

The kinetics of acid-catalyzed decomposition of decanepersulfonic acid

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The kinetics of thermal decomposition of decanepersulfonic acid (RSO_2OOH , $\text{R} = \text{C}_{10}\text{H}_{21}$) in CCl_4 in the presence of cyclohexanesulfonic and trifluoroacetic acids at 323–343 K was studied. The reaction has an autocatalytic character. The kinetics of consumption of the persulfonic acid is described by the equation $-\text{d}[\text{RSO}_2\text{OOH}]/\text{d}t = k_1[\text{RSO}_2\text{OOH}] + k_2[\text{RSO}_2\text{OOH}] \cdot [\text{HX}]$.

Key words: decanepersulfonic acid, decomposition, acid catalysis, kinetics.

It has been established previously¹ that in the decomposition of decanepersulfonic acid (RSO_2OOH , $\text{R} = \text{C}_{10}\text{H}_{21}$) in decane, the reaction of RSO_2OOH with the hydrocarbon solvent is the main channel of its consumption. In this work, we studied the thermolysis of decanepersulfonic acid in a solution of CCl_4 and the influence of acid additives on the reaction kinetics.

Experimental

Decanepersulfonic acid was synthesized according to the procedure described previously.¹ A solution of $\text{C}_{10}\text{H}_{21}\text{SO}_2\text{OOH}$ was thoroughly washed out from admixtures of H_2SO_4 and decanesulfonic acid. The content of the latter in the starting solutions of persulfonic acid did not exceed 1%. The solvent (CCl_4) was purified according to the standard procedure.² Cyclohexanesulfonic acid was obtained by the photochemical sulfoxidation of cyclohexane. CF_3COOH (reagent grade) was used. The reaction kinetics was monitored by the consumption of RSO_2OOH , whose concentration was determined iodometrically.³ Concentrations of decanesulfonic, cyclohexanesulfonic, and trifluoroacetic acids were determined by potentiometric titration. Bu_4NOH was used as the titrant.

Results and Discussion

The thermolysis of decanepersulfonic acid in CCl_4 was studied at 323–343 K. The kinetic curves of consumption of RSO_2OOH have an autocatalytic character. Therefore, the reaction was characterized by the experimental rate constant of consumption of the persulfonic acid (k_{exp} , Table 1), which was determined from the semilogarithmic anamorphoses of the regions of the kinetic curves where the contribution of autocatalysis is not noticeable (conversion of $\text{RSO}_2\text{OOH} < 5\text{--}6\text{ mol.}\%$).

The temperature dependence of k_{exp} is described by the Arrhenius equation (the activation energy is expressed in kJ mol^{-1})

$$\log k_{\text{exp}} = (8.48 \pm 0.56) - (85.3 \pm 3.6)/(2.3RT), r = 0.998.$$

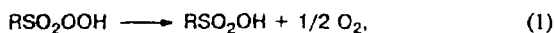
The addition of cyclohexanesulfonic or trifluoroacetic acids to the starting reaction mixture accelerates the reaction and decreases (down to the complete disappearance at a sufficiently high acid concentration) the autoacceleration effect. In this case, the kinetics of consumption of RSO_2OOH is well described by the first-order equation to the almost complete decomposition of the peracid. The k_{exp} values increase proportionally to the content of the acid in the starting reaction mixture (see Table 1). The catalytic effect of trifluoro-sulfonic acid is substantially higher than that of cyclohexanesulfonic acid, which is most likely related to the different strengths of these acids. It can be assumed that the autocatalysis during the decomposition of

Table 1. Dependence of the rate constant (k_{exp}) of decomposition of decanepersulfonic acid on the temperature and acid content $[\text{HX}]$ in the starting reaction medium

T/K	$[\text{RSO}_2\text{OOH}]_0 \cdot 10^2$ mol L^{-1}	$[\text{HX}] \cdot 10^3$	$k_{\text{exp}} \cdot 10^5$ s^{-1}
323	0.5	0	0.46
323	1.3	0	0.47
323	1.3	0	0.44
333	0.2	0	1.28
333	0.5	0	1.27
333	1.0	0	1.28
333	2.5	0	1.30
343	0.25	0	2.88
343	1.0	0	2.95
343	1.0	1.3	3.07 ^a
343	0.3	2.95	3.72 ^a
343	0.4	10.0	7.1 ^a
343	0.2	19.3	11.0 ^a
343	0.2	0.5	3.7 ^b
343	0.2	3.0	8.3 ^b
343	2.4	0	2.95

