EFFECT OF HIGH PRESSURE ON COMPETING REACTIONS OF RADICAL DECOMPOSITION AND REARRANGEMENT OF TRIMETHYL(CUMYLPEROXY)SILANE

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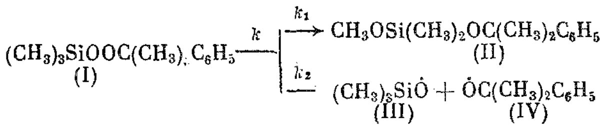
UDC 541.12.034.2:541.515:542.92:547.1'128

As was shown pereviously [1, 2], the thermal rearrangement rate of organosilicon peroxides $-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OO}\overset{|}{\underset{|}{\mathrm{Si}}}- \rightarrow -\mathrm{O}\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}\overset{|}{\underset{|}{\mathrm{Si}}}-$ in anisole increases with increase in the pressure, i.e., a volume decrease occurs when the transition state is formed from the starting peroxide, which corresponds to the known concept that the transition state has a cyclic structure. The volume activation effect of these reactions ($\Delta V^{\neq}$) is -8 ± 2 cm^2/mole.

We found that the thermal transformations of trimethyl(cumylperoxy)silane (I), which lead to the formation of rearrangement product (II) and predominantly the reaction products of the free radicals that arise from (I), are also substantially accelerated by pressure, except for the pressure range of 100-250 MPa, where the reaction rate is practically constant (Fig. 1).



$$\underset{(I)}{(CH_3)_3SiOOC(CH_3)_2C_6H_5} \xrightarrow{k} \begin{cases} \xrightarrow{k_1} \underset{(II)}{CH_3OSi(CH_3)_2OC(CH_3)_2C_6H_5} \\ \xrightarrow{k_2} \underset{(III)}{(CH_3)_3Si\dot{O}} + \underset{(IV)}{\dot{O}C(CH_3)_2C_6H_5} \end{cases}$$

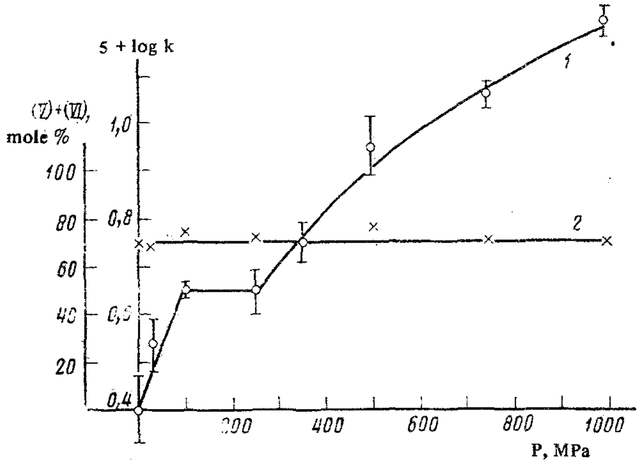


Fig. 1. 1) log K as a function of pressure for thermal transformation of (I) at 443°K in anisole (C_0 = 0.2 mole/liter), k = first-order reaction rate constant; 2) amount of transformation products of radical (IV) in mole % as a function of reacted (I) at various pressures (GLC analysis at 100% conversion of (I)).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1659-1661, July, 1983. Original article submitted December 30, 1982.

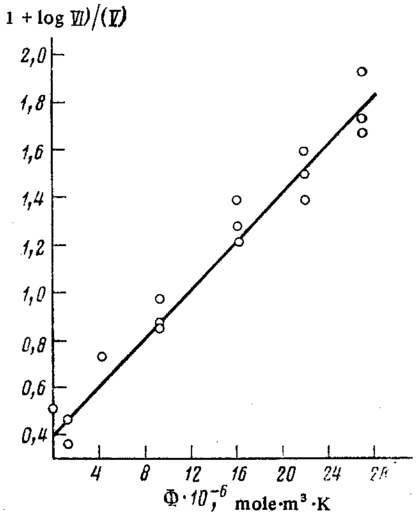
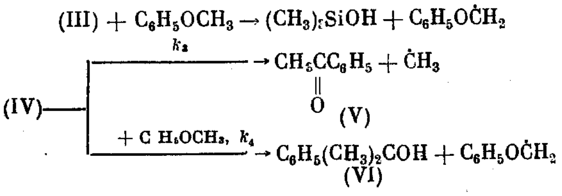


Fig. 2. log (VI)/(V) in moles/mole of reacted (I) as a function of parameter $\Phi = P/R \ln 10(1 + bP)$, $b = 9.2 \cdot 10^{-4}$ MPa^{-1}.

