Tetrahedron. Vol. 26, pp. 3045 to 3049. Pergamon Press 1970. Printed in Great Britain

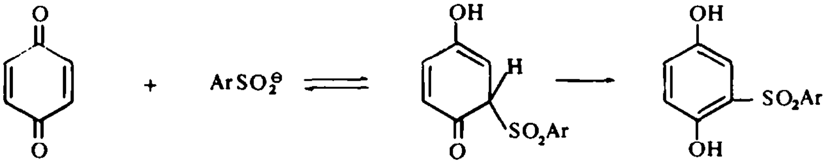
KINETICS OF THE ADDITION OF BENZENESULFINIC ACIDS TO ACRYLONITRILE IN AQUEOUS BUFFERS*

Y. Ogata, Y. Sawaki and M. Isono
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

(*Received in Japan* 7 *January* 1970; *Received in the UK for publication* 24 *February* 1970)

Abstract—Addition of unsubstituted and substituted benzene-sulfinic acids to acrylonitrile in aqueous buffers has been studied kinetically by means of ultraviolet spectrophotometry. The reactions follow the second-order kinetics: $v = k$ [acrylonitrile] × [sulfinate ion]. The reaction is subject to neither general acid nor general base catalysis, the rate being independent of pH. The substituent effect on benzenesulfinic acid fits Hammett's equation, ρ-value at 50° being $-1\cdot15$ ($r = 0\cdot998$) at pH 4·22. The energy and entropy of activation are 21 kcal/mol and -12 e.u., respectively. The nucleophilic reactivity of various sulfur anions are shown to depend on the basicities of the nucleophiles.

Our previous reports have disclosed the addition mechanism of benzenesulfinic acids to *p*-benzoquinone as a nucleophilic addition to α,β-unsaturated compounds.[1, 2, 3] The kinetics suggest a mechanism (1) involving a shift of rate-determining step from addition to deprotonation with increasing pH, characterized by intermediate II similar to the aromatic ring.



I II III (1)

The present paper reports the kinetic study on the addition of benzenesulfinic acids to acrylonitrile.

$$CH_2{=}CHCN + ArSO_2H \rightarrow ArSO_2CH_2CH_2CN \qquad (2)$$

The effects of acidity of media, substituent, and temperature on the rate were estimated, Hammett's ρ-value and activation parameters being calculated. In view of these data, the mechanism and nucleophilic reactivity of aromatic sulfinate ion are discussed in comparison with those of other sulfur anions.

RESULTS AND DISCUSSIONS

Rate law: *Effects of* pH *and buffer concentration.* The active species in the present addition is not free benzenesulfinic acid, but sulfinate ion. The slow disappearance

---

* Contribution No. 150.

of sulfinic acid in conc HCl is regarded as the disproportionation of sulfinic acid.[4] The rates in various buffers follow second-order kinetics at least at pH's below 8.

$$v = k[CH_2{=}CHCN] \times [ArSO_2^-] \tag{3}$$

Here, $[ArSO_2^-]$ is the arylsulfinate ion concentration calculated from the pK_a values of corresponding sulfinic acids in aqueous solution at 25°. Table 1 lists the second-order rate constants, which are independent of hydronium ion and buffer concentrations within experimental error. On the other hand, the rate constants at pH's above 8 decrease as the reaction proceeds. This phenomenon can be explained by assuming that acrylonitrile is consumed by the competitive reactions with hydroxide ion as well as sulfinate ion, the rate being expressed as follows:

$$-d[CH_2{=}CHCN]/dt = [CH_2{=}CHCN] \times (k_{OH}[OH^-] + k[ArSO_2^-]) \tag{4}$$

In fact, Wronski–Bogdanski's kinetic study on the reaction of acrylonitrile with hydroxide ion forming β-hydroxypropionitrile gave a k_{OH} value of $1{\cdot}93 \times 10^{-3}$ M^{-1} sec^{-1} at 50°.[5] Since the value of k for the present reaction is $5{\cdot}85 \times 10^{-4}$ M^{-1} sec^{-1} at 50°, the reaction of acrylonitrile with hydroxide ion tends to become a main pathway with increasing pH, as is the case.

