Because of a parallelism between the acidity and the rates of certain reactions in strong sulfuric acid–water mixtures, these reactions are characterized as acid-catalyzed; the "inhibition" produced by water is ascribed to its basic character.

NEW YORK CITY

THE KINETICS OF THE THIOCYANATE–BROMINATED FATTY ACID REACTIONS

BY VICTOR K. LA MER AND JOSEPH GREENSPAN

In their study of the kinetics of the replacement of bromine in brominated propionic ions by thiosulfate ion, La Mer and Kamner[1] found a greater velocity constant when the bromine was in the beta position than when it was in the alpha position, whereas the customary greater reactivity of the alpha position over the beta position was exhibited when the uncharged fatty acid esters were used instead of the sodium salts. This reversal in reactivity was predicted on the basis of the effect of electrostatic repulsions between the ions of the same sign upon the frequency of collisions.[2]

The analogous reactions in which thiocyanate ion[3] is employed as the replacing ion instead of thiosulfate ion appeared to be well adapted for extending the study, particularly since the analytical method for the determination of thiocyanate published recently by Pagel and Ames[4] possesses the advantages of precision and speed over the tedious method employed by Holmberg.

In Table I are given two typical runs for the reaction

$$SCN^- + CH_2BrCOO^- \longrightarrow CH_2(SCN)COO^- + Br^-$$
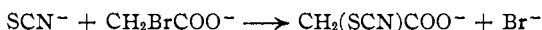
in the presence of sodium as cation. The k values are the bimolecular constants; the units, liters per mole per minute; $T = 25.00 \pm 0.05°$. The concentration of CNS^- in an aliquot at any time, t, was determined

TABLE I

| Run 8 a = 0.1000 m./l. NaCNS b = 0.1000 m./l. NaBrAc | | | | Run 5 a = 0.04980 m./l. NaCNS b = 0.04980 m./l. NaBrAc | | | | |
t	$a - x$	x	% Conv.	k	t	$a - x$	x	% Conv.	k
122	0.07703	0.02297	23	0.0244	260	0.03917	0.01063	22	0.0210
242	.06344	.03656	37	.0238	517	.03247	.01733	35	.0208
362	.05393	.04607	46	.0236	1333	.02096	.02884	58	.0207
482	.04698	.05302	53	.0234	1575	.01898	.03082	62	.0207
662	.03939	.06061	61	.0232	1940	.01674	.03306	66	.0205

[1] La Mer and Kamner, THIS JOURNAL, 53, 2832 (1931).

[2] La Mer, Chem. Reviews, 10, 179 (1932); see pp. 207–210.

[3] Holmberg, Z. physik. Chem., 97, 134–157 (1921).

[4] Pagel and Ames, THIS JOURNAL, 52, 2698 (1930).

by iodimetric oxidation in borax buffer solution under conditions specified by Pagel and Ames.[4]

An examination of this table shows a downward drift for k amounting to about 4% in the region 23 to 60% conversion. Upon attempting to follow the course of this reaction in more dilute solution to compare the Brönsted–Debye limiting slope with the observed values, the drift became greatly magnified, as illustrated in abbreviated form in Table II.
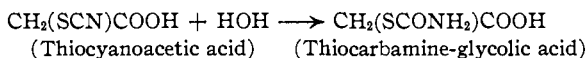
TABLE II

Run 11 NaBr acetate $a = b = 0.004950$ m./l.			Run 18 NaαBr-propionate $a = b = 0.04950$ m./l.			Run 25 NaβBr-propionate $a = b = 0.009910$ m./l.		
t	% Conv.	k	t	% Conv.	k	t	% Conv.	k
3736	23	0.0153	5298	21	0.000973	7319	18	0.00312
9753	40	.0139	15251	25	.000441	21696	25	.00156