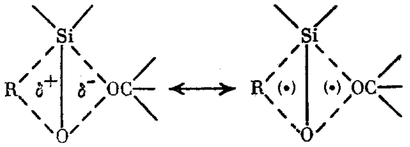


$$(III) + C_6H_5OCH_3 \rightarrow (CH_3)_3SiOH + C_6H_5O\dot{C}H_2$$

$$(IV) \xrightarrow{k_3} CH_3\underset{\underset{O}{\parallel}}{C}C_6H_5 + \dot{C}H_3 \quad (V)$$

$$(IV) \xrightarrow{+ C_6H_5OCH_3,\ k_4} C_6H_5(CH_3)_2COH + C_6H_5O\dot{C}H_2 \quad (VI)$$

Taking the last fact into account it may be stated that the dependence of log k on the pressure has an unusual and as yet unexplained character, but still the amount of radical (IV) that is obtained as a reaction result remains constant (~70%) at all pressures up to 1000 MPa (see Fig. 1). Hence it may be concluded that for (I) in anisole the $\Delta V^{\neq}$ values during rearrangement and decomposition into free radicals are close and have a negative value. This result confirms the assumption that the transition states have the same cyclic structure for both rearrangement and homolysis [3]:



According to the above given scheme of the process, the mole ratio of products (VI) and (V) is expressed as

$$\lambda = \frac{(VI)}{(V)} = \frac{k_4 [C_6H_5OCH_3]}{k_3}$$

and should increase with increase in the pressure, since k_4 characterizes the bimolecular reaction of cleaving an H atom, while k_3 expresses the monomolecular reaction, accompanied by the cleavage of a methyl radical. The obtained data confirm this conclusion: $\lambda = 0.25$ at atmospheric pressure, and $\lambda = 6.0$ at 1000 MPa. The function log λ vs pressure does not exhibit noticeable deviations from the usually observed functions. This can be seen from Fig. 2, where log λ is plotted against parameter Φ, which is the pressure function and characterizes its value in the equation for a linear ratio of the free energies [4]. Within the limits of experimental error, the obtained data satisfy this equation (see Fig. 2), which, employing the method of least squares, was used to calculate the total volume activation effect $\Delta V_c^{\neq}$, which is equal to -21.1 ± 1.8 cm³/mole.

In [5] it was shown that the analogous $\Delta V_c^{\neq}$ value for tert-butoxy radicals is also negative, and in absolute value is greater the higher the reaction rate constant for the cleavage of an H atom from the solvent by the radical. An analysis of the data in [6-8] shows that the tert-butoxy radical is ~1.5 times more active than the cumyloxy radical, while anisole is equally more active than toluene, and consequently it is logical to compare the $\Delta V_c^{\neq}$, obtained in the present paper, with the $\Delta V_c^{\neq}$ for the reactions of the tert-butoxy radical in toluene [5]. The latter at 323°K is -14 cm^3/mole. Calculation by the method given in [4] gives a value of -20.5 cm^3/mole for 443°K (the temperature of our experiments), which coincides with that found when studying the transformations of peroxide (I). As a result, a change in the (VI)/(V) ratio with increase in the pressure does not contradict the scheme of the process, which predicts the formation of (V) and (VI) as the result of the reactions of free radical (IV).

It should be mentioned that in the experiments at atmospheric (or reduced) pressure the sum of products (II), (V), and (VI) in moles per mole of reacted (I) is close to theory, i.e., the character of the transformations of (I) corresponds quantitatively to the above given scheme of reactions. However, as was shown by special experiment, at high pressures the rearrangement product (II) is capable of undergoing further transformations, whose character could not be established, but it was shown that these transformations do not affect the amounts of (V) and (VI). Consequently, the amount of (I) that is converted to give (II) can be determined from the difference (I) − [(V) + (VI)], in which connection this difference is constant at all pressures.

EXPERIMENTAL

Trimethyl(cumylperoxy)silane (I) (99% pure when based on peroxide oxygen) was synthesized as described in [9]. The IR spectra testify to the absence of hydroperoxides and hydroxy compounds in (I).

The experimental procedure and the analysis method for peroxide are described in [1]. It was shown by special experiments that the temperature inside the Teflon ampul reaches the given temperature in 25-30 min after turning on the heat. In addition, there is an uncontrolled period when raising the pressure up to the desired value. Consequently, in calculating the rate constants we took into account the amount of decomposed peroxide while bringing the temperature and pressure up to the given values in the following manner. After raising the pressure up to 10 MPa the heat was turned on and the temperature was brought up to the given value in 30 min, and then the necessary pressure was created and it was reduced to the possible minimum in 1 min, after which the reactor was cooled in 10 min by removing the electric heat, and then under a stream of cold water, to ~20°C. The ampul was emptied and the solution was titrated, and this peroxide concentration was taken as the starting concentration at the given pressure. On the average ~10% of (I) was consumed during the uncontrolled period.

