Induced decomposition of acetylcyclohexylsulfonyl peroxide

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The kinetics of thermal decomposition of acetylcyclohexylsulfonyl peroxide is studied in a *n*-decane solution in an oxygen atmosphere (303—333 K) and under anaerobic conditions (313—333 K); the reaction products are also studied in a cyclohexane solution under oxygen-free conditions (323 K). In the absence of oxygen, the reaction is found to proceed *via* a chain-radical mechanism. Some kinetic parameters of the process are determined.

Key words: acetylcyclohexylsulfonyl peroxide, induced decomposition.

Acetylcyclohexylsulfonyl peroxide (ACSP) was first described by R. Graf.[1] The products of ACSP thermal decomposition were thoroughly studied later[2], and a corresponding effective rate constants were determined for the fixed concentration of ASCP in different solvents in a nitrogen atmosphere.

In this work, the induced decomposition of ACSP is found on the basis of an investigation of the kinetics and reaction products.

Experimental

ACSP and cyclohexanesulfonic acid were synthesized according to the technique described earlier;[1] the content of ACSP in the specimens used was above 96 %. The solvents (*n*-decane and cyclohexane) were purified by the known technique.[3]

The content of ACSP in the solution was determined by iodometric titration.[4] Cyclohexanesulfonic acid was analyzed by potentiometric titration.[5] The total amount of gases evolved (CO_2 and CH_4)[1,2] was measured by the manometric method.[6] Cyclohexyl cyclohexanesulfonate was identified by elemental analysis and also by ^{13}C and ^{1}H NMR spectroscopy.

Reaction products. The products of the anaerobic thermolysis of ACSP were studied at 323 K in a cyclohexane solution. After the reaction was completed (ACSP conversion of 98 %), cyclohexanesulfonic acid was extracted with water, and cyclohexyl cyclohexanesulfonate was isolated from the organic phase. ^{13}C NMR spectrum ($CDCl_3$), δ: 60.56 (d, C(1)); 26.58 (t, C(2), C(6)); 25.11 (t, C(3), C(5)); 25.02 (t, C(4)); 80.25 (d, C(7)); 32.38 (t, C(8), C(12)); 23.67 (t, C(9), C(11)); 25.11 (t, C(10)); ^{1}H NMR spectrum ($CDCl_3$), δ: 2.94 (tt, 1 H, C(1)H, *J* = 12.0, 3.5 Hz); 4.63—4.75 (m, 1 H, C(7)H); 1.2—2.2 (m, 20 H, CH_2). Found (%): C, 58.56; H, 8.50; S, 12.99. Calculated (%): C, 58.54; H, 8.94; S, 13.01.

Under these conditions, the yield of (CO_2+CH_4), $C_6H_{11}S(O_2)OC_6H_{11}$, and $C_6H_{11}S(O_2)OH$ was 184, 83, and 10 mol. %, respectively (based on the ACSP consumed). Together with these products, the $C_6H_{11}S(O_2)OCH_3$ ester is also formed in small amount, the yield estimated by ^{1}H NMR is 2 to 4 %. These data satisfactorily agree with the results obtained earlier[2] for the reaction products.

The reaction kinetics was studied in a glass thermostated reactor by the sampling of the reaction solution to follow the ACSP consumption. When the process was carried out in an oxygen atmosphere, the latter was passed through the solution during the experiment (the reactor was equipped with a reflux condenser). The thermolysis of ACSP in the absence of oxygen was carried out as follows: argon was bubbled through the reaction mixture for 20 to 25 min at room temperature, then the thermostat was switched on, the reflux condenser was replaced by a capillary tube for the removal of the gases evolved, and the Ar bubbling was terminated. Using this technique, the reaction proceeds under a small pressure of CO_2 and CH_4 (traces of oxygen are consumed during the first seconds of the process).

Results and Discussion

Kinetics of ACSP decomposition. The typical kinetic curves of the thermolysis of ACSP in an *n*-decane solution under an O_2 atmosphere and their semilogarithmic anamorphoses are represented in Fig. 1, from which it follows that the rate of thermolysis W_0 is described by the first-order equation:

$$W_0 = k_0 \cdot C, \qquad (1)$$

where k_0 is the rate constant of the reaction in the presence of oxygen, *C* is the concentration of ACSP.

Using the results of determination of k_0 at different temperatures and starting peroxide concentrations C_0 (Table 1), we found:

$$\log k_0 = (16.2\pm0.5) - (123\pm3)/\theta \ (s^{-1}), \qquad (2)$$

where $\theta = 2.3RT$ kJ mol^{-1}.

