TRANSFORMATIONS OF 2-METHYLTHIACYCLOBUTANE IN THE PRESENCE OF ALUMINUM OXIDE

A. K. Yus'kovich, T. A. Danilova,
and E. A. Viktorova

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The transformations of 2-methylthiacyclobutane at 150-350°C in the presence of γ-Al_2O_3 samples with different aprotic acidities were investigated. It was established that the sulfide undergoes isomerization via two pathways, viz., with ring expansion to a five-membered ring and with opening at one C—S bond to give an unsaturated thiol. An experimental confirmation of the consecutive formation of hydrogen sulfide from a one-ring sulfide through a step involving the formation of an unsaturated thiol was obtained for the first time. The transformations are realized as a result of both ionic and polymerization-depolymerization processes.

The expansion of the 2-methylthiacyclobutane (I) ring to a five-membered ring (in 16% yield) in the case of contact with aluminum oxide at 350°C was noted by Yur'ev and co-workers [1]. They did not isolate reaction products other than thiacyclopentane (II) and did not express any ideas regarding the mechanism of this isomerization.

In the present research we studied the transformations of sulfide I on γ-aluminum oxide samples calcined at various temperatures, which made it possible to obtain catalysts with different aprotic acidities. The degree of conversion of sulfide I at 150-350°C* depends directly both on the acidity of the γ-Al_2O_3 sample and the temperature (Table 1).

In contrast to the data in [1], it was established that the isomerization of sulfide I proceeds via two pathways: 1) with ring expansion to sulfide II; 2) with ring opening at one C—S bond to give unsaturated but-1-ene-4-thiol (III). The latter undergoes partial conversion to n-butanethiol (IV), and both compounds are present in the catalyzates in identical amounts.

Ring expansion of sulfide I is promoted by: 1) an increase in the acidity of the catalyst — on a sample of K-0.4 isomerization takes place at 150°C (Fig. 1); 2) an increase in the temperature; however, intensive hydrogen sulfide formation and a decrease in the yield of sulfide II to zero are observed on samples of K-0.3 and K-0.4 at temperatures above 250°C. A 13% yield of sulfide II was obtained on a sample of K-0.1 at 300-350°C (Fig. 1).

On a sample of K-0.1 both processes — ring expansion and the formation of an unsaturated thiol — take place simultaneously up to 250°C with prevalence of the second reaction (Fig. 2). The maximum yield of III and IV combined is 27% (Table 1). The sharp decrease in the yield of thiols and the increase in the yield of hydrogen sulfide and butenes at temperatures above 250°C constitute evidence for the intermediate formation of an unsaturated thiol in the cleavage of sulfide I with the liberation of H_2S.

The direct dependence of the yield of sulfide II, hydrogen sulfide, and butenes (and, consequently, the intermediately formed thiols) on the acidity of the catalyst (Fig. 1 and Table 1) and the absence of a contribution of a thermal process to the transformations of sulfide I constitute evidence in favor of isomerization of the latter via an ionic scheme. Secondary transformations are realized via a polymerization-depolymerization mechanism (see scheme on next page.)

This scheme is in good agreement with the results of our previous studies in which we demonstrated the ability of monocyclic sulfides to split out a hydride ion in the presence

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*In the absence of a catalyst sulfide I remains unchanged at these temperatures.

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 184-187, February, 1982. Original article submitted August 5, 1981.

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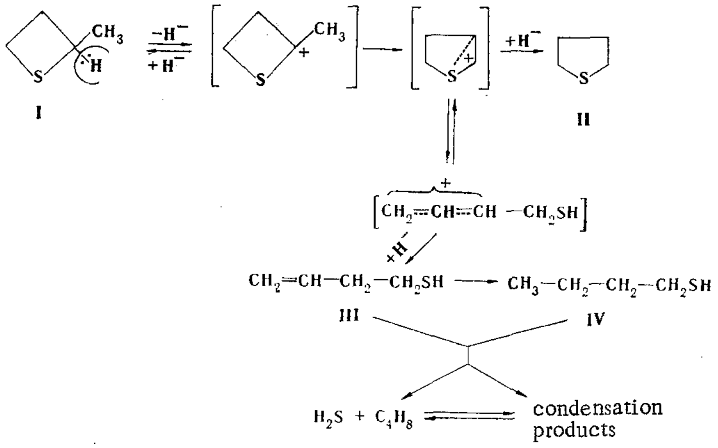
TABLE 1. Dependence of the Degree of Conversion of 2-Methylthiacyclobutane and the Formation of Reaction Products on the Acidity of the Catalyst (at 250°C and space velocity 1.0 h^{-1})

