

Studies on Alkylsulfinylcarboxylic Acids

V. Activation Energies and Entropies for the Reaction between Some β -Alkylsulfinylcarboxylic Acids and Iodide Ions in Acid Solution

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Rate constants obtained from the reduction of some β -alkylsulfinylcarboxylic acids in acidic iodide solution have been determined at 20.0, 25.0, and 30.0°C. From these data the energies and entropies of activation (E_a and ΔS^\ddagger) for the reaction were calculated.

The effect of the substituents R and R' upon the rate of the reaction:

$$\text{R-SO-R}'\text{-CO}_2\text{H} + 2 \text{H}^+ + 2 \text{I}^- \rightleftharpoons \text{R-S-R}'\text{-CO}_2\text{H} + \text{I}_2 + \text{H}_2\text{O}$$

has been discussed earlier by the author; considerable changes in the pseudo first-order rate constants were found to accompany alterations in R as well as R'.¹ This paper will present activation data obtained by measuring the temperature dependence of the rate constants for four various β -alkylsulfinylcarboxylic acids. The reaction was carried out in a 1.00 M perchloric acid solution except for one of the compounds which was studied in 0.50 M perchloric acid in order to obtain more accurate rate constants. The initial concentrations of the sulfoxide compounds and of iodide were 0.005 M and 0.200 M, respectively, so the reaction could in all cases be treated as pseudo first-order and going to completion. The rate constants were calculated by an electronic digital computer using a least squares program. Fig. 1 illustrates, for each case, the use of the Arrhenius expression: $\ln k/dT = E_a/RT^2$ in its integrated form. From the slopes of the lines, corresponding to $-E_a/2.303 R$ and obtained by means of least squares calculations, the values of the activation energies listed in Table 1 were computed.

From the relatively large negative values of the entropy of activation, it can be concluded that for this reaction the internal freedom is less in the transition state than in the reactants, which is consistent with the assumption that the reaction path includes a cyclic intermediate.

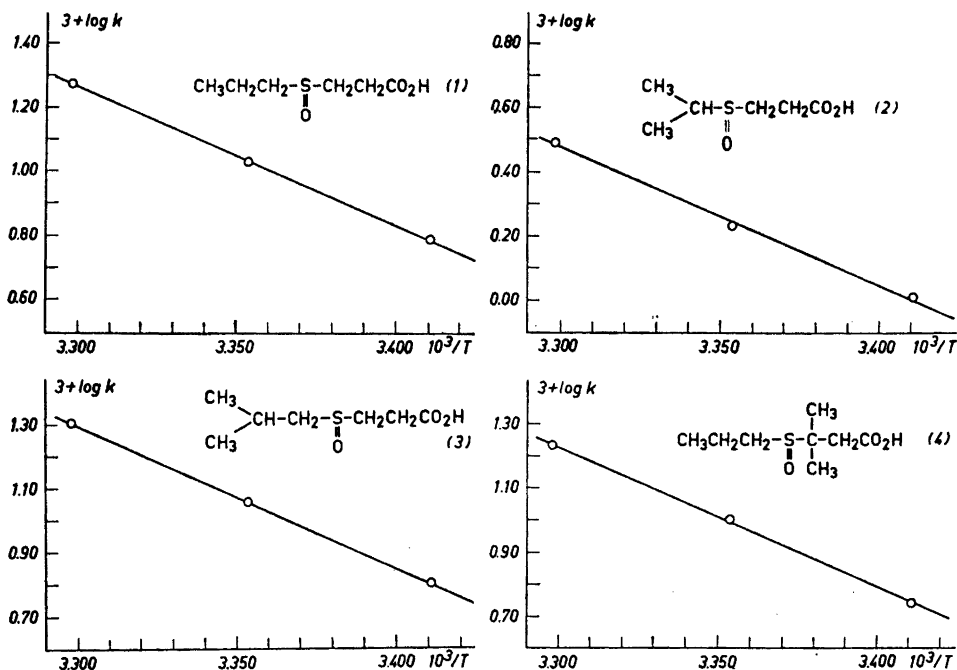
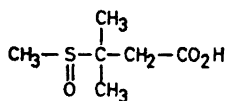


Fig. 1. Arrhenius plots for the various compounds investigated.

