

Studies on Alkylsulfinylcarboxylic Acids

II. Kinetics of the Reactions of Alkylsulfinylcarboxylic Acids with Iodide Ions in Acid Solution

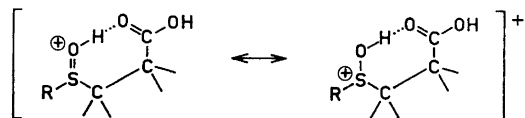
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The rate of the reaction:

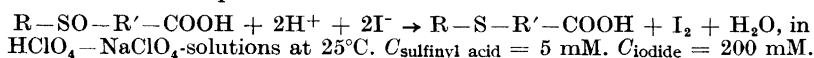
$R-SO-R'-COOH + 2H^+ + 2I^- \rightarrow R-S-R'-COOH + I_2 + H_2O$,
where $R' = -C(CH_3)_2-$, $-CH_2CH_2-$, $-C(CH_3)_2CH_2-$, and $-CH_2CH_2CH_2-$, has been measured in $HClO_4-NaClO_4$ -solutions of various concentrations at 25°C. Only when $R' = -CH_2CH_2-$ and $-C(CH_3)_2CH_2-$ the reaction was found to be fast enough to be measured with accuracy. The nature of the alkyl group (R) greatly influences the reaction velocity.

In a previous paper,¹ the rate of the liberation of iodine from acid solutions of iodide by means of two different β -alkylsulfinylpropionic acids, *viz.* the propyl- and β -carboxyethyl-derivatives, has been reported. In order to investigate the influence of the position of the carboxyl group in relation to the sulfoxide group on the reactivity of the latter one, a series of alkylsulfinylcarboxylic acids was prepared. The compounds which have been kinetically investigated are represented in Table 1. Some of these (II-IX) have been described earlier by the author.^{1,2} The reason why only α,α -dimethyl substituted α -alkylsulfinylacetic acids have been prepared is that monoalkyl- and unsubstituted α -sulfinyl acids are not stable in acid solution.^{3,4} As can be seen in Table 1, the α -acids investigated do not react at all and the γ -sulfinyldibutyric acid reacts about 150 times slower than β -sulfinyldipropionic acid under the same conditions. Thus the most reactive compounds are those with the sulfoxide group in β -position. There is some evidence that this β -effect can be explained by the assumption that intramolecularly hydrogen-bonded structures of the following type



play a part in the reaction mechanism.

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Table 1. The pseudo first-order rate constant k of the reaction:

No.	R	R'	C_{HClO_4}	C_{NaClO_4}	$10^3 k \text{ min}^{-1}$
I	CH ₃ -	-C(CH ₃) ₂ -	2.00	0	0
II	(CH ₃) ₃ C-	->-	2.00	0	0
III	CH ₃ CH ₂ CH ₂ -	-CH ₂ CH ₂ -	2.00	0	36.2 ^a
	->-	->-	1.00	1.00	19.2 ^a
	->-	->-	1.00	0	10.6 ₅ ^a
IV	HOCO·CH ₂ CH ₂ -	->-	2.50	0	43.2
	->-	->-	2.00	0	26.2 ^a
	->-	->-	1.00	0	7.56 ^a
V	HOCO(CH ₂) ₄ -	->-	2.00	0	26.8
	->-	->-	1.00	1.00	13.7
	->-	->-	0.50	0	2.93
VI	(CH ₃) ₂ CH-	->-	2.50	0	9.40
	->-	->-	1.50	0	3.50
	->-	->-	1.00	0	1.81
VII	(CH ₃) ₃ C-	->-	2.00	0	~10 ⁻² ^b
VIII	CH ₃ CH ₂ CH ₂ -	-C(CH ₃) ₂ CH ₂ -	1.00	0	25.8
	->-	->-	0.50	0	9.96
IX	HOCO·CH ₂ CH ₂ -	->-	1.00	0	6.3
X	HOCO·CH ₂ CH ₂ CH ₂ -	-CH ₂ CH ₂ CH ₂ -	2.00	0	0.18

^a Ref.¹^b Somewhat uncertain value.

