N-Chlorosaccharin as a Possible Chlorinating Reagent: Structure, Chlorine Potential, and Stability in Water and Organic Solvents

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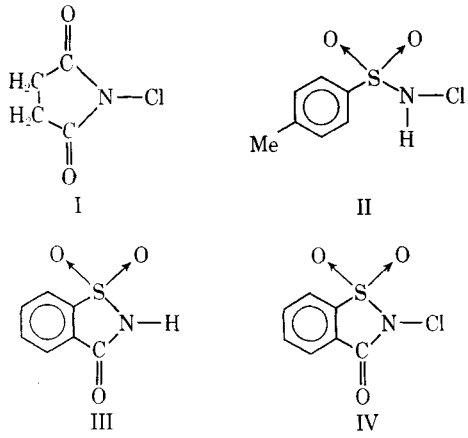
Abstract □ *N*-Chlorosaccharin is shown by its low chlorine potential (pK_{cp} = 4.85 at 25°) to be a stronger chlorinating reagent in water than the commonly used chloramine-T or *N*-chlorosuccinimide. Its possible usefulness as a detoxifying or chlorinating reagent was further indicated by its solubility and stability in a variety of solvents. The mechanism of a reaction in which the imide bond of *N*-chlorosaccharin was cleaved in aqueous hypochlorite solution was also investigated.

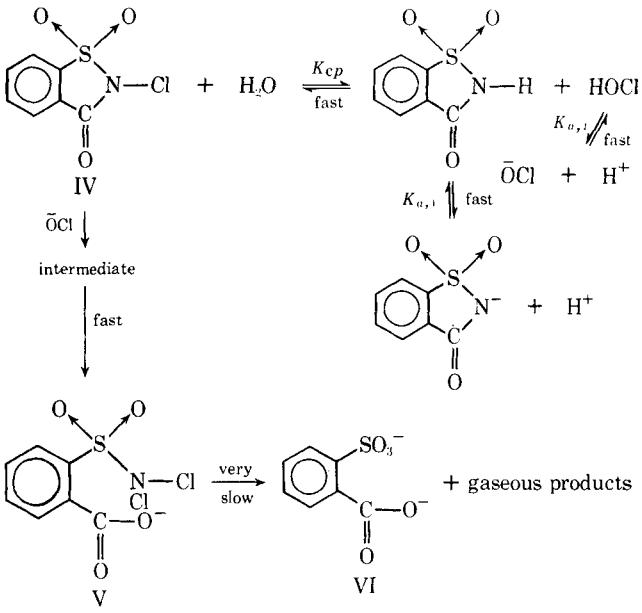
Keyphrases □ *N*-Chlorosaccharin—synthesis □ Chlorine potential—*N*-chlorosaccharin □ Hypochlorite solution—*N*-chlorosaccharin degradation □ IR spectrophotometry—identity □ UV spectrophotometry—identity □ Iodometric titration—analysis

N-Chloro imides [*e.g.*, *N*-chlorosuccinimide (I)] (1) and sulfonamides [*e.g.*, chloramine-T (II)] (2) are widely used as chlorinating and oxidizing reagents. The chlorinating power of these molecules, expressed as their chlorine potential, pK_{cp},[1] has been shown (3) to be related to the acidity of their nonchlorinated conjugates, with the stronger chlorinating agent being derived from the stronger acid. Thus, because saccharin (III) is a stronger acid (pKa = 1.31) (4) than succinimide (pKa = 9.62) (5) or *p*-tolylsulfonamide (pKa = 10.3) (6), it was expected that *N*-chlorosaccharin (IV) would be an even stronger chlorinating reagent than I or II.



I II III IV

When attempting to determine the K_{cp} value of IV, it was found that other reactions were occurring beside the transfer of positive chlorine between IV and water. These included acid dissociation of saccharin, cleavage of the imide bond of IV by the hypochlorite ion, formation of *N*,*N*-dichloro-*o*-sulfamylbenzoic acid (V) (and possibly the monochloro derivative), and slow decomposition of V to yield *o*-carboxylbenzenesulfonic acid (VI) and gaseous compounds. The overall reaction scheme is believed to be as shown in Scheme I.



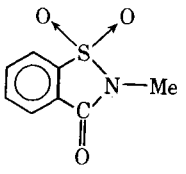
Scheme I

In this communication, evidence is reported for this reaction scheme together with values of the equilibrium constant, K_{cp}, and second-order rate constant, k_1. Approximate values of the solubility of IV in carbon tetrachloride, ethyl acetate, acetone, 1,4-dioxane, and chloroform were also determined, and the stability of its solutions in these solvents and methanol was investigated.

