Oxidation of Styrene by Chlorine Dioxide and by Chlorite in Aqueous Solutions
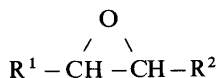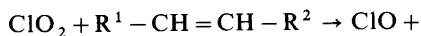
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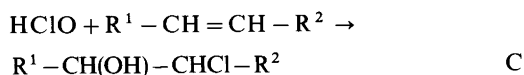Swedish Forest Products Research Laboratory, Box 5604, S-114 86 Stockholm, Sweden

In order to get information about the reactions taking place during chlorine dioxide bleaching of pulp the products of the reaction between styrene and chlorine dioxide in aqueous solutions were analyzed. The result indicates that chlorine dioxide epoxidizes styrene. The monochlorine monoxide thereby formed then oxidizes chlorine dioxide to chlorate and is reduced to hypochlorous acid. The hypochlorous acid either reacts with styrene or can be captured with added sulfamic acid.

The amounts of chlorine dioxide formed when styrene reacted with chlorite and mixtures of chlorite and chlorine dioxide were determined. The reactions were carried out both with and without sulfamic acid present. The results indicate that the chlorite oxidation of styrene follows a chain reaction route in which chlorine dioxide, monochlorine monoxide and hypochlorous acid participate.

When cyclohexene and methyl oleate were treated with chlorine dioxide the formation in small yields of the corresponding 1,2-epoxides was observed.[1,2] trans-Stilbene yielded the epoxide in rather high yield when the reaction was carried out in a carbon tetrachloride solution.[3] When the reaction was carried out in an aqueous solution the formation of the epoxide was not observed but some products were found which could have been formed via the epoxide. Lindgren and Nilsson[4] have suggested that the epoxides are formed from olefines in aqueous solutions according to a reaction route incorporating the reactions A, B and C:

$$ClO_2 + R^1 - CH = CH - R^2 \rightarrow ClO +$$

$$\begin{array}{c} O \\ / \ \backslash \\ R^1 - CH - CH - R^2 \end{array} \qquad A$$

$$ClO + ClO_2 + H_2O \rightarrow HClO + ClO_3^- + H^+ \qquad B$$

$$HClO + R^1 - CH = CH - R^2 \rightarrow$$
$$R^1 - CH(OH) - CHCl - R^2 \qquad C$$

To test this suggestion we have now determined the products formed when styrene is oxidized in aqueous solution with chlorine dioxide. Some of the oxidation experiments were carried out in the presence of sulfamic acid which captures the intermediate hypochlorous acid according to reaction D.

$$HOCl + H_2NSO_3^- \rightarrow HClNSO_3^- + H_2O \qquad D$$

Sulfamic acid has previously been used to capture hypochlorous acid intermediately formed in the chlorite oxidations of vanillin[5] and of lignin preparations[6] as well as in the chlorine dioxide bleaching of wood pulps.[7] Hypochlorous acid reacts very rapidly with sulfamic acid giving the relatively unreactive N-chlorosulfamic acid. The reaction is even more rapid than that between hypochlorous acid and a phenol such as guaiacol.[7]

The rate by which chlorine dioxide delignifies and bleaches wood pulp increases with increasing pH and when chloride is added.[8] In an attempt to explain these effects we have further studied the kinetics of the reaction between chlorine dioxide and styrene.

Because of the close connection between the chlorite and the chlorine dioxide oxidations, the reaction of styrene with chlorite has also been examined.

Table 1. Inorganic products obtained when chloride dioxide was treated with an excess of styrene in water − *tert*-butyl alcohol (3.4:1 v/v) solution.

Product	Yields[a]		
	pH 2	pH 4	pH 6
Chlorate[b]	41	43	47
Chlorite[c]	0	0	5
Hypochlorous acid[d]	46	47	− [e]

[a] Mol % of chlorine dioxide consumed. [b] Determined according to Eriksson and Sjöström.[9] [c] Determined from the difference between the amounts of available chlorine and of residual chlorine dioxide (UV-determination). No sulfamic acid was added. [d] The amount of intermediately formed hypochlorous acid captured as *N*-chlorosulfamic acid by including sulfamic acid in the reaction mixture. The amount of *N*-chlorosulfamic acid was determined iodometrically. The amount of chlorite was here considered to be insignificant in accordance with the result in the line above. [e] This value cannot be obtained due to the rapid reaction between chlorine dioxide and sulfamic acid at pH 6.