TABLE 1. THE SECOND-ORDER RATE CONSTANTS FOR ADDITION OF BENZENESULFINIC ACID TO ACRYLONITRILE AT IONIC STRENGTH 0·24 AND 50 ± 0·5°

		Second-order rate constant ($k \times 10^4$ M^{-1} sec^{-1})		
		Buffer concentration (M)		
No	pH	0·2	0·4	0·6
1	1·98[a]	5·75	—	6·15
2	3·75[b]	4·99	5·20	5·95
3	4·22[b]	6·25	6·50	7·28
4	6·25[b]	—	7·02	—
5	6·00[b]	6·65	7·60	7·60
6	6·90[c]	—	4·67	—
7	7·97[c]	—	5·55–7·08	—
8	8·83[c]	—	(6·24)[d]	—
9	10·35[e]	—	(3·68)[d]	—

[a] Reaction in chloroacetate buffer
[b] Reaction in acetate buffer
[c] Reaction in borate buffer
[d] Initial rate constant
[e] Reaction in carbonate buffer

Effect of temperature. The second-order rate constants for the addition of benzenesulfinate ion to acrylonitrile at 25°, 40° and 50° are $4{\cdot}00 \times 10^{-5}$, $1{\cdot}56 \times 10^{-4}$ and $5{\cdot}85 \times 10^{-4}$ M^{-1} sec^{-1}, respectively. The energy and entropy of activation were calculated on the basis of these data to be 21 kcal/mol and −12 e.u.

Substituent effect. The reactions of substituted benzenesulfinate ions with acrylonitrile were carried out in 0·04 M acetate buffer at ionic strength of 0·24, pH 4·22 and temperature of 50°. The reactions are accelerated by electron-releasing groups on benzenesulfinic acid, second-order rate constants ($k \times 10^4$ M^{-1} sec^{-1}) being as follows: *p*-Me, 11·1; H, 6·50; *p*-Cl, 3·56; *m*-NO_2, 1·06. Hammett's plot of the data gives a good straight line, affording a ρ-value of $-1{\cdot}15$ ($r = 0{\cdot}998$).

Mechanism. At pH 2–9, the addition of arylsulfinic acid to acrylonitrile gives cyanoethylsulfone (IV) alone, neither acid nor base catalysis taking place. Most nucleophilic additions to carbonyl groups and α,β-unsaturated carbonyls are known to follow general acid and general base catalysis.[6] On the other hand, no acid catalysis has been observed for nucleophilic additions of amines,[5,7] mercaptides,[8] alkoxides,[9] bisulfite[10] or thiosulfate[5,11] to acrylonitrile. The same is true of the present reaction. As is obvious from Table 1, the second-order rate constants are invariant with varying pH's and buffer concentrations, within experimental error. These results together with a negative ρ-value of $-1{\cdot}15$ suggest the following mechanism involving an uncatalyzed nucleophilic addition of sulfinate ion, where the rate is determined by step (6).

$$ArSO_2H + H_2O \overset{\text{fast}}{\rightleftharpoons} ArSO_2^- + H_3O^+ \tag{5}$$

$$ArSO_2^- + CH_2{=}CHCN \xrightarrow{\text{slow}} [ArSO_2CH_2\dot{C}HCN] \tag{6}$$

$$[ArSO_2CH_2\dot{C}HCN] + H_3O^+ \overset{\text{fast}}{\rightleftharpoons} \underset{\text{IV}}{ArSO_2CH_2CH_2CN} + H_2O \tag{7}$$

Recently, there have been reports on nucleophilic additions of amino acids,[7] aminothiols,[8,12] alkoxides,[9] and thiols[8,12] to acrylonitrile suggesting that the rate increases linearly with basicities of the nucleophiles, if the nucleophiles have a similar steric environment at the α-carbon. In spite of the presence of steric hindrance, this linearity is observed for the addition of sulfur anions to acrylonitrile. As shown in Fig 1, the nucleophilic additions of sulfur anions (*e.g.*, $ArSO_2^-$, RS^-, $S_2O_3^{2-}$, CS_3^{2-} etc) to acrylonitrile exhibit this linearity of log *k vs.* pK_a with a slope of 0·59 ($r = 0{\cdot}982$), irrespective of the bulkiness of nucleophiles. Furthermore, the plotted line is almost identical with that of primary alkyl mercaptides ($X\text{-}CH_2\text{-}S^-$) but not with that of