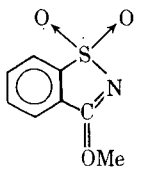
STRUCTURE AND SOLUBILITY OF *N*-CHLOROSACCHARIN

A chlorinated derivative of saccharin was precipitated (7) as a white crystalline powder (m.p. 148–150°) when chlorine gas was passed into cold aqueous solutions of saccharin. This substance was confirmed to be *N*-chlorosaccharin by elemental analysis, iodometric estimation of its positive chlorine content (one equivalent of positive chlorine per molecule), and from a comparison of its IR spectrum to those of saccharin (III), *N*-methylsaccharin (VII), and *o*-methylsaccharin (VIII). The conclusion that the chlorine in the molecule had substituted the imide proton of saccharin was deduced from the facts that: (*a*) the substance liberated positive chlorine in water (this would not be expected if the chlorine atom was substituted in the benzene ring), and (*b*) its IR spectrum contained no peaks above 3000 cm.$^{-1}$ (*i.e.*, in the N—H and O—H stretching region). The conclusion that it was *N*-chlorosaccharin and not the isomeric *o*-chloro derivative came from the observation that its IR spectrum contained a strong peak in the carbonyl stretching fre-

[1] For a chloro compound, R_2NCl, $pK_{cp} = -\log_{10} K_{cp}$, where K_{cp} is the equilibrium constant for the reaction $R_2NCl + H_2O \rightleftharpoons R_2NH + HOCl$.



VII



VIII

quency range (at 1750 cm.$^{-1}$). A similar carbonyl stretching peak was present in the spectra of saccharin (II) and *N*-methylsaccharin (1750 cm.$^{-1}$), but *o*-methylsaccharin did not contain any significant peaks between 1625 and 2000 cm.$^{-1}$. *o*-Chlorosaccharin would have been expected to have similar spectral characteristics to this latter compound (VIII).

Although *N*-chlorosaccharin had very low solubility in water (estimated solubility 0.1 g./l. at 25°), it was considerably more soluble in organic solvents as shown in Table I. UV spectral analysis and iodometric titration indicated that the *N*-chlorosaccharin content of the solutions in Table I did not change more than 3% during 3 hr. at 25°.

Chlorine Potential of *N*-Chlorosaccharin—A substance with a UV spectrum closely resembling that of *N*-chlorosaccharin was rapidly (complete within 30 sec.) formed when a solution of saccharin (1.16×10^{-4} *M*) in 6.8 *N* sulfuric acid was mixed with an equal amount of aqueous hypochlorous acid (1.34×10^{-3} *M*). When similar mixtures were made at higher pH values (in monochloroacetic acid–sodium monochloroacetate buffers), the spectra which were rapidly generated resembled those of mixtures of saccharin, sodium saccharin, and *N*-chlorosaccharin. These rapidly generated spectra did not change more than 3% during 3 min. at pH values below 3.8. They did, however, change appreciably over longer periods because of reactions that will be shown to involve cleavage of the imide bond of *N*-chlorosaccharin followed by slow decomposition of the ring-opened intermediate. Similar spectral behavior was observed when 0.5-ml. aliquots of a solution of *N*-chlorosaccharin in ethyl acetate (9.72×10^{-3} *M*) were mixed with 20 ml. of solutions of hypochlorous acid in various buffers. *N*-Chlorosaccharin was added as its ethyl acetate solution because of its slow rate of dissolution in water.

These initial rapid reactions are believed to be due to the establishment of the equilibria:

$$SH + HOCl \underset{}{\overset{1/K_{cp}}{\rightleftharpoons}} SCl + H_2O \qquad \text{(Eq. 1)}$$

$$SH \overset{K_{a,1}}{\rightleftharpoons} S^- + H^+ \qquad \text{(Eq. 2)}$$

where SH and S^- are the saccharin and saccharin anion, respectively; SCl is *N*-chlorosaccharin; and $K_{cp} = [SH][HOCl]/[SCl]$. The value of K_{cp} was calculated from spectrophotometric measurements of equilibrium concentrations of reactants and products following mixing of aqueous solutions of saccharin with buffered solutions of hypochlorous acid or of ethyl acetate solutions of *N*-chlorosaccharin with buffer solutions. Results from several series of experiments are included in Table II.