Catalyst	Arbitrary designation of the catalyst	Degree of conversion	Yield, %				
			II	H_2S	C_4H_8	III+IV	condensation products
Al_2O_3 (300)*	K-0,1†	91 (57)‡	7	9	14	27	34
Al_2O_3 (550)	K-0,3	96 (83)	8	17	27	17	27
Al_2O_3 (580)	K-0,4	98 (90)	10	21	34	13	20

*The temperature of prior calcination of γ-Al_2O_3 is indicated in parentheses.

†The numbers designate the overall acidities in milliequivalents of n-$C_4H_9NH_2$ per gram of catalyst.

‡For the sake of clarity, the degree of conversion at 200°C is presented in parentheses.



of hydride-ion acceptors [2]; the aprotic centers of γ-Al_2O_3 act as the acceptors in this case. A thermodynamic evaluation of the probability of cleavage of monocyclic sulfides in the absence of hydrogen at one and two C–S bonds to give an unsaturated thiol or hydrogen sulfide and dienes [3, 4], respectively, showed that the first reaction is thermodynamically possible at low temperatures (17-227°C); however, the probability of the second reaction is negligible even at high temperatures. The formation of H_2S from sulfide II is excluded, since it remains unchanged in the presence of γ-Al_2O_3 up to 400-450°C. The material set forth above constitutes evidence in favor of the formation of H_2S from unsaturated thiol III.

The transformations of thiols III and IV and sulfide II in the presence of low-acidity modified samples of an aluminosilicate catalyst [3, 5, 6] may serve as a confirmation of the contribution of polymerization-depolymerization processes. Saturation of unsaturated thiol III to thiol IV and the formation from them and from sulfide II of isomeric C_4H_8 olefins instead of butadiene were also observed on these catalysts, which indicates redistribution of hydrogen with the participation of the condensation products on the catalyst. This process is well known [3, 7, 8]. The formation of such polymeric deposits on a catalyst under the conditions of the present research from thiols III and IV is confirmed by the symbatic change in the yield of the latter and the accumulation of condensation products on the catalyst (Fig. 2 and Table 1).

The presence of unsaturated thiol III in the products of transformation of sulfide I is of particular interest: In the case of aliphatic sulfides a consecutive mechanism for the formation of H_2S from them through thiols has been proved [3, 9-11], whereas this sort of process has only been postulated for monocyclic sulfides [3, 6, 12, 13]. In the present research experimental confirmation of the correctness of this assumption was obtained for the first time.

Thus when sulfide I is placed in contact with γ-Al_2O_3, it is initially converted to sulfide II and thiol III. The formation of the remaining reaction products is a secondary process. For the realization of isomerization it is expedient to use catalysts with a low aprotic acidity at moderate temperatures (250-300°C).

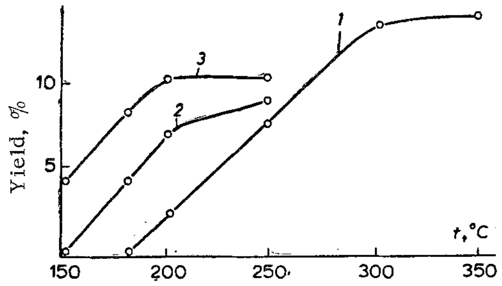


Fig. 1

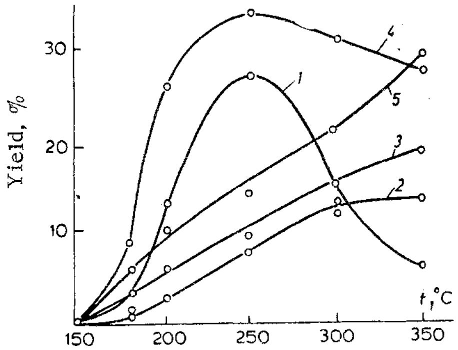


Fig. 2

Fig. 1. Dependence of the yield of thiacyclopentane on the temperature (at a space velocity of 1.0 h^{-1}): 1) K-0.1; 2) K-0.3; 3) K-0.4.