TABLE 2. THE SECOND-ORDER RATE CONSTANTS FOR ADDITION OF VARIOUS SULFUR ANIONS TO ACRYLONITRILE IN WATER

Nucleophile	pK_a*	$k \times 10^4\ M^{-1}\ sec^{-1}$	Reaction temp	ref
$PhSO_2^-$	1·45	0·741	30°	this work
$S_2O_3^{2-}$	2	1·60	50°	lit[11]
SO_3^{2-}	7	2200	30°	lit[10]
S^{2-}	7·24	9·33	30°	lit[5]
CS_3^{2-}	8·18[13]	367	20°	lit[5]
$^-O_2C{-}CH_2{-}S^-$	10·5	42600	30°	lit[8]

* pK_a values of conjugated acids of nucleophiles

secondary and tertiary alkyl mercaptides (X-CRR-S$^-$), where X represents -CH(NH$_2$)CO$_2$$^-$. That is, nucleophilic reactivities of sulfur anions are influenced by alkyl groups (R and R′) on the α-carbon, but not substituents directly substituted on the sulfur anion as observed with compounds 2–9 in Fig. 1. Substituents on the sulfur anion in these compounds seem to have small steric hindrance and little effect on the polarizability of the sulfur anion, since the sulfur atom is rather large in size and quite polarizable.

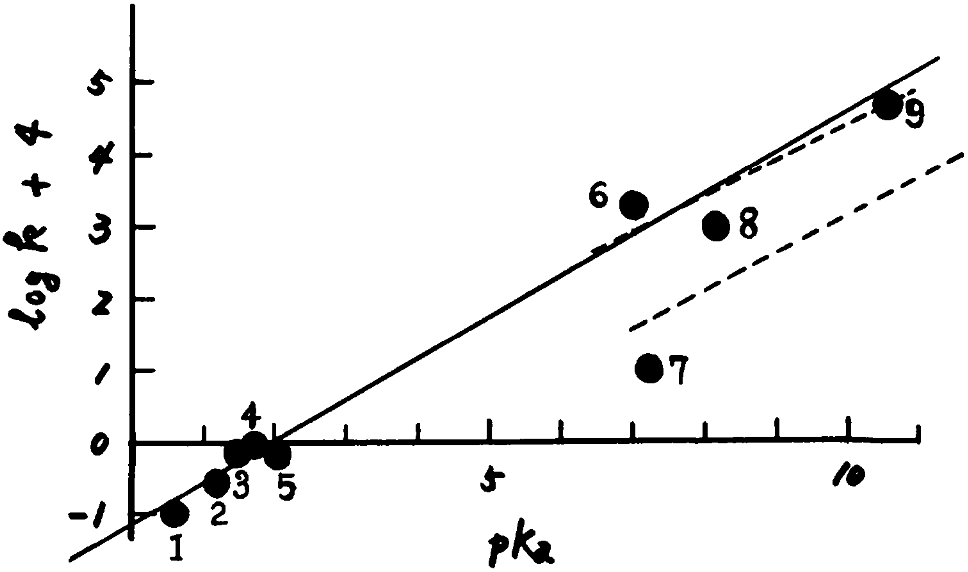


Fig 1. Plot of log k vs pK_a for addition of various sulfur anions to acrylonitrile at 30° (solid line). Nucleophile: 1, m-NO$_2$C$_6$H$_4$SO$_2$$^-$; 2, p-ClC$_6H_4SO_2$$^-$; 3, PhSO$_2$$^-$; 4, p-Me-C$_6H_4SO_2$$^-$; 5, S$_2O_3$$^{2-}$; 6, SO$_3$$^{2-}$; 7, S^{2-}; 8, CS$_3$$^{2-}$; 9, $^-$O$_2$C—CH$_2$S$^-$. Plots 5 and 8 are estimated from the relative rates at 50° and 20°, respectively. The upper dotted line is a plot of log k vs pK_a for the addition of mercaptide groups attached to primary carbon (X—CH$_2$S$^-$) to acrylonitrile at 30°.[8,12] The lower dotted line is that in the case of mercaptide groups attached to secondary and tertiary carbon (X—CRR′—S$^-$).[8,12]

EXPERIMENTAL

Materials. Acrylonitrile (b.p. 73°) was obtained from Toray Ind. Inc. The benzenesulfinic acids substituted by p-Me, H, p-Cl, and m-NO$_2$ groups were prepared and purified as described previously.[2]

