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Chlorination of Aromatic Compounds with Chlorous Acid under Non-Aqueous Conditions

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Summary. The non-aqueous solution of chlorous acid is a versatile chlorinating agent for aromatic compounds, *e.g.* alkylbenzenes, anisoles, and acetanililides. It is also an effective chlorine-substitute for the conversion of aryl bromides into aryl chlorides under mild conditions. The stoichiometry of the chlorination reaction is $ArH+3HOClO \rightarrow ArCl+2ClO_2+2H_2O$, and the mode of dissociation of chlorous acid in dichloromethane is $3HOClO \rightarrow HOCl+2ClO_2+H_2O$.

Keywords. Chlorination; Aromatic substitution; Chlorous acid dissociation.

Chlorierung aromatischer Verbindungen mit chloriger Säure unter nichtwäßrigen Bedingungen

Zusammenfassung. Die nichtwäßrige Lösung von chloriger Säure ist ein vielseitiges Chlorierungsmittel für aromatische Verbindungen wie z.B. Alkylbenzole, Anisole und Azetanilide. Es stellt darüber hinaus auch einen wirkungvollen Ersatz für Chlor für die Umwandlung von Arylbromiden zu Arylchloriden unter milden Bedingungen dar. Die Stöchiometrie der Chlorierung ist $ArH+3HOClO \rightarrow ArCl+2ClO_2+2H_2O$, jene der Dissoziation der chlorigen Säure in Dichlormethan $3HOClO \rightarrow HOCl+2ClO_2+H_2O$.

Introduction

The redox chemistry of the chlorine oxyacids is a vast field and has received considerable attention [1, 2]. Chlorous acid is the least stable of the oxychlorine acids; it cannot be isolated, but it can be obtained in aqueous solution by treating a suspension of barium chlorite with sulfuric acid and filtering off the barium sulfate.

The decomposition of chlorous acid has been the subject of many investigations [1–3]. In aqueous solutions, the decomposition depends sensitively on concentration, *pH*, and the presence of catalytically active ions such as the chloride ion which is itself produced during decomposition. However, the main mode of decomposition, particularly if the chloride ion is present, is to form chlorine dioxide according to $5HOClO \rightarrow 4ClO_2+Cl^-+H^++2H_2O$

Chlorous acid has both oxidizing and chlorinating properties. Benzyl alcohols and aldehydes can be oxidized to the corresponding acids by treatment with

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chlorous acid [4, 5]. The acid also chlorinates active aromatic compounds such as anisole and polycyclic aromatics [6, 7]. In addition to the chloro derivatives, quinones have also been isolated. All oxidation and chlorination reactions so far have been carried out in aqueous solution.

The mechanism and the stoichiometry of the chlorination have not been firmly established, although some reports suggested that chlorine dioxide, resulting from the decomposition of chlorous acid, is the chlorinating species [8]. However, the chlorinating properties and the mode of decomposition of chlorous acid in non-aqueous solutions have not yet been examined.

Results and Discussion

A standard reaction was set up in which a solution of the aromatic substrate and trichloroacetic acid in dichloromethane was treated gradually with solid sodium chlorite. Trichloroacetic acid was preferred to acetic acid due to the low reactivity of the latter with sodium chlorite. The reaction proceeds according to $NaOClO + Cl_3CCO_2H \rightarrow HOClO + Cl_3CCO_2Na$.

Mesitylene was the substrate of the first choice because of its enhanced reactivity, its resistance to oxidation, and its ability to afford only one monochloro derivative. Thus, treatment of mesitylene with chlorous acid for one hour at room temperature yielded 2-chloromesitylene nearly quantitatively. Other reactive aromatic compounds such as anisole and acetanilide gave a 1:2 mixture of 2- and 4-chloro derivatives. Dichlorination of some polyalkylbenzenes and anisole was also achieved using the required stoichiometric amount of chlorous acid. The results of aromatic chlorination are summerized in Table 1. The identity of the products was proven by their melting or boiling points and ^1H NMR spectroscopy.

The overall stoichiometry of the chlorinating reaction may be expressed by $ArH + 3HOClO \rightarrow ArCl + 2ClO_2 + 2H_2O$. Less reactive aromatic compounds, *e.g.* toluene, required longer reaction times. Treatment of toluene with chlorous acid for 12 hours gave benzyl chloride (65%) and a mixture of 2- and 4-chlorotoluenes (35%). When the molar ratio of trichloroacetic acid was doubled and the reaction time reduced to 6 hours, benzyl chloride was isolated only in 20% yield together with 80% of *o*- and *p*-chloro derivatives.

