Kinetics of the Reactions of Picryl Chloride with Substituted Benzoate Ions

By **Triyama Ranjan Mohanty** and **Padina Lochan Nayak,*** Department of Chemistry, Ravenshaw College, Cuttack-3, India

Second-order rate constants have been measured for the reactions of picryl chloride with substituted benzoate ions in 80% methanol–water at several temperatures, and activation parameters have been calculated. The results are compared with corresponding data for the reactions of picryl chloride with anilines and phenoxide ions. For the *meta*- and *para*-substituted compounds a plot of log k against σ gave ρ −1·05 (r 0·965). From a Brönsted-type correlation involving the pK_a values of the corresponding benzoic acids $\beta = 0{\cdot}70$. A linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is indicative of a single mechanism.

THE study of bimolecular nucleophilic substitutions has received considerable attention during the last two decades.[1] The kinetics of the reaction of picryl chloride with anilines have been studied by a number of workers.[2-4] Recently, Ryan and Humffray[5] have reported the reaction of picryl chloride with substituted phenoxide ions and anilines to provide a comparison of the reaction of oxygen with nitrogen nucleophiles. We have reported[6] a comparative account of the reaction of a number of aliphatic, aromatic, and heterocyclic amines with picryl chloride and 1-chloro-2,4-dinitrobenzene. In a recent communication,[7] the rates of reaction of benzoate ions with phenacyl bromide have been reported. We now report a study of the reaction of benzoate ions with an activated halide at an aromatic centre in which the rate constant and activation parameters for the reaction of benzoate ions with picryl chloride were determined. The values of the activation parameters for this reaction have been compared with those of the reaction of picryl chloride with other nucleophiles. An attempt has been made to use some of the linear free energy relationships[8] to throw light on the mechanism of the reaction.

EXPERIMENTAL

Materials.—Sodium salts of benzoic acids were prepared by the usual procedure in ethanol. The sodium salt was filtered off, washed with ethanol, and dried *in vacuo* to a constant weight in a black-painted flask at 100—110°. Picryl chloride (B.D.H.) was recrystallised from alcohol–light petroleum. Baker analysed methanol was used without further purification. Triply distilled water (CO_2 free) was used for dilutions.

Rate Measurements.—The reactions of the substituted benzoate ions with picryl chloride were studied under second-order conditions. Stock solutions of sodium benzoates (0·05M) and picryl chloride (0·025M) were prepared in 80% methanol. The reactions at different temperatures were followed by pipetting portions (5 ml) into aqueous 5% nitric acid (10 ml) and titrating the chloride ion by Volhard's method according to our previous procedure.[6,7] In every case, the kinetic runs were followed to at least 70% completion and the second-order rate constants k_2 were determined at three different temperatures and computed by least-squares using Tobey's method.[9] The rate constants were accurate to within 1—2% for duplicate experiments. The activation energies and log A values were computed from the rate constants at different temperatures by the method of least squares, the plot of log k against $1/T$ being linear for all cases. The entropies of activation $\Delta S^{\ddagger}$ were calculated by the usual procedure. The estimated pre-

---

[1] (*a*) J. Miller, *Rev. Pure Appl. Chem.*, 1951, **1**, 171; (*b*) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 273; J. F. Bunnett, (*c*) *Quart. Rev.*, 1958, **12**, 1; (*d*) *Ann. Rev. Phys. Chem.*, 1963, **14**, 271; (*e*) J. Sauer and R. Huisgen, *Angew. Chem.*, 1960, **72**, 294; (*f*) S. Ross, *Progr. Phys. Org. Chem.*, 1963, **1**, 31; (*g*) J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, New York, 1968.

[2] C. W. L. Bevan and J. Hirst, *J. Chem. Soc.*, 1956, 254.

[3] R. E. Parker and T. O. Read, *J. Chem. Soc.*, 1962, 9.