The best description of the kinetic curves of the decomposition of ACSP under an Ar atmosphere is

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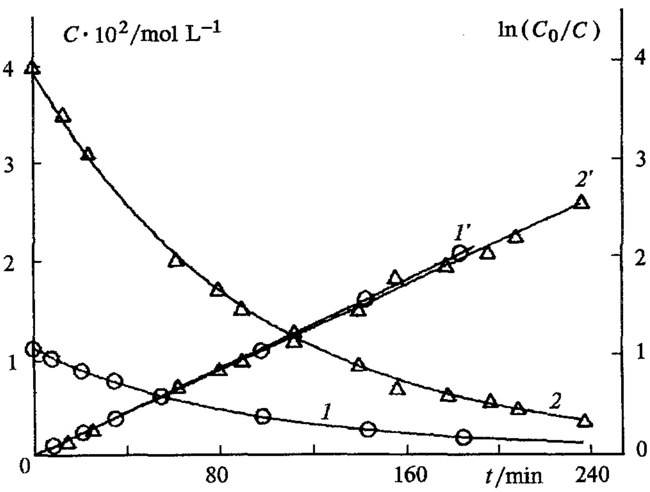


Fig. 1. Typical kinetic curves (*1, 2*) for the decomposition of ACSP in oxygen atmosphere (50 °C) and their semilogarithmic anamorphoses (*1', 2'*).

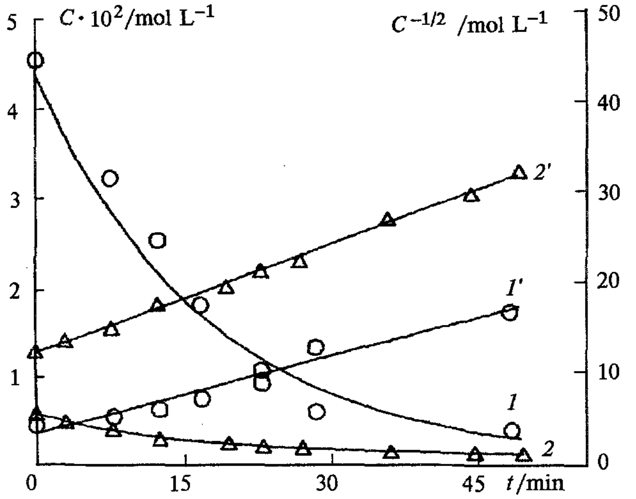


Fig. 2. Typical kinetic curves (*1, 2*) for the decomposition of ACSP in oxygen atmosphere (50 °C) and their linearization in the coordinates of kinetic sesqui-order equation (*1', 2'*).

achieved by a sesqui-order equation (Fig. 2):

$$W_{Ar} = k_{Ar} \cdot C^{1.5}, \tag{3}$$

where W_{Ar} and k_{Ar} are the rate constant and effective rate constant, respectively, of the reaction in an inert atmosphere.

Taking account the effective rate constant k_{Ar} under the different starting conditions listed in Table 1, we obtain

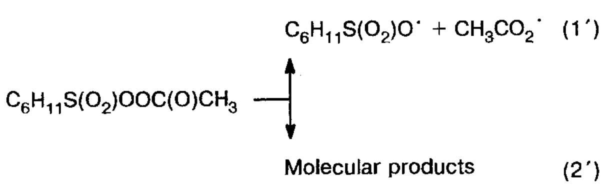
$$\log k_{Ar} = (13.2 \pm 0.5) - (93 \pm 3)/\theta \ (\mathrm{L^{0.5}\ mol^{-0.5}\ s^{-1}}). \tag{4}$$

It follows from equations (1)—(4) that

$$W_{Ar} / W_0 = k_{Ar}\sqrt{C} / k_0 = 10^{-3.11+30.6/\theta} \cdot \sqrt{C}. \tag{5}$$

As seen from Table 1, $W_{Ar}/W_0 \approx 5 \div 23$, *i.e.* , the decomposition of ACSP in an inert atmosphere is significantly faster than that in an oxygen atmosphere.

Mechanism of the process. Using the obtained results and literature data[2], the chain-radical mechanism can be proposed for the decomposition of ACSP under anaerobic conditions that is analogous to the scheme of the decomposition of acetyl peroxides:[7]



$$\mathrm{C_6H_{11}S(O_2)OOC(O)CH_3} \rightarrow \mathrm{C_6H_{11}S(O_2)O^{\bullet} + CH_3CO_2^{\bullet}} \quad (1')$$

$$\mathrm{C_6H_{11}S(O_2)OOC(O)CH_3} \rightarrow \text{Molecular products} \quad (2')$$

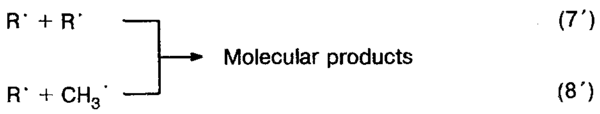
$$\mathrm{C_6H_{11}S(O_2)O^{\bullet} + RH \longrightarrow C_6H_{11}S(O_2)OH + R^{\bullet}} \quad (3')$$

$$\mathrm{CH_3CO_2^{\bullet} \longrightarrow CH_3^{\bullet} + CO_2} \quad (4')$$

$$\mathrm{CH_3^{\bullet} + RH \longrightarrow CH_4 + R^{\bullet}} \quad (5')$$

$$\mathrm{R^{\bullet} + C_6H_{11}S(O_2)OOC(O)CH_3 \longrightarrow CH_3CO_2^{\bullet} + C_6H_{11}S(O_2)OR} \quad (6')$$

