HYDROLYSIS OF TRICHLOROMETHANESULFENYL CHLORIDE

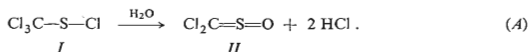J.ŠILHÁNEK and M.ZBIROVSKÝ

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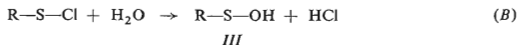*Prague Institute of Chemical Technology, 166 28 Prague 6*

The rate of hydrolysis of trichloromethanesulfenyl chloride *I* in a heterogenous system, *i.e.* a mixture of a solution of *I* in organic solvent and water, has been studied under kinetic conditions, giving rise to thiophosgene-S-oxide (*II*, dichlorosulfine). It was found that the reaction is of the first order with respect to *I* and of minus first order with respect to the hydrolytically formed hydrogen chloride. The inhibitory effect of hydrogen chloride is neither a function of proton, nor of the Cl^- ion, and it is probably connected with the assumed first reaction step, *i.e.* the formation of free trichloromethanesulfenic acid (*IIIa*) which decomposes to *II* and hydrogen chloride in the subsequent rapid step. The preparation is described in detail of the so far the only simpler sulfine, *II*.
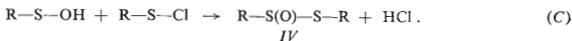
As shown earlier[1], during the hydrolysis of trichloromethanesulfenyl chloride (*I*), carried out by stirring the heterogeneous mixture with water, thiophosgene-S-oxide (*II*, dichlorosulfine) is formed in the sense of equation (*A*):

$$\text{Cl}_3\text{C}-\text{S}-\text{Cl} \xrightarrow{\text{H}_2\text{O}} \text{Cl}_2\text{C}=\text{S}=\text{O} + 2\,\text{HCl} . \qquad (A)$$
$$\quad I \qquad\qquad\qquad II$$

Compound *II* formed in the reaction is of limited stability. However, it can be isolated from the reaction mixture by careful distillation in an almost pure state. After the preliminary communication[1] on the preparation of this so far simplest known representative of the sulfine group[2], the preparation of this compound by oxidation of thiophosgene with *m*-chloroperbenzoic acid[3] has been described. Physico-chemical constants and spectral characteristics are in agreement with those which have been found in our paper[1].

Hence, the hydrolysis of *I* gives in principle a different result from that which could be expected on the basis of analogy with the hydrolysis course of all sulfenyl chlorides studied so far. It has been demonstrated[4-6] that sulfenyl chlorides are hydrolysed via the stage of the unstable sulfenic acid *III* which immediately gives with the unreacted sulfenyl chloride present the corresponding thiosulfinate *IV* (equation (*B*) and (*C*)):

$$\text{R}-\text{S}-\text{Cl} + \text{H}_2\text{O} \rightarrow \text{R}-\text{S}-\text{OH} + \text{HCl} \qquad (B)$$
$$\qquad\qquad\qquad\qquad III$$

$$R—S—OH + R—S—Cl \rightarrow R—S(O)—S—R + HCl . \qquad (C)$$
$$IV$$

The formation of further products of hydrolysis, isolated in individual cases, as for example disulfides, thiosulfonates, sulfinic and sulfonic acids, or even mercaptans, has been explained satisfactorily by subsequent conversions of the primarily formed thiosulfinate *IV*. In this paper we have tried to elucidate this anomalous course of hydrolysis by studying the kinetics of this reaction.

EXPERIMENTAL

The starting trichloromethanesulfenyl chloride (*I*) was prepared by chlorination of carbon disulfide in hydrochloric acid[7]. It was purified by repeated column distillation under reduced pressure. Gas chromatographic analysis was carried out on a W. Giede GCHF 18·3 apparatus, using a thermal conductivity detector and a 2 m × 5 mm column packed with 10% SE-30 on Chromaton N-AW-HMDS. The determination of the acidity and of the chlorides was carried out alkalimetrically and argentometrically, with potentiometric indication.

