HOMOGENEOUS CATALYSIS IN THE HETEROLYTIC CHLORINATION OF UNSATURATED COMPOUNDS

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Abstract

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CHEMISTRY

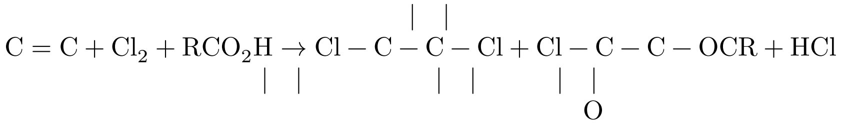
The kinetic parameters of the chlorination of unsaturated compounds depend extraordinarily strongly on the nature of the solvent.

Our experiments showed that in aprotic solvents, in particular in carbon tetrachloride, chlorine in the dark and at low temperatures does not add at all to allyl chloride, stilbene, cyclohexene, tolane, and, evidently, to other olefins and acetylenes. In benzene solutions a slow reaction occurs, apparently on the surface of the glass.

Table 1

Q	[Q], mol/l	k_D, l^2 · mol^{-2} · min^{-1}	k_E, l^2 · mol^{-2} · min^{-1}	k_D/k_E
CH_3CO_2H	0.1–0.2	0.9	1.1	0.82
CH_2ClCO_2H	0.01	22	20	1.1
CCl_3CO_2H	0.009–0.017	133	97	1.4
CF_3CO_2H	0.012–0.017	1240	760	1.6
HCl	0.02–0.05	18	0	
C_5H_5N	0.12–0.24	1.1	2.2	0.5
$(CH_3)_3COH$	0.2	0.84	1.26	0.66

The addition reaction of chlorine is initiated and accelerated by additions of compounds capable of forming acceptor-donor complexes, in particular carboxylic acids, hydrogen chloride, tert-butyl alcohol, and pyridine. As a result of chlorination in the presence of catalysts, mixtures of dichlorides and mixed chlorine-substituted products are obtained. Thus, upon addition of carboxylic acids, dichlorides and chloro esters are formed:



$$C = C + Cl_2 + RCO_2H \rightarrow Cl - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - Cl + Cl - \underset{|}{C} - \underset{\underset{O}{|}}{C} - C - OCR + HCl$$

Fig. 1

Figure 1: Fig. 1

We found that the rate of these reactions increases proportionally to the concentration of the unsaturated compound (S) and of chlorine and approximately proportionally to the concentration of the added catalyst (Q). Taking into account the appearance of hydrogen chloride during the formation of mixed forms and the noncatalytic reaction with rate constant k_0, the reaction rate must be represented by the general equation (1)

$$-\frac{d[\mathrm{Cl_2}]}{dt} = k_2[S][\mathrm{Cl_2}] = k[S][\mathrm{Cl_2}]\{k_D[Q] + k_E[Q] + k'[\mathrm{HCl}] + k_0\} \qquad (1)$$

Table 1 compares the values of the constants of equation (1) for the reaction of allyl chloride with chlorine in benzene at 20°; k_0 for these experiments is equal to 0.055, and the initial concentrations of Cl_2 and S are close to 0.02 mol/l.

We note that chlorinated carboxylic acids give an especially significant accelerating effect, and that there is a clear correlation between the strength of the carboxylic acids and their catalytic action. From the data of Table 1 it further follows that the catalyst accelerates both the formation of dichloride and the formation of the mixed adduct. The less acidic (or the more basic) the catalyst, the relatively less dichloride is formed and the more mixed adduct.

Carboxylic acids in aprotic solvents are found, as is known, in the form of an equilibrium mixture of monomeric and dimeric molecules.

We found that the dependence of the chlorination rate constant on the catalyst concentration is linear, provided that the values of the constant k_2 are referred to the concentration of the monomer, and not to the analytical concentration of the added acid (Fig. 1). It may therefore be assumed that the catalyst for the chlorination of unsaturated compounds in aprotic solvents is only the monomeric form of the carboxylic acid.*

Fig. 1. Monomeric and dimeric forms of monochloroacetic acid in the chlorination of allyl chloride in benzene. The values of k_2 are referred, for I, to the concentration of the monomer of monochloroacetic acid, and, for II, to its analytical concentration.