The tendency of chlorous acid to chlorinate the aromatic ring and the methyl group of toluene indicates that the reaction may proceed *via* electrophilic substitution and free radical mechanisms. A possible mechanism for the ring chlorination and the methyl radical reaction may involve disproportionation of chlorous acid to chlorine dioxide and hypochlorous acid according to $3HOClO \rightarrow HOCl + 2ClO_2 + H_2O$. Hypochlorous acid is a well-known chlorinating agent for aromatic compounds [9]. The radical chlorination mechanism of the methyl group in toluene to give benzyl choloride may proceed *via* homolytic bond fission of hypochlorous acid by the paramagnetic chlorine dioxide to give a chlorine radical according to $HOCl \xrightarrow{ClO_2} HO^{\cdot} + Cl^{\cdot}$. Homolytic C–O bond fission of hypochlorous acid may also be achieved photochemically [10].

The fact that the free radical chlorination of the methyl group is predominant and restricted to toluene when one equivalent of trichloroacetic acid is used (see Table 1) may be attributed to the low reactivity of hypochlorous acid with the aromatic ring [11]. Consequently, the reaction of hypochlorous acid with the weakly-activated toluene ring is rather slow compared with the more reactive polyalkylbenzenes, *e.g.* xylene and mesitylene. This allows chlorine dioxide to react with

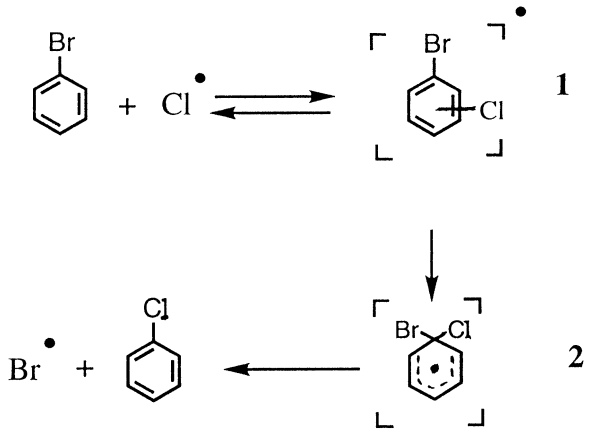
Table 1. Chlorination of aromatic compounds with chlorous acid

Educt	Product	Molar ratio (substrate: ClO_2^-:H^+)	Time (h)	Yield (%)
Benzene	Chlorobenzene	1:3:6	24	20
Toluene	*o*-Chlorotoluene	1:3:3	12	20
	p-Chlorotoluene			15
	Benzyl chloride			65
Toluene	*o*-Chlorotoluene	1:3:6	6	30
	p-Chlorotoluene			50
	Benzyl chloride			20
m-Xylene	4-Chloro-*m*-xylene	1:3:3	3	62
	2-Chloro-*m*-xylene			38
Mesitylene	2-Chloromesitylene	1:3:3	1	95
Mesitylene	2,4-Dichloromesitylene	1:6:12	1	96
Durene	3,6-Dichlorodurene	1:6:6	1	95
Anisole	2-Chloroanisole	1:3:3	1	35
	4-Chloroanisole			65
Anisole	2,4-Dichloroanisole	1:6:12	3	96
Acetanilide	2-Chloroacetanilide	1:3:3	1	40
	4-Chloroacetanilide			60
Bromobenzene	Chlorobenzene	1:3:3	3	92
4-Bromotoluene	4-Chlorotoluene	1:3:3	3	20
	4-Chlorobenzyl chloride			18
	4-Chlorobenzyl bromide			17
	4-Bromobenzyl chloride			25
	4-Bromobenzyl bromide			20
Styrene	α-Chloroacetophenone	1:3:3	1	93