Preparative Hydrolysis of Trichloromethanesulfenyl Chloride (*I*)

A mixture of 85 g (0·46 mol) of *I* and 350 ml of water was stirred at 20°C for 24 h. The organic layer was separated (50 g) and dried over anhydrous sodium sulfate. GLC analysis was used for the determination, by repeated experiments, in the organic layer of 60—70% of *II*, 20—30% of the unreacted *I*, and small amounts of volatile fractions (HCl, phosgene, COS), further thiophosgene, trichloromethanesulfonyl chloride[8], chlorocarbonylsulfenyl chloride[9], bis(tri-chloromethyl) disulfide[10] in addition to a further three still unidentified higher-boiling compounds; the total amount of these by-products did not exceed 2—3%. The organic layer was distilled on a column provided with a low-temperature distillation head under reduced pressure. First a red liquid distilled, with b.p. 20°C/1·60 kPa (12 Torr, 4·2 g), which according to GLC contained about 5% of thiophosgene in addition to ClC(O)SCl. The main fraction is *II*. Next a yellow liquid (23·7 g) distilled at 47—49°C/3·73 kPa (28 Torr), which solidified in the distillation head cooled at −60°C. The main component is *II* (86%), in addition to unreacted *I*. The analytically determined yield of *II* was 43%. The further fraction distilled at 36°C/1·46 kPa (11 Torr), which according to GLC consists of the unreacted *I*. Repeated distillation of the second fraction under the same conditions afforded 18·0 g (30%) of *II* the purity of which according to GLC is higher than 95%. Unreacted *I* represents the main impurity. Product *II* is a yellow liquid possessing a very strong lachrymatory effect, n_D^{20} 1·5588 (lit.[3], n_D^{20} 1·5583). Its IR spectrum contains only 3 strong absorption bands at 1156, 1059 and 950 cm^{-1} (Zwannenburg and co-workers[3] give 1155, 1055 and 955 cm^{-1}). For CCl$_2$OS (131·0) calculated: 54·14% Cl, 24·48% S; found: 54·14% Cl, 24·14% S. Extraction of the aqueous layer after hydrolysis with dichloromethane and evaporation of the solvent gave an oily residue which gave by distillation under the same conditions as above a further 8·5 g of a more than 95% *II* (the residue is dichloromethane). In view of the instability of *II* the total yield depends on the conditions of separation, mainly on the time of distillation, column efficiency and bath temperature which should not exceed 90°C. A decrease of the temperature of distillation by a decrease of pressure leads to an imperfect separation of the unreacted *I*, and the distillation temperatures and pressures mentioned represent an experimentally verified compromise.
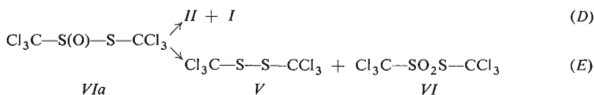
Kinetic Measurement

A mixture of 200 ml of water, or KCl or H_2SO_4 solutions, and 200 ml of a solution of I in organic solvent (concentrations are given in Table I) was stirred with a perforated teflon blade stirrer at 1 300 rpm (for the determination of the conditions of the kinetic course of the reaction 900 rpm were sufficient). During the experiments samples of the aqueous phase were withdrawn which were rapidly extracted with dichloromethane and titrated with 0·1M-NaOH. In preliminary experiments chlorides were determined in the aqueous phase argentometrically and the content of I in the organic phase by GLC, thus checking the stoichiometry of the reaction. The rate constants were calculated from the equation (I):

$$kt = c_{HCl} + 2c_0 \ln \frac{c_0}{c_0 - 0 \cdot 5c_{HCl}}, \qquad (I)$$

where c_0 is the starting concentration of the solution I and c_{HCl} is the concentration of HCl formed in the reaction in time t.