RESULTS

Reaction products. The products formed in the reaction between styrene and chlorine dioxide were analyzed for runs in which styrene was in excess. The yields of inorganic compounds are given in Table 1. Slightly less than half of the chlorine dioxide consumed was oxidized to chlorate and about the same amount was reduced to the intermediate hypochlorous acid, which was captured as N-chlorosulfamic acid. (Chlorine dioxide reacted only slowly with sulfamic acid except when the pH was
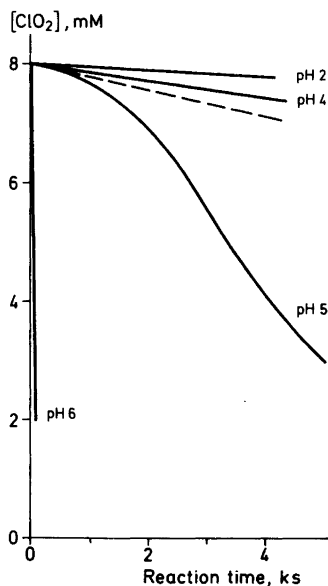

Fig. 1. The consumption of chlorine dioxide by sulfamic acid at different pH-values. The initial concentration of sulfamic acid was 8.8 mM. Temperature was 30 °C. Phosphate buffer solutions (0.28 M). The concentration of chlorine dioxide was determined by following continuously the UV-absorptivity at 357 nm. The dashed line refers to an experiment at pH 6 in the absence of sulfamic acid.

above 4, see Fig. 1.) Only minor amounts of chlorite were formed.

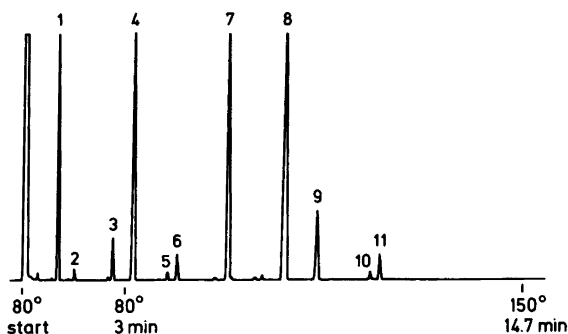The organic products were analyzed by gas chromatography (see Fig. 2) and mass spectrometry.

Fig. 2. Gas chromatogram of products from styrene oxidation by chlorine dioxide at pH 6, no sulfamic acid added. The chromatograms were run on an OV 17 fused silica column (25 m) installed in Carlo Erba 4100 gas chromatograph. The program used was 3 min isothermally at 80 °C, then 6 °C/min to 150 °C. Split injection was applied. Naphthalene was used as internal standard. Peak 1 is ascribed to styrene and peak 7 to naphthalene. The designations of the other peaks are given in Table 2.

Table 2. The organic products obtained when chlorine dioxide was treated with an excess of styrene in water − *tert*-butyl alcohol (3.4:1 v/v) solution.

Peak in Fig. 2	Product	Yields[a]				
		Sulfamic acid Absent			Present	
		pH 2	pH 4	pH 6	pH 2	pH 4
Chlorinated products						
8	2-Chloro-1-phenyl-1-ethanol[b]	34	36	34	5	2
6	2-Chloro-1-phenyl-ethene	1.4	1.5	1.7	0.3	0.3
12[c]	α-Chloro-acetophenone	0.8	0.6	0	0.7	0.6
5	1-Chloro-1-phenyl-ethene	0.6	0.5	0.5	<0.1	<0.1
	Total	37	39	36	6	3
Products from the epoxide						
4	Phenyl-oxirane	0.1	0.3	26	0.1	0.2
9	1-Phenyl-1,2-ethanediol[d]	14	27	6	21	22
3	Phenylacetaldehyde[d]	7	0.1	1.1	3	0.2
10, 11	Dimers (total)[d]	8	3.6	2.6	6	2.2
	Total	29	31	36	30	25
Other oxidation products						
2	Benzaldehyde[e]	0.5	0.5	0.5	1.0	0.8

[a] Mol % of chlorine dioxide added (the yields of the dimers were calculated on C_8 basis, *i.e.* twice the mol % yields). The yield figures are only approximate as they were determined from the peak areas of GLC assuming that the response factors were proportional to the number of carbon atoms in the molecule of the compound. [b] Mixed with a small amount of 1,2-dichloro-1-phenyl-ethane. [c] Peak 12 is not presented in Fig. 1 because the corresponding compound is not formed at pH 6. In other cases peak 12 is located between peaks 8 and 9. [d] These compounds were also formed when the epoxide was kept under the reaction conditions used. [e] Benzoic acid was also found in the reaction mixture.

