The Kinetics of Thermal Decomposition of Acetyl-*cyclo*-hexylsulfonylperoxide

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Received October 23, 2000

Abstract—The kinetics of the decomposition of acetyl-*cyclo*-hexylsulfonylperoxide (SP, $RS(O_2)OOC(O)CH_3$, $R = cyclo\text{-}C_6H_{11}$) was studied in a $C_6H_4Cl_2$ solution in an O_2 atmosphere at 323–353 K and in an Ar atmosphere at 323–343 K. The rate constants of SP monomolecular decomposition (k_1) and SP reaction with $CH_3^\bullet$ radicals (k_3) were determined. The temperature dependences of these rate constants are described by equations $\log k_1 = (14.5 \pm 2.9) - (115.4 \pm 19.0) - (2.3RT)$ and $\log k_3 = (11.6 \pm 2.2) - (44.6 \pm 14.2)/(2.3RT)$, where the activation energies are expressed in kJ/mol.

INTRODUCTION

The synthesis and some properties of acetyl-*cyclo*-hexylsulfonylperoxide (SP) were described for the first time by Graf [1]. The products and kinetics of the thermal decomposition of SP in some saturated and aromatic hydrocarbons, alcohols, and in CCl_4 were studied more recently [2–4]. It has been found that, under anaerobic conditions in decane and cyclohexane solutions, alkyl radicals induce SP decomposition and O_2 is an inhibitor of this process [3].

In this work, the kinetics of SP decomposition was studied in a 1,2-dichlorobenzene solution in the presence and absence of O_2.

## EXPERIMENTAL

SP $RS(O_2)OOC(O)CH_3$, where $R = cyclo\text{-}C_6H_{11}$, was synthesized and purified using the procedure described in [1]. $C_6H_4Cl_2$ solvent ("chemically pure") was distilled at a low pressure. The reaction was carried out in a glass reactor at a constant temperature. The reactor was equipped with a Teflon cover, through which O_2 or Ar were supplied and bubbled continuously though the solution and samples were taken with a microsyringe. The reaction kinetics was determined by the monitoring of SP consumption. The SP concentration was measured by iodometric titration.

RESULTS AND DISCUSSION

SP consumption in the presence of O_2 is described well by the first-order rate law. The kinetics was characterized by the rate constant (k', s^{-1}). This rate constant (in an O_2 atmosphere) was calculated from the semilogarithmic anamorphosis of kinetic curves (Fig. 1, line *1*). The values of k' are independent of $[SP]_0$ within the experimental error (see table). The substitution of Ar for O_2 leads to an increase (~2–3 times) in the SP decomposition rate (see table) and to an increase in the apparent reaction order n to 1.3–1.5. Figure 1 illustrates the linearization of the kinetic curve at $n = 1.5$ (line *2*). We determined k_{exp} from these data (in the absence of O_2), calculated the initial reaction rate $w_0 = k_{exp}[SP]_0^n$, and found k' using formula $k' = w_0/[SP]_0$. In contrast to experiments carried out in the presence of O_2, an increase in $[SP]_0$ under anaerobic conditions leads to an increase in k' (table). The constant k' as a function of $[SP]_0$ can be linearized in the k'–$[SP]_0^{0.5}$ coordinates (Fig. 2).
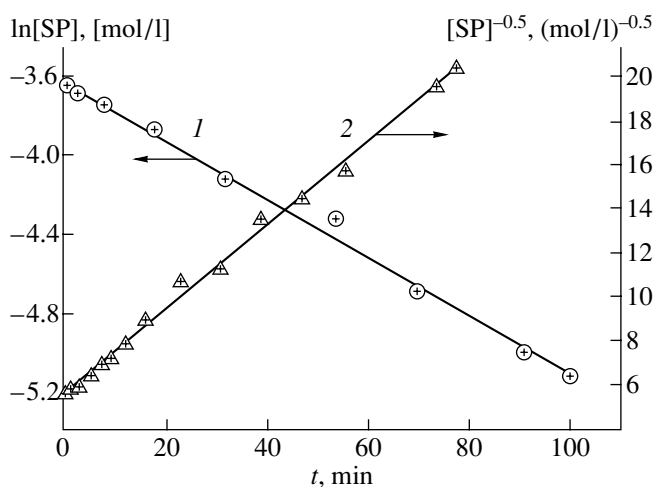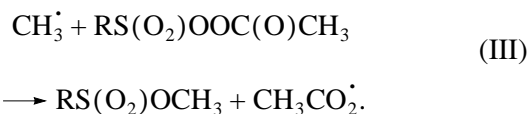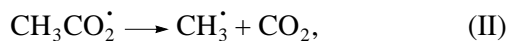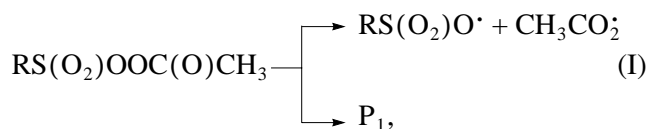

