

Kinetics and Mechanism of the Reaction of *N*-Chlorosuccinimide with I^- and OH^-

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ABSTRACT: In this kinetic study of the reaction between the iodide ion and the *N*-chlorosuccinimide, we have found that the reaction is first order in *N*-chlorosuccinimide: namely, first order with respect to the iodide ion and first order with respect to the proton concentration. Based on the experimental results, we propose a mechanism consistent in Cl^+ transfer from the *N*-chlorosuccinimide to the iodide ion. We have found that the reaction presents general acid catalysis with a Brönsted exponent value of 0.10. In addition, given that the *N*-chloro compounds are not stable in aqueous solution, we have carried out a study on the influence of bases in the presence of *N*-chlorosuccinimide. We have found that the reaction is first order in hydroxide ion, as well as in the 1,1,1,3,3,3-hexafluoroisopropanoxide ion and the 2,2,2-trifluoroethoxide ion, which shows that the reaction is general-base catalyzed. © 2005 Wiley Periodicals, Inc. *Int J Chem Kinet* 37: 243–252, 2005

INTRODUCTION

The general class of organic compounds known as chloramines has received much attention as a possible source of chlorating agents for water treatment [1,2]. These compounds generally have an advantage over chlorine gas in that they do not appreciably chlorinate organic impurities to produce toxic haloforms.

Although much information is available on the formation of chlorine and bromine containing trihalomethanes [3–5], very little research has been performed on the formation and occurrence of iodinated trihalomethanes [6]. This is reasonable, given that the iodine is the least active of the three significant halo-

gens in this regard. However, it has been shown that iodoform was formed in the presence of chloramines, in a region where the formation of the most classical chlorinated or brominated trihalomethanes is usually unfavoured [7].

Besides, the characteristic medicinal odors that appear quite frequently in chlorinated finished drinking waters have been shown to be associated with the formation of iodinated trihalomethanes [8,9].

Formation of various halomethanes in chlorination of river water with added bromide and iodide was first report by Bun et al. [10]; they found all possible single halogen and mixed halogen-containing trihalomethanes.

If iodide is present in natural waters that are chlorinated, the added chlorine will oxidize the iodide very rapidly [11]. This reaction forms the basis for many

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analytical methods for determining chlorine (for example, the iodometric method). Molecular iodine (I_2) hydrolyzes readily to hypoiodous acid [12].

This study examines the reactivity of a chloramine, *N*-chlorosuccinimide (NCS), compared with the iodide ion, comparing it with the reactivity against the bromide ion (see Scheme 1).

In addition, given that one of the main characteristics of the NCS is its instability in an aqueous solution, perhaps due to its radical decomposition in light [13], we have carried out a kinetic study of its reactivity against different bases, such as the hydroxide, trifluoroethoxide, and hexafluoroisopropanoxide ions.

EXPERIMENTAL SECTION

N-chlorosuccinimide (Aldrich) has been recrystallized prior to use [14]. A stock solution of concentration 0.015 M was freshly prepared and stored in a UV-opaque flask in order to avoid decomposition.

Ionic strength was kept constant ($I = 0.5$ M) using $NaClO_4$ (Aldrich), and a solution of perchloric acid 3.0 M was prepared from commercial perchloric acid at 70% (Merck).

All sodium iodide solutions were prepared daily, by direct weighing of commercial product, Aldrich, to minimize the formation of triiodides.

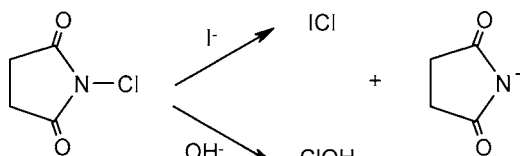
The different buffer solutions have been prepared from the corresponding acid or alcohol, by direct weight of the commercial products (Aldrich), adding the necessary amount of sodium hydroxide solution, until the desired pH value is reached.

The concentration of alkoxide in the reaction mixture was determined from

$$[B] = \frac{[B]_T}{(1 + 10^{(pK - pH)})}$$

where $[B]$ and $[B]_T$ are the concentrations of alkoxide and total alcohol, respectively, and the pK corresponds to the pK_a of the alcohol.

The kinetic experiments for the most rapid reactions were carried out in a sequential stopped-flow Applied Photophysics DX-17MV, while for the slower reactions we have used a double-beam spectrophotome-



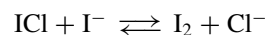
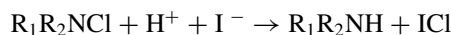
Scheme 1

ter Kontron UVIKON 930, both equipped with a thermostated cell carrier, which allows the temperature of the solutions to remain constant at $25.0 \pm 0.1^\circ C$.

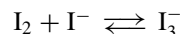
pH measurements were made with a radiometer PHM82 pHmeter using a combined electrode radiometer GK2401C. The pHmeter was calibrated with buffer solutions of pH 4.01 and 7.00 (Crison) and 10.01 and 12.45 (Beckman).