^a $\text{HX} = \text{C}_6\text{H}_{11}\text{SO}_2\text{OH}$. ^b $\text{HX} = \text{CF}_3\text{COOH}$.

persulfonic acid is due to the accumulation of the corresponding sulfonic acid, whose yield (calculated per decomposed peracid) is ~85% (343 K, $[\text{RSO}_2\text{OOH}]_0 = 2.1 \cdot 10^{-2} \text{ mol L}^{-1}$). When hydrocarbons are added to the reaction mixture, the yield of sulfonic acid reaches the quantitative value.¹ The kinetic regularities of the reaction can be explained in terms of the following formal scheme:



According to this scheme, the consumption of the persulfonic acid can be described by the equation

$$\begin{aligned} d[\text{RSO}_2\text{OOH}]/dt = \\ = -k_1[\text{RSO}_2\text{OOH}] - k_2[\text{RSO}_2\text{OOH}] \cdot [\text{RSO}_2\text{OH}], \end{aligned}$$

where k_1 and k_2 are the rate constants of the corresponding stages.

Under the experimental conditions, when $[\text{HX}]_0 \gg [\text{RSO}_2\text{OOH}]_0$, the accumulation of sulfonic acid at the initial stages of the reaction can be neglected. After integration, we obtain the expression

$$\ln([\text{RSO}_2\text{OOH}]_0/[\text{RSO}_2\text{OOH}]) = (k_1 + k_2[\text{HX}])t$$

($[\text{HX}]$ is the concentration of sulfonic or other acid).

Taking into account that $k_1 + k_2[\text{HX}]$ is, in fact, the experimental rate constant of consumption of persulfonic acid, i.e.,

$$k_{\text{exp}} = k_1 + k_2[\text{HX}],$$

we can expect a linear dependence of k_{exp} on the content of acids in the system, which is observed experimentally (see Table 1). According to this equation, we found from the dependences of k_{exp} on $[\text{HX}]$: $k_2(70^\circ\text{C}) = (4.3 \pm 0.5) \cdot 10^{-3} \text{ L (mol s)}^{-1}$, $r = 0.998$ for cyclohexanesulfonic acid and $k_2(70^\circ\text{C}) = (1.8 \pm 0.6) \cdot 10^{-2} \text{ L (mol s)}^{-1}$, $r = 0.999$ for trifluoroacetic acid. It is found from the intercepts on the Y axis: $k_1(70^\circ\text{C}) = (2.7 \pm 0.5) \cdot 10^{-5} \text{ s}^{-1}$ and $(2.9 \pm 1.1) \cdot 10^{-5} \text{ s}^{-1}$ at $\text{HX} = \text{C}_6\text{H}_{11}\text{SO}_3\text{H}$ and CF_3COOH , respectively. These k_1 values agree well with the k_{exp} values determined from the initial regions of the kinetic curve of consumption of RSO_2OOH (see Table 1) in the absence of acids in the starting mixture when reaction (2) can be neglected.

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Electrochemical hydrogenation of citral

6.* Voltammetric measurements in DMF solutions of citral and acetic acid

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The electrochemical behavior of citral at Hg, Au, Pt, Cu, and glassy carbon electrodes was studied by cyclic voltammetry in DMF solutions containing acetic acid. Electrocatalytic hydrogenation of citral is the predominant reaction route at Pt and Cu electrodes.

Key words: citral, electrocatalytic hydrogenation, cyclic voltammetry.

Despite the substantial interest in the preparative electrochemical reduction of citral (Cit) both in aqueous

alcohols² and aqueous DMF,^{3,4} the mechanism of its electroreduction, unlike those of other α,β -unsaturated carboxyl compounds,⁵ has not been studied. The purpose of this work is to study this aspect and to verify the

* For Part 5, see Ref. 1.