HYDROLYSIS OF METHANE-, CHLOROMETHANE-, AND DICHLOROMETHANESULFONYL CHLORIDES

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Hydrolysis of the title sulfonyl chlorides has been studied in water–dioxane solvent mixtures with the use of conductometry. Hydrolyses of methanesulfonyl chloride and chloromethanesulfonyl chloride have a similar course, obey the rate equation of a pseudomonomolecular, reaction, and proceed by the S_N2 mechanism. On the other hand, the hydrolysis of dichloromethanesulfonyl chloride has a quite different course. Deuterolysis of the title sulfonyl chlorides has been also performed. Methyl esters of methane-, chloromethane-, and dichloromethanesulfonic acids have been prepared.

Chlorinations of many sulfur-containing compounds in the presence of the aqueous phase to the corresponding sulfonyl chlorides are usually accompanied by hydrolysis as the side-reaction. In the aliphatic series, this hydrolysis has been studied with methanesulfonyl chloride[1-3] and some higher alkanesulfonyl chlorides[1-6]. In the present paper, we wish to compare the hydrolysis of the two chlorinated methanesulfonyl chlorides with that of the unsubstituted methanesulfonyl chloride (all these three sulfonyl chlorides are for example formed in chlorinations of compounds containing the methylthio group).

EXPERIMENTAL

Materials. Methanesulfonyl chloride (Loba-Chemie, Wien) was purified by distillation and the fraction boiling at 58—59°C/21 Torr was used. Chloromethanesulfonyl chloride (b.p. 75—76°C : : 25 Torr) was prepared from sodium chloromethanesulfonate and phosphorus pentachloride[7]. Dichloromethanesulfonyl chloride (b.p. 78—79°C/25 Torr) was prepared by chlorination of sodium dichloromethanesulfinate[8,9]. Dioxane (Analytical Reagent Grade, Lachema, Brno) was purified by refluxing with sodium for 8 h, distillation, and rectification of the distillate in the presence of sodium (b. p. 99·5—105·5°C). The purity of the above compounds was checked by gas chromatography. Sodium chloride, sodium perchlorate, sodium hydroxide, silver nitrate, hydrochloric acid, and sulfuric acid were of the A. R. grade (Lachema, Brno). Redistilled water was used. Deuterium oxide (99·7%) was imported from Soviet Union.

Kinetic measurements. The course of hydrolysis was followed conductometrically on a Radelkis OK 102/1 apparatus with a conductometric platinum electrode. Time dependence of the degree of conversion (x) was calculated from the equation

$$x = (\lambda_t - \lambda_0)/(\lambda_\infty - \lambda_0)$$

wherein λ_0, λ_t, and λ_∞ are conductivities of reaction mixtures at the beginning, in time t, and in the moment of a complete conversion. Measurements were performed in the region of the linear relation between concentration of hydrogen ions and conductivity, namely, up to the concentration of 0·005M of the starting sulfonyl chloride. Thermostated (accuracy, ±0·1°C) water–dioxane solvent mixtures of various ratios were used as the reaction medium. When the concentration of water in the solvent mixture was lower than 80% by weight, the starting sulfonyl chloride was added into the volumetric flask which was almost full with the solvent mixture and the flask was then made up to the graduation mark. When the concentration of water in the solvent mixture was higher than 80% by weight, the sulfonyl chloride was dissolved in the volumetric flask in 1 g of dioxane and the content made up to the graduation mark with the thermostated water–dioxane solvent mixture (these different procedures are necessary to dissolve the sulfonyl chloride at the required rate). When the flask was made up to the mark, the content was thoroughly shaken without delay (this moment was taken as the initial time) and poured into the measuring vessel of the conductometer. The conductivity was then measured up to the moment of the complete conversion (when conductivity does not change with time; the control was also performed titrimetrically). Maximum relative errors in determinations of rate constants do not exceed 2·4%.