The products and their yields are given in Table 2. These products consisted partly of compounds which are formed when hypochlorous acid reacts with styrene and partly of styrene oxide (= phenyl-oxirane) and compounds which are formed when styrene oxide is kept in aqueous solution. Considerable amounts of styrene oxide were obtained only when the oxidation was carried out at pH 6. When sulfamic acid was added the yields of the chlorinated products decreased greatly.

We conclude from these results that the main reaction route for the reaction between styrene and chlorine dioxide is that shown in reactions A, B and C, $R^1 = C_6H_5$ and $R^2 = H$.

Kinetics. The rate of the reaction between styrene and chlorine dioxide was determined by following the decrease in chlorine dioxide concentration. The styrene concentration was then taken as the initial styrene concentration minus the styrene consumption. In the absence of sulfamic acid (reaction sequence A, B, C) this consumption was assumed

to be equimolar with the chlorine dioxide consumption. In the presence of sulfamic acid (sequence A, B, D) it was assumed to be half that of the chlorine dioxide.

We concluded in the following way that the epoxidation (reaction A) is the rate-determining step in both the routes A, B, C and A, B, D. Reaction B must be very rapid due to the instability of monochlorine monoxide. Reaction C was found to be about 100 times more rapid than the reaction between chlorine dioxide and styrene. Reaction D is almost instantaneous as it is more rapid than the chlorination of phenols.[7] The slow step is therefore the epoxidation (reaction A). When one mol of chlorine dioxide epoxidizes styrene another mol of chlorine dioxide is oxidized by monochlorine monoxide (reaction B). The epoxidation rate is therefore half of the rate of chlorine dioxide consumption.

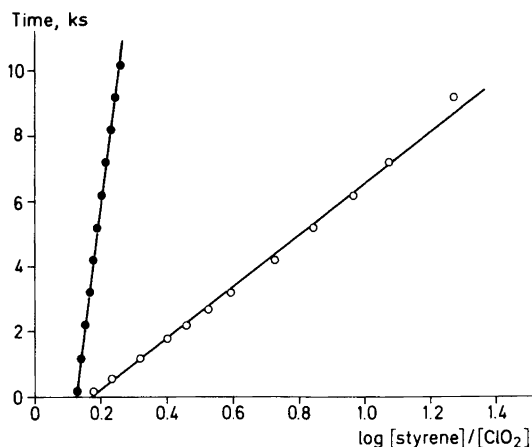When the reaction time was plotted in a diagram as a function of log [styrene]/[ClO₂], straight lines

Time, ks

Fig. 3. The reaction time *versus* log [styrene]/ [ClO$_2$] for the reaction between chlorine dioxide and styrene. $\bigcirc$, Solvent: water — *tert*-butyl alcohol 3.4:1 v/v; pH 2; [ClO$_2$]$_o$ = 10.16 mM; [styrene]$_o$ = 14.05 mM. $\bullet$, Solvent: water — *tert*-butyl alcohol 1:4 v/v; pH 3.5; [ClO$_2$]$_o$ = 11.30 mM; [styrene]$_o$ = 14.80 mM.

were obtained up to a consumption of 90 – 95 % of the chlorine dioxide (an example is given in Fig. 3). The kinetics of the reaction was therefore of the second order. The values for the rate constants of the epoxidation were calculated from the gradients of the lines (Table 3). They were about the same for pH 2, 4 and 6 and they did not change significantly when sulfamic acid was added. Chloride (concentration 0.5 M) decreased the rate distinctly.