The mean value for K_{cp} in water was 1.4×10^{-5} *M* at 25° (excluding the K_{cp} values calculated from Experiments 6 and 7 where 2.4% ethyl acetate was present).

Thus, *N*-chlorosaccharin has a lower chlorine potential ($pK_{cp} = -\log K_{cp} = 4.85$) than *N*-chlorosuccinimide (8) ($pK_{cp} = 7.91$) and chloramine-T (8) ($pK_{cp} = 7.77$). Its value is very close to that which would be predicted (3) (5.27) on the basis that *N*-chlorosaccharin is a complex between a polarizable nitrogen containing anion (S^-) and the Lewis acid (Cl^+). For such a case the chlorine potential would be

Table I—Solubility of *N*-Chlorosaccharin at 25°

Solvent	Solubility, g./l.$^{-1}$
Carbon tetrachloride	4.3
Ethyl acetate	81.1
Chloroform	112.0
Acetone	173.0
1,4-Dioxane	287.0

Table II—Hydrolytic Constant,[a] K_{cp}, for *N*-Chlorosaccharin at 25°

Exp. No.	$[HOCl]_{added}$, *M*	$[Saccharin]_{added}$, *M*	$[SCl]_{added}$, *M*	$K_{cp} \times 10^5$ *M*
1	7.23	1.81	—	1.4
2	10.6	1.77	—	1.4
3	13.8	1.73	—	1.3
4	9.55	3.54	—	1.3
5	4.66	2.72	—	1.4
6[b]	—	0.379	1.58	1.8
7[b]	—	0.948	1.74	2.0

[a] Calculated as described in *Experimental* section. [b] Solutions contain 2.4 vol.-% ethyl acetate.

expected to be related to the pKa of saccharin by the identity $pK_{cp} = 0.28\ pKa + 4.90$.

Degradation of *N*-Chlorosaccharin in Aqueous Hypochlorite Solution—The previously mentioned changes in the UV spectrum of an equilibrium mixture of saccharin, saccharin anion, and *N*-chlorosaccharin increased in rate when the pH of the solution was raised or when the concentration of hypochlorous acid was increased. These changes are believed to be due to a relatively fast cleavage of the imide bond of *N*-chlorosaccharin followed by a slower decomposition of the chlorinated *o*-sulfamylbenzoic acid. Results in Fig. 1 show the change in UV absorbance at 282 mμ in a 2-cm. cell plotted against time following the mixing of a solution of saccharin (5.60×10^{-4} *M*) in an acetic acid–sodium acetate buffer at pH 3.9 with an equal volume of aqueous hypochlorous acid (1.05×10^{-2} *M*). After the reaction had proceeded for longer than 40 min., unidentified gases were evolved. The UV spectrum, which was measured 3 min. after mixing the reactants, is shown in Fig. 2 to be almost identical to that obtained 3 min. after mixing equal volumes of solutions of *o*-sulfamylbenzoic acid (6.00×10^{-4} *M*) and hypochlorous acid (1.37×10^{-2} *M*).

The reactions occurring in the hypochlorous acid–saccharin system could be quenched by adding drawn samples to excess sodium bisulfite to reduce the positive chlorine. When the drawn samples were added to sodium bisulfite at progressively longer time intervals after the reactants had been mixed, and the solution was placed on a silicic acid–sulfuric acid column, saccharin and *o*-sulfamylbenzoic acid (identified by their UV spectra in chloroform and their retention time on the column as compared to authentic materials) were eluted with a chloroform–butanol mixture. The amount of saccharin obtained decreased, and the amount of *o*-sulfamylbenzoic acid increased initially and then decreased as the time elapsed before the addition to sodium bisulfite increased. Results of the amounts of saccharin and *o*-sulfamylbenzoic acid obtained are plotted as a function of time before addition to sodium bisulfite in Fig. 3. *o*-Carboxylbenzenesulfonic acid, which was also expected to be a product of the degradation of *N*-chlorosaccharin, could not be eluted from the column with chloroform–butanol mixtures because of its high acidity. It was, however, eluted with aqueous phosphate buffer after the saccharin and *o*-sulfamylbenzoic acid had been removed. It was identified by the similarity of its UV spectra in 1 *M* HCl and 0.1 *M* NaOH to that of authentic material. Thus, the changes in UV absorbance and product analysis are consistent with the proposed reaction scheme for degradation of *N*-chlorosaccharin.