Deuterolysis of sulfonyl chlorides and preparation of methyl esters. The particular sulfonyl chloride (2 g) was stirred at 25°C with deuterium oxide (20 ml) for 12 hours and the excess deuterium oxide was then evaporated at max. 50°C/20 Torr. The residual concentrate of the corresponding sulfonic acid was diluted with 10 ml of deuterium oxide and treated with excess silver oxide. The solid (silver chloride and unreacted silver oxide) was then filtered off and the filtrate evaporated to dryness at 50°C/20 Torr. The residual silver salt of the corresponding sulfonic acid was treated with benzene (65 ml) and a three fold molar excess of methyl iodide. The resulting suspension was stirred at room temperature for 6 h, the silver iodide filtered off and the filtrate evaporated at 20 Torr (bath temperature up to 40°C) to remove benzene and the excess methyl iodide. The residue was then distilled at 0·2 Torr (bath temperature up to 90°C); the b.p. of the methyl esters varied in the range of 60—70°C/0·2 Torr and the yields were about 70%. The following methyl esters were obtained by this procedure.

Methyl methanesulfonate. For $C_2H_6O_3S$ (110·13) calculated: 24·02% C, 6·05% H, 32·06% S; found: 23·83% C, 6·17% H, 32·28% S. IR spectrum: characteristic bands at 3025, 2960, 2940, and 2845 cm^{-1} in the region of valence C—H vibrations. NMR spectrum: two singlets δ_{OCH_3} 3·01 and δ_{CH_3-S} 3·90 in 1 : 1 integral intensity ratio (all the measurements were performed on a Varian 100 MC apparatus in tetrachloromethane; tetramethylsilane as internal standard).

Methyl chloromethanesulfonate. For $C_2H_5ClO_3S$ (144·58) calculated: 16·61% C, 3·48% H, 24·52% Cl, 22·18% S; found: 16·80% C, 3·63% H, 24·19% Cl, 22·44% S. IR spectrum: characteristic bands at 3020, 2960, 2910, and 2845 cm^{-1} in the region of valence C—H vibrations. NMR spectrum: singlets δ_{OCH_3} 4·07 and δ_{ClCH_2-S} 4·62 in 3 : 2 integral intensity ratio.

Methyl deuterodichloromethanesulfonate. For $C_2H_3DCl_2O_3S$ (179·02) calculated: 13·42% C, 2·25% H+D, 39·61% Cl, 17·91% S; found: 13·19% C, 2·34% H+D, 39·22% Cl, 17·60% S. IR spectrum: characteristic bands at 3 025, 3 005, 2 960, and 2850 cm^{-1} (region of valence C—H vibrations) and at 2230 cm^{-1} (C—D vibrations). NMR spectrum: a singlet δ_{OCH_3} 4·21.

Methyl dichloromethanesulfonate: In this preparation, water was used instead of deuterium oxide. IR spectrum: the band at 2230 cm^{-1} is absent. NMR spectrum: singlets δ_{OCH_3} 4·21 and

δ_{Cl_2CH-S} 6·37 in 3 : 1 integral intensity ratio. The methyl esters of methanesulfonic acid and chloromethanesulfonic acid were prepared and analyzed similarly to methyl dichloromethanesulfonate and were found identical with methyl esters obtained by the above mentioned deuterolysis.

Attempted deuteration of dichloromethanesulfonic acid and 1,1-*dichlorodimethyl sulfone.* Dichloromethanesulfonic acid (2 g; prepared by hydrolysis of dichloromethanesulfonyl chloride and evaporation of excess water at 20 Torr) was dissolved in deuterium oxide (50 ml) and the resulting solution kept at 25°C for 75 h. Most deuterium oxide was evaporated and the remaining acid converted to the methyl ester as described above. As shown by IR and NMR spectra, no deuteration took place. The attempted deuteration of 1,1-dichlorodimethyl sulfone (for the preparation *cf.*[10]) was performed similarly and the product was extracted with dichloromethane. No deuteration occurred as indicated by NMR spectrum (singlets $\delta_{CH_3-SO_2}$ 3·09 and δ_{Cl_2CH} 6·06 in 3 : 1 integral intensity ratio).