All reactions were carried out using the isolation method; the concentration of the iodide ion, hydroxide ion, or alkoxides being at least ten times that of the NCS. The observed first-order rate constants were obtained by nonlinear regression of the absorbance-time data; report values are the mean of 6–10 kinetic runs.

The stoichiometry of the reaction between *N*-chlorosuccinimide and iodide ion can be represented by the following equation:

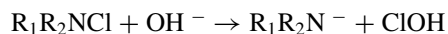


In the presence of iodide ion, the iodine formed during the reaction can be found to be in equilibrium with the triiodide ion according to the reaction:



The formation of the triiodide ion is less rapid than the reaction which is the object of the study, taking place as soon as iodine appears in the reaction medium. The spectrum of the triiodide ion presents two clear absorption maximum at 287 nm and 353 nm, with very high molar absorptivity coefficients [15], $\epsilon = 38,800$ $M^{-1} cm^{-1}$ and $\epsilon = 25,750$ $M^{-1} cm^{-1}$, respectively, so that with very low concentrations of triiodide ion we can obtain high absorbance values. In the study carried out in acidic solutions, the reactions were monitored by the formation of the triiodide ion at 287 nm.

The stoichiometry of the reaction between *N*-chlorosuccinimide and hydroxide ion can be represented by the equation:



In aqueous solution hypochlorous acid is found to be dissociated with a pK_a of 7.5 to $25^\circ C$ [16].

Reactions were followed by spectrophotometrically monitoring the development of a band at 292 nm due to the sodium hypochlorite ($\epsilon = 350$ $M^{-1} cm^{-1}$ [17]).

The reaction with alkoxides takes place in a similar way, given that a similar stoichiometry treatment can be applied.

EXPERIMENTAL RESULTS

Reaction with Iodide Ion

We studied first the effect of the concentration of NCS on the rate constant, varying its concentration and keeping all the other parameters constant. The observed rate constants are not affected by variations of the NCS concentration.

To investigate the influence of the iodide ion concentration on the rate constant, we carried out several experiments in which its concentration varied between 2.5×10^{-4} M and 1.5×10^{-3} M. The observed rate constants varied linearly with the iodide ion concentration (Table I); hence, the reaction is first order in iodide ion. The plot of k_{obs} against iodide ion concentration is a straight line with a slope of $(2.33 \pm 0.10) \times 10^5$.

On the basis of spectrophotometric measurements, we can determine the value of the equilibrium constant ($K_{I_3^-}$) for the triiodide ion at 25°C and $I = 0.5$ M. For this, we use the infinite time absorbance values, obtained in the study of the influence of the iodide ion concentration at the wavelength used, 287 nm.

The characteristic equilibrium constant is shown in Eq. (1):

$$K_{I_3^-} = \frac{[I_3^-]}{[I_2][I^-]} \quad (1)$$

The relationship obtained between the absorbance values observed and the concentration of the species which absorbs is given by Eq. (2):

$$A_{287} = \frac{K_{I_3^-} \varepsilon_{287} [\text{NCS}]_0 [I^-]}{1 + K_{I_3^-} [I^-]} \quad (2)$$

in which ε ($\text{M}^{-1} \text{cm}^{-1}$) represents the molar absorptivity coefficient of the reactive species, $[\text{NCS}]_0$ refers to the initial concentration of NCS, and A_{287} is the experimental absorbance obtained at this wavelength.

Figure 1 shows the variation of absorbance at 287 nm with the concentration of iodide ion. By adjusting Eq. (2), we have obtained a value of $748.7 \pm$

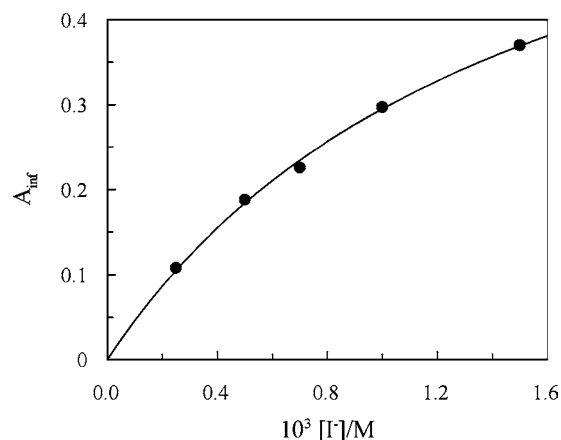


Figure 1 Spectrophotometric data for the measurement of $K(I_3^-)$ in 0.1 M de HClO_4 $\lambda = 287$ nm, $T = 25.0 \pm 0.1^\circ\text{C}$. The solid line shows the fit of Eq. (3) for $K_1 = 748.7 \pm 13.5$.

13.5 M^{-1} for the equilibrium constant of the triiodide ion, in accordance with the data found in the literature [18].

We carried out five series of experiments varying the concentration of iodide ion between 2.5×10^{-4} M and 1.5×10^{-3} M at different acid concentrations (0.005–0.5 M), keeping the temperature, ionic strength, and NCS concentration constant. We have found that there exists a linear relationship without an appreciable intercept between the observed rate constant and iodide ion concentration. The slopes obtained are shown in Table II, observing an increase in the slopes as the acid concentration increases.

