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Abstract

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PHOTOCHEMICAL SULFOOXIDATION OF *n*-HEPTANE WITH GASEOUS SULFUR DIOXIDE AND OXYGEN

Direct sulfonation of *n*-heptane with sulfuric acid or oleum is only slightly effective. *n*-Heptane reacts with fuming sulfuric acid with the formation of only a small amount of heptanesulfonic acids (1). They are also formed in the process of sulfooxidation of *n*-heptane with sulfur dioxide and oxygen in the presence of organic peracids (2). The present work was carried out in order to study the direct photochemical reaction of sulfooxidation of *n*-heptane in the liquid phase.

Sulfooxidation of *n*-heptane was carried out at a temperature of 20° in a vertical quartz tube 30 mm in diameter, provided in its upper part with a reflux condenser. Through the hydrocarbon, charged into the tube in an amount of 300–400 ml, an equimolecular mixture of sulfur dioxide and oxygen was bubbled; it was dispersed into small bubbles by means of a capillary opening in the tube serving for the admission of the gases. The reaction mixture was irradiated with ultraviolet light of wavelength 3650 Å. A PRK-2 mercury-quartz lamp was arranged vertically and was located at a distance of 125 mm from the reactor. During the experiments, liquid reaction products separated from the hydrocarbon layer and were collected in the lower part of the tube.

In all the experiments we carried out, the yield of reaction products did not depend on the concentration of sulfur dioxide and oxygen in the gas mixture and was directly proportional to the time for which they were passed through the layer of *n*-heptane, which indicates that the yield is proportional to the number of light quanta absorbed by the reacting substances. The degree of utilization of sulfur dioxide and oxygen is in a linear dependence on the height of the hydrocarbon layer through which the gases are bubbled.

The reaction products separating from the hydrocarbon layer and collecting in the lower part of the quartz tube were a mixture of substances, the composition of which is given in Table 1.

Table 1

Composition of the products of the photochemical sulfooxidation reaction of *n*-heptane

Formula of substance	$C_7H_{15}SO_3H$	$C_7H_{14}(SO_3H)_2$	$C_7H_{15}OH$	H_2SO_4
Content, wt. %	67	5-6	5-9	18

The preliminary introduction of benzoyl peroxide into *n*-heptane has no noticeable effect on the rate of separation of the reaction products. The process under study apparently has no induction period. In the presence of toluene, which, according to our investigations, does not undergo photochemical sulfooxidation by gaseous sulfur dioxide and oxygen either in the liquid or in the vapor phase, the sulfooxidation reaction of *n*-heptane practically did not proceed. It was established that *n*-heptane under these conditions induces the oxidation of toluene, whereas even a small amount of the latter or of the products of its oxidation inhibits the photochemical sulfooxidation reaction of *n*-heptane.

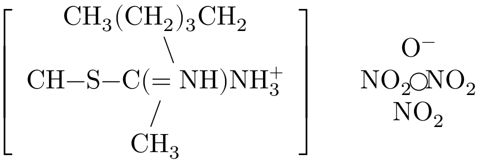
The results of the experiments carried out by us in a flow system showed that the photochemical sulfooxidation reaction of *n*-heptane with gaseous sulfur dioxide and oxygen is a consecutive reaction proceeding with the intermediate formation of mono- and disulfinic acids. We succeeded in obtaining these acids in the course of bubbling sulfur dioxide through *n*-heptane while irradiating it with ultraviolet light. Heptanesulfinic acids are readily soluble in *n*-heptane and, in its solution, are readily oxidized by oxygen with the formation of heptanesulfonic acids, which separate from the hydrocarbon and contain no sulfuric acid. In a special series of experiments carried out in a stationary closed system, it was experimentally established that the photochemical sulfooxidation reaction of *n*-heptane proceeds with the intermediate formation of heptanesulfinic acids.