Partial deuterolysis of dichloromethanesulfonyl chloride. Dichloromethanesulfonyl chloride (3·0 g) was stirred at room temperature with deuterium oxide (50 ml). When the conversion was 33%, the unreacted portion was separated, dried over anhydrous magnesium sulfate, distilled at 20 Torr, and analyzed with the use of pure dichloromethanesulfonyl chloride and deuterodichloromethanesulfonyl chloride as standards. The content of deuterodichloromethanesulfonyl chloride was determined by means of IR spectroscopy with the use of valence vibration absorption bands of C—H bonds (2990 cm^{-1} and 2960 cm^{-1}) and C—D bonds (2230 cm^{-1} and 2210 cm^{-1}). The spectra were measured in substancia (concentration, 100%) on a Perkin-Elmer apparatus in KBr cell (0·018 cm). The observed content (37·3% by weight) is in good accordance with that (37·7% by weight) determined by mass spectrometry. Measurements were performed on a Mass Spectrometer-Gas Chromatograph LKB 9000 apparatus (70 eV) with the use of "base peak" spectrum corresponding to the ionic fragment Cl_2CH^+ (*m/e* 83, 85, 87) or Cl_2CD^+ (*m/e* 84, 86, 88).

RESULTS AND DISCUSSION

Under the conditions stated, the hydrolysis of sulfonyl chlorides $R—SO_2Cl$ (R = = CH_3, $ClCH_2$, Cl_2CH) proceeds according to the equation

$$R—SO_2Cl + H_2O \rightarrow R—SO_2—OH + HCl . \qquad (1)$$

The rate increases in the order chloromethanesulfonyl chloride < methanesulfonyl chloride ≪ dichloromethanesulfonyl chloride (Fig. 1). The corresponding halftimes of hydrolyses at 20°C in aqueous dioxane containing 40% by weight of water (respectively 80%) are as follows: 270·8 (145·6), 253·0 (92·3), and 6·7 (0·8) min. The hydrolysis of methanesulfonyl chloride[1-3] and chloromethanesulfonyl chloride obeys the first order rate equation of a pseudomonomolecular reaction. The rate constants depend on composition of the hydrolytical medium (Fig. 2) and on the temperature (Table I). The primary effect of salts added does not interfere in these cases, *i.e.*, the rate of hydrolysis does not depend on the presence of an electrolyte either with a common ion (addition of sodium chloride or hydrochloric acid) or without a common ion (addition of sodium perchlorate). On the other hand, the presence of hydroxylic ions accelerates the hydrolysis in a such a manner that the measurement is not possible. From the temperature dependence of rate constants, there were calculated by means of the Arrhenius equation the values of activation energy, frequence factor, and activation entropy (Table II).

The hydrolysis of dichloromethanesulfonyl chloride does not obey the simple rate equation of an integral order. The presence of hydrogen ions formed (or added) leads to a retardation of the reaction (Fig. 3). On the other hand, the influence of the chloride ions (addition of sodium chloride in concentration of 0·01M) is negligible; these ions rather accelerate (but not convincingly) than retard the hydrolysis. Also the addition of an electrolyte without a common ion (0·01M sodium perchlorate) does not exert any influence.

