APPLICATION OF GAS CHROMATOGRAPHY TO STUDY THE RESISTANCE OF SI-C BONDS TOWARD SULFURIC ACID

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Usually one definite Si-C bond is cleaved when β -trialkylsilylpropionic acids, containing several various alkyl radicals on the Si atom, are treated with H₂SO₄. However, in [1] it was shown that in the case of β -methyldi-n-hexylsilylpropionic acid the reaction products are simultaneously hexane and methane, in which connection their total amount testifies to the cleavage of only one Si-C bond in each molecule. The reaction with β -dimethylbutylsilylpropionic acid also proceeds in a similar manner.

The kinetic data on the reaction of $R_2Si(CH_3)_2$ [2] and $(CH_3)_3Si(CH_2)_2COOH$ [3, 4] with H_2SO_4 were obtained by the volumetric method. However, this method does not give data on the composition of the gaseous reaction products, which in many cases is necessary in order to understand the mechanism of the process. In the present paper we employed the method of reaction gas chromatography [5], which makes it possible to determine the composition of the liberated gases, and also to calculate the values of the rate constants of the reactions.

In the scheme employed by us to run the experiments the gaseous reaction products were blown out with a gas stream into the batcher of the chromatograph. Each sample contained an amount of reaction products that is equal to their increase in a definite time interval. For first order reactions this increase can be expressed as

$$\Delta x = a e^{-Kt} \left(e^{K\Delta t} - 1 \right) \tag{1}$$

Solving the system of Eqs. (1) for t_1 and t_2 , with $\Delta t = \text{const}$, relative to K, we obtain

$$K = \frac{1}{t_2 - t_1} \ln \frac{\Delta x_1}{\Delta x_2} \tag{2}$$

In the linear range of the sensitivity of the detector the area of the chromatographic peak is proportional to the amount of substance. Then in the case of the liberation of one gaseous product

$$K = \frac{1}{t_2 - t_1} \ln \frac{S_1}{S_2} \tag{3}$$

and in the case of the liberation of n gaseous products

$$K = \frac{1}{t_2 - t_1} \ln \frac{\sum_{i=1}^{n} f_i S_i^{(1)}}{\sum_{i=1}^{n} f_i S_i^{(2)}}$$
(4)

where f_i are the molar correction factors. Taking $t_1 = 0$, we obtain

$$\ln S_2 - \ln S_1 = -Kt_2 \tag{5}$$

Equation (5) makes it possible to calculate the rate constants from the chromatographic data. Employing this method, the rate constants of the following reactions were determined at $t = 20^{\circ}C$.

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TABLE 1

H ₂ SO ₄ concen- tration,%	K·10-4, sec-1	
	chromatography	from [3]
95,0 94,0 93,0 92,0 90,0	14,513,612,411,58,3	15,3 13,1 13,0 12,0 8,0

Fig. 1. Change in volume of liberated gas with time: 1) TMSPA in 96% H_2SO_4 ; 2) TMSPA in 92% H_2SO_4 ; 3) DMBSPA in 96% H_2SO_4 ; V_{∞} is the limiting volume of gaseous reaction products; V_t is the volume of gas liberated in time t.

 $(CH_3)_3 \operatorname{Si} (CH_2)_2 \operatorname{COOH} + H_2 \operatorname{SO}_4 \rightarrow (CH_3)_2 \operatorname{Si} (CH_2)_2 \operatorname{COOH} + CH_4$ (I) $| \\ OSO_2 OH$

 $(C_{4}H_{9}) (CH_{3})_{2} Si (CH_{2})_{3} COOH + H_{2}SO_{4} \rightarrow nC_{4}H_{40} + n (CH_{3})_{2} Si (CH_{2})_{2} COOH + m (CH_{3}) (C_{4}H_{9}) Si \\ | \\ OSO_{2}OH + MOSO_{2}O | (CH_{2})_{2} COOH + mCH_{4}$ (II)

With a large excess of H_2SO_4 these reactions are pseudomonomolecular, as is evidenced by the experimental data given in [3,4], and also by the data obtained by us (Fig. 1). The obtained values of the constants for reaction (I) (Table 1) are in good agreement with the data given in [3].

The rate constant of reaction (II) was determined at a H_2SO_4 concentration of 96% by two methods: chromatographically and volumetrically. The agreement in the values of the constants, $K_{chrom.} = 28.8 \cdot 10^{-4}$ and $K_{volum.} = 25 \cdot 10^{-4}$ (sec⁻¹), can be considered to be quite satisfactory. Based on the GLC data, the gas liberated in reaction (II) contained 59 ± 2 mole % of CH₄ and 41 ± 2 mole % of C₄H₁₀. A change in the composition of the gas during the reaction process was not observed.

EXPERIMENTAL METHOD

The β -trimethylsilylpropionic (TMSPA) and β -dimethylbutylsilylpropionic (DMBSPA) acids were synthesized as described

in [6], and had the following constants: TMSPA, bp 114-116° (20 mm); n_D^{20} 1.4290; d_4^{20} 0.9177; DMBSPA, bp 122-124°C (5 mm); n_D^{20} 1.4440; d_4^{20} 0.9115.

A diagram of the apparatus is shown in Fig. 2. For the experiments we used a Tswett-4 chromatograph, which was equipped with a detector based on the heat conductivity. For the separation of the gases we used two columns, with a length of 1 and 2 m, that were connected in series and respectively filled with 1-3% of Apiezon L deposited on Chezosorb 0.20-0.36 and 2-10% of poly(ethylene glycol) 2000 deposited on Chezosorb 0.20-0.36. The reaction vessel represented a three-necked flask that was equipped with a rubber seal and tubes for the entrance and exit of the gas. The sample of the studied acid (0.1-0.2 g) was added by means of a syringe through the rubber seal into the reaction vessel, which contained 25 ml of H_2SO_4 and was thermostatted at $20 \pm 0.5^\circ$. The gas samples were taken at 1-min intervals. The flow rate of the gas through the reactor was maintained constant at 176 ml/min. Helium was used as the carrier gas and for purging the reaction vessel. The rate constant of reaction (II) was determined volumetrically using the method described in [2].



Fig. 2. Block diagram of apparatus: G = gas for purging the reaction vessel; V = precision control valve; Fm = flow meter; S = sample of studied substance; R = reaction vessel; B = batcher; CG = carrier gas; CC = chromatographiccolumn; <math>D = detector; A = automatic recorder.

CONCLUSIONS

It was shown that the reaction gas chromatography method can be used to determine the rate constants for the cleavage of the Si-C bonds in β -trialkylsilylpropionic acids under the influence of sulfuric acid. We determined the rate constants for the cleavage of the Si-C bonds in the β -trimethylsilylpropionic and β -dimethylbutylsilylpropionic acids under the influence of sulfuric acid.

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