To determine the structure of heptanemonosulfinic acid, the latter, together with heptanedisulfinic acid, was separated from sulfuric acid by the salt method in the form of barium salts; from these, upon treatment with phosphorus pentachloride, a mixture of mono- and disulfochlorides was then obtained. This mixture was dissolved in an equal volume of dry isopentane, the solution was cooled in a Dewar vessel to a temperature of −54°, after which the precipitated heptanedisulfochloride, poorly soluble even in warm isopentane, was filtered off at the same temperature. After removal of the solvent, the filtrate was a mixture of 64 wt. % monoheptanesulfochloride and 36% heptyl chloride, apparently formed mainly during the very process of obtaining the acid chlorides of heptanesulfonic acids, through interaction with phosphorus pentachloride (3):

$$C_7H_{15}SO_2Cl + PCl_5 \rightarrow C_7H_{15}Cl + SOCl_2 + POCl_3.$$

Heptanemonosulfochloride was subjected to thermal desulfination at a temperature of 195-200°. This gave 2-chloroheptane, distilling at 146-149° and having refractive index n_D^{20} 1.4212 (according to the literature data, b.p. 147-150° and n_D^{20} 1.4222 (4)).

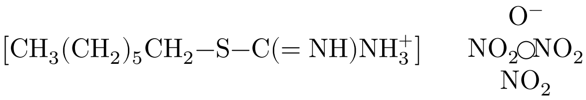
In addition to identification by physicochemical constants, from the isolated heptyl chloride we obtained, by the method of Levy, Brown, and Campbell (5), crystalline picrate of S-heptylisothiourea, having m.p. 116.5-117°.



$$\left[\begin{array}{c} \mathrm{CH_3(CH_2)_3CH_2} \\ \backslash \\ \mathrm{CH{-}S{-}C(=NH)NH_3^+} \\ / \\ \mathrm{CH_3} \end{array}\right] \quad \begin{array}{c} \mathrm{O^-} \\ \mathrm{NO_2}\bigcirc\mathrm{NO_2} \\ \mathrm{NO_2} \end{array}$$

The picrate was prepared as follows. Thiourea, in an amount of 0.5 g, was dissolved in 5 ml of 95% ethyl alcohol, and 0.53 g of heptyl chloride was added to the solution. The resulting solution was boiled with a reflux condenser for 1 hour, after which 0.5 g of picric acid, m.p. 120.9-121°, was added to it, and boiling was continued for another 10 min. After cooling, the alcoholic solution was diluted with 45 ml of distilled water; the picrate thereby formed crystallized as yellow plates, which were filtered off with suction and recrystallized from 50% methyl alcohol.

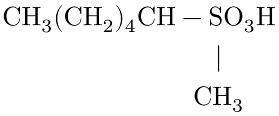
A mixed sample of the obtained picrate with picrate prepared by the same method from *n*-heptyl bromide and having m.p. 127-127.5°,



$$[\mathrm{CH_3(CH_2)_5CH_2{-}S{-}C(=NH)NH_3^+}] \quad \begin{array}{c} \mathrm{O^-} \\ \mathrm{NO_2}\bigcirc\mathrm{NO_2} \\ \mathrm{NO_2} \end{array}$$

melted at a temperature of 110.5-111.5°.

Thus, the heptanemonosulfonic acid obtained by us in the process of photochemical sulfooxidation of *n*-heptane is α-methylhexanesulfonic acid



$$\begin{array}{l} \mathrm{CH_3(CH_2)_4CH - SO_3H} \\ \qquad\qquad\quad | \\ \qquad\qquad\ \mathrm{CH_3} \end{array}$$

From the potassium salt of heptanesulfonic acid, obtained by treating its barium salt with an equimolecular amount of potassium sulfate, we synthesized the benzylthiuronium salt of heptanesulfonic acid, which has not been described in the literature. This synthesis was carried out as follows. The potassium salt of heptanesulfonic acid, in an amount of 1.16 g (0.0053 g-mol), was dissolved in 4 ml of distilled water; the solution was cooled in ice and then mixed and shaken well with an ice-cooled solution of 1.32 g (0.0065 g-mol) of benzylthiuronium chloride (m.p. 173-174°) in a small amount of water. On cooling, crystals of the benzylthiuronium salt of heptanesulfonic acid separated; these were collected on a filter and washed with cold water. After repeated recrystallization from 50% ethyl alcohol, the derivative was obtained in the form of scaly crystals, having m.p. 105.5-106.5°.

