

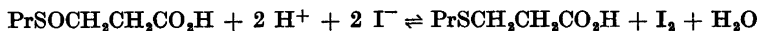
Studies on Alkylsulfinylcarboxylic Acids

III. A Kinetic Study of the Effect of Iodide Concentration upon the Reaction between Alkylsulfinylcarboxylic Acids and Iodide Ions in Acid Solution

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The influence of the iodide ion concentration upon the rate of the reaction:



has been studied. At low iodide concentrations the reaction becomes reversible and an equilibrium constant can be calculated. At high iodide concentrations, however, the equilibrium is far to the right, so the reaction can be treated as going essentially to completion. Furthermore the rate of the reaction is then very little affected by changes in iodide concentration.

As a part of a study concerning the mechanism of the reduction of the sulfoxide group in alkylsulfinylcarboxylic acids by means of iodide ions in perchloric acid solutions, the dependence of the rate upon the iodide ion concentration was investigated. Previously the influence of the hydrogen ion concentration has been reported.¹ It was found, that at constant ionic strength and with both hydrogen and iodide ions in excess, the rate of the reaction was directly proportional to the hydrogen ion concentration and when the ionic strength was varied, the logarithms of the rate constants, when plotted against $-H_0$ (the Hammett acidity function), gave straight lines with unit slope for the β -alkylsulfinylcarboxylic acids investigated. From this it was concluded that the protonation of the sulfoxide group cannot be a rate-determining step. However, at high iodide concentrations (80–10 times the sulfoxide concentration), the attack of an iodide ion cannot be rate determining either, because if this were the case, the pseudo first-order rate constant would show much greater variations with changing iodide concentration than actually is found. The results are shown in Table 1. The rate constants have been calculated according to the expression:

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

Table 1. The pseudo first-order rate constant k for the reaction between β -propylsulfinylpropionic acid and iodide ions in 2.00 M perchloric acid at 25°C. $C_{\text{sulfinyl acid}} = 5.00$ mM.

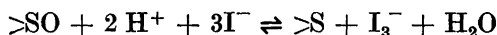
C_{iodide} M	$10^3 k \text{ min}^{-1}$
0.4	39.8
0.2	36.2
0.1	32.2
0.05	28.6

where a and $a - x$ denote the sulfoxide concentrations at $t = 0$ and t respectively. It is obvious that the variation in the rate constants is not more than what can be expected from the change in ionic strength.

At lower iodide concentrations the reaction reaches a measurable equilibrium. An equilibrium constant K has been calculated from the expression:

$$K = \frac{[>\text{SO}][\text{I}^-]^3}{[>\text{S}][\text{I}_3^-]}$$

which corresponds to the overall reaction:



Because the concentrations of hydrogen ions and water remain constant during the reaction, they can be neglected. If the concentrations of sulfoxide and iodide at the start of the reaction are denoted by a and b respectively, then at equilibrium *i.e.* at $t = \infty$ they will have obtained the values $a - x_\infty$ and $b - 3x_\infty$ if the triiodide ion concentration then is called x_∞ . Consequently the equilibrium constant can be written:

$$K = \frac{(a - x_\infty)(b - 3x_\infty)^3}{x_\infty^3} \quad (1)$$

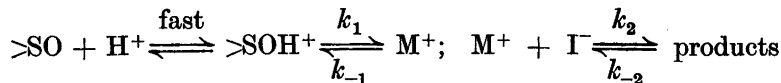
The values of x_∞ have been measured for the reaction of β -propylsulfinylpropionic acid with iodide ions in perchloric acid-sodium perchlorate solution at 25°C and at different iodide concentrations. The equilibrium constant was calculated using eqn. (1). The results are shown in Table 2. Reversibility in the reaction between sulfoxides and hydriodic acid in acetic acid-water mixtures also has been reported recently by Landini *et al.*²

Table 2. The equilibrium constant K for the reaction between β -propylsulfinylpropionic acid and iodide ions in 1.50 M perchloric acid + Y M sodium perchlorate at 25°C. $C_{\text{sulfinyl acid}} = 5.00$ mM. $Y + C_{\text{iodide}} = 0.789$ M.

C_{iodide} mM	x_∞	$a - x_\infty$	$b - 3x_\infty$	K
20.0	2.94	2.05	11.30	342
25.0	3.57	1.46	14.44	345
30.0	4.03	1.00	18.09	365
35.0	4.40	0.64	22.01	353
40.0	4.65	0.40	26.29	336

mean value: $K = 348$

In order to interpret the kinetic data found in the reactions, the following scheme is suggested:



If k_{-2} is neglected, which can be done for not too low iodide concentrations and by considering only the initial velocity of the reaction, the following kinetic expressions can be obtained:

$$d[\text{M}^+]/dt = k_1[>\text{SOH}^+] - k_2[\text{M}^+][\text{I}^-] - k_{-1}[\text{M}^+] \quad (2)$$

and

$$dx/dt = k_2[\text{M}^+][\text{I}^-] \quad (3)$$

where x denotes the triiodide ion concentration at the time t .