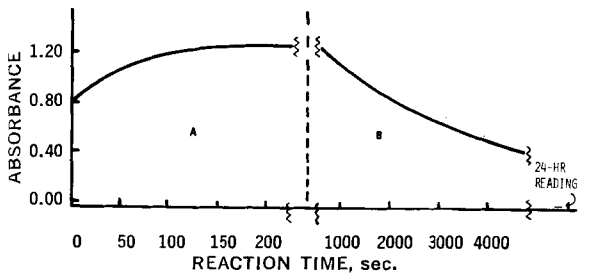


Figure 1—*Observed change in absorbance at 282 mμ in a 2-cm. cell containing initially 5.25×10^{-3} M HOCl and 2.8×10^{-4} M saccharin in pH 3.9, 0.03 M acetate buffer at 25°.*

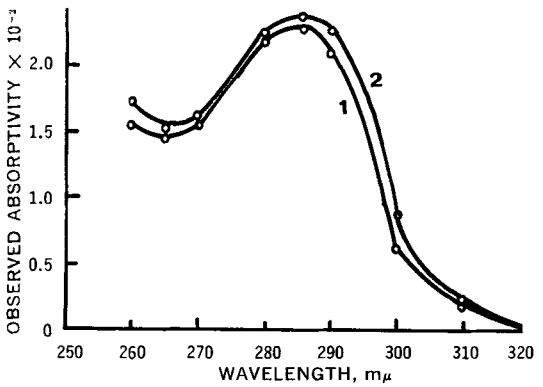


Figure 2—*UV spectra:* (1) *Mixture of saccharin and hypochlorous acid in 3 × 10⁻² M acetate buffer after 3 min. (with same concentration of hypochlorous acid as reference), pH 4.9.* (2) *Mixture of hypochlorous acid and o-sulfamyl benzoic acid (with same concentration of hypochlorous acid as reference), pH 3.30. Observed absorptivities were calculated by dividing absorbances by [saccharin]added or [o-sulfamyl benzoic acid] and the pathlength of the cell.*

Kinetic data for the ring-cleavage reaction were obtained from measurements of changes in UV absorbance at 282 mμ following addition of 1 ml. of solutions of saccharin ($1.74 - 2.18 \times 10^{-3}$ *M*) and 1 ml. hypochlorous acid ($5.78 - 2.88 \times 10^{-2}$ *M*) to 4.6 ml. acetate buffer of ionic strength, I, 0.5 *M*. Under these conditions (where the initial concentration of hypochlorous acid, $[HOCl]_{added}$, was greatly in excess of the added concentration of saccharin, $[SH]_{added}$), the ring-cleavage reaction was pseudo-first-order; a pseudo-first-order rate constant, k_1', was calculated by taking the maximum absorbance as the absorbance of the pure product. Because it is not known whether this product was *N,N*-dichloro-*o*-sulfamylbenzoic acid, *N*-chloro-*o*-sulfamylbenzoic acid, or an isomer of these, an unspecified intermediate was included in the reaction scheme. However, it is believed that irreversible ring cleavage was the rate-determining step in the reaction. On this basis, the rate equation for consumption of total saccharin species, SH_{total} $\{[SH_{total}] = [SH] + [S^-] + [SCl]\}$ would be:

$$\text{rate} = \frac{k_1 K_{a,2} [HOCl]_{added}^2 [SH_{total}]}{\{[H^+][HOCl]_{added} + K_{a,1} K_{cp} + K_{cp} [H^+]\}} \quad \text{(Eq. 3)}$$

where $K_{a,1}$ and $K_{a,2}$ are the acid dissociation constants of saccharin and hypochlorous acid ($K_{a,2} = 2.82 \times 10^{-8}$) (9). Thus the second-order rate constant would be related to the pseudo-first-order rate constant k_1' at different pH values and added hypochlorous acid concentrations by the identity

$$k_1 = k_1' \frac{[H^+][HOCl]_{added} + K_{a,1} K_{cp} + K_{cp} [H^+]}{K_{a,2} [HOCl]_{added}^2} \quad \text{(Eq. 4)}$$