In a CCl_4 solution the effect of the catalysts is smaller than in benzene, although, as stated, in the absence of catalysts the chlorination reactions do not proceed at all in this solvent. Data on the chlorination of allyl chloride in CCl_4 at 20° are given in Table 2.

The ratio k_D/k_E was determined for additions of CCl_3CO_2H; it varies with temperature: 2.0 at 1°, 1.3 at 10°, and 0.92 at 20°.

In the chlorination of tolan in benzene and in CCl_4, analogous kinetic relationships are observed, but the noncatalytic reaction develops more strongly in the case of tolan. Experimental values for a solution of tolan in benzene are collected in Table 3; temperature 20°, $k_0 = 0.15$.

At the same time, k_D/k_E for the chlorination of tolan is considerably higher than for the chlorination of allyl chloride: in the presence of trichloroacetic acid in benzene and in CCl_4, about 80% cis- and trans-dichlorostilbenes and only about 20% chloroether are formed.

In the case of tolan, it becomes possible to determine the stereodirection of chlorine addition. We found that the mixture of dichlorides obtained in the presence of trichloroacetic acid in benzene contains 65% cis- and 35% trans-dichlorostilbene.

Table 2

	$[Q]$, mol/l	$(k_D + k_E)$, $l^2 \cdot mol^{-2} \cdot min^{-1}$
–	0	0
CH_2ClCO_2H	0.04–0.08	1.2
CCl_3CO_2H	0.02–0.04	13
HCl	0.027–0.054	10

Table 3

Q	$[Q]$, mol/l	$(k_D + k_E)$, $l^2 \cdot mol^{-2} \cdot min^{-1}$
CH_2ClCO_2H	0.01	40
CCl_3CO_2H	0.005–0.02	285
HCl	0.019–0.038	43

In proton-donor solvents (acetic acid, water), chlorination reactions proceed much faster than in aprotic ones. Therefore, for kinetic measurements it is necessary to take less active unsaturated compounds, for example β-chloroallyl chloride instead of allyl chloride. As a result of the reaction, mixed adducts are formed primarily. They are accompanied by dichlorides, the amount of which increases as the concentration of HCl increases.

The acceleration effects of chlorination upon addition of acids and salts are not as large as in aprotic solvents, especially in benzene. The increase in the reaction rate, as in aprotic solvents, is proportional to the concentration of the added binary compound. The overall kinetic–

* For the calculations, modern data on the equilibria between monomers and dimers of carboxylic acids in solutions were used (1).

the kinetic equation is conveniently represented in the form:

$$-d[\mathrm{Cl_2}]/dt = [\mathrm{S}][\mathrm{Cl_2}]\{k_0 + k[\mathrm{Q}] + k'[\mathrm{HCl}]\},$$

where k_0 and k refer to the formation of dichlorides and mixed adducts together.

According to the degree of acceleration of the chlorination of β-chloroallyl chloride in glacial acetic acid at 20°, the additives are arranged in the following series:

Q	LiCl	LiO_2CCl_3	HCl	$LiNO_3$	LiO_2CCH_3	H_2O	CCl_3CO_2H
k, $l^2 \cdot mol^{-2} \cdot min^{-1}$	0.12	0.04	0.031	0.028	0.024	0.02	0.01

For these experiments k_0 is equal to 0.017 $l \cdot mol^{-1} \cdot min^{-1}$, $[\mathrm{S}]_0 = [\mathrm{Cl_2}]_0 = 0.1\ M$, Q from 0.05 to 0.5 M.

Considering this series, we find that salts act more strongly than the corresponding free acids and that chlorides accelerate the reaction more than other compounds of anions. Meanwhile, the nucleophilicity of the anion apparently has no special significance for the reaction rate.

During chlorination in aprotonic solvents, carboxylic acids and other catalysts lead, as shown above, to the formation of both mixed adducts and dichlorides. Does the catalytic mode of dichloride formation have significance in proton-donor solvents, where formation of mixed esters predominates?

To resolve this question, we determined in parallel the dichloride and chloro ester (from the fall in chlorine titer and the increase in HCl content) during the chlorination of β-chloroallyl chloride in acetic acid. It turned out that the amount of dichloride formed does not tend to zero when the percentage of dichloride is extrapolated to zero time, but gives a value of about 12% of the chlorine entering into reaction (Fig. 2). Thus, catalytic formation of dichlorides without participation of hydrogen chloride does indeed occur in proton-donor solvents.