Table 3. The bimolecular rate constant for the epoxidation of styrene with chlorine dioxide (reaction A). Solvent: water — *tert*-butyl alcohol (3.4:1 v/v).[a]

pH	$10^2 \times k_{II}$ [M^{-1} s^{-1}] Sulfamic acid Absent	Present[b]
2	4.22[c]	4.49:4.21
4	4.13:4.01	4.17:4.16
6	4.34	– [d]

[a] Reactions conditions: [ClO$_2$]$_o$ about 10 mM; [styrene]$_o$ about 15 mM; 30 °C; the solvent was buffered with phosphate buffers (0.28 M). [b] [Sulfamic acid]$_o$ = 10.3 mM. [c] The value was 2.98 when NaCl was added, [Cl$^-$]$_o$ = 0.5 M. [d] This experiment was not carried out because sulfamic acid reacted rapidly with chlorine dioxide at this pH.

Table 4. The bimolecular rate constant for the epoxidation of styrene with chlorine dioxide (reaction A). Solvent: water — *tert*-butyl alcohol (1:4 v/v).[a]

pH	[Styrene]$_o$ mM	[ClO$_2$]$_o$ mM	$10^2 \times k_{II}$ M^{-1} s^{-1}
Acid[b]	25.4	1.9	0.45
Acid[b]	37.3	1.7	0.49[c]
3.5	14.8	11.3	0.42:0.45[d]
4	11.8	0.9	0.47
6	37.3	1.7	0.49[c]

[a] Reaction conditions: temperature 33.2 °C except for the run at pH 3.5 where the temperature was 30 °C, phosphate buffers. [b] Unbuffered solvent. [c] When sulfamic acid was added ([sulfamic acid]$_o$ = 3 mM) the value was unchanged. When LiCl was added ([Cl$^-$]$_o$ = 40 mM) the value was 0.46. [d] The run was carried out at a slightly lower temperature than the others (see *a*).

The solvent in the runs described in Table 3 was water — *tert*-butyl alcohol in the volume proportions 3.4:1. When the proportion was changed to 1:4 the rate was still of the second order (Fig. 3) but the values for the rate constant were only about a tenth of those obtained in the first solvent (Table 4). The influence of the chloride ion (concentration 40 mM) and of sulfamic acid (concentration 3 mM) on the rate was studied in runs with a large excess of styrene. The rate constant did not change significantly when these compounds were added.

The large decrease in the rate when a less polar solvent was used indicates that the transition state for the epoxidation (reaction A) is more polarized than the reactants. A possibility is that the transition state has a structure close to the structure 1. This structure may be more polarized than chlorine
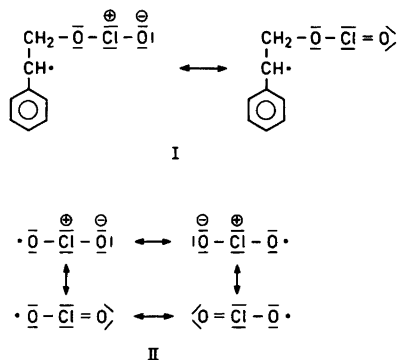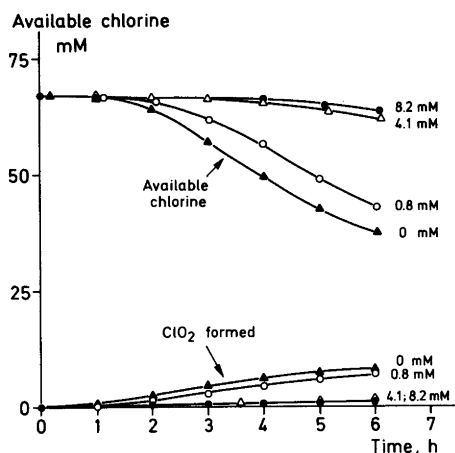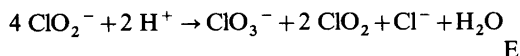
Fig. 4. The concentrations of available chlorine and chlorine dioxide (as available chlorine) versus time when styrene was treated with chlorite. Different amounts of sulfamic acid have been added. The figures in the diagram denote its concentration. Reaction conditions: temperature 30 °C, $[ClO_2^-]_o$ = 33.6 mM; $[styrene]_o$ = 18.3 mM, solvent: water −tert-butyl alcohol (3:1 v/v), pH 4 (phosphate buffer, 0.33 M).
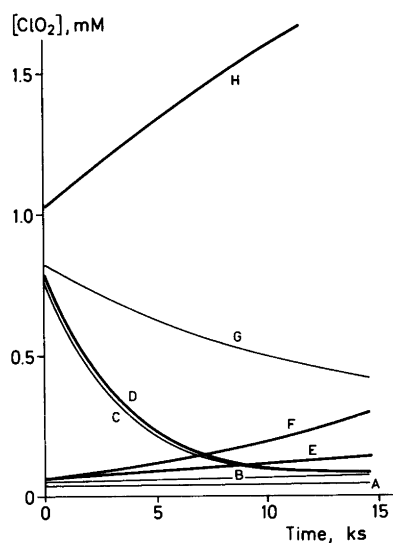