According to the steady-state approximation $d[\text{M}^+]/dt = 0$ is assumed, which leads to an expression for $[\text{M}^+]$:

$$[\text{M}^+] = \frac{k_1[>\text{SOH}^+]}{k_2[\text{I}^-] + k_{-1}}$$

But $[>\text{SOH}^+] = K_b[>\text{SO}][\text{H}^+]$ which gives:

$$\frac{dx}{dt} = \frac{K_b k_1 k_2 [>\text{SO}][\text{H}^+][\text{I}^-]}{k_2[\text{I}^-] + k_{-1}}$$

$K_b k_1 [\text{H}^+]$ can be called k_1' , for $[\text{H}^+]$ is constant during the reaction:

$$\frac{dx}{dt} = \frac{k_1' k_2 [>\text{SO}][\text{I}^-]}{k_2[\text{I}^-] + k_{-1}} \quad (4)$$

From eqn. (4) it can easily be seen that at higher iodide concentrations where $k_2[\text{I}^-] \gg k_{-1}$, it reduces to:

$$\frac{dx}{dt} = k_1' [>\text{SO}]$$

which is the pseudo-unimolecular reaction previously studied by the author.^{1,3,4}

The following symbols are introduced:

At $t = 0$: $[>\text{SO}] = a$, $[\text{I}^-] = b$

At the time t : $[>\text{SO}] = a - y$, $[\text{M}^+] = y - x$, $[\text{I}^-] = b - 3x$, $[>\text{S}] = [\text{I}_3^-] = x$

Substituting in eqn. (2) and putting $d[\text{M}^+]/dt = 0$ gives:

$k_1 K_b (a - y)[\text{H}^+] = k_{-1}(y - x) + k_2(y - x)(b - 3x)$, *i.e.* solving y as a function of x and using the earlier notations:

$$y = \frac{3k_2 x^2 - bk_2 x - k_1' a - k_{-1} x}{3k_2 x - bk_2 - k_1' - k_{-1}} \quad \text{so} \quad [\text{M}^+] = y - x = \frac{k_1' (a - x)}{k_2 (b - 3x) + k_1' + k_{-1}}$$

Introducing $[\text{M}^+]$ in eqn. (3) leads to:

$$\frac{dx}{dt} = k_1' k_2 \frac{(a - x)(b - 3x)}{k_2 (b - 3x) + k_1' + k_{-1}}$$

Separation of the variables yields:

$$\frac{k_2(b-3x) + k_1' + k_{-1}}{(a-x)(b-3x)} dx = k_1'k_2 dt$$

which can easily be integrated:

$$k_2 \int \frac{dx}{a-x} + (k_1' + k_{-1}) \int \frac{dx}{(a-x)(b-3x)} = k_1'k_2 t + C$$

Evaluation of the integrals and determination of the integration constant C gives the final expression:

$$\frac{k_1'k_2}{k_1' + k_{-1}} = \frac{2.303}{(b-3a)t} \log \frac{a(b-3x)}{(a-x)b} + \frac{2.303k_2}{(k_1' + k_{-1})t} \log \frac{a}{a-x}$$

Now $\frac{k_2}{k_1' + k_{-1}}$ can be called k_2' , so the equation will be further simplified:

$$k_1'k_2' = \frac{2.303}{t} \left(\frac{1}{b-3a} \log \frac{a(b-3x)}{(a-x)b} + k_2' \log \frac{a}{a-x} \right) \quad (5)$$

from which k_2' can be determined graphically by plotting $2.303/[t(b-3a)] \log [a(b-3x)]/[(a-x)b]$ as a function of $2.303/t \log [a/(a-x)]$. This has been done in Fig. 1. From the value of k_2' thus obtained, $k_1'k_2'$ can be calculated for all t -values of the kinetic runs. The results are shown in Table 3. As mentioned earlier only the initial velocity was considered within each run, otherwise the reversibility has to be taken into account, which cannot easily

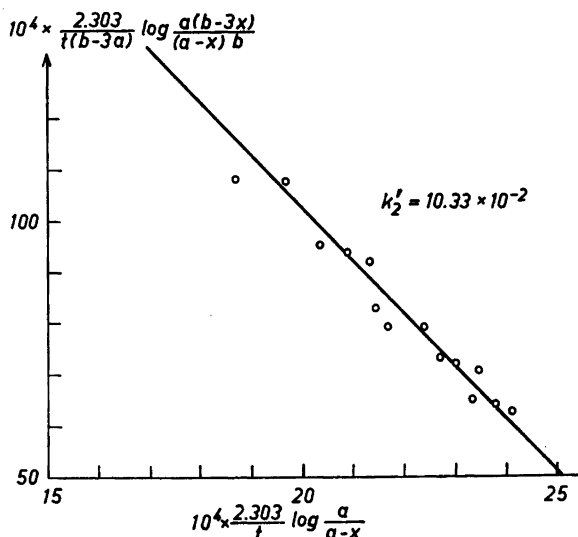


Fig. 1. Graphical determination of k_2' in eqn. (5).

