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# Effect of the solvent on the kinetics of thermal decomposition of acetylcyclohexylsulfonyl peroxide

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The kinetics of the decomposition of acetylcyclohexylsulfonyl peroxide (ACSP) in $CCl_4$, benzene, toluene, ethylbenzene, cumene, acetonitrile, ethanol, and 2-propanol in an atmosphere of $O_2$ were studied at 40—70 °C. The rate constants ($k_0$) and activation parameters of the monomolecular decomposition of ACSP were determined. A linear dependence between $\log A_0$ and activation energy $E_0$ (compensation effect) was established. The dependence of $k_0$ on the nature of a solvent is described by the four-parameter Koppel—Palm equation.

**Key words:** alkylsulfonyl peroxides, thermal decomposition, kinetics, solvent effect; compensation effect.

The thermal decomposition of acetylcyclohexylsulfonyl peroxide (ACSP) in a medium of saturated hydrocarbon (*n*-decane, cyclohexane) in the absence of oxygen proceeds *via* a radical chain mechanism.[1] The following reactions are the primary stages of the decomposition of ACSP:

$$1.\ RSO_2OOC(O)Me \longrightarrow RSO_2O^{\cdot} + MeCO_2^{\cdot},$$

$$2.\ RSO_2OOC(O)Me \longrightarrow P_2,$$

where $P_2$ is the molecular product of the corresponding (second) stage.

Oxygen is a strong inhibitor of the induced chain decomposition of ACSP in alkanes. In the presence of $O_2$, the rate of decomposition of ACSP is described by the equation[1]

$$-dC/dt = (k_1 + k_2)C = k_0C, \qquad (1)$$

which can be used to determine the rate constant of monomolecular decomposition ($k_0$) ($C$ is the concentration of ACSP, $k_1$ and $k_2$ are the rate constants of the corresponding stages).

In the present work, the dependence of $k_0$ on the nature of the solvent was studied.

## Experimental

The reaction was carried out in an atmosphere of oxygen at 40—70 °C in the following solvents (the maximum range of change in the initial concentration of ACSP is indicated in parentheses, $C_0$/mmol $L^{-1}$): $CCl_4$ (4—37), PhH (5—27), PhMe (6—40), PhEt (3—53), $PhCMe_2H$ (4—39), MeCN (3—35), EtOH (2—35), MeCHOHMe (3—29). The kinetics of the process were studied by analyzing the consumption of ACSP using a procedure described previously.[1]

Acetylcyclohexylsulfonyl peroxide was synthesized and purified by the procedure presented in the same work.[1] The solvents used were purified by known methods.[2]

## Results and Discussion

The kinetics of the thermal decomposition of ACSP obey the first-order equation:

$$-dC/dt = k'C. \qquad (2)$$

The rate constant $k'$ was calculated from the semilogarithmic anamorphoses of the curves of the consumption of ACSP (30—50% conversion).

In relatively inert solvents ($CCl_4$, PhH, and MeCN), within the accuracy of the determination (±15—20%) the rate constant $k'$ is almost independent of the initial concentration and coincides with $k_0$ according to Eqs. (1) and (2).

However, in other solvents, a weak increase in $k'$ is observed as $C_0$ increases, which indicates that ACSP is involved in reactions with the active intermediates formed (the dependence of $k'$ on $C_0$ for the reaction in a solution of ethylbenzene at 60 °C is presented in Fig. 1 as an example). In this case, the $k_0$ constant was determined by extrapolation of this dependence to the zero concentration of ACSP, *i.e.*, to the conditions under which secondary processes involving ACSP are ruled out:

$$k' = k_0 + \alpha C_0, \qquad (3)$$

where $\alpha$ is a proportionality coefficient.

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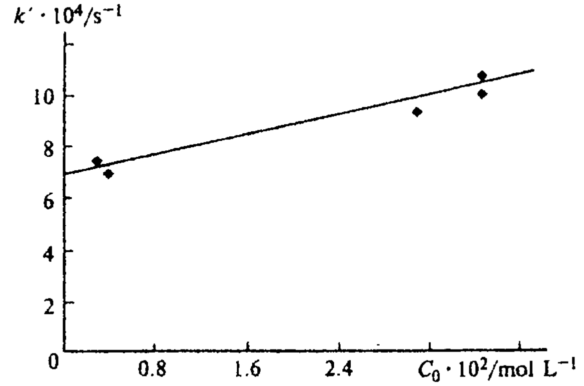

**Fig. 1.** Dependence of the experimental rate constant of the decomposition of ACSP ($k'$) on its initial concentration ($C_0$) (ethylbenzene, 60 °C).