Given that we have shown in the previous study that there exists an influence of the proton concentration on the observed rate constant, we have carried out the study in a wider range, in an interval of $-\log [H^+]$ comprised between 0.2 and 2.4, keeping the NCS concentration, the iodide ion concentration, the temperature, and the ionic strength constant.

The experimental results obtained are shown in Fig. 2, where we can observe that a decrease in the rate constant occurs as the pH of the medium increases,

Table I Variation of the Rate Constant Observed with the Concentration of Iodide Ion. $[\text{NCS}] = 2 \times 10^{-5}$ M, $[H^+] = 5 \times 10^{-3}$ M, $T = 25.0 \pm 0.1^\circ\text{C}$, $I = 0.5$ (NaClO_4)

$10^3 [I^-]$ (M)	k_{obs} (s^{-1})	A_{287}
0.25	72.8	0.108
0.50	122.4	0.188
0.70	164.8	0.226
1.0	246.7	0.297
1.5	362.7	0.370

Table II Values of the Slopes Obtained in the Study of the Variation of the Observed Rate Constant with the Concentration of Iodide Ion at Different Acid Concentrations

$[H^+]$ (M)	10^{-5} Slope
5×10^{-3}	2.33
0.02	2.42
0.05	2.46
0.2	2.59
0.5	2.93

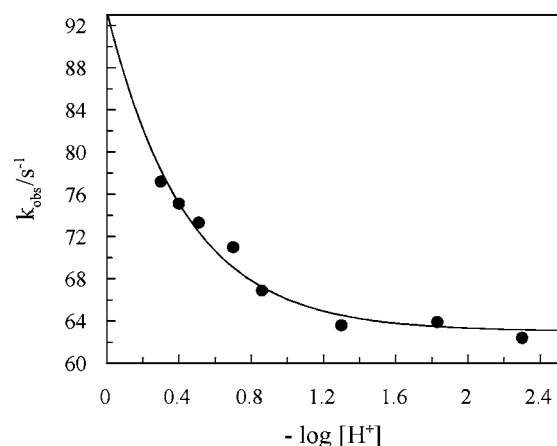


Figure 2 Influence of the pH of the medium on the rate constant. $[NCS] = 2 \times 10^{-5}$ M, $[INa] = 2 \times 10^{-4}$ M, $T = 25.0 \pm 0.1^\circ\text{C}$, $I = 0.5$ (NaClO_4).

reaching a pH value which is approximately greater than 2, where the rate constant becomes independent of the pH value.

Continuing with the study systematics of the influence of the concentrations of the species which take part in the reaction on the rate constant, we have studied the effect of the buffer concentration used to control the pH of the medium. We have observed that the values of the rate constant increase with buffer concentration, which suggests the occurrence of a catalytic effect. In addition, we have studied the influence of the nature of the buffer using for this purpose different buffer solutions, observing the catalytic effect on all of them. Table III shows the results obtained in the presence of buffers.

In order to calculate the experimental activation parameters of the reaction, the effect of the temperature on the rate constant observed was studied. The study has been carried out in acidic solutions at five different temperatures: 16, 20, 25, 30, and 40°C , and it was found

that the rate constant increases as does the temperature. The results obtained are shown in Fig. 3.

Reaction with Hydroxide Ion and Alkoxides

As in the study carried out for the reaction between NCS and iodide ion, we analyzed the possible influence of the concentration of NCS on the rate constant, varying that concentration while keeping all the other parameters constant. The observed rate constants are not affected by variations of the NCS concentration.

To investigate the influence of the concentration of the sodium hydroxide on the rate constant, we have carried out a series of experiments in which we varied the concentration of sodium hydroxide between 0.003 and 0.02 M. The experimental results obtained are shown in Fig. 4, in which we can see that there is a linear increase in the rate constant as the concentration of sodium hydroxide increases, showing an intercept which is compatible with zero and a slope with a value of $(9.3 \pm 0.4) \times 10^3$ at 25°C .

Similar behavior is observed in the presence of hexafluoroisopropanoxide ion (HFP) and trifluoroethoxide ion (TFE) (Fig. 5). The observed rate constants increase linearly with increasing concentrations of trifluoroethoxide ion and hexafluoroisopropanoxide ion in buffer solutions at constant pH. The hydrolysis of TFE causes changes in the pH value [19], which leads to modifications in the contribution of the hydroxide ion catalysis to the value of the observed rate constant. Thus, the catalytic rate constant for trifluoroethoxide ion was calculated by plotting $k_{\text{obs}} - k_{\text{OH}}[\text{OH}^-]$ versus the trifluoroethoxide ion concentration.

Although slight modifications of the pH values take place when hexafluoroisopropanol buffer is used, no correction was carried out; the influence of the hydroxide ion catalysis at pH 9 becomes negligible.

