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Abstract

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SULFOOXIDATION OF METHANE WITH GASEOUS SULFUR DIOXIDE AND OXYGEN

The reaction of the sulfooxidation of methane has scarcely been described in the literature; there are only isolated indications of the transformation of methane under the action of certain sulfonating agents. Methane dissolves slowly in fuming sulfuric acid ([1]), but the compounds formed in this process have not been isolated. With sulfur dioxide, methane reacts thermally and thermocatalytically with the formation of sulfo derivatives and oxidation products ([2,3]).

Methanesulfonic acid and its derivatives are usually prepared by other methods. Alkali salts of methanesulfonic acid can be obtained from salts of sulfurous acid and methyl iodide ([4]), or from methyl iodide and diethyl sulfite in the presence of caustic potash ([5]). On heating dimethyl sulfate with alkali-metal sulfites ([6]), the corresponding salts of methanesulfonic acid and methylsulfuric acid are also formed, and are difficult to separate from one another.

Indirect methods for obtaining methanesulfonic acid have also been described ([7,8]); however, the literature contains no indications of the possibility of direct sulfooxidation of methane with gaseous sulfur dioxide and oxygen in order to obtain methanesulfonic acid. The present work, which we carried out using as initiating influences on the reaction various additives, ultraviolet light, X-ray radiation, and a high-frequency electric discharge, was aimed at clarifying this possibility of sulfooxidation of methane.

As a result of experiments carried out in quartz apparatus in static and flow systems, it was established that the reaction of sulfooxidation of methane with gaseous sulfur dioxide and oxygen under the action of ultraviolet light practically does not proceed. Under these conditions, only processes of photochemical oxidation of methane and sulfur dioxide took place. Methane likewise did not undergo photochemical sulfooxidation in the presence of metallic mercury, acetic anhydride, palladium black, and benzoyl peroxide at low temperatures; however, at elevated temperatures (200–400°C) methanesulfonic acid was formed with a yield of about 0.02% of the theoretical. In this case, the principal processes were the oxidation of methane and sulfur dioxide. The yield of sulfuric acid in this process exceeded the yield of methanesulfonic acid by 30–40 times. Under the action of X-rays, the initial gaseous substances reacted only with the formation of carbon monoxide and dioxide, hydrogen, water, and sulfur dioxide in amounts of the order of 2–5% each. We were unable to observe the formation of methanesulfonic acid under these conditions.

The inertness of methane in the sulfooxidation reaction can be explained by the fact that, under the action of ultraviolet light with a wavelength greater than 3000 Å, no noticeable dissociation of methane molecules occurs with the formation of methyl radicals; only at elevated temperatures (200–400°C) under the action of ultraviolet light can dissociation of methane molecules occur to some extent. Under these conditions, as noted above, we succeeded in obtaining small amounts of methanesulfonic acid.

In the sulfooxidation of methane with gaseous sulfur dioxide and oxygen in a flow system in the field of a high-frequency electric discharge (the duration of exposure of the reaction mixture to the discharge in different experiments varied from 1.4 to 4.5 min., calculated wavelength 357.6 m), we succeeded in increasing the yield of methanesulfonic acid to 2–3% based on methane. These experiments were carried out in reactors with an internal electrode in the form of platinum wire 0.05 and 0.19 mm in diameter. The source of high-frequency damped oscillations was a "Tesla" transformer with an output power of 200 W, at a voltage of 1,000,000 V, fed from a 1 kW oil transformer with a voltage of 10,000 V.

Analysis of the liquid reaction products established that 1 g of them contained 0.001145–0.001247 g-eq. of methanesulfonic acid (10.99–11.97%), 0.005089–0.006261 g-eq. of sulfuric acid (24.94–30.68%), 0.1–5.5 wt. % methyl alcohol, and the remainder was water. Hydrogen sulfide, mercaptans, carbon disulfide, and carbon oxysulfide could not be detected in the reaction products. During passage of the gaseous reaction mixture through the zone of the electric discharge, sulfur was deposited in considerable quantity on the walls of the reactors. In the gases leaving the reactor, formaldehyde, acetylenic hydrocarbons (in an amount of 0.60–0.65 vol. %), carbon monoxide (9.0–12.5%), carbon dioxide (4.8–5.0%), ethylenic hydrocarbons (~0.1%), and hydrogen (14.0–19.0%) were found.