As it may be seen from the dependence of rate constants of pseudomonomolecular hydrolysis of methanesulfonyl chloride and chloromethanesulfonyl chloride on composition of the hydrolytical medium (Fig. 2), there is a good agreement in data of the earlier authors[3] on kinetics of the hydrolysis of methanesulfonyl chloride and our measurements except for the region of the highest rates. The rate of the hydrolysis of chloromethanesulfonyl chloride is lower in all solvent mixtures used, especially

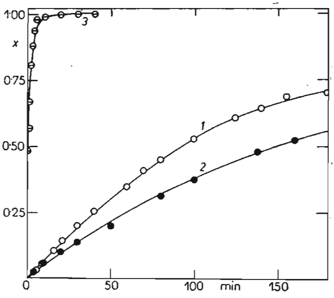

FIG. 1

The Course of Hydrolysis of Methanesulfonyl Chloride *1*, Chloromethanesulfonyl Chloride *2*, and Dichloromethanesulfonyl Chloride *3* in 80 : 20 (by weight) Water–Dioxane at 20°C (initial concentration of the sulphonyl chloride, 0·002M)

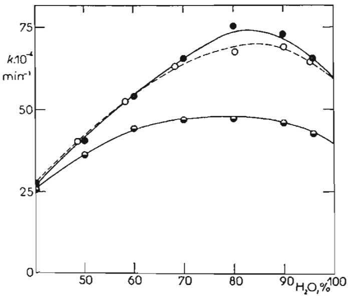

FIG. 2

Dependence of Rate Constants of the Hydrolysis of Methanesulfonyl Chloride (● our results, ○ reported[3] results) and Chloromethanesulfonyl Chloride (◒) on the Composition of Water–Dioxane Solvent Mixtures at 20°C (initial concentration of the sulfonyl chloride, 0·002M and 0·05M (*cf.*[3]), resp.)

in those containing a higher percentage of water. Methanesulfonyl chloride was shown[3] to hydrolyze by the S_N2 mechanism. As suggested by the similar course of hydrolysis, by the independence on the presence of electrolytes added (with or without a common ion), by a considerable acceleration of hydrolysis in the presence of hydroxylic ions, and by retardation of hydrolysis in media of the highest ionisation ability (*i.e.*, in media containing almost exclusively water), also chloromethanesulfonyl chloride may be assumed to hydrolyze by the S_N2 mechanism. The slower hydrolysis of chloromethanesulfonyl chloride (when compared with that of methanesulfonyl chloride) cannot be ascribed in view of the small negative activation entropy value to sterical hindrance (replacement of a hydrogen atom in the methyl

TABLE I

Rate Constants $k \cdot 10^4$ (min^{-1}) of Hydrolyses of Methanesulfonyl Chloride and Chloromethanesulfonyl Chloride in Water–Dioxane Solvent Mixtures (*I*, 40% by weight of water; *II*, 80% by weight of water) at Various Temperatures

Temperature °C	CH_3SO_2Cl		$ClCH_2SO_2Cl$	
	I	*II*	*I*	*II*
15	16·5	10·4	15·4	33·2
20	27·4	75·1	25·6	47·0
25	44·7	118·8	44·7	81·5
30	71·6	194·6	69·9	148·0
35	111·0	342·0	110·0	255·0
40	166·5	—	166·0	—

TABLE II

Activation Energy (*E*), Frequence Factor (*A*), and Activation Enthropy ($\Delta S^{\neq}$) of Hydrolyses of Methanesulfonyl Chloride and Chloromethanesulfonyl Chloride in Water–Dioxane Solvent Mixtures (*I*, 40% by weight of water; *II*, 80% by weight of water)

Quantity	CH_3SO_2Cl		$ClCH_2SO_2Cl$	
	I	*II*	*I*	*II*
E (kcal/mol)	16·83	18·83	16·02	20·46
log *A* (s^{-1})	8·19	10·11	7·88	11·14
$-\Delta S^{\neq}$ (cal/deg) 25°C	23·0	14·3	24·5	9·6