Table III Values of the Rate Constants Obtained in the Study of the Influence of the Concentration of Buffer and of the Slopes Obtained in that Study

[Buffer] (M)	$k_{\text{obs}} (s^{-1})$					
	Boric (pH = 8.87)	Phosphate (pH = 6.32)	Acetic (pH = 4.56)	Monochloroacetic (pH = 2.86)	Dichloroacetic (pH = 1.86)	Trichloroacetic (pH = 0.85)
0.40	69.9 ± 0.1	70.0 ± 0.1	69.1 ± 0.2	73.4 ± 0.2	69.0 ± 0.1	74.9 ± 0.2
0.30	69.0 ± 0.1	67.5 ± 0.1	67.1 ± 0.1	69.4 ± 0.1	64.1 ± 0.1	71.4 ± 0.2
0.20	68.6 ± 0.1	64.2 ± 0.1	64.7 ± 0.1	66.4 ± 0.1	60.0 ± 0.1	65.9 ± 0.1
0.10	67.7 ± 0.1	60.0 ± 0.1	62.2 ± 0.1		55.1 ± 0.1	61.5 ± 0.1
0.05	67.5 ± 0.1	58.5 ± 0.1	61.0 ± 0.1	61.1 ± 0.1	53.0 ± 0.1	59.0 ± 0.1
Slope of k_{obs} vs [Buffer] plot	6.8 ± 0.1	33.8 ± 0.1	23.4 ± 0.2	34.9 ± 0.1	45.7 ± 0.1	46.2 ± 0.2

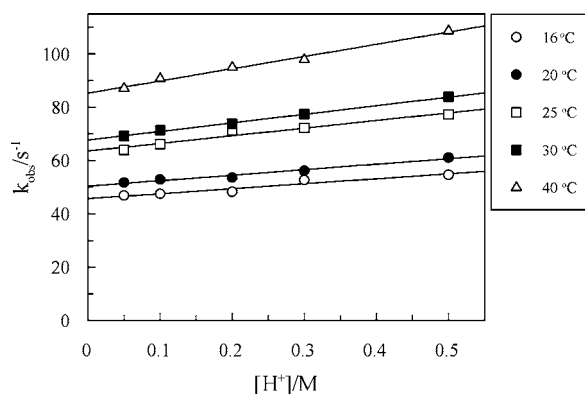


Figure 3 Influence of the temperature on the rate constant [NCS] = 2×10^{-5} M, [INa] = 2.5×10^{-4} M, $I = 0.5$ (NaClO₄).

The slopes obtained from Fig. 5 allow us to determine the values for the catalytic constants by HFP, $k_{\text{HFP}} = (1.1 \pm 0.1) \text{ M}^{-1} \text{ s}^{-1}$ and TFE, $k_{\text{TFE}} = (5.4 \pm 0.1) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$.

The study of the effect of the temperature has been carried out on the influence of the concentration of the hydroxide ion on the rate constant at five different temperatures: 16, 25, 30, 35, and 40°C (Fig. 4).

MECHANISM AND DISCUSSION

Reaction with Iodide Ion

The rate dependence for the reaction of the *N*-chlorosuccinimide, in a buffered solution, with excess iodide, is first order in NCS:

$$-d[\text{R}_1\text{R}_2\text{NCl}]/dt = k_{\text{obs}} [\text{R}_1\text{R}_2\text{NCl}] \quad (3)$$

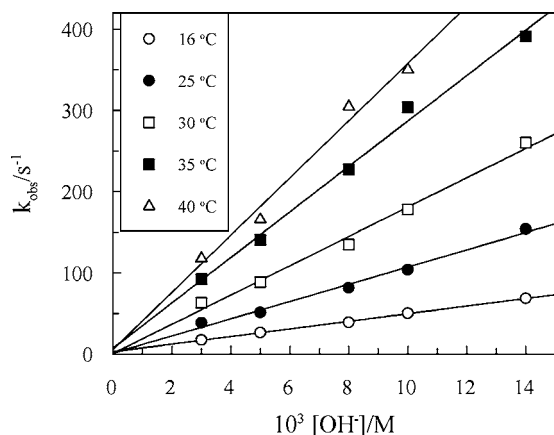


Figure 4 Influence of NaOH concentration on the rate constant at different temperatures [NCS] = 2×10^{-4} M, $I = 0.5$ (NaClO₄).

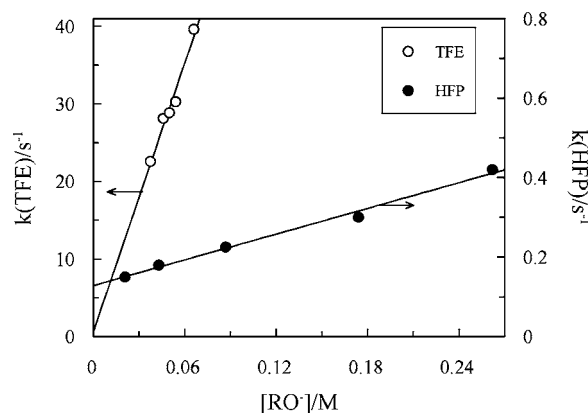
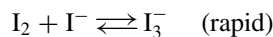
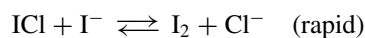
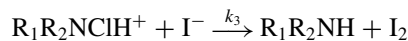
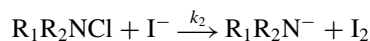


Figure 5 Influence of the concentration of HFP and TFE on the observed rate constant [NCS] = 2.5×10^{-4} M, $T = 25.0 \pm 0.1^\circ\text{C}$, $I = 0.5$ (NaClO₄).