Fig. 2. Dependence of the yield of products of the conversion of 2-methylthiacyclobutane on the temperature (on K-0.1 at a space velocity of 1.0 h^{-1}): 1) $C_4H_7SH + C_4H_9SH$; 2) thiacyclopentane; 3) H_2S; 4) condensation products; 5) C_4H_8.

EXPERIMENTAL

2-Methylthiacyclobutane (I) was synthesized in 42% yield by the method in [14] and had bp 105°C (756 mm), d_4^{20} 0.9537, and n_D^{20} 1.4882.

Preparation of the Catalysts (Table 1). Industrial-grade aluminum oxide was calcined at 300, 550, and 580°C in a muffle furnace for 6 h. The grain diameter was 1-2 mm. The acidity of the catalyst surface and its character were determined by nonaqueous titration with n-butylamine in the presence of Hammett indicators (overall acidities H_0) or in the presence of arylmethanols (protic acidities H_R) [15].

The method used to carry out the experiments in a flow apparatus was described in [16]. The experiments were carried out at 150, 180, 200, 250, 300, and 350°C at a space velocity of 1.0 h^{-1}.

The liquid reaction products were analyzed by gas-liquid chromatography (GLC) [with a column filled with 10% Apiezon N on Chromosorb W, 60-80 mesh (300-400 μ) at 90-100°C with helium as the carrier gas, a flow rate of 40-50 ml/min, a column length of 7 m, and a column diameter of 4 mm; with a column filled with 15% PEGA (polyethylene glycol adipate) on Chromaton (40-60 mesh) at 90-100°C with helium as the carrier gas, a flow rate of 40-50 ml/min, a column length of 1.8 m, and a column diameter of 4 mm] and chromatographic mass spectrometry with an LKB-2091 spectrometer (Sweden) (with a column filled with 10% PEGA on Sferokhrom at 50-150°C with helium as the carrier gas, a flow rate of 40 ml/min, a column length of 6 m, and a column diameter of 5 mm). The hydrocarbon gases were analyzed with a Khrom-2 chromatograph (the liquid phase was triethylene glycol n-butyl ether, the column length was 50 m, and the temperature was 50°C), while the hydrogen sulfide was trapped in the form of CdS and was determined by iodometric titration [17].

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DEPENDENCE OF THE COMPOSITION OF THE PRODUCTS OF THERMAL FRAGMENTATION OF THIACYANINE DYES ON THE LENGTH OF THEIR POLYMETHINE CHAIN

V. G. Khesin, M. A. Al'perovich,
P. I. Abramenko, R. D. Raikhina,
and T. D. Medvedeva

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The pathways of thermal fragmentation of thiacyanine dyes with different lengths of the external polymethine chain were investigated. The results of thermolysis of the thiacyanines are compared with the results of quantum-chemical calculations of their molecules.

When thiapolycarbocyanines I are heated above their melting points, they are converted to dyes with a shorter polymethine chain; when the chain length is increased (when n is increased), the yields of the dyes decrease markedly, and larger amounts of products that absorb in the UV portion of the spectrum, the structures of which have not been established, are formed [1]. In thiapolycarbocyaninium iodide series I when n is increased, the temperature at which the compounds melt (accompanied by decomposition of the dyes) gradually decreases, which constitutes evidence for lability of the bonds.

To estimate the strength of the bonds in dyes I (n = 1-5) we subjected the indicated compounds in the S_0 state to quantum-chemical calculation by the Pariser—Parr—Pople (PPP) method with the program in [2]. The results of the calculation are given in Table 1.

An analysis of the data in Table 1 shows that the magnitude of the positive charge on the nitrogen and sulfur atoms of the thiazole rings and on the odd-numbered carbon atoms of the polymethine chain decreases as the polymethine chain becomes longer; in the case of all of the examined dyes the carbon atoms in the 2 and 2' positions, which are closer to the center of symmetry of the molecule, have the greatest q_r values. The negative charges on the even-numbered carbon atoms change only slightly for the various n values: In contrast to the $+q_r$ values, the $-q_r$ values decrease from the ends to the center of the polymethine chain. It is interesting that the bond orders decrease as the polymethine chain of the thiacyanines becomes longer, and the polarities of the bonds in the thiazole rings increase; the μ values and the uniformity of the p_{rs} values along the polymethine chromophore decrease. In conformity with the F values [3], the ring nitrogen atoms and the carbon atoms in the 8 and 8' positions should be most susceptible to the effect of radical reagents; as n increases, this

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