Fig. 2. Change in the composition of the product of chlorine addition to β-chloroallyl chloride during the reaction. **I** —decrease in chlorine concentration, **II** —increase in HCl concentration, **III** —ratio of dichloro adduct (1,1,2,3-tetrachloropropane) to consumed chlorine (in percent).

This result should be compared with an old observation, when it was shown that in the reaction of ethylene and chlorine in aqueous solution, 3.4% of the reacting chlorine is converted into dichloroethane, independently of the concentration of chloride ion (^{2}).

Fig. 2. Change in the composition of the product of chlorine addition to β-chloroallyl chloride during the reaction. I —decrease in chlorine concentration, II —increase in HCl concentration, III —ratio of dichloro adduct (1,1,2,3-tetrachloropropane) to consumed chlorine (in percent)

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In discussing the mechanism of chlorination in solutions, we note that the catalytic effect of carboxylic acids increases with increasing acid strength. This leads to the suggestion that acids activate the chlorine molecule, imparting to it greater polarity through formation of a complex

$$\mathrm{Cl} \cdots \mathrm{Cl} \cdots \mathrm{H} \cdots \mathrm{A}.$$

An idea of this kind has recently been developed by Andrews and Keefer in their work on the chlorination of unsaturated and aromatic compounds with iodine benzenedichloride and, sometimes, elemental chlorine in CCl_4 (^{3}).

We think that this scheme is insufficient for interpreting the reaction mechanism. It overlooks the fact that not only acids, but also anions and compounds of basic character, play a role in catalysis of chlorination in solutions. We consider these reactions as a case of bifunctional catalysis, including the formation of acceptor-donor cycles. It is possible to pred—

represent this idea by the following schemes of transition complexes:

Formation of the dichloride *Formation of the chloro ester*

These forms of transition complexes are consistent with the particulars of the catalytic action of carboxylic acids and connect chlorination with other known reactions in which acids act as a bifunctional catalyst (^{4}).

Experimental procedure

To avoid loss of chlorine by volatilization in the kinetic experiments, we prepared mixtures in 20-ml glass medical syringes enclosed in a jacket through which water from a thermostat was passed. Samples were discharged through a ground-glass stopcock into weighed solutions of KI in water or, in the case of aprotonic solutions, into solutions of HI in benzene or in CCl_4. After weighing, the sample was titrated with thiosulfate solution. The accuracy of the chlorine determination was about 1%. To determine HCl in acetic-acid solutions, HCl was blown out of the sample with a stream of air through water, and the HCl solution was titrated by Volhard' s method. This method can be used only on the condition that chlorination of the substrate proceeds relatively slowly. In determining HCl in aprotonic solvents, the reaction was brought almost to complete disappearance of chlorine, the sample was poured into a weighed amount of water, and the mixture was titrated with silver nitrate.

The unsaturated compounds were obtained and purified by known procedures. Preparative chlorination experiments were carried out in benzene with allyl chloride and tolane, with additions of trichloroacetic acid (molar ratio of reagents 1 : 1 : 1), at a concentration of 0.5-0.8 M. After the usual work-up, the chlorination products of allyl chloride were separated by distillation under reduced pressure. The fraction with b.p. 24–26° at 5 mm was 1,2,3-trichloropropane. Yield 50%. The fraction with b.p. 95–98° at 5 mm, n_D^{20} 1.5040, was the dichloropropyl ester of trichloroacetic acid.

Found, %: Cl 63.5, 63.7
$C_5H_5Cl_5O_2$. Calculated, %: Cl 64.6

It has not yet been established exactly which isomer is obtained from the two possible adducts. The solid product of chlorination of tolane was recrystallized from alcohol. trans-Dichlorostilbene separates first, yield 30%. A considerable portion of cis-dichlorostilbene, m.p. 62°, is isolated from the filtrate. On distillation of the residue at 0.05 mm, a fraction of cis-dichlorostilbene boils at 110° (overall yield 50%); at 140° α-chloro-α'-trichloroacetoxystilbene passes over, m.p. 128°, yield 16%.

Found, %: Cl 37.45, 37.62
$C_{16}H_{10}Cl_4O_2$. Calculated, %: Cl 37.8

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Note: Figure translations are in progress. See original paper for figures.