Fig. 1. The linearization of SP consumption curves in coordinates of the first-order rate equation (line *1*, O_2 atmosphere) and the 1.5-order equation (line *2*, Ar atmosphere), $T = 333$ K.

Kinetic parameters of SP decomposition

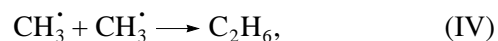| T, K	Atmosphere	$[SP]_0 \times 10^2$, mol/l	$k' \times 10^4$, s^{-1}	$k_1' \times 10^4$, s^{-1}	$k_3 \sqrt{\dfrac{e_1 k_1}{2k_4}} \times 10^2$, l$^{0.5}$ mol$^{-0.5}$ s^{-1}	$k_3 \times 10^{-4}$, l mol^{-1} s^{-1}
323	O$_2$	0.13	0.58 ± 0.07	0.58 ± 0.22	–	–
		0.80	0.66 ± 0.02			
		3.00	0.81 ± 0.05			
	Ar	0.15	1.1 ± 0.1	0.74 ± 0.30	0.09 ± 0.02	2.2
		0.90	1.5 ± 0.2			
		2.30	2.1 ± 1.2			
		3.40	2.3 ± 1.2			
333	O$_2$	0.12	2.22 ± 0.13	2.20 ± 0.04	–	–
		0.80	2.31 ± 0.01			
		2.60	2.53 ± 0.02			
	Ar	0.16	4.15 ± 0.40	2.4 ± 2.2	0.42 ± 0.20	3.55
		0.66	5.7 ± 0.9			
		2.80	9.5 ± 0.6			
343	O$_2$	0.16	8.00 ± 0.05	8.0 ± 0.9	–	–
		0.79	8.50 ± 0.03			
		2.90	9.70 ± 0.05			
	Ar	0.16	16.2 ± 1.8	11.1 ± 4.7	1.25 ± 0.43	5.8
		0.75	21.7 ± 1.7			
		2.70	31.7 ± 1.5			
353	O$_2$	0.14	21.9 ± 1.4	21.7	–	–
		0.75	22.5 ± 2.9			

By analogy with data reported in [2, 3, 5], the acceleration of SP decomposition in the absence of oxygen in an inert solvent can be explained by the activation of the chain-radical channel of SP decomposition (reactions (II) and (III)):

$$RS(O_2)OOC(O)CH_3 \longrightarrow \begin{cases} RS(O_2)O^{\bullet} + CH_3CO_2^{\bullet} \\ P_1, \end{cases} \quad (I)$$

$$CH_3CO_2^{\bullet} \longrightarrow CH_3^{\bullet} + CO_2, \quad (II)$$

$$CH_3^{\bullet} + RS(O_2)OOC(O)CH_3$$
$$\longrightarrow RS(O_2)OCH_3 + CH_3CO_2^{\bullet}. \quad (III)$$

Henceforth, P are nonradical products.