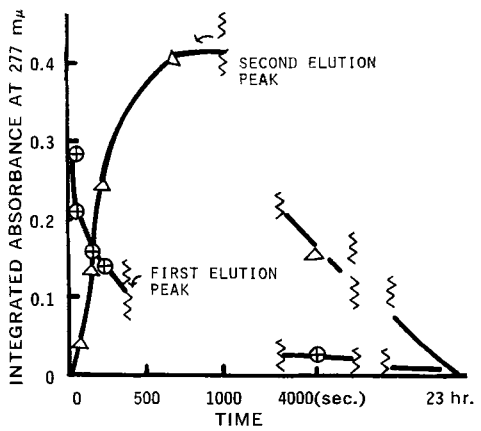


Figure 3—*Integrated absorbance areas under the first and second elution peaks obtained at various reaction times for mixture of hypochlorous acid and saccharin. The system initially contained 3.90 × 10⁻³ M hypochlorous acid and 4.85 × 10⁻⁴ M saccharin, pH 3.4.*

Table III—Rate Constants for Cleavage of Imide Bond of *N*-Chlorosaccharin

pH	$[Saccharin]_{added} \times 10^4$ *M*	$[HOCl]_{added} \times 10^3$ *M*	$10^2 k_1'$ Sec.$^{-1}$	$10^{-5} k_1$ M^{-1} Sec.$^{-1}$
5.4	3.30	7.28	3.63	1.9
	3.30	5.82	2.32	1.8
	3.30	5.09	1.98	2.0
	3.30	4.36	1.52	2.1
4.9	3.30	7.28	3.30	1.6
	3.30	5.82	2.32	1.7
	3.30	4.36	1.35	1.8
	2.64	5.82	2.24	1.7
	2.64	8.74	4.88	1.7
4.3	3.30	7.28	2.77	1.6
	3.30	5.82	1.79	1.6
	3.30	5.09	1.63	1.8
	3.30	4.36	1.26	1.9
Av.				1.8 ± 0.2

Values of k_1 calculated in this way are included in Table III.

The consistency of values of k_1 in Table III is strong evidence in support of the proposed reaction scheme. The kinetics of degradation of the chlorinated *o*-sulfamylbenzoic acid were not determined.

The overall reaction scheme is essentially the same as that proposed by Chattaway (7) to account for the degradation of *N*-chlorosaccharin in solutions of caustic alkalis.

Stability of *N*-Chlorosaccharin in Methanol—Methanolysis of *N*-chlorosaccharin to saccharin and methyl hypochlorite was a more favorable reaction than hydrolysis to saccharin and hypochlorous acid. Thus, when *N*-chlorosaccharin was dissolved in anhydrous methanol, it was quantitatively converted to saccharin and methyl hypochlorite by the following reaction:

$$SCl + MeOH \rightarrow SH + MeOCl \quad \text{(Eq. 5)}$$

When this reaction was complete (after 20 min.), the titer of iodine against positive chlorine was within 6% of theoretical, indicating that the reaction mixture was still a potential chlorinating system.

The rate of consumption of *N*-chlorosaccharin and the rate of formation of saccharin were pseudo-first-order reactions; from measurements of changes in concentration with time, a pseudo-first-order rate constant, k_m^1, with a value 4.1×10^{-3} sec.$^{-1}$ at 25° was calculated. When known amounts of water were added to the methanol, the rate of conversion of *N*-chlorosaccharin to saccharin increased linearly as shown in Fig. 4. The catalytic rate constant for water was calculated from this plot to be 10^{-2} M^{-1} sec.$^{-1}$. No further studies were undertaken to determine the mechanism of this reaction.

The chemical literature contains what the authors believe to be erroneous references (2, 9) to a reaction between *N*-chlorosaccharin and methanol to yield *N*-methylsaccharin. Although these references are apparently based on studies of Remsen and Dohme (10), the original work makes no mention of this reaction and treats instead the reaction between methanol and the product formed by reaction

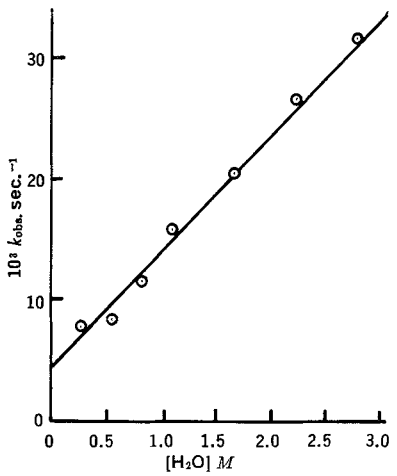


Figure 4—*Plot of* $k_{obs.}$ *against concentration of water in methanol for reaction of* N*-chlorosaccharin in aqueous methanol.*