Titration of the solutions initially neutral showed that both the α- and β-bromopropionate–thiocyanate solutions had become acid (approximately P_H 3) whereas the bromoacetate–thiocyanate solutions still remained neutral. This clearly demonstrated the occurrence of side or consecutive reactions. In one run (No. 18 above), SCN$^-$ was found to be regenerated, indicating either an hydrolysis of the resultant thiocyano compound

$$CH_3CH(SCN)COO^- + H_2O \longrightarrow CH_3CH(OH)COO^- + HSCN$$
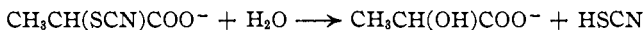
with consequent increase in acidity of the solution, or an interference of secondary products with the analytical determination of SCN$^-$.

Ostwald,[5] using conductivity methods, showed that the reaction

$$CH_2(SCN)COOH + HOH \longrightarrow CH_2(SCONH_2)COOH$$
(Thiocyanoacetic acid)   (Thiocarbamine-glycolic acid)

was 90% complete in five days (room temperature) at a concentration of 1 mole in 1024 liters. In a recent paper, Fredga[6] demonstrated that the α- and β-thiocyanopropionic acids were also unstable in aqueous solution, undergoing hydration to the corresponding thiocarbamine acids, which might interfere with the analytical method. The increasing acidity of the solution can be explained by the direct hydrolysis of the brominated acids, the monomolecular constants for the α and β cases being of the order of 10^{-5} and 10^{-4}, respectively.[7]

Holmberg's[3] studies involved the reaction $CH_2ICOO^- + SCN^- \xrightarrow{K^+} CH_2SCNCOO^- + I^-$ for concentrations as dilute as 0.0125 M in the iodoacetic salt. The iodo derivative reacts about 50% faster than does the corresponding bromo derivative,[8] so that measurements could be completed within forty-eight hours. Within this period Holmberg obtained no drift in k, whereas we observed a perceptible drift over this same time interval

[5] Ostwald, Z. physik. Chem., **3**, 179–181 (1889).

[6] Fredga, J. prakt. Chem., **231** (N. F.), **123**, 110–128 (1929).

[7] Ref. 1, p. 2844.

[8] See Ref. 2, p. 203.

(Table I). We attribute this difference to the more precise analytical method used by us. In but one measurement extending over fifty hours did Holmberg[9] observe a drift; this he attributes to the formation of the thiocarbamine acid.

TABLE III

Na α-bromopropionate $a = 0.05215$ m./l. NaSCN $b = 0.03528$ m./l.			Na β-Bromopropionate $a = 0.05223$ m./l. NaSCN $b = 0.03017$ m./l.		
t	% Conv.	k	t	% Conv.	k
1297	6	0.000899	1342	20	0.00326

Since interference from end-products will be at a minimum during the first few hours of reaction, we may conclude from Table III that the β-ion reacts about 3.4 times more rapidly than the α-bromopropionate ion, a result in good accord with that obtained for the thiosulfate reaction.[1]

Summary

Side and consecutive reactions obscure the kinetics of the halogen replacement by thiocyanate ion in the halogenated fatty acids when the elapsed time exceeds 1500 minutes. The greater reactivity of halogen in the beta position in an ion has been confirmed for the thiocyanate ion replacement reaction.

[9] Ref. 3, p. 155.

NEW YORK CITY

TRANSFERENCE NUMBERS OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE, SODIUM CHLORIDE, LITHIUM CHLORIDE AND HYDROCHLORIC ACID AT 25° BY THE MOVING BOUNDARY METHOD[1]

BY L. G. LONGSWORTH

Introduction

In the paper following this one, the conductance and transference data for aqueous solutions of some binary electrolytes will be interpreted from the standpoint of the modern theories of solutions. The transference data obtained for that study were determined by the moving boundary method. The experimental work involved in their measurement is the subject of this paper. An equation which is useful for interpolation and extrapolation to zero concentration is also given.

[1] A portion of the work here reported was completed while the author was a National Research Council Fellow.