Branched alkyl groups (R) lower the reaction rate considerably which can be seen by comparing the rate constants of three different β -alkylsulfinylpropionic acids: *viz.* the propyl-, isopropyl- and *tert.*-butyl-compounds. The k -values for these acids under the same conditions are: 0.0362, 0.0060 and $\sim 10^{-5} \text{ min}^{-1}$, respectively, *i.e.* the ratio is of the order 3600:600:1. It is obvious that this behaviour must be due to steric effects from the branched alkyl groups. However, when the other neighbour carbon atom of the sulfoxide group, *i.e.* the β -carbon atom, carries methyl substituents no such decrease of the reaction rate is observed but instead an acceleration of the reaction velocity. The k -values for β -propylsulfinylpropionic acid and β -propylsulfinylisovaleric acid are: 0.01065 and 0.0258 min^{-1} , respectively, under the same conditions, which means that the β,β -dimethyl substituted compound reacts about 2.4 times faster than the unsubstituted one.

Table 2. Infra-red stretching vibration frequencies of the sulfoxide group for the compounds investigated.

Compound	Wave number cm^{-1}	
	In H_2O	In 2 M HCl
$\text{CH}_3-\text{SO}-\text{C}(\text{CH}_3)_2\text{COOH}$	1017-1019	1005-1010
$\text{CH}_3\text{CH}_2\text{CH}_2-\text{SO}-\text{CH}_2\text{CH}_2\text{COOH}$	995-999	970-998
$\text{HOCO}(\text{CH}_2)_4-\text{SO}-\text{CH}_2\text{CH}_2\text{COOH}$	1000	986-999
$(\text{CH}_3)_2\text{CH}-\text{SO}-\text{CH}_2\text{CH}_2\text{COOH}$	1000	985-1002
$(\text{CH}_3)_3\text{C}-\text{SO}-\text{CH}_2\text{CH}_2\text{COOH}$	1003	985-996
$\text{HOCO}\cdot\text{CH}_2\text{CH}_2-\text{SO}-\text{CH}_2\text{CH}_2\text{COOH}$	1008-1011	1004
$\text{CH}_3\text{CH}_2\text{CH}_2-\text{SO}-\text{C}(\text{CH}_3)_2\text{CH}_2\text{COOH}$	994	980
$\text{HOCO}(\text{CH}_2)_3-\text{SO}-\text{C}(\text{CH}_3)_2\text{COOH}$	995	965-980
$\text{CH}_3-\text{SO}-\text{CH}_3$	1015	1003

The infra-red stretching vibration frequencies of the $>\text{SO}$ groups of some different sulfinyl compounds are represented in Table 2. The measurements have been carried out in water and in 2 M hydrochloric acid. It is noticeable that the $>\text{SO}$ -absorption of the β -alkylsulfinylcarboxylic acids generally occurs at a lower frequency than in dimethyl sulfoxide.

EXPERIMENTAL

The kinetic measurements have been carried out in the same way as previously described.¹

The infra-red spectra were recorded with a Perkin-Elmer model 221 spectrophotometer equipped with a grating monochromator and a sodium chloride prism. Cells with windows of Irtran-2 and with spacers of 12.5 μ platinum foil were used.

The instrument was operated with the "automatic gain control" characteristic of the model. The following settings were used: slit program 940, corresponding to a slit width of 152 μ at 1000 cm^{-1} , scale 25 cm^{-1}/cm , speed about 25 $\text{cm}^{-1}/\text{min}$ with a properly attenuated pen.

α -Methylsulfinylisobutyric acid was prepared according to Tananger.⁵ The acid was recrystallized from ethanol. M.p. 109-111°. (Found: C 39.8; H 6.63; S 21.15; equiv. wt. 150.1 (NaOH); 75.7 (KBrO₃); 75.1 (HBr). Calc. for C₅H₁₀O₃S: C 40.0; H 6.71; S 21.35; equiv. wt. 150.15 (NaOH); 75.1 (KBrO₃; HBr)).

γ -Sulfinyldi-butyric acid was prepared according to Larsson,⁶ with the exception that the oxidation was carried out in a solution of acetone instead of glacial acetic acid. M.p. 96°. (Found: C 42.9; H 6.25; S 14.25; equiv. wt. 110.9 (NaOH). Calc. for C₈H₁₄O₅S: C 43.2; H 6.35; S 14.4; equiv. wt. 111.1 (NaOH)).

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