It has also been proved experimentally that the observed rate constants are directly proportional to the iodide ion concentration and to the hydrogen ion concentration. The k_{obs} values are not affected by variations in *N*-chlorosuccinimide concentration. The k_{obs} values do increase with buffer concentration when hydrogen ion and iodide ion concentrations are constant. This behavior is consistent with that other buffer-catalyzed reactions.

Based on the experimental results, we can propose a reaction mechanism in which Cl⁺ transfer from the *N*-chlorosuccinimide to iodide ion to give an ICl intermediate, which reacts very rapidly with excess iodide ion to give I₂ and I₃⁻. The mechanism proposed is the following:



On the basis of the proposed mechanism, we obtain the following rate equation:

$$\begin{aligned} v &= -\frac{d[\text{R}_1\text{R}_2\text{NCl}]}{dt} \\ &= k_2[\text{I}^-][\text{R}_1\text{R}_2\text{NCl}] + k_3[\text{I}^-][\text{R}_1\text{R}_2\text{NClH}^+] \quad (4) \end{aligned}$$

Taking account of the equilibrium corresponding with the protonation of the *N*-chlorosuccinimide and that the total concentration of *N*-chlorosuccinimide, $[R_1R_2NCl]_T$, is the sum of the concentration of the protonated *N*-chlorosuccinimide, $[R_1R_2NClH^+]$, and the unprotonated *N*-chlorosuccinimide $[R_1R_2NCl]$, the rate equation takes the following form:

$$v = \frac{k_2 K_1 [I^-] + k_3 [H^+] [I^-]}{K_1 + [H^+]} [R_1R_2NCl]_T \quad (5)$$

Therefore, the rate constant observed is related to the rate constants of the elemental processes through the equation:

$$k_{\text{obs}} = \frac{k_2 K_1 [I^-] + k_3 [I^-] [H^+]}{K_1 + [H^+]} \quad (6)$$

If we suppose that in our working conditions $K_1 \gg [H^+]$, the concentration of protons can be considered negligible compared with term K_1 , the rate constant observed will then take the form:

$$k_{\text{obs}} = k_2 [I^-] + \frac{k_3}{K_1} [I^-] [H^+] \quad (7)$$

We can see then that this mechanism leads to an equation in accordance with all the results obtained experimentally. Hence, the representation of the observed rate constant compared with proton concentration should be a straight line, of ordinate $k_2 [I^-]$ and slope $k_3/K_1 [I^-]$. We have obtained values for $k_2 = (2.52 \pm 0.02) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and for $k_3/K_1 = (1.2 \pm 0.1) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$.

These constants can also be calculated on the basis of the representation of the observed rate constant compared with iodide ion concentration, obtaining an intercept zero and an slope equal to $(k_2 + k_3/K_1 [H^+])$. By carrying out the study at different proton concentrations, we can represent the value of each one of the slopes obtained against each proton concentration (the experimental data are shown in Table II), obtaining of the intercept a value for $k_2 = (2.36 \pm 0.01) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and of the slope a value for $k_3/K_1 = (1.27 \pm 0.03) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$.

We can show that the values for the constants k_2 and k_3/K_1 obtained separately agree acceptably, not exceeding an error of 6%.

Brönsted Relationship. In the experimental study of the reaction of the *N*-chlorosuccinimide with iodide ion, we had found that the buffer-catalyzed rates increase with the strength of the general acids that are present in the solution. This behavior is typical of pro-

cesses subject to general acid–base catalysis. Bearing this in mind the rate constant will be expressed by Eq. (8):

$$k_{\text{obs}} = k_2 [I^-] + \sum_i \frac{k_{3i}}{K_1} [I^-] [HA] \quad (8)$$

Equation (9) expressed in terms of the total buffer concentration and the dissociation constant of the buffer would take the form

$$\frac{k_{\text{obs}}}{[I^-][H^+]} = \frac{k_2}{[H^+]} + \frac{k_3}{K_1} + \frac{k_{\text{HA}}}{K_1} \frac{[\text{Buffer}]_T}{(K_a + [H^+])} \quad (9)$$

On the basis of the representation of $k_{\text{obs}}/[I^-][H^+]$ against $[\text{Buffer}]_T/(K_a + [H^+])$, we would obtain through the slope the value of the catalytic constant (Table IV) for the different acids studied. The value of the catalytic constant by H_3O^+ could be obtained from the influence of the proton concentration. In Fig. 6, we can observe the good fit of the experimental results for the case of the reaction in the presence of the trichloroacetic, dichloroacetic, and monochloroacetic buffers. As we can observe in Fig. 6, the intercept does not remain constant, which is due to the fact that term k_2 depends on proton concentration. Taking the values of k_2 and k_3/K_1 calculated previously, we can obtain the values for the theoretical intercepts, finding that they coincide acceptably well, within the experimental error margin, with those obtained from experimental results.