Table IV—Determination of Hydrolytic Constant, K_{cp}, at 25° under the Condition where $[HOCl]_{added}$ Was Much Greater than $[SH]_{added}$[a]

pH	A_0	A	L[b]	Slope × 10^{-4}	Intercept × 10^{-4}	K_{cp} × 10^5 M	ϵ^{270}_{SCl}
2.30	0.611	0.950	3.47×10^3				
2.37	0.613	0.939	3.81×10^3				
2.48	0.616	0.925	4.62×10^3				
2.69	0.619	0.819	6.79×10^3	−7.22	7.19	1.38	2652
2.94	0.622	0.857	1.00×10^4				
3.34	0.624	0.774	1.55×10^4				
3.67	0.625	0.774	2.03×10^4				

[a] $[SH]_{added} = 1.77 \times 10^{-4}$ M, $[HOCl]_{added} = 1.06 \times 10^{-3}$ M. Buffer concentration = 0.04 M (monochloroacetate). Absorbance measured at 270 mμ in a 2-cm. cell. [b] $L = [(A - A_0)(K_{a,1} + [H]^+)]/([H^+][HOCl]_{added})$.

of saccharin and phosphorous pentachloride at 70–75°. This latter product is presumably pseudosaccharin chloride (11, 12) and not chlorosaccharin.

CONCLUSION

N-Chlorosaccharin is likely to have only limited usefulness as a chlorinating agent in water because of its poor solubility and slow rate of dissolution. On the other hand, it is readily soluble in several organic solvents and, because it readily releases its positive chlorine in water, it is expected to be a good chlorinating agent in these solvents. The reactions of *N*-chlorosaccharin in aqueous hypochlorite solution or methanol do not reduce the availability of positive chlorine appreciably and these solutions also should be useful chlorinating systems.

EXPERIMENTAL

Reagents and Equipment—All reagents used were of the highest grade commonly available and were normally subjected to further purification before use. Saccharin (Aldrich) was recrystallized from acetone (m.p. 228–229°). *N*-Chlorosaccharin was prepared and purified according to Chattaway (7). The purity of the recrystallized product (m.p. 148–150°), determined iodometrically, was 98% based on active chlorine content. Hypochlorous acid was prepared essentially according to Higuchi and Hasegawa (13). Commercially available bleaching solution (containing 5% sodium hypochlorite) was acidified with boric acid and distilled under vacuum at 50°. The distillate was redistilled under vacuum at the same temperature. A diluted solution of the second distillate was used in the reactions. The diluted solutions fell in the concentration range of 2×10^{-2} to 4×10^{-2} M. Monochloroacetic acid (J. T. Baker, A. R. grade) was recrystallized from benzene before use. Water used throughout this study was finally distilled from acid permanganate to remove possible volatile nitrogenous contaminants.

Table V—Determination of Hydrolytic Constant, K_{cp}, at 25° in Water under the Condition where $[HOCl]_{added}$ Was Not Much Greater than $[SH]_{added}$[a]

pH	A_0	A	A_∞	K_{cp} × 10^5 M
2.30	0.861	1.245	1.453	1.5
2.40	0.866	1.236	1.453	1.3
2.47	0.868	1.217	1.453	1.4
2.59	0.872	1.187	1.453	1.4
2.81	0.867	1.140	1.453	1.3
3.06	0.880	1.070	1.453	1.4
3.20	0.881	1.032	1.453	1.4
3.30	0.882	1.015	1.453	1.4
3.47	0.882	0.976	1.453	1.5
			Av.	1.4 ± 0.1

[a] $[SH]_{added} = 2.72 \times 10^{-4}$ M, $[HOCl]_{added} = 4.66 \times 10^{-4}$ M. Buffer concentration = 0.04 M (monochloroacetate). Absorbances were measured at 270 mμ in a 2-cm. cell.