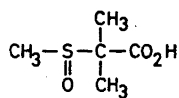
Table 1. Rate constants and activation data for the reaction.

Compound No.	C_{HClO_4} , M	Temp. °C	$10^3 k \text{ min}^{-1}$	E_a kcal/mole	ΔS^\ddagger e.u.
1	1.00	20.00	6.15 ± 0.03	19.63 ± 0.13	-11.8 ± 0.5
		25.00	10.62 ± 0.02		
		30.00	18.7 ± 0.05		
2	1.00	20.00	1.02 ± 0.02	19.62 ± 0.86	-15.5 ± 2.9
		25.00	1.70 ± 0.04		
		30.00	3.10 ± 0.09		
3	1.00	20.00	6.29 ± 0.05	20.52 ± 0.21	-8.7 ± 0.7
		25.00	11.40 ± 0.06		
		30.00	20.1 ± 0.08		
4	0.50	20.00	5.46 ± 0.05	20.17 ± 0.27	-10.2 ± 0.9
		25.00	9.97 ± 0.04		
		30.00	17.1 ± 0.10		

This is further illustrated by a comparison between the two compounds β -methylsulfinylisovaleric acid (a) and α -methylsulfinylisobutyric acid (b). The only difference between these acids is a methylene group:



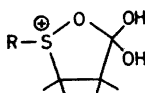
(a)



(b)

The failure of (b) to react at any observable rate with iodide in 2 M perchloric acid at 25°C has been reported earlier.¹ On the other hand, the author studied (a) in 1 M perchloric acid at this temperature and under the conditions given above and obtained a rate constant, $k = 0.0151 \text{ min}^{-1}$.

This difference in reactivity is further support for the hypothesis that a five-membered ring of the type:



exists as an intermediate in the reduction of a β -alkylsulfinylcarboxylic acid in acidic iodide solution, and that the formation of this intermediate is a rate-determining step. Therefore, the geometric configuration of α,β -unsaturated sulfoxide-acids is of the greatest importance for the rate of reduction, a fact recently pointed out.²

Because a change of the alkyl group from a propyl to an isopropyl group for β -alkylsulfinylpropionic acids caused a sixfold decrease in the pseudo first-order rate constant,¹ it was of interest to see if a similar decrease would occur in β -alkylsulfinylisovaleric acids. Therefore, the reaction of β -isopropylsulfinylisovaleric acid with iodide in 1 M perchloric acid at 25°C and under the conditions written above was studied. A rate constant $k = 0.00655 \text{ min}^{-1}$ was obtained. Comparing this value with the value found earlier for the propyl derivative under identical conditions,^{1,3} $k = 0.0258 \text{ min}^{-1}$, reveals a change in rate of about 4 times. The isovaleric acid compounds are accordingly only slightly less susceptible to changes in R than the propionic acid derivatives.

CALCULATIONS OF RATE CONSTANTS, ACTIVATION PARAMETERS AND ERRORS

The pseudo first-order rate constants satisfy the simple expression: $k = (1/t) \ln [a/(a-x)]$, where $a - x$ denotes the sulfoxide concentration at time t . Thus, a plot of $\log(a - x)$ against t will give a straight line of slope $-k/2.303$. From the least squares program a line, best adapted to the experimental points, was obtained. The errors in k were estimated in the following manner: By calculation of k for all points of time t , using the formula given above,

a maximum and a minimum value of k is obtained (k_{\max} and k_{\min}). The error $\pm \Delta k$ is then taken as $\pm (k_{\max} - k_{\min})/2$. It is roughly $\pm (0.5-2)$ % of k for the reactions studied.

The computation of the activation energies already has been described. The error in E_a was estimated by using similar operations as given above. The extreme values of E_a were considered as the maximum and minimum slopes obtained when the errors in k at the highest and lowest temperature, respectively, were taken into account.

The values of ΔS^\ddagger were obtained from the expression:⁴

$$\Delta S^\ddagger = 2.303 R (\log k - \log 5.665 \times 10^{10} T) + (E_a/T)$$

where k is expressed in the unit of sec^{-1} . From the errors in k and E_a a largest and smallest value of ΔS^\ddagger could be found, giving the error as above.