As can be seen, k_{HA} values obtained increase with the acid strength in the following order: $\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{H}_2\text{PO}_4^- > \text{H}_3\text{BO}_3$, in accordance with the results obtained in previous studies [20,21].

Table IV Values of the Catalytic Constants Obtained for the Reaction of Iodide Ion with NCS

Species	pK_a	p	q	$k_{\text{HA}} (\text{M}^{-2} \text{s}^{-1})$
H_3O^+	-1.74^a	3	2	$(1.20 \pm 0.10) \times 10^5$
Cl_3CCOOH	0.66^b	1	2	$(4.72 \pm 0.05) \times 10^5$
Cl_2CHCOOH	1.26^b	1	2	$(3.66 \pm 0.05) \times 10^5$
ClCH_2COOH	2.60^b	1	2	$(2.80 \pm 0.05) \times 10^5$
CH_3COOH	4.50^c	1	2	$(1.87 \pm 0.02) \times 10^5$
H_2PO_4^-	6.80^b	2	3	$(1.80 \pm 0.02) \times 10^5$
H_3BO_3	8.97^d	1	4	$(5.44 \pm 0.05) \times 10^4$

^a After Bell, R. P. The Proton in Chemistry; Chapman and Hall: London, 1973.

^b After Martell, A. E.; Smith, R. M. Critical Stability Constants; Plenum: New York, 1982; Vol. 5, p. 287.

^c After Deneux, M.; Meillous, R.; Benoit, R. L. Can J Chem 1968, 46, 1383–1388.

^d After Owen, B. B.; King, E. J. J Am Chem Soc 1943, 65, 1612–1620.

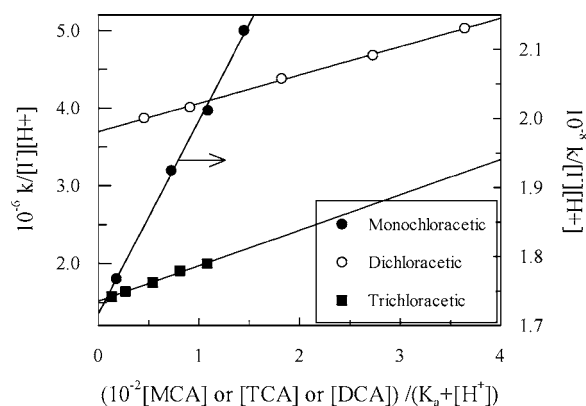


Figure 6 Fit of $k_{\text{obs}}/([\text{H}^+][\text{I}^-])$ against the total concentration of the buffer.

The acid dissociation constants (K_a) and the rate constants for the buffer-catalyzed reactions (k_{HA}) can be correlated by using the Brønsted relationship [22], which is shown in Eq. (10):

$$\frac{k_{\text{HA}}}{p} = G_A \left(\frac{K_a q}{p} \right)^\alpha \quad (10)$$

in which p is the number of equivalent acidic positions in HA, q is the number of equivalent basic positions in the conjugated base, A, G_a is the Brønsted proportionality constant, and α is the degree of proton transfer in the transition state. The reasoning consists of the interpretation of whether the transition state resembles the reactants or the products. The values of α , for different reactions in aqueous solution, are usually found in the interval $0 < \alpha < 1$. This equation is a linear-free energy relationship, between the free energies of activation for the proton transfer reactions and the free energies of acid ionizations. A plot of $\log(k_{\text{HA}}/p)$ vs $\log(K_a q/p)$ should give a line with a slope equivalent to the α value (Fig. 7).

We have obtained a value for $\log G_a = 5.47 \pm 0.03$ and a value for the Brønsted parameter (α) of 0.13 ± 0.01 . The value found reflects the fact that the proton transfer is in the vicinity of 13%, which shows a small degree of proton transfer in the transition state. The low α value is indicative of a weakly basic site that influences but does not dominate the reactivity with iodide ion. The $k_{\text{H}_2\text{O}}$ point was not used in the calculation of α since it obviously does not fit the trend shown in the other points. It is not clear that H_2O actually acts as an acid in these reactions [23], and this may be the reason it does not fit the Brønsted relationship. We have found an effect of the same type in the study of the reaction of the NCS with bromide ion (Fernández Fernández I., Tesina de Licenciatura, June 1997) which was to be expected given the similarity of both reactions.