RESULTS AND DISCUSSION

If considering that the given scheme of hydrolysis of sulfenyl chlorides has a general validity (Eqs (B) and (C)), it would mean that the expected primarily formed S-tri-chloromethyl ester of trichloromethanesulfinic acid (IVa) should decompose immediately selectively to II under regeneration of I (Eq. (D)), instead of the expected decomposition to disulfide V and S-trichloromethyl ester of trichloromethanethio-sulfonic acid (VI) (Eq. (E)):

$$Cl_3C—S(O)—S—CCl_3 \nearrow^{II\ +\ I} \qquad (D)$$
$$\searrow_{Cl_3C—S—S—CCl_3\ +\ Cl_3C—SO_2S—CCl_3} \qquad (E)$$

$$VIa \qquad\qquad V \qquad\qquad\qquad VI$$

Attempts at direct synthesis of IVa were quite unsuccessful so far. The only method coming into consideration, i.e. the oxidation of V, met with an unusual resistance of this disulfide to oxidizing reagents[11]. The following of the course of hydrolysis of I by means of gas and thin-layer chromatography has shown that up to a high degree of conversion of the starting I (60%) the sole components of the reaction mixture are only II and the unreacted I, in addition to hydrogen chloride the amount of which corresponded to the amount of II formed. Bis(trichloromethyl) disulfide (V) was found in a small amount only after prolonged hydrolyses (2—3%), and also among the products of thermal decomposition of II; thiosulfonate VI was not found among the hydrolytic products at all. The rate of hydrolysis can be measured to a considerable degree of conversion by determining the increase in hydrogen chloride content.

In view of the solubility properties of both reacting substances the reactions were investigated in a heterogeneous system, *i.e.* in a stirred mixture of a solution of *I* in an inert solvent and a large excess of water. Preliminary experiments confirmed that at a sufficiently low concentration of *I*, and a sufficient excess of water, conditions can be achieved without difficulty when the reaction rate no longer depends on the intensity of the stirring. Even though this fact alone does not guarantee that macro-kinetic factors have been eliminated, the results of the measurement, *i.e.* the very good agreement of the experimental data with the simple kinetic equation, and the high value of activation energy found on the basis of the measurements of the rate at various temperatures (*i.e.* 109 kJ mol^{-1}), further support this assumption. In experiments aimed at the study of the kinetics of hydrolysis in homogeneous systems of the dioxane-water type we have found that in this system a much faster decomposition of product *II* takes place, which considerably complicates and decreases the accuracy of the results.

When interpreting the results of the measurement we considered the relative hydrolytic inertness of *I* against more concentrated solutions of hydrochloric acid, determined earlier[7]. Therefore we followed the effect of hydrogen chloride formed in the reaction on the reaction rate. The inhibitory effect of hydrogen chloride determined on a macroscale was also fully confirmed when the reaction rate was followed, and it became obvious that hydrogen chloride should be included into the rate equation; this should be done in a very simple and defined form. The results of the kinetic measurement of the hydrolysis under the above mentioned conditions can be expressed by equation (2):

$$\mathrm{d}c_I/\mathrm{d}t = -k \cdot c_I \cdot c_{HCl}^{-1}. \tag{2}$$

The rate constants calculated from the integrated form of this equation (Eq. (*1*)) are listed in Table I. In addition to the following of the rate of hydrolysis in water alone the effect of the Cl$^-$ ions was also investigated, by adding KCl into the hydrolytic medium, and the general effect of the acidity of the aqueous phase by adding sulfuric acid. The question of the effect of the character of the organic solvent was also studied.

From the results obtained the considerable independence of the reaction rate of the conditions applied is evident. No differences appear in the series of rather non-polar solvents, cyclohexane, benzene, tetrachloromethane and chloroform. However, an acceleration by more than one order of magnitude was observed in the case of diethyl ether. These results are generally in agreement with experiences so far with the chemistry of compound *I*, where the use of a more polar solvent, (and at that most commonly in the case of diethyl ether) is a necessary condition for the carrying out of some reactions[12]. It may also be judged that in the heterogeneous hydrolytic system the main reaction takes place predominantly in the organic phase. The effect

of addition of sulfuric acid is negligible and remains within the limits of experimental error. Hence a slowing down of the hydrolysis is evidently a function of the undissociated molecule of hydrogen chloride and not a function of the proton. This is also confirmed by the fact that an addition of Cl⁻ ion is also without any effect on the reaction rate of hydrolysis.

