Kinetics of Reaction of Picryl Bromide with Substituted Naphthoate Ions

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Second-order rate constants have been measured for the reactions of picryl bromide with 6- and 4-substituted 1-naphthoate and 6-substituted 2-naphthoate ions in 80% methanol–water at several temperatures and activation parameters have been calculated. The Hammett equation applies very well to these reactions. The rate constants are correlated with the pK_a values of the corresponding naphthoic acids *via* the Brönsted equation giving a β value of 0.30 for the 1-series and 0.56 for the 2-series. Electron-withdrawing groups decrease and electron-donating groups increase the rate. A linear correlation between $\Delta H^‡$ and $\Delta S^‡$ is indicative of a single mechanism.

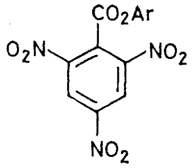
ALTHOUGH the study of bimolecular nucleophilic substitutions employing benzene derivatives as nucleophiles has received much attention,[1] very few studies have so far been undertaken with naphthalene derivatives. We have recently reported a study of the kinetics of the reaction of 6-substituted 2-naphthoate ions with phenacyl bromide.[2] We now report our study of the reaction of several naphthoate ions with picryl bromide, a compound containing an activated halogen at the reaction centre. Our original intention was to study the reactions of picryl bromide with substituted naphthoxide ions and substituted naphthylamines to provide a comparison of the reaction of oxygen with that of nitrogen nucleophiles. But these reactions were found to be too fast under our conditions for kinetic investigation by conventional methods.

EXPERIMENTAL

Materials.—Picryl bromide was prepared as described [3] and recrystallized from ethanol, m.p. 123—124°. The naphthoic acids were prepared by literature methods.[4,5] *6-Iodo-1-naphthoic acid* was crystallized from ethanol, m.p. 159—160° (Found: C, 44.3; H, 2.4. $C_{11}H_7O_2I$ requires C, 44.3; H, 2.35%). Methanol was purified by the method of Lund and Bjerrum.[6] Triply distilled water was used for dilution. Sodium salts of the naphthoic acids were prepared by the usual procedure in ethanol.

Rate Measurements.—The solvent used was 80% methanol–water. The temperature was controlled to ±0.1°. The reactions were studied under second-order conditions. Low concentrations of the reactants (0.01M in both) were found to be suitable for following the kinetics satisfactorily. The reactions were followed by pipetting portions (10 ml) into aqueous 5% nitric acid and titrating the bromide ion by Volhard's method after removing the organic matter with benzene. In every case the kinetic runs were followed to at least 75% completion and the second-order rate constants were calculated using the equation $k = x/at(a - x)$. The rate constants are reproducible to within 2%.

Reaction Path and Products.—We followed the liberation of bromide ion which may arise from nucleophilic attack by naphthoate ion at C-1 of picryl bromide. Bromide ion could also arise by attack of OH^- formed by the hydrolysis of the sodium salts of the acids. There is a further possibility of liberation of Br^- by general base catalysed attack of water or methanol. Given these possibilities, the situation is not simple. However, that the process being followed is mainly nucleophilic attack on picryl bromide by naphthoate ion is confirmed by almost quantitative isolation of the picryl ester (1) in all cases. The product did not contain methyl picryl ether. The amount of picric acid formed is so small that it does not affect the overall order of the reaction.



(1)

Standard solutions of the appropriate sodium naphthoate and picryl bromide were mixed in equimolar ratio and maintained at the kinetic temperature until completion. After concentration of the solution to small volume under reduced pressure, the picryl esters precipitated were filtered, and recrystallized from suitable solvents. In all cases the amount of ester formed was *ca.* 95%. Table 1 lists the new compounds isolated, their m.p.s, and analyses.

RESULTS AND DISCUSSION

It was observed that the reactions followed second-order kinetics, first order in each reactant. The usual procedure was employed to establish this in a few representative cases. The data in Tables 2 and 3 indicate that electron-withdrawing groups decrease and electron-donating groups increase the rate showing that it depends on the electron density on the oxygen atom of the nucleophile. The observation that naphthoxide ions and naphthylamines reacted very rapidly with picryl bromide shows that naphthoxide ions and naphthylamines are stronger nucleophiles than naphthoate ions.