The rate constants $k_0$ obtained by Eq. (3) are presented in Table 1 along with the $k_0$ values determined in solutions of $CCl_4$, PhH, and MeCN. The activation parameters of the reaction calculated using these values are presented in Table 2.

**Table 1.** Dependences of the rate constant of the monomolecular decomposition of ACSP ($k_0$) on the nature of the solvent and on the temperature

| Solvent | $k_0 \cdot 10^4$/s$^{-1}$ | | | |
|---|---|---|---|---|
| | 40 °C | 50 °C | 60 °C | 70 °C |
| $CCl_4$ | 0.21 | 1.0 | 3.9 | — |
| PhH | 0.38 | 1.4 | 5.0 | 17.5 |
| PhMe | 0.50 | 1.8 | 6.3 | 18.6 |
| PhEt | 0.60 | 1.9 | 6.9 | 19.2 |
| $PhCMe_2H$ | 0.37 | 1.4 | 5.3 | — |
| MeCN | 0.06 | 0.4 | 1.1 | — |
| EtOH | 0.22 | 0.7 | 2.4 | — |
| MeCHOHMe | 0.15 | 0.6 | 2.2 | 6.5 |

**Table 2.** Dependence of the activation parameters ($\log A_0$ and $E_0$) of the decomposition of ACSP on the nature of the solvent

| Solvent | $\log A_0$ | $E_0$ /kJ mol$^{-1}$ |
|---|---|---|
| $n$-$C_{10}H_{22}$* | 16.2 | 123 |
| $CCl_4$ | 16.5 | 127 |
| PhH | 14.5 | 114 |
| PhMe | 13.8 | 108 |
| PhEt | 13.1 | 104 |
| $PhCMe_2H$ | 14.7 | 115 |
| MeCN | 15.8 | 126 |
| EtOH | 12.5 | 103 |
| MeCHOHMe | 14.0 | 113 |

*Note.* The errors of the determination of $\log A_0$ and $E_0$ are 0.1—0.6 and 2—10 kJ mol$^{-1}$, respectively.
* Ref. 1.