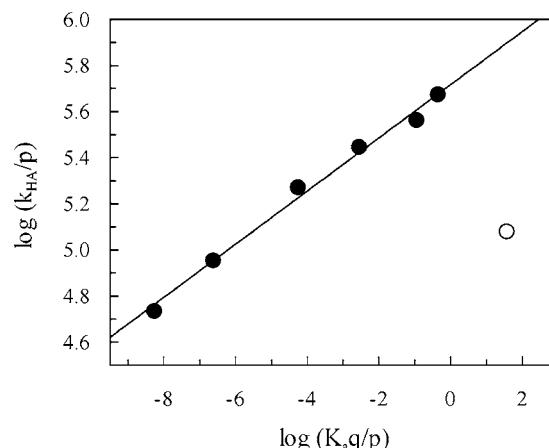


Figure 7 Representation of the Brønsted equation, $\log k$ against the $\text{p}K_a$ of the different acids studied, for the reaction of NCS with iodide ion. (\bullet) = $k_{\text{H}_2\text{O}}$.

It is important to realize that in these processes the proton from HA cannot be transferred to *N*-chlorosuccinimide in a pre-equilibrium step, because the rates involved would result in specific catalysis, where the rates are dependent only on hydrogen ion concentration and not on the HA concentration. This means that the transition state must contain three species, HA, $\text{R}_1\text{R}_2\text{NCl}$, and I^- . The nitrogen would thus accept a proton from HA, while it transfers Cl^+ to I^- . To reach this transition state it is not necessary for there to be a trimolecular collision, it is enough for the species AH to approach a weakly associated ($\text{R}_1\text{R}_2\text{NClI}^-$) species, or perhaps I^- to approach ($\text{AHNR}_1\text{R}_2\text{Cl}$) species. In any case, a complete proton transfer prior to the reaction with iodide ion would be impossible in a general acid–base catalytic process such as the present one.

In the studies carried out in the present article and in similar ones [25], we found that second-order rate constants for the reactions of the type $\text{R}_1\text{R}_2\text{NCl} + \text{X}^-$, in which X^- refers to bromide, iodide, cyanide ions, etc., which are found to be related to the nucleophilicity of these anions by means of the Swain–Scott relationship [26], shown in Eq. (11), in which n is the nucleophilicity of the different anions (X^-) and s is the sensitivity of the reaction site, compared with C which presents in the species CH_3Br for which $s = 1.00$

$$\log \left(\frac{k}{k_0} \right) = sn \quad (11)$$

For the reaction of NCS with iodide ion, which presents a parameter $n = 5.04$, we have calculated a value for bimolecular rate constant of $2.52 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and we have found a Brønsted exponent value of $\alpha = 0.12$.

For the reaction of NCS with bromide ion, which presents a parameter $n = 3.89$, the value calculated for the bimolecular constant is $0.96 \text{ M}^{-1} \text{ s}^{-1}$, whereas the Brönsted exponent value is $\alpha = 0.40$.

If we relate the values of $\log k$ against the nucleophilicity (n) of the anions, I^- and Br^- , we can see that an increase occurs in the bimolecular constant as n increases. We can also calculate an approximate value for the slope of that relationship, using the value calculated for the bimolecular constant for the reaction with hydroxide ion, $k = 9.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, which presents a parameter $n = 4.02$. The value of the slope is 3.5, which is the value which will be assigned to parameter s .

The Swain–Scott relationship was obtained on the basis of the reaction which corresponds with a nucleophilic attack at carbon, where the typical values for s are 1.0 ± 0.5 . On the basis of the value of s obtained for our reaction ($s = 4.0$) and the extremely high value for s found in the reaction with HOCl [27], in which $s = 4.7$, we can show that the nucleophilic reactions at chlorine are far more sensitive to the nucleophilic strength of the anions than the reactions at carbon and they are also much more rapid. This can be attributed in part to the much easier expansion of the number of valence electrons around chlorine.

In addition, we must bear in mind that the Brönsted α values for Br^- and I^- decrease as the nucleophilicity of X^- increases, $\alpha = 0.40$ for Br^- and $\alpha = 0.12$ for I^- . When the n values are large, the reactions are very favorable and the degree of proton transfer from HA is small because there is less need for acid assistance. On the other hand, if the nucleophilicity is small, the reaction needs larger degree of assistance by proton transfer, as reflected by larger α values.

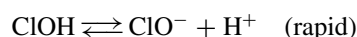
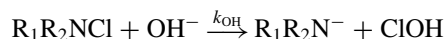
The reactivity of the bromide ion is less than that of the iodide ion given that the bromide is less nucleophilic than the iodide. The similarity of the reactions of the NCS with iodide and bromide suggests that there should exist a parallel with the transfer mechanisms of Cl^+ .

Reaction with Hydroxide Ion and Alkoxides

When introducing the solution of *N*-chlorosuccinimide in a very alkaline medium, in the presence of OH^- ions, a decomposition reaction occurs. We have found a first-order dependence on the reaction rate with regard to the *N*-chlorosuccinimide, showing that the values of k_{obs} are not affected by variations in its concentration. The experimental studies carried out show that an increase occurs in the rate constant observed as the concentration of sodium hydroxide increases, when the rest

of the reagents remain constant. Similar behavior has been observed in the presence of trifluoroethoxide and hexafluoropropanoxide ions, in which a linear increase occurs in the rate constant with the concentration of alkoxide in buffered solutions at a constant pH value. These results show the existence of a general-base catalytic process.