Activation Parameters.—The activation energies were computed from the linear plots of log k against $1/T$. The values of the activation energies show a regular variation with substituents: electron-withdrawing groups increase and electron-donating groups decrease E_a.

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The entropies of activation are negative as for bimolecular reactions.

TABLE 1

Picryl naphthoates

Substituent	M.p. (°C)	Recryst. solvent	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
		Picryl 4- (or 6-)substituted 1-naphthoates					
H	156—157	A	53.3	2.5	$C_{17}H_9N_3O_8$	53.3	2.3
4-F	180—181	B	51.2	2.1	$C_{17}H_8N_3O_8F$	50.9	2.0
4-Cl	184—185	A	48.5	2.1	$C_{17}H_8N_3O_8Cl$	48.9	1.9
6-Cl	150—151	A	49.1	2.0	$C_{17}H_8N_3O_8Cl$	48.9	1.9
4-Br	160—161	B	43.9	2.0	$C_{17}H_8N_3O_8Br$	44.2	1.7
6-Br	114—115	A	44.0	1.9	$C_{17}H_8N_3O_8Br$	44.2	1.7
4-NO_2	172—173	A	47.7	2.0	$C_{17}H_8N_4O_{10}$	47.7	1.9
4-CH_3	134—135	A	54.7	2.9	$C_{18}H_{11}N_3O_8$	54.4	2.8
6-CH_3	94—95	A	54.7	2.7	$C_{18}H_{11}N_3O_8$	54.4	2.8
4-OCH_3	224—225	B	52.7	2.8	$C_{18}H_{11}N_3O_9$	52.3	2.7
6-OCH_3	140—141	A	52.2	2.8	$C_{18}H_{11}N_3O_9$	52.3	2.7
6-I	98—99	A	40.3	1.6	$C_{17}H_8N_3O_8I$	40.1	1.6
		Picryl 6-substituted 2-naphthoates					
H	137—138	A	53.4	2.6	$C_{17}H_9N_3O_8$	53.3	2.3
F	179—180	B	50.8	2.2	$C_{17}H_8N_3O_8F$	50.9	2.0
Cl	215—216	B	48.7	2.1	$C_{17}H_8N_3O_8Cl$	48.9	1.9
$COCH_3$	210—211	B	54.0	2.7	$C_{19}H_{11}N_3O_9$	53.6	2.6
CH_3	188—189	B	54.4	2.7	$C_{18}H_{11}N_3O_8$	54.4	2.8
OCH_3	159—160	B	51.9	2.8	$C_{18}H_{11}N_3O_9$	52.3	2.7

A, Aqueous methanol; B, aqueous ethanol.

Linear Free Energy Relationship.—The applicability of the Hammett equation [7] was tested in the reactions of picryl bromide with 6- and 4-substituted 1-naphthoate ions and 6-substituted 2-naphthoate ions. The σ constants used are those evaluated from the alkaline hydrolysis of the substituted methyl naphthoates.[4] The value of ρ was computed as —0.52 (r 0.997) for the reaction of 6- and 4-substituted 1-naphthoate ions and —0.78 r (0.996) for the reaction of 6-substituted 2-naphthoate ions at 30 °C. These values, according to the significance generally attached, seem to indicate that the substituent effect is not high.

TABLE 2

Second-order rate constants and activation parameters for the reaction of substituted 1-naphthoate ions with picryl bromide in 80% (v/v) methanol

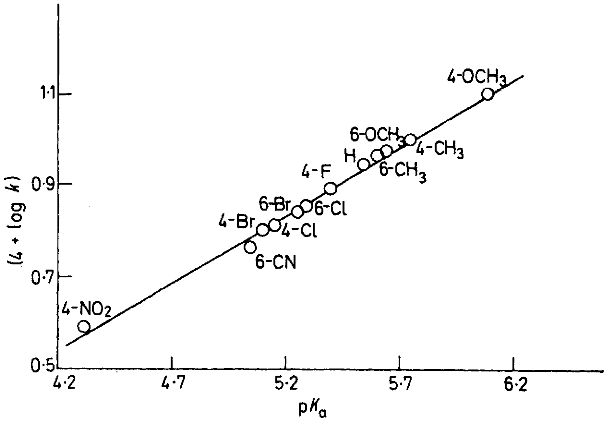
Substituents	10^3k/l mol^{-1} s^{-1} 30°	40°	50°	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}	log (A/s^{-1})
H	0.89	1.85	3.83	14.2	−26	7.59
4-F	0.79	1.71	3.60	14.6	−24	7.90
4-Cl	0.65	1.54	3.36	15.8	−21	8.65
4-Br	0.64	1.51	3.31	15.9	−21	8.71
4-NO_2	0.38	1.07	2.60	18.8	−12	10.54
4-CH_3	1.03	2.04	4.12	13.2	−29	6.95
4-OCH_3	1.26	2.33	4.62	12.1	−32	6.30
6-Cl	0.72	1.63	3.55	15.2	−23	8.29
6-Br	0.70	1.60	3.52	15.4	−22	8.42
6-I	0.68	1.58	3.49	15.5	−22	8.48
6-CN	0.58	1.42	3.28	16.6	−19	9.14
6-CH_3	0.93	1.91	3.92	13.5	−28	7.13
6-OCH_3	0.96	1.94	3.94	13.3	−29	6.98