Fig. 5. $[ClO_2]$ versus time when styrene was treated with chlorine dioxide, chlorite and a mixture of them. Some runs were also carried out with sulfamic acid added. For comparison, the corresponding curves for the oxido-reduction of chlorite are included. Reaction conditions: pH 4 (phosphate buffer; 0.33 M); temperature 30.0 °C; solvent: water − tert-butyl alcohol (3:1 v/v).

Reactants present				Curve
Styrene 10.2 mM	ClO$_2^-$ 20.5 mM	ClO$_2$ ~1 mM	Sulfamic acid 20.5 mM	
	+			E
	+		+	A
+	+			F
+	+		+	B
+		+		D
+		+	+	C
+	+	+		H
+	+	+	+	G

dioxide, in which the negative charge is distributed between the two oxygen atoms (structure II).

Our kinetic experiments thus show that the chlorine dioxide oxidation of styrene differs from that of lignin in that its rate does not increase either with increase in pH or when chloride is added.

Chlorite oxidation of styrene. The oxidation of styrene with chlorite as judged from the consumption of available chlorine was retarded by the addition of sulfamic acid (Fig. 4). The amount of sulfamic acid needed was small in comparison with the amounts of other reactants. The chlorite oxidation of phenols and lignin preparations is similarly retarded by a comparatively small amount of sulfamic acid.[6] The reason for this behaviour is due to the fact that chlorite itself is not the oxidizing agent. The oxidizing agent is chlorine dioxide which is formed by a chain process from the chlorite. The initiating reaction in this process may be the acid-catalyzed oxido-reduction of chlorite

$$4 ClO_2^- + 2 H^+ \rightarrow ClO_3^- + 2 ClO_2 + Cl^- + H_2O \qquad E$$

(The properties of this complicated reaction are reviewed in Ref. 10.) The chlorine dioxide formed

then reacts with the organic material and is thereby partly reduced to hypochlorous acid. The hypochlorous acid regenerates chlorine dioxide by oxidizing chlorite

$$HOCl + 2 ClO_2^- \rightarrow HO^- + Cl^- + 2 ClO_2 \qquad F$$
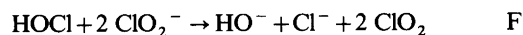
(This reaction is also reviewed in Ref. 10.) The chlorite oxidation of styrene should then consist of

the initiating reaction E and the chain sequence of the reactions A, B and F.

When chlorite was added to a styrene solution at pH 4, chlorine dioxide was however formed (curve F in Fig. 5). This does not fit with the reaction sequence A, B, F the sum of which does not yield chlorine dioxide. Nor could the chlorine dioxide have been formed by acid catalyzed oxido-reduction of chlorite (reaction E) as the formation of chlorine dioxide from chlorite in the absence of styrene was too slow under these conditions (curve E).

A similar formation of chlorine dioxide was obtained when styrene was treated with a mixture of chlorite and chlorine dioxide. Further amounts of chlorine dioxide were formed rapidly (curve H) in spite of the fact that chlorine dioxide when treated with styrene in the absence of chlorite was rapidly consumed (curve D). To obtain a chain mechanism which yields chlorine dioxide we have assumed that the intermediately formed monochlorine monoxide oxidizes not only chlorine dioxide to chlorate (reaction B) but also chlorite to chlorine dioxide.

$$ClO + ClO_2^- + H^+ \rightarrow HClO + ClO_2 \qquad G$$

The sum of the reactions A, G and F yields two mol of chlorine dioxide for every mol of chlorine dioxide which epoxidizes styrene.