The composition of the solid, liquid, and gaseous reaction products indicates the great variety and complexity of the processes occurring with the substances present in the electric-discharge zone. We believe that, in the field of a high-frequency electric discharge, the synthesis of methanesulfonic acid proceeds by a chain mechanism with the intermediate formation of methanepersulfonic acid; however, owing to the large number of different side processes not considered in the present communication, the specific role of the sulfooxidation reaction of methane nevertheless remains very small.

The process initiating the sulfooxidation reaction of methane is evidently the decomposition of a methane molecule excited in the electric discharge in one way or another:

$$\mathrm{CH_4} \rightsquigarrow \mathrm{CH_4^*} \rightarrow \mathrm{CH_3^\bullet} + \mathrm{H^\bullet} \tag{1}$$

The methyl radical reacts with sulfur dioxide, as a result of which a methanesulfonyl radical is formed:

$$CH_3^\bullet + SO_2 \rightarrow CH_3{-}SO_2^\bullet, \tag{2}$$

which is then oxidized by oxygen with formation of the methanepersulfonic-acid radical:

$$CH_3SO_2^\bullet + O_2 \rightarrow CH_3SO_2O_2^\bullet. \tag{3}$$

This radical reacts with methane, giving a molecule of methanepersulfonic acid and a new methyl radical:

$$CH_3SO_2O_2^\bullet + CH_4 \rightarrow CH_3SO_2O_2H + CH_3^\bullet. \tag{4}$$

The molecule of methanepersulfonic acid, like all alkanepersulfonic acids, is unstable. In aqueous solution it is very rapidly reduced by sulfurous acid to methanesulfonic acid with formation of an equimolecular amount of sulfuric acid:

$$CH_3SO_2O_2H + SO_2 + H_2O \rightarrow CH_3SO_3H + H_2SO_4. \tag{5}$$

Water is formed mainly at the expense of the reactions described by equations (6), (7), and (13), and also partly at the expense of reaction (10).

$$\begin{array}{r} CH_3^\bullet + O_2 \rightarrow CH_2O + {}^\bullet OH \\ {}^\bullet OH + CH_4 \rightarrow CH_3^\bullet + H_2O,\ \text{etc.} \end{array} \quad \text{chain.} \tag{6}$$

This scheme agrees with the data of A. B. Nalbandyan (9) on the photochemical oxidation of methane in the presence of mercury vapor. The formaldehyde obtained under the conditions of our experiments in considerable quantity could be further oxidized by atomic oxygen:

$$HCHO + O^{\cdot} \rightarrow CO + H_2O. \tag{7}$$

The possibility is not excluded that methanesulfonic acid is also formed through the interaction of methane with radicals arising as a result of the decomposition of unstable methane persulfonic acid:

$$CH_3SO_2O_2H \rightarrow CH_3SO_2O^{\cdot} + {}^{\cdot}OH; \tag{8}$$

$$CH_3SO_2O^{\cdot} + CH_4 \rightarrow CH_3SO_3H + CH_3{}^{\cdot}; \tag{9}$$

$$CH_4 + {}^{\cdot}OH \rightarrow H_2O + CH_3^{\cdot}. \qquad (10)$$

The excess amount of sulfuric acid in the reaction products, compared with the amount capable of being formed according to equation (5), is obtained, in all probability, as a result of the following processes:

a) through the reaction of sulfur dioxide with ozone, whose formation in electric discharges has been proved by us experimentally:

$$SO_2 + O_3 \rightarrow SO_3 + O_2; \qquad (11)$$

b) as a result of disproportionation of the oxygen of sulfur dioxide contained in the reacting gas mixture, which is accompanied by the simultaneous formation of sulfur (10):

$$3SO_2 \rightarrow S + 2SO_3, \qquad (12)$$

the main amount of which is nevertheless apparently obtained through the reaction of reduction of sulfur dioxide by hydrogen (10):

$$SO_2 + 2H_2 \rightarrow 2H_2O + S; \qquad (13)$$

c) upon oxidation of sulfur dioxide by oxygen (10):

$$2SO_2 + O_2 \rightarrow 2SO_3. \qquad (14)$$

As a result of the work carried out, it has been established that in the field of a high-frequency electric discharge the sulfooxidation of methane by gaseous sulfur dioxide and oxygen takes place. The reaction is accompanied by a number of parallel processes.

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