TABLE 3

Second-order rate constants and activation parameters for the reaction of 6-substituted 2-naphthoate ions with picryl bromide in 80% (v/v) methanol

Substituents	10^3k/l mol^{-1} s^{-1} 30°	40°	50°	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}	log (A/s^{-1})
H	0.74	1.48	2.99	13.8	−27	7.25
F	0.66	1.38	2.85	14.2	−26	7.49
Cl	0.59	1.29	2.73	15.1	−23	8.09
Br	0.57	1.26	2.66	15.3	−23	8.22
$COCH_3$	0.45	1.11	2.49	16.3	−20	8.82
SO_2CH_3	0.37	0.96	2.21	17.0	−18	9.29
CH_3	0.89	1.68	3.27	12.6	−31	6.36
OCH_3	0.96	1.79	3.36	11.8	−33	5.92

Brönsted Relationship.—The Brönsted equation has been widely employed in numerous general acid–base catalysis reactions.[8] It has been shown to be of great importance in the study of nucleophilic reactions.[9,10]



Plot of the rate constant (4 + log$k$) of the reaction of picryl bromide with 6- and 4-substituted 1-naphthoate ions at 30° *versus* the pK_a of the corresponding naphthoic acids [11]

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In the Figure the log of the rate constants of the reaction with 6- and 4-substituted 1-naphthoate ions are plotted against the pK_a values of the corresponding conjugate acids in 50% *eth*anol–water.[11,12] A good correlation is obtained with β 0.30 (r 0.994). The Brönsted coefficient β of 0.56 (r 0.975) is obtained for the reaction of 6-substituted 2-naphthoate ions with picryl bromide. Generally in such reactions the magnitude of the Brönsted coefficient is taken as a measure of the extent of bond formation in the transition state.[13] Brönsted coefficients between 0.6 and 1.5 have been taken as indicative of extensive bond formation whereas those between 0.0 and 0.3 are indicative of little bond formation. The value of β obtained in this study for the 1-series compares with a value of 0.36 reported in the reaction between 4-substituted 1-naphthoate ions and phenacyl bromide.[14] Though the conditions are different in these experiments, the extent of bond formation in both reactions is very nearly the same. Fairly extensive bond formation has been noted in the reaction of 6-substituted 2-naphthoate ions with picryl bromide. This may be due to the absence of a *peri*-hydrogen interaction in the 2-series.

The rate data given in Tables 2 and 3 show that 1-naphthoate ion reacts faster than 2-naphthoate ion. It is difficult to rationalize this on the basis of the σ constants [15] of the 2,3- (σ 0.5) and 3,4-benzo groups (σ 0.04). 1-Naphthoic acid has a higher ionization constant than 2-naphthoic acid [16] due to steric inhibition of resonance caused by the *peri*-hydrogen in the 1-acid. Based on the ionization constants, the rate with 1-naphthoate ion would be expected to be lower than with 2-naphthoate ion. The observed results can be explained in terms of the greater electron density at C-1 than at C-2 of naphthalene.[17]

Isokinetic Relationship.—As outlined by Exner,[18,19] the isokinetic relationship has been examined in these reactions through plots 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 take T_1 323 and T_2 303 K in these series, the plots are linear and they gave values of 338 and 345 K respectively for the 1- and 2-series for the isokinetic temperature. These closely agree with the values calculated from linear plots 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.[20]

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