The order of the reaction with respect to SP is higher than unity; therefore, we should conclude that the lim-

ing step of the chain process is reaction (III). Therefore, $CH_3^{\bullet}$ radicals participate in chain termination

$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow C_2H_6, \quad (IV)$$

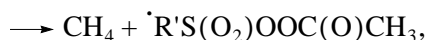$$CH_3^{\bullet} + RS(O_2)O^{\bullet} \longrightarrow RS(O_2)OCH_3. \quad (V)$$

Apparently, $RS(O_2)O^{\bullet}$ radical decay takes place not only as a result of reaction (V), but also as a result of their self-recombination ($RS(O_2)O^{\bullet} + RS(O_2)O^{\bullet} \longrightarrow$ products). The participation of $CH_3CO_2^{\bullet}$ radicals in chain termination can be neglected, because these radicals decompose quickly via reaction (II); according to the published data [6], $k_2 \sim 10^9$ s^{-1}.

The reactions of $CH_3^{\bullet}$ and $RS(O_2)O^{\bullet}$ radicals with a cyclohexyl ring of SP were also excluded from consideration:

$$CH_3^{\bullet} + RS(O_2)OOC(O)CH_3$$
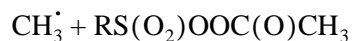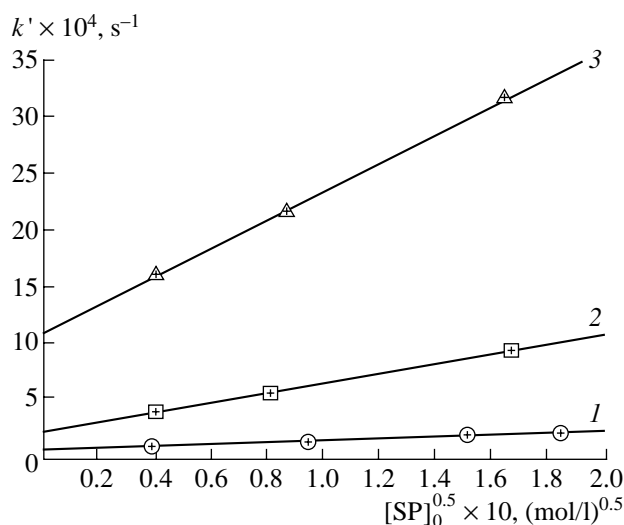
Fig. 2. The rate constant of SP consumption k' as a function of $[SP]_0^{0.5}$ in an Ar atmosphere at (*1*) 323, (*2*) 333, and (*3*) at 343 K.

Fig. 3. Arrhenius plots of rate constants k_1 and k_3.

$$\longrightarrow CH_4 + {}^\cdot R'S(O_2)OOC(O)CH_3,$$

$$RS(O_2)O^\cdot + RS(O_2)OOC(O)CH_3$$

$$\longrightarrow RS(O_2)OH + {}^\cdot R'S(O_2)OOC(O)CH_3.$$
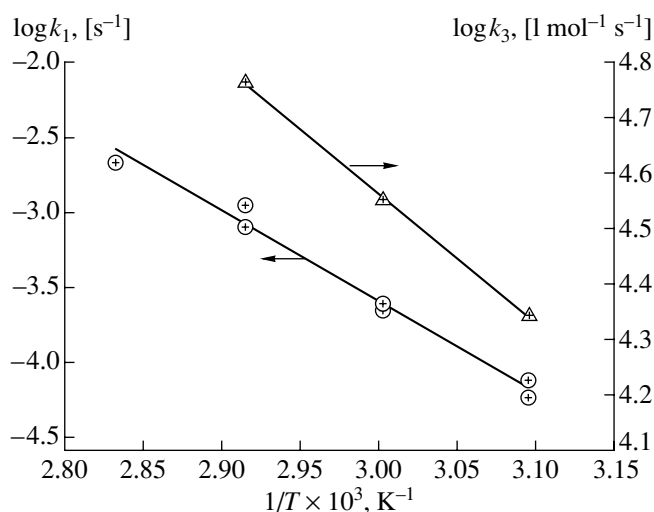
Similar reactions of these radicals with nonsubstituted hydrocarbons occur with rates constants of $\sim 10^2$ for $CH_3^\cdot$ [7] and $> 10^8 \, l \, mol^{-1} \, s^{-1}$ for $RS(O_2)O^\cdot$ [8] radicals. It is known that the introduction of the $S-O_3H$ group into a linear hydrocarbon molecule deactivates the neighboring $> CH_2$ groups of this hydrocarbon up to the fourth carbon atom counting from the substituent [9]. In cyclohexane sulfoxidation, the main product of the reaction is monosulfo acid; the products of di- and polysubstitution were not found [1]. The same influence of the first substituent was also observed in other chain-radical substitution processes, such as chlorination, sulfochlorination, and nitration [10, 11]. Probably, the influence of the $-S(O_2)OOC(O)CH_3$ group is analogous.