Reaction products. To ArSO$_2$Na·XH$_2$O (0·02 mol) in aq acetate buffer (30 ml) was added acrylonitrile (0·03 mol), stabilized by addition of a small amount of hydroquinone. The reaction mixtures were kept standing at 50° for 1 h to yield substituted cyanoethyl aryl sulfones, X-C$_6$H$_4$SO$_2$CH$_2$CH$_2$CN. The following data describe, successively, substituent, m.p. crystallized from EtOH, and UV absorption peaks in mμ (log ε) in water. p-Me, 94–94·5° (lit[14] 93–94°), 228 (4·14), 268 (2·78), 276 (2·47); H, 94–94·5 (lit[15] 93–94°), 218 (3·97), 265·5 (3·06), 272·5 (2·99); p-Cl, 93–94° (lit[15] 92–93°), 231 (4·24), 263 (2·88), 273·5 (2·69); m-NO$_2$, 116·5–117·5° (lit[16] 113–115°), 253 (3·82). These products were identified by their IR spectra.

Rate measurement. Since these products, ArSO$_2$CH$_2$CH$_2$CN, have similar UV peaks and absorbances as those of benzenesulfinic acids, it is difficult to determine directly the concentrations of products and reactants. Hence, rate of disappearance of benzenesulfinic acid was determined indirectly after its conversion to diphenyl sulfone.[2] Purified benzenesulfinic acids (approx 0·18 g, 0·05 M) was added to an aq buffer (25 ml) containing acrylonitrile (1 ml, 0·608 M) at 50°. Aliquots were taken out at regular intervals of time and diluted with water. Then excess aqueous *p*-benzoquinone was added to the soln to convert remaining sulfinic acids to diphenyl sulfones, which were determined by means of UV spectrophotometry.[2] Since a large excess of acrylonitrile was used, the rate is pseudo-first-order with respect to arylsulfinic acid, the concentration of which is estimated as diphenyl sulfone. The second-order rate constant was calculated by (pseudo-first-order rate constant)/[acrylonitrile].

Acknowledgement—The authors are grateful to Toray Ind. Inc. for their gift of acrylonitrile.

REFERENCES

[1] Y. Ogata, Y. Sawaki and S. Gotoh, *J. Am. Chem. Soc.* **90**, 3469 (1968)
[2] Y. Ogata, Y. Sawaki and M. Isono, *Tetrahedron* **25**, 2715 (1969)
[3] Y. Ogata, Y. Sawaki and M. Isono, *Ibid.* **26**, 736 (1970).
[4] J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.* **84**, 605 (1962); J. L. Kice, D. C. Hampton and A. Fitzgerald, *J. Org. Chem.* **30**, 883 (1965)
[5] M. Wronski and J. Bogdanski, *Zeszyl Nauk. Uniw. Lodg.* **14**, 153 (1963)
[6] Y. Ogata, A. Kawasaki and I. Kishi, *J. Chem. Soc.* (B), 703 (1968)
[7] M. Friedman and J. S. Wall, *J. Am. Chem. Soc.* **86**, 3735 (1964)
[8] M. Friedman, *Ibid.* **89**, 4709 (1967)
[9] B. A. Feit and A. Zilkha, *J. Org. Chem.* **28**, 406 (1963); B. A. Feit and A. Zilkha, *Ibid.* **28**, 3245 (1963); R. N. Ring, G. C. Tesoro and D. R. Moore, *Ibid.* **32**, 1091 (1967)
[10] M. Morton and H. Landfield, *J. Am. Chem. Soc.* **74**, 3523 (1952)
[11] R. Kerber and J. Sarnik, *Tetrahedron Letters* **26**, 3007 (1966)
[12] M. Friedman, J. F. Cavins and J. S. Wall, *J. Am. Chem. Soc.* **87**, 3672 (1965)
[13] G. Gattow and B. Krebs, *Z. Anorg. Allgem. Chem.* **322**, 13 (1963)
[14] I. Kh. Fel'dmann and V. N. Mikhailova, *Zh. Obsh. Khim.* **32**, 944 (1962).
[15] N. Borisova and D. Stankevich, *Zh. Organ.* **2** (8), 1437 (1966)
[16] I. Kh. Fel'dmann and V. N. Mikhailvoa, *Zh. Obsh. Khim.* **33**, 2111 (1963)