.155, 0.150, and 0.160 at 55, 70, and 80° respectively. For comparison the *m* values for phenacyl bromide and alkyl bromides are included in Table 3. The Grunwald–Winstein *m* value measures the sensitivity of the substrate to the ionising power of the solvent and increases as the carbonium ion character of the transition state increases. The *m* values in Table 3 indicate that the

TABLE 2

ω-Bromo-2-acetonaphthone

Compound	Solvent	$10^6k/s^{-1}$ 55°	70°	80°
ω-Bromo-2-acetonaphthone	70% Ethanol	4.3	14.0	25.3
ω-Bromo-2-acetonaphthone	80% Ethanol	3.0	11.3	28.6
ω-Bromo-2-acetonaphthone	90% Ethanol	2.4	8.5	20.9

---

[15] (*a*) A. C. Cope and M. E. Synerholm, *J. Amer. Chem. Soc.*, 1950, **72**, 5228; (*b*) A. C. Cope and E. S. Graham, *ibid.*, 1951, **73**, 4702.

[16] J. W. Baker, *Trans. Faraday Soc.*, 1941, **37**, 632.

[17] F. J. Ozog, V. Comte, and L. C. King, *J. Amer. Chem. Soc.*, 1952, **74**, 6225.

[18] M. R. Crampton, *J.C.S. Perkin II*, 1975, 185.

[19] W. J. Bover and P. Zuman, *J.C.S. Perkin II*, 1973, 786; *J. Amer. Chem. Soc.*, 1973, **95**, 2531.

[20] M. R. Crampton, M. A. El Ghariani, and M. J. Willison. *J.C.S. Perkin II*, 1974, 441.

[21] (*a*) P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, London, 1968; (*b*) J. Shorter, *Chem. in Britain*, 1969, **5**, 269; (*c*) 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum, London, 1972.

carbonium ion character of the transition state for the solvolysis of ω-bromo-2-acetonaphthone is less than that for the solvolysis of phenacyl bromide.

TABLE 3

Grunwald–Winstein *m* values in aqueous ethanol

Compound	Temp (°C)	*m*
ω-Bromo-2-acetonaphthone [a]	55	0.155 [b]
ω-Bromo-2-acetonaphthone [a]	70	0.150 [b]
ω-Bromo-2-acetonaphthone [a]	80	0.160 [b]
Phenacyl bromide	55	0.20 [c]
Phenacyl bromide	70	0.19 [c]
Phenacyl bromide	80	0.21 [c]
Methyl bromide	50	0.258
Isopropyl bromide	50	0.544

[a] Present investigation. [b] Accurate within ±0.005. [c] Ref. 6.

Isokinetic Relationship.—As explained by Exner,[23,24] the isokinetic relationship in the solvolysis of 6-substituted ω-bromo-2-acetonaphthones has been examined through a plot of log k_1 *versus* log k_2 where k_1 refers to the rate constants at temperature T_1 and k_2 to the constants at temperature T_2, with $T_1 > T_2$. If we take T_1 353 and T_2 328 K in this series, the plot is linear and is of slope $b = 0.358$ (by least squares). This gives a value of 368 K for the isokinetic temperature, which agrees with the value calculated from a linear plot between enthalpy of activation ($\Delta H^\ddagger$) and 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.[25]

We thank the managing board of the V.H.N.S.N. College, Virudhunagar, for support.

[6/349 *Received, 18th February*, 1976]

---

[22] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

[23] O. Exner, *Nature*, 1964, **201**, 488; 1970, **227**, 366.

[24] O. Exner, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1094.

[25] K. Bowden, N. B. Chapman, and J. Shorter, *J. Chem. Soc.*, 1964, 337.