[4] E. V. Titov, L. M. Litvinenko, N. F. Levchenko, and N. A. Izmailov, (*a*) *Ukrain. khim. Zhur.*, 1961, **24**, 481; (*b*) *Bull. Acad. Sci. U.S.S.R.*, 1962, 1653.

[5] J. J. Ryan and A. A. Humffray, *J. Chem. Soc.* (*B*), 1967, 1300.

[6] P. L. Nayak, *J. Indian Chem. Soc.*, 1974, **51**, 231.

[7] P. Mishra, P. L. Nayak, and M. K. Rout, *Indian J. Chem.*, 1973, **11**, 452.

[8] (*a*) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323; (*b*) S. Ehrenson, *ibid.*, 1968, **6**, 195; (*c*) P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, London, 1968; (*d*) J. Shorter, *Chem. in Britain*, 1969, **5**, 269.

[9] S. W. Tobey, *J. Chem. Educ.*, 1962, **39**, 473.

cision is *ca.* ±0·5 kcal mol^{-1} in $\Delta H^\ddagger$ and *ca.* ±1·5 cal mol^{-1} K^{-1} in $\Delta S^\ddagger$.

RESULTS AND DISCUSSION

We found that the reaction between picryl chloride and benzoate ions follows second-order kinetics, first-order in each reactant. The substituent effect on the rate constant (Table 1) shows that the reaction rate depends on the electron density on the oxygen atom of the benzoate ion: electron-donating substituents increase the rate, while electron-withdrawing groups decrease it. The observed rate conforms to the following order of reactivity: *p*-OMe > *m*-OMe > *p*-Me > *m*-Me > H > *p*-Br > *p*-Cl > *m*-Cl > *m*-Br > *m*-NO_2 > *p*-NO_2.

TABLE 1

Second-order rate constants for the reaction of substituted benzoate ions with picryl chloride in 80% (v/v) methanol

	10^3k_2/l mol^{-1} s^{-1}		
Substituents	35°	40°	45°
p-OMe	2·455	3·38	4·52
m-OMe	1·925	2·787	3·68
p-Me	1·712	2·456	3·59
m-Me	1·52	2·25	3·236
H	1·38	2·15	3·20
p-Br	1·15	1·77	2·70
p-Cl	1·10	1·67	2·60
m-Cl	0·708	1·29	1·995
m-Br	0·631	1·273	1·80
m-NO_2	0·38	0·60	1·00

A comparison of our results with those of the reaction of picryl chloride with phenoxide ions and anilines[5] shows that benzoate ions react more slowly than the other series of compounds, *i.e.* phenoxide ions and anilines are stronger nucleophiles than benzoate ions.

Activation Parameters.—The activation parameters are noted in Table 2. The trends in variation of the activation parameters are the same as with phenoxide ions and anilines. The values of the activation energies show a regular variation with substituents in benzoate ions; electron-donating substituents decrease and electron-withdrawing groups increase E_a. The activation energies are larger in the benzoate ion series than in phenoxide ion and aniline series; this can be accounted for, in part at least, by differences in the energy required for rehybridisation of the oxygen or nitrogen, and by differences in stabilisation by solvation.[5]

TABLE 2

Activation parameters for the reaction of picryl chloride with substituted benzoate ions

Substituents	E_a/ kcal mol^{-1}	$\Delta H^\ddagger$/ kcal mol^{-1}	$-\Delta S^\ddagger$/ cal mol^{-1} K^{-1}	log (A/s^{-1})
p-OMe	12·00	11·40	39·40	10·50
m-OMe	13·30	12·70	31·80	11·50
p-Me	14·30	13·70	30·50	12·10
m-Me	15·20	14·60	27·00	12·90
H	16·10	15·50	25·30	13·50
p-Br	18·00	17·40	19·50	14·90
p-Cl	18·20	17·60	18·00	14·80
m-Cl	18·90	18·30	17·70	15·6
m-Br	19·80	19·20	15·10	15·10
m-NO_2	20·20	19·60	13·70	16·80

