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Abstract

Full Text

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CHEMISTRY

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SULFOCHLORINATION OF METHANE WITH GASEOUS SULFUR DIOXIDE AND CHLORINE

At the present time no methods are known for obtaining methanesulfonic acid chloride by direct sulfochlorination of methane. This compound is usually prepared from salts of methanesulfonic acid by the action of phosphorus pentachloride ([1]), or from free methanesulfonic acid and thionyl chloride ([2]); in the latter case, up to 80% of methanesulfonic anhydride is formed simultaneously ([3]). Methanesulfonyl chloride is obtained with the best result by chlorination of methylisothiourea ([4]).

The sulfochlorination reaction proceeds with difficulty with ethane and still more difficultly with methane. We carried out experiments on the photochemical sulfochlorination of methane in quartz apparatus. In the course of the experiments we observed the change in the composition of the reaction mixture, which was in the gaseous and vapor states. Irradiation of the reaction gas mixture was carried out with ultraviolet light of wavelength 3650 Å or with X-rays ($\lambda_{\text{eff}} = 1.6$ Å).

In the gas phase, under the action of ultraviolet light and powerful X-ray radiation (beam intensity at the window of the tube $12.6 \cdot 10^{15}$ eV/cm$^2 \cdot$ sec, or $\sim$ 2000 r/sec), no noticeable amounts of methanesulfonic acid chloride were formed. The main reaction products under these conditions were chlorinated derivatives of methane and sulfuryl chloride, which was liberated in a small amount.

We believe that photochemical sulfochlorination of aliphatic hydrocarbons can proceed not only by a chain mechanism ([5]), but, as our experiments have shown, there may also occur a process of formation (as intermediate compounds) of alkanesulfinic acids.

Under the action of activating radiation, an aliphatic hydrocarbon reacts with an activated molecule of sulfur dioxide with formation of an alkanesulfinic acid

$$\mathrm{RH} + \mathrm{SO}_2^* \xrightarrow{h\nu} \mathrm{RSO}_2\mathrm{H}$$

and its oxidation by chlorine, leading to formation of the sulfonic acid chloride and hydrogen chloride

$$RSO_2H + Cl_2 \rightarrow RSO_2Cl + HCl.$$

In the sulfochlorination of methane, the most difficult stage is the formation of methanesulfinic acid, which is formed from methane and sulfur dioxide in a yield tens of times lower than from other hydrocarbons. The quantum yield of methanesulfinic acid reaches only 0.006, whereas in the formation of butanesulfinic acid it is about 0.23 ([6]). The very low content of methanesulfonyl chloride in the products of the photochemical reaction of sulfochlorination of methane with gaseous sulfur dioxide and chlorine is evidently due to the low specific role of the reaction of formation of methanesulfinic acid in comparison with the simultaneously proceeding photochemical reaction of chlorination of methane.

For a more successful direct synthesis of methanesulfonic acid chloride, the process of sulfochlorination of methane must be carried out under conditions that make it possible to obtain higher degrees of dissociation of methane with the formation of methyl radicals than is observed under the action of ultraviolet radiation.

To confirm this conclusion, we carried out special experiments on the sulfochlorination of methane with gaseous sulfur dioxide and chlorine in a flow system in the field of a high-frequency electric discharge (calculated wavelength 357.6 m). The generator of high-frequency damped oscillations was a "Tesla" transformer with an output power of 200 W at a voltage of 1,000,000 V. This transformer was supplied by an oil transformer of 1 kW power, giving a voltage of 10,000 V.

The apparatus used for these experiments consisted of a vertically arranged glass tube, along the axis of which passed a second glass tube 2 mm in diameter, filled with mercury and serving as the electrode to which the high voltage was applied. The external grounded electrode was made in the form of a wire spiral immersed in a conductor washing the reaction tube.

Under the conditions described, the yield of methanesulfonic acid chloride reached 2-3% calculated on methane. The formation of methanesulfonyl chloride was proved by preparing from it methanenaphthylsulfamide.

The initial reaction gases were fed into the reactor in equimolecular amounts. The rate of gas feed in different experiments was varied so that the residence time of the reaction mixture in the discharge field ranged from 0.8 to 4.4 min.

In the process of sulfochlorination of methane, sulfur was deposited in considerable quantity on the reactor walls. In the liquid reaction products, in addition to methanesulfonyl chloride, an insignificant content of methionic acid dichloride ($CH_2(SO_2Cl)_2$) and fairly large amounts of mono- and trichloromethanesulfonyl chloride ($ClCH_2SO_2Cl$, Cl_3CSO_2Cl), methylene chloride, chloroform,

carbon tetrachloride, sulfuryl chloride, and carbon disulfide were found.

The formation under these conditions of methanesulfonic acid chloride may be represented as a chain process initiated mainly by methyl radicals formed in the process of dissociation of methane molecules excited in the field of a high-frequency electric discharge:

$$CH_4 \rightsquigarrow CH_4^{\bullet} \longrightarrow CH_3^{\bullet} + H^{\bullet} \tag{1}$$

and also as a result of the interaction of methane molecules with chlorine atoms

$$CH_4 + Cl^{\bullet} \rightarrow CH_3^{\bullet} + HCl.$$

Methyl radicals interact with sulfur dioxide molecules with formation of methanesulfinyl radicals

$$CH_3^{\bullet} + SO_2 \rightarrow CH_3SO_2^{\bullet},$$

which, reacting with chlorine, give methanesulfonyl chloride

$$CH_3SO_2^{\bullet} + Cl_2 \rightarrow CH_3SO_2Cl + Cl^{\bullet}.$$

The preparation of methanesulfonic acid chloride in the field of a high-frequency electric discharge confirmed our supposition that the reaction of sulfochlorination of methane with gaseous sulfur dioxide and chlorine can proceed with appreciable yields only under such conditions in which the experimental method ensures the possibility of forming a relatively large excess of methyl radicals in comparison with ato-

chlorine atoms. Under the conditions of our experiments, owing to insufficient formation of methyl radicals according to scheme (I), and also to the comparatively high concentration of molecular and atomic chlorine in the reaction mixture, the chain process of methane sulfochlorination does not undergo appreciable development, evidently because of chain termination through absorption of radicals in the processes:

$$SO_2 + Cl\cdot \rightarrow \cdot SO_2Cl;$$

$$CH_3\cdot + \cdot SO_2Cl \rightarrow CH_3SO_2Cl;$$

$$\cdot SO_2Cl + Cl\cdot \rightarrow SO_2Cl_2.$$

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The relative role of the methane sulfochlorination process was reduced, moreover, by various side reactions (including the chain reaction of methane chlorination), as a result of which the above-mentioned compounds were liberated.

Thus, two mechanisms may occur in the sulfochlorination reaction of saturated aliphatic hydrocarbons:

1. Photochemical sulfochlorination proceeds through the stage of formation of sulfinic acid and its oxidation by chlorine to the sulfonyl chloride.
2. Sulfochlorination in the field of electrical discharges proceeds through the stage of radical formation and has a chain mechanism.

The fundamental possibility of obtaining methanesulfonyl chloride by direct sulfochlorination of methane with gaseous sulfur dioxide and chlorine has been shown experimentally.

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

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