Table VI—Determination of Hydrolytic Constant, K_{cp}, at 25° under the Condition where *N*-Chlorosaccharin Was Added to Buffered Solutions of Saccharin[a]

pH	A_0	A	A_∞	K_{cp}[b] × 10^5 M
2.29	0.604	0.760	1.028	1.9
2.33	0.606	0.753	1.028	2.0
2.47	0.611	0.751	1.028	1.6
2.70	0.617	0.707	1.028	2.1
3.02	0.621	0.683	1.028	1.8
3.30	0.623	0.671	1.028	1.4
3.46	0.624	0.658	1.028	1.5
3.57	0.624	0.646	1.028	2.0
			Av.	1.8 ± 0.3

[a] $[SCl]_{added} = 1.58 \times 10^{-4}$ M, $[SH]_{added} = 3.79 \times 10^{-5}$ M. Buffer concentration = 0.05 M (monochloroacetate). All solutions contained 2.4 vol.-% of ethyl acetate. Absorbances were measured at 270 mμ in a 2-cm. cell. [b] Using Eq. 9 and 10 to calculate K_{cp}, the values 1.96×10^{-4} M (added concentration of SCl + added concentration of SH) and 1.58×10^{-4} M (added concentration of SCl) were used for the terms "$[SH]_{added}$" and "$[HOCl]_{added}$."

Methanol (Allied Chemical, reagent grade) was dried according to Vogel (14). *o*-Methylsaccharin (VIII) was prepared by following the procedure used by Meadow and Reid (12) (m.p. 180–181°). *N*-Methylsaccharin (VII) was synthesized according to Brackett (15) (m.p. 131–132°). 1,4-Dioxane (Allied Chemical, reagent grade) was purified according to Vogel (14).

Cary 11, 14, or 15 recording spectrophotometers, which were thermostated at 25.0 ± 0.2° by circulating water, were used to measure absorbances. pH values were measured using a Corning 12 research pH meter.

CALCULATIONS AND PROCEDURES

Solubility of *N*-Chlorosaccharin in Organic Solvents—Solubility was estimated by measuring the maximum concentration of *N*-chlorosaccharin that could be dissolved by stirring with the solvent in a sealed vessel at 25°. Samples of solution were removed every 15 min. and analyzed by UV spectrophotometry and iodometric titration for *N*-chlorosaccharin and positive chlorine, respectively. When the concentration of the solution in the presence of undissolved crystals did not change during 45 min., it was assumed to be saturated.

Acid Dissociation Constant and Molar Absorptivity of Saccharin—Because saccharin is a strong acid, the absorbance of the neutral molecule in water was difficult to measure. Its acid dissociation constant, $K_{a,1}$, could not be calculated directly by using the relationship:

$$K_{a,1} = \frac{(A - A_{SH})\,[H^+]}{(A_S^- - A)} \qquad \text{(Eq. 6)}$$

where A is the absorbance of an equilibrium solution of saccharin and saccharin anion, and A_{SH} and A_S^- are the absorbances of the same solution at pH values where 99% of the saccharin is in the form of its neutral molecule and anion, respectively. Although the value of A_{SH} could not be measured, values of A_S^-, A (both in a 5-cm. cell at 270 mμ) and $[H^+]$ were measured for the equilibrium solutions formed when 1-ml. aliquots of aqueous solutions of saccharin (3.80×10^{-3} M) were added to 20 ml. of solutions of HCl and KCl (total concentration 2×10^{-1} M) at 25°. Plots of $(A_S^- - A)/[H^+]$ against A gave a straight line with a slope of 20.4 and an intercept on the Y-axis when $A = O$ of 21.7. From Eq. 6 it can be seen that the slope of this line and the intercept of the Y-axis are related to $K_{a,1}$ and the molar absorptivity of saccharin, ϵ^{270}_{SH}, by the identities

$$K_{a,1} = \frac{1}{\text{slope}} \quad \text{and} \quad \epsilon^{270}_{SH} = -\frac{\text{intercept}}{\text{slope} \times [SH]_{added} b} \qquad \text{(Eq. 7)}$$

where b is the pathlength of the spectrophotometer cell. From results of the experiment, values of $K_{a,1} = 4.91 \times 10^{-2}$ (lit. 2.5×10^{-2} at 18°) (16) and $\epsilon^{270}_{SH} = 1119$ in water at 25.0 ± 0.2° were calculated.