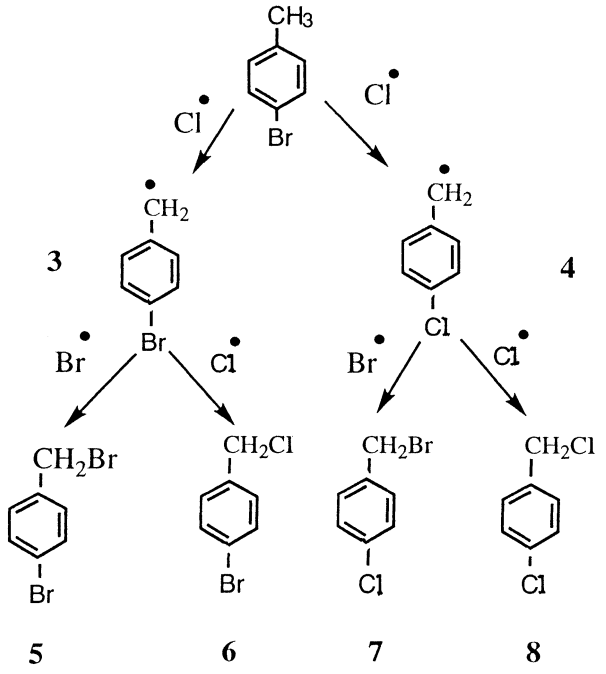
hypochlorous acid to give a chlorine radical in a rate faster than the rate of the electrophilic reaction. On the other hand, the electrophilic substitution becomes the predominant reaction when an additional equimolar amount of trichloroacetic acid is used; the acid converts hypochlorous acid into the more reactive chlorinating agent acetyl hypochlorite according to $HOCl+Cl_3CCO_2H \rightarrow CH_3CCO_2Cl+H_2O$ [12].

Further evidence that hypochlorous acid dissociates to the chlorine radical in the presence of chlorine dioxide is manifested by the reaction of chlorous acid with bromobenzene (see Table 1). The latter undergoes a halogen exchange reaction to give chlorobenzene in high yield. This process, *i.e.* the displacement of a halogen by another halogen of lower atomic number, is well established and can be performed photochemically by irradiation of a mixture of bromobenzene and chlorine gas with light [13]. The mechanism is believed to proceed *via* the formation of a π- or σ-complex intermediate **1** to **2** which dissociates to chlorobenzene and the bromine radical (Scheme 1) [14].

In support of the previous mechanistic speculations that the chlorine-bromine exchange yields a bromine radical (Scheme 1) we found that the reaction of chlorous acid with *p*-bromotoluene gave *p*-bromobenzyl bromide (**5**) and *p*-chlorobenzyl bromide (**7**) in addition to *p*-bromobenzyl chloride (**6**) and *p*-chlorobenzyl chloride (**8**). Similar results were obtained when *p*-bromotoluene was reacted with sulfuryl chloride in carbon tetrachloride at reflux temperature in the presence of benzoyl peroxide [15]. The possible mechanism is illustrated in



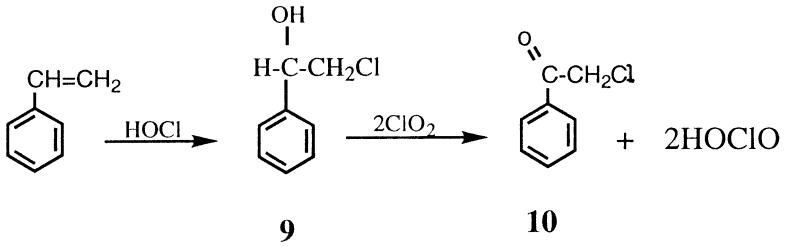
Scheme 1



Scheme 2

(Scheme 2). It may involve generation of *p*-bromobenzyl and *p*-chlorobenzyl radicals (**3** and **4**) which subsequently combine with bromine radicals resulting from the displacement by chlorine to give the benzyl bromides **5** and **7**.

Further evidence in support of the dissociation of chlorous acid to hypochlorous acid and chlorine dioxide was obtained by treatment of styrene with an equimolar amount of chlorous acid in dichloromethane. The olefin undergoes an addition reaction with hypochlorous acid, followed by subsequent oxidation of the resultant chlorohydrine **9** by chlorine dioxide to give α-chloroacetophenone (**10**; Scheme 3).



Scheme 3

Experimental

Melting points were recorded on an electrothermal melting point apparatus and are uncorrected. The ^{1}H NMR spectra were determined on a Varian Model E390 NMR spectrometer (90 MHz) in $CDCl_3$ relative to internal *TMS*. Product mixtures were analyzed by GLC on a Hitachi Model 163 flame ionization instrument equipped with an SE-30 chromosorb WAW column. The structures of the various products were established by comparison by their NMR spectra with those of authentic samples. Sodium chlorite was obtained from Aldrich Chemical Company (technical grade); iodometric analysis showed 80% sodium chlorite content [16].

Typical procedure

1.7 g, sodium chlorite (80%) (15 mmol) were added in portions over 10 min to a vigorously stirred solution of the aromatic substrate (5 mmol) and 2.1 g trichloroacetic acid (15 mmol) in 100 cm^3 CH_2Cl_2. The mixture was stirred in the dark for the specified time (Table 1) and then transferred to a separatory funnel. The organic phase was washed three times with water and dried (Na_2SO_4). Evaporation *in vacuo* afforded the chloro compound.

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