The rate determining reaction in the sequence A, G, F should be the reaction A. During chlorine dioxide oxidation of styrene (sequence A, B, C) this reaction is also rate determining. This oxidation consumes two mol of chlorine dioxide; the sequence A, G, F produces the same amount. If, therefore, the oxidation of styrene with a mixture of chlorite and chlorine dioxide strictly followed the sequence A, G, F, the rate of this chlorine dioxide *production* should be equal to the rate of the chlorine dioxide *consumption* when the oxidation is carried out with chlorine dioxide alone. As shown by the gradients of the curves D and H at zero time, that was not the case; the production rate was lower than the consumption rate. This leads to the conclusion that *under the conditions used by us in the H run* the monochlorine monoxide formed reacted both with chlorine dioxide (reaction B) and with chlorite (reaction G).

When the oxidation of styrene with a mixture of chlorite and chlorine dioxide was carried out in the presence of sulfamic acid, a consumption of chlorine dioxide was observed (curve G) but not as great as that in the chlorine dioxide oxidation (curve D). This

suggests that the reaction route was a mixture of the sequences A, G, D and A, B, D and thus agrees with our assumption that reactions B and G were competing.

Our results thus indicate that the chlorite oxidation of styrene follows the chain routes described by the reaction sequences A, B, F and A, G, F. The initiating reaction is probably the oxido-reduction of chlorite into chlorine dioxide, chlorate and chloride (reaction E). The chlorine dioxide formed then reacts with styrene. The monochlorine monoxide and the hypochlorous acid intermediately formed react with chlorite giving an increasing concentration of chlorine dioxide which should speed up the oxidation. In agreement with this the gradient of the curve F increases with time, which indicates that the rate really increases. When the chlorine dioxide concentration becomes greater an increasing part of the monochlorine monoxide should oxidize chlorine dioxide to chlorate. In agreement with this, the gradient of the curve H decreases with time.

CONCLUSIONS

The routes of chlorine dioxide reactions. Evidence has earlier been presented which shows that chlorine dioxide is reduced by a one-electron reduction to chlorite when it reacts with phenols.[11,12] This article presents a principally different route for the chlorine dioxide oxidation of organic materials, since the reaction with styrene is a two-electron oxido-reduction by which chlorine dioxide is reduced to monochlorine monoxide. Stilbene and other olefinic compounds may react similarly.

The delignification of pulp lignin. It has been suggested that monochlorine monoxide is formed during the chlorine dioxide bleaching of wood pulps and that it may oxidize chlorine dioxide to chlorate, which should explain a part of the chlorate formation during the bleaching.[4] These experiments have shown that monochlorine monoxide can be formed when olefinic materials react with chlorine dioxide and that it can oxidize chlorine dioxide to chlorate.

Chlorite. Chlorite oxidizes directly neither phenols,[6,12] lignin material[6,12] nor styrene. It must first be transformed into chlorine dioxide. At moderate acidity this transformation is a chain process (at low pH the formation of chlorine dioxide from chlorite by the acid-catalyzed oxido-reduction

may dominate over the chain process). As shown in this paper, more chlorine dioxide can be formed in this process from reactions of chlorite with monochlorine monoxide and hypochlorous acid than is consumed in reactions with the organic material.

EXPERIMENTAL

Styrene oxidation by chlorine dioxide and chlorite. The reaction conditions are given in note *a* to Table 3 and in the legend to Fig. 4.

The analyses of the inorganic products obtained from the chlorine dioxide oxidation of styrene. The concentration of chlorine dioxide was determined from the UV-absorptivity at 357 nm ($\varepsilon = 1250$ M^{-1} cm^{-1}). The determinations of the other compounds are described in Table 1.

The analyses of the organic products obtained from the chlorine dioxide oxidation of styrene. When nearly all the chlorine dioxide was consumed, the reaction mixture was extracted with dichloromethane (3 times). The extract was dried with sodium sulfate and analyzed by gas chromatography and mass spectrometry. The gas chromatography conditions are given in the legend to Fig. 2. The peaks were identified by mass spectrometry and compared with authentic samples of the compounds.

The kinetics of the chlorine dioxide oxidation of styrene. The reaction was carried out in cuvettes kept thermostated in a Cary 118 spectrophotometer. The absorptivity at 357 nm was recorded continuously. The UV-light did not affect the rate of the reaction.

The rate of hypochlorous acid reaction with styrene. A solution of hypochlorous acid (10.35 mM) and styrene (13.94 mM) in water − *tert*-butyl alcohol (3.4:1 v/v, buffered to pH 6.4) was prepared and kept at 30 °C. The chlorine concentration determined iodometrically was 0.90 mM after 1 min.

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