EXPERIMENTAL

The syntheses and physical constants of the β -propylsulfinylpropionic, β -isopropylsulfinylpropionic, and β -propylsulfinylisovaleric acids as well as their corresponding sulfides were reported previously by the author.^{3,5} All sulfinyl compounds described here were prepared by oxidation of the sulfide-acids with hydrogen peroxide in acetone solution. A 10 % excess of the amount calculated for the oxidation to sulfoxide was used.

β -Isobutylthiopropionic acid (I). β -Mercaptopropionic acid was treated with isobutylbromide in an alkaline water-ethanol solution. When the reaction was complete the ethanol was distilled, the residue acidified and extracted with ether. After removal of the ether the product was vacuum-distilled. B.p. 147 - 147.5°/9 mm. Starting with 26.5 g (0.25 mole) β -mercaptopropionic acid the yield was 29.0 g (71.5 %). (Found: C 51.6; H 8.66; S 19.8. Calc. for $C_5H_{10}O_2S$: C 51.8; H 8.70; S 19.8).

β -Isobutylsulfinylpropionic acid (II). This acid was recrystallized from ethyl acetate + light petroleum. M.p. 73.5-74.5° (Found: C 47.2; H 7.97; S 18.3; equiv. wt. 177.9. Calc. for $C_5H_{10}O_3S$: C 47.2; H 7.92; S 18.0; equiv. wt. 178.3).

β -Methylthioisovaleric acid (III). β -Mercaptoisovaleric acid, obtained by the method of Földi and Kollonitsch,⁶ was reacted with dimethyl sulfate in an alkaline water-ethanol mixture. The rest of the synthesis was performed as described for the preparation of I. Starting with 13.4 g (0.1 mole) of β -mercaptopisovaleric acid, a product with b.p. 126.5 - 127°/8 mm was obtained in an amount of 9.12 g (61.5 %). The acid solidified in the receiver to well-formed crystals.

β -Methylsulfinylisovaleric acid (IV). One recrystallization from ethyl acetate + light petroleum and another from a toluene-ethanol mixture gave a m.p. of 86.0 - 87.5°. (Found: C 43.9; H 7.37; S 19.4; equiv. wt. 164.4. Calc. for $C_5H_{10}O_3S$: C 43.9; H 7.37; S 19.5; equiv. wt. 164.2).

β -Isopropylthioisovaleric acid (V). β -Mercaptoisovaleric acid was treated with isopropylbromide and alkali in the same way as described for the preparation of III. B. p. 93°/0.15 mm. (Found: C 54.3; H 9.13; S 18.0. Calc. for $C_5H_{10}O_2S$: C 54.5; H 9.15; S 18.2).

β -Isopropylsulfinylisovaleric acid (VI). The acid was recrystallized from ethyl acetate + light petroleum. M.p. 91.5 - 92.2°. (Found: C 50.1; H 8.41; S 16.7; equiv. wt. 192.0. Calc. for $C_5H_{10}O_3S$: C 50.0; H 8.39; S 16.7; equiv. wt. 192.3).

The kinetic experiments were carried out in the same way as described earlier.³ A nitrogen atmosphere was used in all cases and blank solutions were titrated with sodium thiosulfate in order to correct for the very slow concurrent air oxidation of iodide. These corrections, which always have to be made were, however, quite small. The initial concentrations were determined in the following way: The stock solution of the sulfoxide compound dissolved in perchloric acid was prepared in such a way that a certain volume of it gave an initial concentration of 0.005 M when diluted in the reaction vessels. A more accurate value of the sulfoxide-content could, in the case of the propionic

acid derivatives, be obtained by using the method of bromide-bromate titration.^{5,7} In cases of the most rapidly reacting compounds, the reaction with iodide in ~ 3 M acid concentration is so fast that it is completed within a fairly short time so that the initial concentration can be determined in this way. In the least squares calculations this initial concentration has been varied in the vicinity of the experimental value.

The temperature of the thermostat has been constant within $\pm 0.02^\circ\text{C}$.

Perchloric acid and sodium iodide of p.a. quality were used.

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