There are statements in the literature that the photochemical sulfooxidation reaction of paraffinic and cycloparaffinic hydrocarbons proceeds by a chain mechanism. Thus, Graf ([6]) and Ortner ([7]) consider that this reaction is a chain reaction and proceeds with the intermediate formation of alkanepersulfonic acids, which in aqueous solution are instantaneously reduced by sulfurous acid to alkanesulfonic acids, giving an equimolecular amount of sulfuric acid

$$\mathrm{RSO_2O_2H + SO_2 + H_2O \rightarrow RSO_3H + H_2SO_4}. \tag{1}$$

The formation of sulfinic acids observed by us, as well as the much higher content of heptanesulfonic acids in the reaction products in comparison with the amount of sulfuric acid that should be present according to this scheme, does not support the formation of heptanesulfonic acids and sulfuric acid through decomposition of heptanepersulfonic acids by sulfurous acid according to equation (1). The formation of sulfuric acid according to equation (1) in our experiments is in general unlikely, since the water necessary for this reaction to proceed could have been introduced into the reaction medium only in the most negligible amounts together with the reacting gases. As Graf ([6]) indicates, water may arise as a result of the reaction

$$\mathrm{C_nH_{2n+1}SO_2O_2H + C_nH_{2n+2} \rightarrow C_nH_{2n+1}SO_3H + C_nH_{2n} + H_2O}, \tag{2}$$

but in our experiments no appreciable formation of unsaturated compounds occurred.

We believe that the photochemical sulfooxidation reaction of *n*-heptane by gaseous sulfurous anhydride and oxygen is a consecutive reaction proceeding by the following route. *n*-Heptane reacts with a molecule of sulfurous anhydride activated by ultraviolet light, with the formation of heptanesulfinic acid

$$\mathrm{SO_2 + h \ \rightarrow SO_2^*}, \tag{3}$$

$$\mathrm{C_7H_{16} + SO_2^* \xrightarrow{h} C_7H_{15}SO_2H}. \tag{4}$$

This process of formation and accumulation of heptanesulfinic acids is the slow stage of the reaction. In the presence of oxidizing agents, which under the conditions of our experiments may be molecular and atomic oxygen, as well as ozone, there occurs a continuous process of oxidation of heptanesulfinic acids into heptanesulfonic acids, which separate from the hydrocarbon:

$$2C_7H_{15}SO_2H + O_2 \rightarrow 2C_7H_{15}SO_3H, \tag{5}$$

$$C_7H_{15}SO_2H + O^{\cdot} \rightarrow C_7H_{15}SO_3H, \tag{6}$$

$$C_7H_{15}SO_2H + O_3 \rightarrow C_7H_{15}SO_3H + O_2. \tag{7}$$

Simultaneously with the consecutive reaction described, there may also proceed, to some extent, the process of formation of heptanesulfo acids from heptane persulfo acids according to scheme (1). In addition, sulfur trioxide, under the conditions of our experiments, is apparently also formed through oxidation of sulfur dioxide by the hydroperoxide of *n*-heptane

$$C_7H_{16} + O_2^{*} \rightarrow C_7H_{15}OOH, \tag{8}$$

$$C_7H_{15}OOH + SO_2 \rightarrow C_7H_{15}OH + SO_3. \tag{9}$$

The scheme presented, although not definitive, nevertheless makes it possible to interpret the experimental data most fully. To establish the mechanism of the photochemical sulfooxidation reaction of aliphatic hydrocarbons with gaseous sulfur dioxide and oxygen, the experimental data obtained by us are insufficient, and additional special investigations are necessary. Work in this direction is continuing.

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