group by the chloro atom). The effect might be due to a greater electrostatic repulsion between the neutral molecule of the nucleophile (water) and the increased positive charge on the central sulfur atom in the transition state as assumed in some analogous cases where the rate of hydrolysis decreases in the order ethanesulfonyl chloride > > methanesulfonyl chloride > β-chloroethanesulfonyl chloride > α-chloroethanesulfonyl chloride. Dependence of the rate of hydrolysis of chloromethanesulfonyl chloride on composition of the water–dioxane solvent mixtures may be explained analogously to the hydrolysis of methanesulfonyl chloride[3,5] by the different transportability of particular molecules of water to the molecule of the sulfonyl chloride, or water required for the formation of the transition state (with both sulfonyl chlorides, the increasing content of water in the hydrolytical medium leads to an increase of the activation energy and to a decrease of the negative activation entropy, see Table II).

Concerning the hydrolysis of dichloromethanesulfonyl chloride, the dependence on the presence of hydrogen ions (they retard the hydrolysis) suggests involvement of the methine proton of dichloromethanesulfonyl chloride in the mechanism of the hydrolysis:

$$\mathrm{Cl_2CHSO_2Cl} \rightleftharpoons \mathrm{Cl_2\bar{C}SO_2Cl} + \mathrm{H^+} \qquad (2)$$

To elucidate the role of the assumed proton, we performed the deuterolysis of dichloromethanesulfonyl chloride, converted the thus-obtained acid to the methyl ester, and measured the infrared and NMR spectra which confirmed the exclusive formation of deuterated dichloromethanesulfonic acid:

$$\mathrm{Cl_2CHSO_2Cl} + \mathrm{D_2O} \rightarrow \mathrm{Cl_2CDSO_2OD} + \mathrm{HCl} \qquad (3)$$

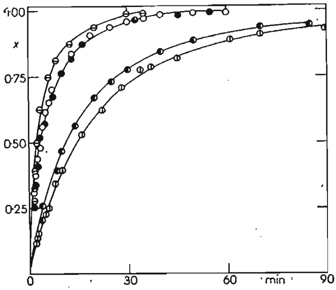

FIG. 3

Influence of Additions of Various Electrolytes on the Course of Hydrolysis of Dichloromethanesulfonyl Chloride (initial concentration, 0·0025M) in the Medium of 1 : 1 (by weight) Water–Dioxane at 15°C; ⊖ 0·01M Sodium Chloride, ● 0·01M Sodium Perchlorate, ○ without any Electrolyte added, ◐ 0·01N Sulfuric Acid, ⦶ 0·01M Hydrochloric Acid.

On the other hand in the case of methanesulfonyl chloride and chloromethanesulfonyl chloride, the hydrolysis does not occur in spite of analogous conditions (the exchange at the methyl or chloromethyl group does not take place). Also in the model compounds, namely, dichloromethanesulfonic acid and 1,1-dichlorodimethyl sulfone the hydrogen atoms in C—H bonds are not exchanged for deuterium atoms even when prolonged reaction times are used. The reversibility of the first step (equation (2)) of the proposed mechanism was confirmed in the case of the partial deuterolysis of dichloromethanesulfonyl chloride: the unreacted portion contained a considerable amount of deuterodichloromethanesulfonyl chloride.

On the basis of the above mentioned findings we assume that the first step of hydrolysis of dichloromethanesulfonyl chloride is an equilibration (equation (2)) which is then followed by removal of the chloride ion from the carbanion under the formation of an intermediate of the sulfene type:

$$Cl_2^-CSO_2Cl \rightarrow (Cl_2C{=}SO_2) + Cl^- \qquad (4)$$

This intermediate very quickly adds water (or deuterium oxide) under the formation of dichloromethanesulfonic acid:

$$(Cl_2C{=}SO_2) + H_2O \rightarrow Cl_2CHSO_2OH\,. \qquad (5)$$

The formation of the sulfene intermediate is also assumed in the hydrolysis of benzylsulfonyl chloride in the presence of trimethylamine[11], *i.e.*, a considerably stronger nucleophile than water which is sufficient in case of dichloromethanesulfonyl chloride.

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