The reaction products were analyzed by GLC on a Tsvet-104 instrument using a 100 × 0.4 cm steel column packed with 15% Carbowax 20 M deposited on Chromatone N-AW-HMDS (0.2-0.25 mm), a temperature of 180°, and helium as the carrier gas at a flow rate of 67 ml/min.

The rearrangement product (II) of peroxide (I) was mixed with acetophenone and dimethylphenylcarbinol in anisole (0.2 mole/liter of (II)) and kept at 1000 MPa and 443°K for 10 half-lives of (I). After experiment the concentration of acetophenone and dimethylphenylcarbinol did not change, while the concentration of (II) decreased by 4-5 times.

CONCLUSIONS

1. The character of the change in the ratio of the amounts of dimethylphenylcarbinol and acetophenone, obtained by the transformations of trimethyl(cumylperoxy)silane in anisole, with increase in the pressure indicates that they are formed by reactions that directly involve the free cumyloxy radicals.

2. The rate constants of the competing reactions for the radical decomposition and rearrangement of trimethyl(cumylperoxy)silane increase the same in a broad range of increasing the pressure, which testifies that the transition states of these reactions have close structures.

LITERATURE CITED

1. V. A. Yablokov, A. V. Ganyushkin, M. Ya. Botnikov, and V. M. Zhulin, Izv. Akad. Nauk SSSR, Ser. Khim., 484 (1978).
2. V. A. Yablokov, A. V. Ganyushkin, M. Ya. Botnikov, and V. M. Zhulin, Izv. Akad. Nauk SSSR, Ser. Khim., 950 (1980).
3. V. A. Yablokov, Usp. Khim., 49, 1711 (1980).
4. B. S. El'yanov and E. M. Vasylvitskaya, Rev. Phys. Chem. Jpn., 50, 169 (1980).
5. V. M. Zhulin and B. I. Rubinshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 2201 (1976).
6. J. H. T. Brook, Trans. Faraday Soc., 53, 327 (1957).
7. K. Uneyama, H. Namba, and Sh. Oae, Bull. Chem. Soc. Jpn., 41, 1928 (1968).
8. E. Niki, Y. Kamiya, and N. Ohta, Bull. Chem. Soc. Jpn., 41, 1466 (1968).
9. E. Buncel and A. E. Davies, J. Chem. Soc., 1550 (1958).

ETHYNYLATION OF SALTS OF PHOSPHORUS THIOACIDS WITH ETHYNYL BROMIDES IN THE PRESENCE OF CuCl

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UDC 542.97:547.1'118

The substituted S-ethynyl esters of thiophosphoric acids are of interest as potential insecticides and acaricides. Previously [1] we described a method for obtaining such esters, which consists in reacting magnesium bromoacetylides with dialkoxyphosphorylsulfenyl chlorides, but here the S-ethynyl thiophosphates are obtained in low yield.

We attempted to obtain the S-hexyne and ethylmercaptopropyne esters of diethylthiophosphoric acid by the alkynylation of potassium diethyl thiophosphate with the appropriate substituted ethynyl bromides, but only the starting reactants were isolated.

$$(EtO)_2P(S)OK + BrC \equiv CX - // \rightarrow (EtO)_2P(O)SC \equiv CX$$

where X = Bu, CH_2SEt.

It is known that many ethynylation reactions are catalyzed by metal chlorides. In this connection we studied the catalytic effect of cuprous chloride when ethynyl bromides are reacted with the salts of phosphorus monothioacids. It proved that the reaction of a potassium dialkyl thiophosphate with substituted ethynyl bromides can be run in the presence of equimolar amounts of CuCl in polar solvents with a 60-80% yield of the S-ethynyl esters (Table 1).

$$(RO)_2P(S)OK + Br{-}C{\equiv}C{-}X \xrightarrow{CuCl} (RO)_2P(O)SC{\equiv}C{-}X \qquad (A)$$

where R = alkyl and X = alkyl, alkylmercaptomethyl, alkoxymethyl, hydroxymethyl, acyloxymethyl, and phenyl.

The reaction can only be run in polar solvents like alcohol, acetone, THF or MeCN. It does not go in less polar solvents like ether or benzene. The structure of the obtained compounds is confirmed by the IR spectra, which have absorption bands in the 1270 (P=O) and 2195–2210 cm^{-1} (C≡C) regions for all of the compounds (Table 2).

Compounds containing an OH group in the unsaturated radical, proved to be unstable and their structure, besides the IR spectra, was proved by converting them to the stable

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