Determination of the Hydrolytic Constant, K_{cp} Value, for *N*-Chlorosaccharin—The K_{cp} value was calculated from the ab-

sorbance, A, of an equilibrium solution of saccharin (SH), saccharin anion (S^-), *N*-chlorosaccharin (SCl), and hypochlorous acid by using the equation:

$$\frac{(A - A_0)(K_{a,1} + [H^+])}{[H^+]\{[HOCl]_{added} - [(A - A_0)/(A_\infty - A_0)][SH]_{added}\}} = \frac{A_\infty}{K_{cp}} - \frac{A}{K_{cp}} \quad \text{(Eq. 8)}$$

A_0 and A_∞ were the absorbances of the solution under conditions where >99% of the added saccharin was in the form of saccharin plus saccharin anion and *N*-chlorosaccharin, respectively, and $K_{a,1}$ was the acid dissociation constant of saccharin. Values of A_0, A, and $[H^+]$ could be measured directly, but values of A_∞ could not be because of the difficulty of working at pH values where the saccharin would not be dissociated to an appreciable extent. Also, A_∞ could not be calculated from the identity

$$A_\infty = \epsilon_{SCl}[SH]_{added}\,b + \epsilon_{HOCl}([HOCl]_{added} - [SH]_{added})b \quad \text{(Eq. 9)}$$

until a sufficiently accurate value of the molar absorptivity of *N*-chlorosaccharin, ϵ_{SCl}, was available.

Inspection of Eq. 8 shows that when $[HOCl]_{added}$ is much larger than $[SH]_{added}$ and at a wavelength where $\epsilon_{SCl} > \epsilon_{SH}$ or ϵ_{S^-} a plot of

$$\frac{(A - A_0)(K_{a,1} + [H^+])}{[H^+][HOCl]_{added}}$$

against A at different pH values would give a straight line from which values of K_{cp} [= − (1/slope)] and A_∞ [= (−intercept/slope)] could be calculated. A value of ϵ_{SCl} could then be calculated from this A_∞ value and used to calculate A_∞ values for subsequent experiments where $[HOCl]_{added}$ was not much greater than $[SH]_{added}$. This was the method used to compute K_{cp} values. Typical sets of results for experiments carried out under conditions where: (*a*) $[HOCl]_{added} \gg [SH]_{added}$; (*b*) $[HOCl]_{added}$ was not much greater than $[SH]_{added}$, and (*c*) *N*-chlorosaccharin was added to buffered solution of saccharin are shown in Tables IV, V, and VI, respectively.

Determination of the Rate Constant for the Cleavage of Imide Bond of *N*-Chlorosaccharin—A saccharin stock solution, acetate buffer solutions (0.5 *M* with ionic strength adjusted to 0.5 by adding sodium sulfate) of different pH values, and hypochlorous acid of various concentrations were prepared and brought to 25°. Then 4.6 ml. of buffer solution of desired acidity was mixed with 1.0 ml. of saccharin solution in a 2-cm. cell. Into this cell 1.0 ml. of hypochlorous acid of desired concentration was injected. The cell was quickly shaken and placed in a spectrophotometer. The change of absorbance at 282 mμ was then recorded. At the end of the fast reaction (after the absorbance had passed its maximum reading), the pH of the mixture was determined.

Chromatographic Separation of the Components of the Reaction Mixture of Saccharin and Hypochlorous Acid—A partition column was prepared as follows: 20 ml. of 2 *N* sulfuric acid was added to 20 g. of silicic acid and mixed well. A slurry was made with 40 ml. of chloroform and packed into a glass column (50 cm. long, 2 cm. in diameter) containing a plug of glass wool and having a Teflon stopcock.

A 10-ml. portion of the reaction mixture was added to 2 ml. of 4 *N* sulfuric acid which contained sufficient sodium bisulfite to quench the reaction by reducing the positive chlorine and, consequently, *N*-chlorospecies were converted into their conjugate nonchlorinated derivatives. Five milliliters of the quenched reaction mixture was then chromatographed according to the following procedure: 5 g of silicic acid was added to the mixture and a slurry was made with 10 ml. of chloroform. The slurry was then packed on the top of the column.

Saccharin was eluted with 100 ml. of 2% butanol in chloroform and *o*-sulfamyl benzoic acid with 100 ml. of 6% butanol in chloroform. The integrated absorbance was obtained by adding the absorbances of all fractions (10 ml. eluate in each fraction) that contained the same component.

Alcoholysis of *N*-Chlorosaccharin to Saccharin in Methanol—A stock solution of *N*-chlorosaccharin was made up in ethyl acetate (4.00×10^{-2} *M*). Then 0.02 ml. of this solution was injected into a 1-cm. stoppered cell containing 2.0 ml. of methanol or aqueous methanol. The disappearance of *N*-chlorosaccharin was then followed spectrophotometrically at 276 mμ.

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