Entropies of activation are negative as expected for bimolecular reactions. In comparing the activation entropy values between the reactions of anilines and benzoate ions, it is evident that there is a difference between the two series (average values −24 and −34 cal mol^{-1} K^{-1} for the benzoate ion and aniline series respectively). The difference may be due to greater solvent participation in the transition state of the reaction of picryl chloride with anilines than with benzoate ions. In the case of benzoate ion, there is already a formal charge on the oxygen atom and the change from reactants to transition state results only in the spreading out of an already existing charge. The solvation contribution to the activation entropy would then be expected to operate in the opposite sense to that in the aniline series, leading to a smaller decrease of entropy.

Linear Free Energy Relationships.—Application of Hammett relationship. The rates of reactions of picryl chloride with various *m*- and *p*-substituted benzoate ions were correlated by means of the σ–ρ Hammett relationship using the statistical method recommended by Jaffé[10] and on the basis of the data treatment suggested by Wepster and his co-workers[11] and by Taft and his co-workers.[12]

The value of ρ was computed to be −1·05 (r 0·965) for the reaction of *meta*- and *para*-substituted benzoate ions with picryl chloride. Ryan and Humffray[5] found ρ −4·70 (r 0·96) and −2·57 (r 0·74) for the reactions of anilines and phenoxide ions with picryl chloride respectively. The value of ρ is comparatively small in the present reaction series, *i.e.* the effect of substituents is more pronounced in the other cases than with benzoate ions. Nayak and his co-workers[7] found ρ −0·70 (r 0·96) for the reaction of benzoate ions with phenacyl bromide showing still lower sensitivity of the rates to substituents.

Following the procedure recommended by Taft and Lewis,[12] a regression line was fitted to the log k against σ^0 data for the *meta*-substituted compounds. Effective substituent constants ($\bar{\sigma}$) were then evaluated from the relationship $\bar{\sigma} = (\log k - \log k_0)/\rho_0$ for different substituents. Nevertheless, Wepster and his co-workers[11] have pointed out that $\bar{\sigma}$ is not a good measure of the interaction between substituents and reaction centre and they prefer to express the influence of *para*-resonance in terms of the free-energy differences, $-\Delta\Delta F_p = 2{\cdot}303\,RT\,\rho(\bar{\sigma} - \sigma^n)$. In this relationship not only σ values but also ρ and T are taken into account. The values of $\Delta\Delta F_p$, calculated for different substituents are

---

[10] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[11] (*a*) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1959, **78**, 815; (*b*) N. Rout, P. L. Nayak, and M. K. Rout, *J. Indian Chem. Soc.*, 1970, **47**, 217.

[12] R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343.

given in Table 3. Positive values of $\Delta\Delta F_p$ signify a decrease in *para*-interaction energy, and negative values an increase.

Brönsted relationships. In recent years, much attention has been focused on the use of the extended Brönsted relationship as a probe for determining the mechanistic pathway.[13-21] The magnitude of the Brönsted coefficient has usually been related to the extent of bond formation in the transition state and when an intermediate is formed along the reaction pathway, a large Brönsted coefficient is expected.[22] Values ranging from 0·6 to 1·5 have been considered as indicative of extensive bond formation while values from 0 to 0·3 have been related to little bond formation.

TABLE 3

Effective σ values and *para*-resonance interaction values for different substituents

Substituents	$\bar{\sigma}$	$\Delta\Delta F_p$/kcal mol^{-1}
p-OMe	−0·2143	−0·2086
m-OMe	−0·0867	
p-Me	−0·0714	+0·1372
m-Me	+0·007	
p-Br	+0·1053	+0·310
p-Cl	+0·1290	+0·222
m-Cl	+0·293	
m-Br	+0·357	
m-NO_2	+0·721	