For this reaction, bearing in mind that the study has been carried out also with other bases other than the hydroxide ion, we could propose a mechanism:



On the basis of the proposed mechanism, we obtain the rate equation (12), in which k_{OH} refers to the catalytic rate constant for hydroxide ion and k_{B} is the catalytic rate constant for any other base

$$-\frac{d[\text{R}_1\text{R}_2\text{NCl}]}{dt} = (k_{\text{OH}}[\text{OH}^-] + k_{\text{B}}[\text{B}])[\text{R}_1\text{R}_2\text{NCl}]_{\text{T}} \quad (12)$$

The rate constant observed will then take the form

$$k_{\text{obs}} = k_{\text{OH}}[\text{OH}^-] + k_{\text{B}}[\text{B}] \quad (13)$$

We will suppose that the predominant species in the reaction medium for such high pH values is the NCS which is found entirely in a unprotonated form.

Brönsted Relationship. It is well known that strongly basic alkoxide and hydroxide ions show negative deviations from Brönsted plots, hence we have carried out these correlations with the data obtained experimentally in our study. Although curvature cannot be established from three points, Brönsted plot of $\log k_{\text{OH}}$ against the $\text{p}K_{\text{a}}$ of the attacking base (Fig. 8) shows that the system presents the characteristic curvature of these ions [28]. The curvature in Brönsted plots reflects some type of nonlinear relationship between the changes in basicity and reactivity.

This curvature in the structure-reactivity correlations may represent a change in rate-determining step or a change in transition state structure. It is important therefore to examine critically the reasons for nonlinear structure-reactivity correlations. Although there exists an explanation for the Brönsted curvature based on the

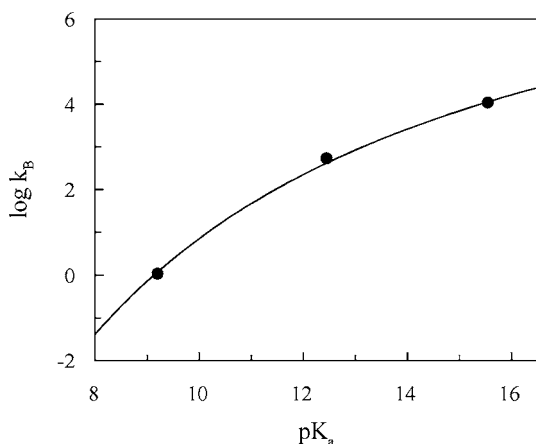


Figure 8 Brønsted correlation obtained for the reaction of NCS with different bases.

hypothesis of solvation effects of the alkoxides, it is important to emphasize that this effect can be used to explain almost anything. Hupe and Wu's [29] conclusion is that most of the curvatures in Brønsted plots of oxygen anions depends on the basicity of the oxygen bases rather than the difference in energies of the reactants and products. The same curvature is observed for correlations of several reactions of oxygen anions and elimination reactions [28,30].

If we observe the resulting correlation, it seems that the data for bases of pK_a between 8 and 12.45 fall close to a straight line with a greater slope than those which are between the pK_a values of 12.45 and 16, which would form another line with a less pronounced slope. This curvature might be interpreted as a dramatic example of the Hammon postulate in which the transition state structure becomes the reactant-like for higher pK_a.

On the other hand, given that the hydroxide ion seems to have a smaller reactivity than we would expect, we could also interpret these results as an "anomalous" behavior of this ion. However, given that there exist studies carried out with similar systems in which it has been found that the hydroxide ion correlates with bases with a similar pK_a, we could discard this interpretation.

The simplest explanation of the above observation is that OH⁻ and RO⁻ act as nucleophiles (analogously to I⁻ and Br⁻ in acidic solution) to give succinimide and ROCl. So the "curved" Brønsted plot would then simply result from sterical hindrance.

Activation Parameters. We have carried out the study of the influence of the temperature on the rate constant observed with the purpose of calculating the activation parameters, for the reaction studied. We have seen

Table V Values of the Activation Parameters Calculated as Much for the Reaction with Iodide Ion as for the Reaction with the Hydroxide Ion

	Reaction with Iodide Ion		Reaction with Hydroxide Ion
	k ₂	k ₃ /K ₁	k _{OH}
E _a (kJ mol ⁻¹)	20 ± 2	29 ± 2	57 ± 5
ΔH [#] (kJ mol ⁻¹)	19 ± 2	26 ± 2	54 ± 5
ΔS [#] (J mol ⁻¹ K ⁻¹)	-153 ± 20	-130 ± 10	-49 ± 12

on the basis of the experimental results that the rate constants comply with the Arrhenius equation and the equation derived from the theory of the transition state, using these constants to calculate the energy values, enthalpy values, and entropy activation values for the processes of the reactions studied, which are shown in Table V.

The enthalpy values calculated show that the process corresponds with a chemical control of the reaction. With regard to the entropies, they present negative values, which show that the transition state is more orderly than the reactives. Besides, the high values found for the reaction with iodide ion show that the transition state is highly solvated.

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