Thus it follows that aqueous hydrolysis of I is inhibited by the specific effect of hydrogen chloride, while the whole-number exponent in the rate equation indicates its role in some elementary step of the mechanism. The slowing down of the hydrolysis of sulfenyl chlorides by the hydrogen chloride formed has already been observed, it is true, in the case of hydrolysis of p-toluenesulfenyl chloride with moist chloroform[13], but this effect has not been expressed in an explicit form, and it was explained as a suppressing of the basic catalysis by ion Cl⁻ in aprotic solvents, which does not come into consideration in our case. A similar specific function of hydrogen chloride, however, is the characteristic and decisive character of the preparation of I by chlorination of carbon disulfide in aqueous solutions of hydrochloric acid[7]. It was demonstrated by model experiments that the reaction between II and HCl in no case leads to the starting I; on the contrary, mineral acids rather increase the decomposition of II.

A detailed mechanism of this inhibitory effect of hydrogen chloride on the rate of hydrolysis cannot safely be derived from the observed preparative and kinetic

TABLE I

Rate Constant Values for Hydrolysis of I at 18°C

Conc. of I in org. phase mol/l	Solvent	Hydrolytic medium	$k \cdot 10^8$ mol l^{-1} s^{-1}
0·1	benzene	water	2·07 ± 0·03
0·08	benzene	water	2·00 ± 0·04
0·04	benzene	water	2·08 ± 0·03
0·01	benzene	water	2·05 ± 0·03
0·01	tetrachloromethane	water	2·17 ± 0·05
0·01	chloroform	water	2·12 ± 0·05
0·01	cyklohexane	water	1·97 ± 0·04
0·01	diethyl ether	water	45·8 ± 1·8
0·1	benzene	water/KCl 0·05M	2·25 ± 0·05
0·1	benzene	water/KCl 0·1M	2·08 ± 0·03
0·1	benzene	water/H₂SO₄ 0·01M	1·95 ± 0·05
0·1	benzene	water/H₂SO₄ 0·05M	2·02 ± 0·04
0·1	benzene	water/H₂SO₄ 0·1M	1·93 ± 0·04

dependences. However, it seems probable that the inhibitory function of hydrogen chloride already intervenes in the first step of hydrolysis, *i.e.* during the direct attack of a water molecule on *I*; in the absence of some other suitable idea and in agreement with tradition this is formulated as the formation of an unstable free trichloromethanesulfenic acid $(IIIa)$, (Eq. (F)):

$$Cl_3C—S—Cl + H_2O \; \rightleftarrows \; [Cl_3C—S—OH] + HCl \qquad (F)$$
$$IIIa$$
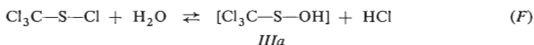
As a further step in the mechanism leading to the final product, the rapid monomolecular decomposition of this intermediary sulfenic acid may be assumed $(Eq. (G))$:

$$Cl_3C—S—OH \xrightarrow{\text{rapidly}} II + HCl \qquad (G)$$
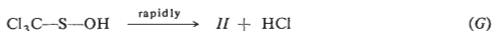
Hence, the course of hydrolysis of *I* differs distinctly from the mechanism of hydrolysis of other sulfenyl chlorides, mainly in the fact that the expected thiosulfinate *IVa* is not formed, even transitorily. In the light of the knowledge of the chemistry of *I* this fact can be easily explained, however, because it is known that in spite of its considerable reactivity, *I* displays a distinctly higher selectivity in the choice of nucleophilic reagents as partners with which it reacts willingly, than the majority of other sulfenyl halogenides. Thus, for example, *I* does not by far reach such a universality and ease of reaction as 2,4-dinitrophenylsulfenyl chloride. Therefore it may be judged that in the sense of the theory of hard and soft acids and bases, *I* is a "harder" substrate which reacts easily only with a nucleophile with corresponding properties giving rise transitorily to sulfenic acid *IIIa* which need not posses a corresponding disposition for an easy reaction with the starting *I*.

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Translated by Ž. Procházka.