The correlation can be represented graphically by plotting the logarithm of the rate constants against pK_a values of the corresponding conjugate acids in water. A good Brönsted plot was obtained for our reaction. The value of β, the Brönsted coefficient, was 0·70 (*r* 0·997). Thus, a correlation exists between rate and basicity for nucleophiles of the same type and the dependence, as measured by β 0·70, is pronounced. The Brönsted coefficients were computed to be 0·80 and 1·25 for the reactions of phenoxide ions and anilines with picryl chloride. The value of β was 0·85 for the reaction of anilines with 1-chloro-2,4-dinitrobenzene.[6] Recently Nayak and his colleagues [7] found β 0·50 and 1·1 for the reactions of benzoate ions and anilines with phenacyl bromide. This, according to the significance generally attached to the Brönsted β values, seems to indicate that more bond formation between the nucleophile and the reaction centre at the rate-limiting transition state is involved for reactions with neutral nucleophiles than for the reaction with anionic nucleophiles.[23] This is in accordance with the prediction of the Ogg–Polanyi–Hammond principle.[24]

Isokinetic relationship. A linear relationship between the entropy of activation ($\Delta S^\ddagger$) and the enthalpy of activation ($\Delta H^\ddagger$) has been observed for the reaction. The data can be fitted in the equation $\Delta H^\ddagger = \Delta H_0^\ddagger + \beta\Delta S^\ddagger$.[25] $\Delta H_0^\ddagger$ Has the value 21·5 kcal mol^{-1} and β, the isokinetic temperature, is 400 K for the reaction (*r* 0·988). The values of β are 480 and 400 K for the reactions of anilines and phenoxide ions with picryl chloride.[5] The linear relationship shown by the majority of the substituents indicates that one mechanism prevails in all cases.[26]

[4/384 *Received*, 26*th February*, 1974]

---

[13] (*a*) R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1962, 1062; (*b*) R. F. Hudson and G. Loveday, *ibid.*, p. 1068; (*c*) R. F. Hudson, *Chimia*, 1963, **16**, 173.

[14] M. J. Gregory and T. C. Bruice, *J. Amer. Chem. Soc.*, 1967, **89**, 4400.

[15] F. Pietra, *Quart. Rev.*, 1969, **23**, 504.

[16] T. C. Bruice and S. Benkovic, 'Bioorganic Mechanisms,' Benjamin, New York, 1966, p. 231.

[17] R. F. Hudson, 'Structure and Mechanism in Organic Phosphorus Chemistry,' Academic Press, London, 1965, p. 110.

[18] S. J. Benkovic and P. A. Benkovic, *J. Amer. Chem. Soc.*, 1966, **88**, 5504.

[19] O. Rogne, *J. Chem. Soc.* (*B*), (*a*) 1972, 489; (*b*) 1971, 1855.

[20] K. Okamoto, H. Kushiro, I. Nitta, and H. Shingu, *Bull. Chem. Soc.* (*Japan*), 1967, **40**, 1900.

[21] K. K. Satpathy and P. L. Nayak, *J. Indian Chem. Soc.*, 1971, **49**, 615.

[22] (*a*) L. Senatore, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, 1970, **72**, 3035; (*b*) E. Ciuffarin and L. Senatore, *J. Chem. Soc.* (*B*), 1970, 1680.

[23] G. Biggi and F. Pietra, *J. Chem. Soc.* (*B*), 1971, 44.

[24] (*a*) R. A. Ogg, jun., and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 1375; (*b*) G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[25] (*a*) J. E. Leffler, *J. Org. Chem.*, 1955, **20**, 1202; (*b*) J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963, p. 291.

[26] (*a*) P. L. Nayak and M. K. Rout, *J. Indian Chem. Soc.*, 1970, **47**, 807; (*b*) K. K. Satpathy, P. L. Nayak, and M. K. Rout, *Indian J. Chem.*, 1971, **9**, 680; (*c*) K. Bowden, N. B. Chapman, and J. Shorter, *J. Chem. Soc.*, 1964, 337.