Table 3. Values of $k_1'k_2'$ calculated from eqn. (3). Reaction conditions are the same as in Table 2.

C_{iodide} mM	t min	A^*	B^{**}	$k_1'k_2' \times 10^4$
20.0	13	10.77	197.0	31.11
	22	10.81	187.1	30.13
25.0	13	9.20	213.3	31.23
	20	9.38	209.1	30.97
	28	9.51	203.6	30.53
30.0	12	7.92	224.2	31.06
	21	7.92	216.9	30.32
	31	8.27	214.5	30.42
35.0	12	7.06	234.7	31.29
	21	7.20	230.2	30.96
	29	7.32	227.2	30.78
40.0	10	6.26	241.3	31.18
	19	6.40	238.0	30.97
	29	6.49	233.5	30.60

Mean value $k_1'k_2' = 0.00308$

$$* A = \frac{2.303}{t(b-3a)} \log \frac{a(b-3x)}{(a-x)b} \times 10^4$$

$$** B = \frac{2.303}{t} \log \frac{a}{a-x} \times 10^4$$

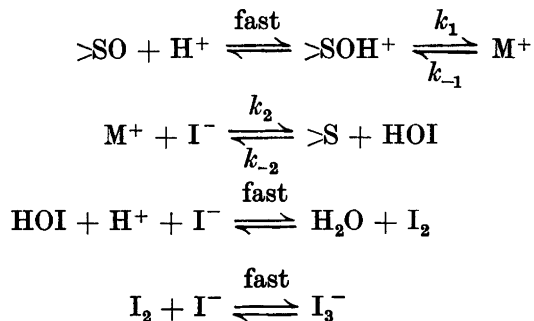
be done. The small discrepancy within each run from following the straight line in Fig. 1, is probably due to the fact, that this reversibility has been neglected. Accordingly the first values within each run show the best constancy, as found in Table 3.

From the mean value of $k_1'k_2' = 0.00308$, $k_1' = 0.0299 \text{ min}^{-1}$ is obtained, which is in good agreement with the value of the pseudo first-order rate constant $k_1' = 0.0290 \text{ min}^{-1}$, that can be calculated from earlier kinetic studies on the same compound in 1.50 M perchloric acid at 25°C by putting $C_{\text{NaClO}_4} + C_{\text{iodide}} = 0.789 \text{ M}$ as in the present case, but with an initial iodide concentration $C_{\text{iodide}} = 0.200 \text{ M}$.¹

Concerning the mechanism of this reaction, it will require further study. Landini *et al.*² have proposed a mechanism for the reduction of sulfoxides by means of hydriodic acid in acetic acid containing some water, where a third-order rate process has been observed. The question of changes in the reaction medium and type of sulfoxide compound and their effect on the mechanism should, however, be considered here. The nature of the intermediate M^+ , proposed by the present author, is also a matter of question, but it seems very likely that it should possess a cyclic structure. Leonard and Rippie⁵ have observed transannular cyclisations of cyclic sulfoxide ketones in perchloric acid to form bicyclic compounds, and it is possible that the intermediate M^+ , formed in the first step of the reaction between β -alkylsulfinylcarboxylic

acids and iodide ions in perchloric acid, has an analogous, but monocyclic structure.

From the calculation of the equilibrium constant for the reaction it is found that the formation of hypoiodous acid during the reaction is possible:



This scheme is in agreement with the kinetic data as well as the equilibrium constant and should not be left out of consideration. It also indicates an attack of an iodide ion upon an oxygen atom and not on sulfur as proposed by Landini *et al.* However, the nucleophilic attack on sulfoxide-oxygen in acid solutions, resulting in sulfur-oxygen bond cleavage, has been reported earlier by Bordwell and Pitt⁶ for the oxygen exchange reaction between sulfoxides and sulfides. It therefore seems reasonable that an analogous attack of an iodide ion on oxygen with the formation of hypoiodous acid can be a plausible step in the reaction under discussion, and also serve as an explanation for the observed reversibility, because hypochlorous acid has been found to oxidise sulfides rapidly.⁷

EXPERIMENTAL

All reactions were carried out in a nitrogen atmosphere in the same way as earlier described, and the β -propylsulfinylpropionic acid used was of the same purity as previously reported.¹ Perchloric acid, sodium perchlorate and sodium iodide were of *p.a.* quality.

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