Using the steady-state approximation and assuming that chain termination occurs in the absence of O_2 mainly via reaction (IV) ($e_1k_1[SP] = 2k_4[CH_3^\cdot]^2$, where e_1 is the escape of radicals into the volume in reaction (I)), the following equation is valid for the rate of SP consumption (w):

$$w = -\frac{d[SP]}{dt} = k_1[SP] + k_3\sqrt{\frac{e_1k_1}{2k_4}}[SP]^{1.5}. \quad (1)$$

According to this equation, the order of the overall reaction of SP decomposition should be between 1

and 1.5. This is observed experimentally. At the initial instant ($[SP] = [SP]_0$), we obtain from (1)

$$k' = \frac{w_0}{[SP]_0} = k_1 + k_3\sqrt{\frac{e_1k_1}{2k_4}}[SP]_0^{0.5}. \quad (2)$$

The plot of k' as a function of $[SP]_0^{0.5}$ is a straight line (Fig. 2). This is in accordance with Eq. (2). The values of k_1 and parameter $k_3\sqrt{e_1k_1/2k_4}$ were calculated from these lines (see table).

The introduction of O_2 into the system practically stops reaction (III), because the main channel of $CH_3^\cdot$ radical decay becomes reaction

$$CH_3^\cdot + O_2 \longrightarrow CH_3O_2^\cdot, \quad (VI)$$
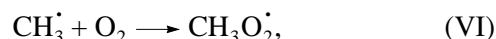
occurring with the diffusion rate constant ($k_6 > 10^9 \, l \, mol^{-1} \, s^{-1}$ [7]). Methylperoxy radicals formed in reaction (VI) are not active with respect to SP [4] and decay in the reaction

$$CH_3O_2^\cdot + CH_3O_2^\cdot \longrightarrow P_7. \quad (VII)$$
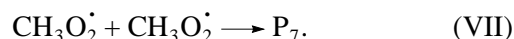
Therefore, in the presence of O_2, k' is the rate constant of monomolecular SP decomposition, that is, k_1. The values of k_1 measured in aerobic and anaerobic experiments agree with each other. The temperature dependence of k_1 (Fig. 3) is described by equation

$$\log k_1 = (14.5 \pm 2.9) - (115.4 \pm 19.0)/2.3RT. \quad (3)$$

(Henceforth, the activation energy is expressed in kJ/mol.)

The values of the preexponential factor and the activation energy correlate with published data for benzene and toluene [4].

Equation (3) was used to determine the rate constant k_3 from the values of parameter $k_3\sqrt{e_1 k_1/2k_4}$ found above (see table). In these calculations, we used the following values: $e_1 = 0.5$ and $2k_4 = 8.9 \times 10^9$ l mol^{-1} s^{-1} [7].

Note that the values of k_3 for the $\overset{\bullet}{C}H_3$ radical determined in this work (table) are ~4 times lower than the values of an analogous constant for the secondary $C_{10}H_{21}^{\bullet}$ radical [3]. The temperature dependence of k_3 (Fig. 3) is described by the equation

$$\log k_3 = (11.6 \pm 2.2) - (44.6 \pm 14.2)/2.3RT.$$

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