**Table 3.** Dependence of the rate constant $k_0$ on the properties of solvent

| Solvent | $Y$ | $P$ | $E$ | $B$ | $-\log k_0$ | |
|---|---|---|---|---|---|---|
| | | | | | experiment | calculation[a] |
| | | | $T$ = 40 °C | | | |
| $n$-$C_{10}H_{22}$ | 0.1946 | 0.2393 | 0 | 0 | 4.4[b] | 4.4 |
| $CCl_4$ | 0.2222 | 0.2670 | 0 | 0 | 4.7 | 4.6 |
| PhH | 0.2266 | 0.2860 | 2.1 | 48 | 4.5 | 4.4 |
| PhMe | 0.2351 | 0.2845 | 1.3 | 58 | 4.2 | 4.4 |
| PhEt | 0.2379 | 0.2846 | 1.3 | 58 | 4.3 | 4.4 |
| $PhCMe_2H$ | 0.2358 | 0.2828 | 1.3 | 58 | 4.5 | 4.4 |
| MeCN | 0.4784 | 0.2057 | 5.2 | 160 | 5.2 | 5.2 |
| EtOH | 0.4672 | 0.2170 | 11.6 | 235 | 4.7 | 4.7 |
| MeCHOHMe | 0.4579 | 0.2259 | 8.7 | 236 | 4.8 | 4.7 |
| | | | $T$ = 50 °C | | | |
| $n$-$C_{10}H_{22}$ | 0.1989 | 0.2368 | 0 | 0 | 3.7[b] | 3.8 |
| $CCl_4$ | 0.2204 | 0.2642 | 0 | 0 | 4.0 | 4.0 |
| PhH | 0.2246 | 0.2829 | 2.1 | 48 | 3.8 | 3.8 |
| PhMe | 0.2329 | 0.2819 | 1.3 | 58 | 3.7 | 3.8 |
| PhEt | 0.2356 | 0.2819 | 1.3 | 58 | 3.7 | 3.8 |
| $PhCMe_2H$ | 0.2338 | 0.2803 | 1.3 | 58 | 3.9 | 3.8 |
| MeCN | 0.4773 | 0.2031 | 5.2 | 160 | 4.6 | 4.6 |
| EtOH | 0.4651 | 0.2148 | 11.6 | 235 | 4.1 | 4.2 |
| MeCHOHMe | 0.4543 | 0.2238 | 8.7 | 236 | 4.2 | 4.1 |
| | | | $T$ = 60 °C | | | |
| $n$-$C_{10}H_{22}$ | 0.1911 | 0.2344 | 0 | 0 | 3.1[b] | 3.1 |
| $CCl_4$ | 0.2186 | 0.2614 | 0 | 0 | 3.4 | 3.3 |
| PhH | 0.2226 | 0.2797 | 2.1 | 48 | 3.3 | 3.2 |
| PhMe | 0.2307 | 0.2790 | 1.3 | 58 | 3.1 | 3.2 |
| PhEt | 0.2333 | 0.2791 | 1.3 | 58 | 3.2 | 3.3 |
| $PhCMe_2H$ | 0.2317 | 0.2778 | 1.3 | 58 | 3.3 | 3.2 |
| MeCN | 0.4754 | 0.2005 | 5.2 | 160 | 4.0 | 4.0 |
| EtOH | 0.4629 | 0.2126 | 11.6 | 235 | 3.6 | 3.7 |
| MeCHOHMe | 0.4499 | 0.2219 | 8.7 | 236 | 3.6 | 3.6 |
| | | | $T$ = 70 °C | | | |
| $n$-$C_{10}H_{22}$ | 0.1893 | 0.2319 | 0 | 0 | 2.5[b] | 2.5 |
| $CCl_4$ | 0.2167 | 0.2585 | 0 | 0 | 2.8[c] | 2.8 |
| PhH | 0.2205 | 0.2765 | 2.1 | 48 | 2.8 | 2.7 |
| PhMe | 0.2288 | 0.2761 | 1.3 | 58 | 2.6 | 2.7 |
| PhEt | 0.2309 | 0.2764 | 1.3 | 58 | 2.7 | 2.7 |
| $PhCMe_2H$ | 0.2299 | 0.2753 | 1.3 | 58 | 2.8[c] | 2.7 |
| MeCN | 0.4739 | 0.2979 | 5.2 | 160 | 3.4[c] | 3.4 |
| EtOH | 0.4603 | 0.2103 | 11.6 | 235 | 3.2[c] | 3.2 |
| MeCHOHMe | 0.4449 | 0.2195 | 8.7 | 236 | 3.1 | 3.1 |

[a] Calculated by Eq. (4) from the data in Table 4 to illustrate the quality of the description.
[b] Ref. 2.
[c] Calculated from the data in Table 2.

As can be seen from the data in Table 2, the determined values of the pre-exponential factors are characteristic of monomolecular reactions. The analysis of the values presented in Table 2 shows a linear dependence between $\log A_0$ and $E_0$ with the correlation coefficient $r = 0.980$ (compensation effect):

$$\log A_0 = -(2.7\pm1.3) + (1.5\pm0.1) \cdot 10^{-4} E_0.$$

**Table 4.** Temperature dependence of the parameters of Eq. (4)

| $T$/°C | $-\log k_0$ | $y$ | $p$ | $e \cdot 10^3$ | $b \cdot 10^3$ | $r$ |
|---|---|---|---|---|---|---|
| 40 | 2.5 | −6.872 | −1.667 | 1.303 | 6.111 | 0.946 |
| 50 | 1.6 | −6.455 | −3.324 | −3.817 | 5.069 | 0.966 |
| 60 | 1.2 | −5.761 | −3.575 | −6.699 | 4.306 | 0.977 |
| 70 | 0.7 | −5.1063 | −3.959 | −7.965 | 3.237 | 0.987 |

The effect of the solvent on the rate constant $k_0$ is described by the four-parameter Koppel—Palm equation,[3] which takes into account both nonspecific and specific solvations:

$$\log k_0 = \log k_0{}^\circ + yY + pP + eE + bB. \qquad (4)$$

Here $Y = (\varepsilon - 1)/(2\varepsilon + 1)$; $P = (n^2 + 2)$; $E$ and $B$ are empirical parameters of the electrophilicity and nucleophilicity of the solvent, respectively; $k_0{}^\circ$ is the rate constant of the gas-phase reaction; $y$, $p$, $e$, and $b$ are coefficients characterizing the sensitivity of the reaction to the corresponding parameter.

The results of the analysis of the kinetic data in terms of Eq. (4) are presented in Tables 3 and 4. For the calculations, the $E$ and $B$ values were taken from Ref. 3, the $\varepsilon$ and $n$ values were taken from Refs. 4 and 5, and the refractive index of nonadecane was used for decane.[5]

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