The limiting stage of the three-centered chain process is reaction (6') that is indicated by the reaction order with respect to ACSP. This fact means that the chain break involves the R$^{\bullet}$ radicals:



$$\mathrm{R^{\bullet} + R^{\bullet}} \rightarrow \text{Molecular products} \quad (7')$$

$$\mathrm{R^{\bullet} + CH_3^{\bullet}} \rightarrow \text{Molecular products} \quad (8')$$

The role of the $\mathrm{CH_3CO_2^{\bullet}}$ radicals in the chain break can be neglected, because they decompose very quickly by reaction (4'); according to the data published earlier,[8] k_4 ~10^9 s^{-1}. The rate constant of the reaction between oxysulfonyl radicals and hydrocarbons $k_3 > 10^8$ L (mol s)$^{-1}$ (see Ref. 9); hence, under the conditions of our experiments, they are virtually completely consumed in reaction (3') and do not recombine with radicals R$^{\bullet}$. Considering that the yield of $\mathrm{C_6H_{11}S(O_2)OCH_3}$ is rather small, we can also ignore the reaction

$$\mathrm{CH_3^{\bullet} + C_6H_{11}S(O_2)OOC(O)CH_3 \rightarrow CH_3CO_2^{\bullet} + C_6H_{11}S(O_2)OCH_3}.$$

Table 1. Dependence of rate constants (k_0/c^{-1} and k_{Ar}/L$^{0.5}$ mol$^{-0.5}$ s^{-1}) on temperature and starting concentration of ACSP (C_0 /mol L^{-1})

T/K	$C_0 \cdot 10^2$	$k_0 \cdot 10^4$	$k_{Ar} \cdot 10^3$	W_{Ar}/W_0[a]
303	0.50	0.10	—	—
	4.40	0.10	—	—
313	1.10	0.44	—	—
	3.30	—	4.5	18.1
	4.00	—	4.6	19.9
	4.30	0.43	—	—
	5.40	—	4.2	23.1
323	0.15	1.80	—	—
	0.60	—	13.0	5.3
	1.10	1.80	—	—
	2.30	—	13.5	10.3
	2.90	—	12.9	11.8
	4.00	1.90	—	—
	4.60	—	13.0	14.8
	4.60	—	13.2	14.8
	15.40[b]	1.40	—	—
333	0.63	7.40	—	—
	1.27	7.40	—	—
	1.74	—	36.1	6.5
	2.70	—	36.1	8.1
	2.80	—	39.0	8.2
	4.67	8.60	—	—
	4.80	—	38.1	10.7
	4.90	8.00	—	—
	4.90[c]	8.40	—	—

[a] Calculated by formula (5). [b] In a cyclohexane solution. [c] In air.

Thus, the reaction rate in the stationary regime is described by the following equation under the condition of long chains:

$$W_{Ar} = \frac{k_0 C\sqrt{2k_1 C}}{\sqrt{2k_7 + (k_6 C / k_5[\mathrm{RH}]) \cdot 2k_8}} \quad (6)$$

From (3) and (6), we obtain:

$$k_{Ar} = \frac{k_6\sqrt{2k_1}}{\sqrt{2k_7 + (k_6 C / k_5[\mathrm{RH}]) \cdot 2k_8}}.$$

Since the experimental effective rate constant k_{Ar} is independent, within the error of its determination, of the C value (Table 1), we can conclude that $2k_7 >> (k_6C/k_5[\mathrm{RH}])\ 2k_8$. Therefore, the chain break virtually occurs only *via* reaction (7'). With this result, the expression for the rate constant of the decomposition of ACSP takes the following form in the absence of oxygen:

$$W_{Ar} = k_{Ar}C^{1.5} \approx (k_6\sqrt{2k_1 / 2k_7}) \cdot C^{1.5}. \quad (7)$$

Oxygen inhibits the induced chain decomposition of ACSP due to the fast reaction

$$r^{\cdot} + O_2{}^{\cdot} \rightarrow rO_2{}^{\cdot}, \quad (9')$$

($k_9 \sim 10^9$ L (mol s)$^{-1}$, see Ref.10) resulting in peroxide radicals (r = CH_3 or R), which are inactive with respect to ACSP. Under our experimental conditions (moderate temperature), $rO_2^{\cdot}$ radicals mainly react with each other:

$$rO_2{}^{\cdot} + rO_2{}^{\cdot} \rightarrow \text{Molecular products} \quad (10')$$

The kinetics of ACSP consumption in oxygen atmosphere can be described by the equation:

$$W_0 = k_0 \cdot C = (k_1 + k_2) \cdot C.$$

Finally, we estimate the rate constant of reaction (6') assuming that $2k_1$ k_0 (the eficiency of initiation e 0.5); under this assumption, we obtain from (7), (2), and (4):

$$\log k_6 \approx \log\ k_{Ar}\sqrt{2k_7 / k_0}) = 10.8 - 36 / \theta \quad (\mathrm{L\ (mol\ s)^{-1}});$$

in this calculation we used
$\log(2k_7) = 11.68 - 10.9/\theta$ (L (mol s)$^{-1}$) [11].

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