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Kinetics of oxidation of alkanes and their derivatives by *n*-decanepersulfonic acid

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The kinetics of interaction of *n*-decanepersulfonic acid with linear, branched, and substituted hydrocarbons was studied. The oxidation of *cyclo*-C_6H_{12}/C_6D_{12} occurs with a moderate kinetic isotope effect, $k^H/k^D = 2.2\pm0.3$. A satisfactory correlation between the partial rate constants and the structure of hydrocarbons in terms of the Okamoto—Brown equation was found.

Key words: persulfonic acid, alkanes, oxidation, kinetics.

It has previously[1] been found for decane and cyclohexane that *n*-decanepersulfonic acid (RSO_2OOH) efficiently oxidizes hydrocarbons to alcohols. The main channel of RSO_2OOH consumption is its reaction with the oxidized substrate (R′H). It has been shown[2] for some alcohols and hydrocarbons that the kinetics of RSO_2OOH consumption is described by the following equation:

$$-dC/dt = k'C = (k_1 + k_2[R'H])C, \qquad (1)$$

where C is the concentration of RSO_2OOH; R′H is the oxidized substrate; k'/s^{-1} is the experimental rate constant calculated from the semilogarithmic anamorphoses of the kinetic curves of RSO_2OOH consumption ($\ln(C_0/C) = k't$); and k_1/s^{-1} and $k_2/L\ mol^{-1}\ s^{-1}$ are the rate constants of the following overall reactions, respectively:

$$RSO_2OOH \longrightarrow RSO_2OH + 1/2\ O_2,$$
$$RSO_2OOH + R'H \longrightarrow RSO_2OH + P$$

(P is the reaction product).

The reaction product P is an alcohol in hydrocarbon oxidation or ketone in alcohol oxidation. We have measured the k_2 rate constants for some hydrocarbons and alcohols and observed a correlation between their values and the substrate structure in terms of the Okamoto—Brown equation.[2] In this report, which continues our previous work,[2] we studied the influence of the nature of substituents at the CH group on its reactivity in the oxidation by decanepersulfonic acid for a wide range of substrates.

Experimental

n-Decanepersulfonic acid was synthesized by a known procedure.[1] Carbon tetrachloride and the hydrocarbons were purified by standard procedures.[3] Kinetic experiments were carried out as described previously.[2] The reaction kinetics was monitored by the consumption of persulfonic acid whose concentration was determined iodometrically.[4] Alcohols and ketones were analyzed by GLC and, in particular cases, by GC-MS.[1]

Results and Discussion

The reaction kinetics was studied in the 303—343 K temperature range in air using CCl_4 as the solvent. All experiments were carried out with the substrate concentration $[R'H]_0 \gg C_0$. Under these conditions, the k' values are almost independent of the C_0 value and increase proportionally to increase in the amount of substrate added to the solution, *i.e.*, in full correspondence with Eq. (1). The rate constant k_1 has been previously[5] determined (at 323—343 K): $\log k_1 = (8.48\pm0.56) - (85.3\pm3.6)/\theta$ ($\theta = 2.303RT$ kJ mol^{-1}). The k_1 value estimated from the dependence of k' on $[R'H]_0$ satisfactorily agrees with this equation. The k_2 values and its Arrhenius parameters (A_2 and E_2) for various substrates and temperatures are presented in Table 1. It follows from these data that the linear dependence between the $\log A_2$ and E_2 values is fulfilled (the compensation effect) within particular classes of the substrates under study:

$$\log A_2 = -6.4 + 0.19E_2\ (r = 0.954,\ \text{hydrocarbons}),$$
$$\log A_2 = -9.0 + 0.22E_2\ (r = 0.9999,\ \text{nitro compounds}),$$
$$\log A_2 = -0.6 + 0.13E_2\ (r = 0.992,\ \text{alcohols}).$$

The reaction of *n*-decanepersulfonic acid with *n*-decane results in the formation of a mixture of secondary decyl alcohols with the almost statistical distribution of the hydroxyl group along the hydrocarbon chain.[6] The yield of the alcohols per consumed RSO_2OOH is ~90 mol.%. The products of hydroxylation of primary C—H bonds are absent. The oxidation of

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Table 1. Reaction rate constant (k_2) as a function of the temperature and nature of the substrate

Substrate	$[R'H]_0$ /mol L^{-1}	T/K	$k_2 \cdot 10^5$	$k_2^{CH} \cdot 10^5$	log A_2	E_2 /kJ mol^{-1}
			L mol^{-1} s^{-1}			
Cyclohexane	1—4	313	1.2±0.1	0.10	7.8±0.8	76±5
		323	3.3±0.9	0.28		
		333	8.2±0.6	0.62		
		343	15.0±1.1	1.18		
Cyclohexane-d_{12}	1.0—9.2	323	1.7±0.6	0.14	5.42±0.63	63±4
		333	3.2±0.03	0.26		
		343	6.8±0.3	0.57		
n-Hexane	0.5	323	2.1±0.4	0.26	—	—
n-Heptane	1—4	323	2.3±1.3	0.23	8.5	81.5
		343	13.5±1.1	1.35		
n-Decane[a]	4.9	313	2.5	0.15	8.3±0.4	77.0±0.3
		333	13.6	0.85		
		343	34.6	2.16		
3-Methylhexane	0.03—0.70	303	2.86±0.12	2.86	8.4±1.1	75.1±6.3
		313	8.8±0.8	8.84		
		323	18.04±3.9	18.04		
2,3-Dimethylbutane	0.03—0.30	303	5.8±0.9	2.88	10.1±0.6	83.5±3.8
		313	14.96±0.54	7.48		
		323	45.03±0.26	22.5		
2,4-Dimethylpentane	5	50	25.6±0.1	12.8	—	—
3,3-Dimethylpentane	4.1	50	5.3±0.1	1.35	—	—
1,4-*trans*-Dimethylcyclohexane	1.3	50	5.0±0.1	5.0	—	—
1,4-*cis*-Dimethylcyclohexane	7	50	7.6±0.1	7.6	—	—
2,2,4-Trimethylpentane	6.1	313	2.7±0.3	2.7	6.7±0.7	67±4
		323	6.7±0.8	6.7		
		333	11.8±0.1	11.8		
		343	27.5±0.3	27.5		
Chloroform	0.02—9.90	323	0.03±0.01	0.031	—	—
Nitromethane	1.1—6.7	323	0.10±0.01	0.033	2.47±0.58	52.5±3.7
		333	0.16±0.03	0.05		
		343	0.31±0.09	0.10		
1-Nitropropane	0.9—9.0	323	2.26±0.48	1.13	7.72±0.03	76.5±0.2
		333	5.29±0.74	2.65		
		343	11.89±6.9	5.94		
2-Nitropropane	0.1—9.8	323	0.58±0.49	0.59	5.36±0.25	65.5±1.6
		333	1.2±0.2	1.17		
		343	2.4±1.9	2.43		
Ethanol[b]	0.05—0.50	313	35±0.3	17.5	8.65±1.0	72.4±6.2
		323	97±12	48.5		
		333	185±23	92.5		
1-Octanol[b]	0.1—1.0	313	40±6	20	6.9±0.6	62±4
		323	76±2	38		
		333	167±18	83.5		
Isopropyl alcohol[b]	0.02—0.30	313	43±28	43	8.5±2.7	71±16
		323	154±20	154		
		333	219±67	219		
Cyclohexanol[b]	0.02—0.20	313	600±73	600	4.8±0.4	42±3
		323	920±100	920		
		333	1580±280	1580		

[a] Data in Ref. 1.

[b] Data in Ref. 2.

2-methylbutane affords only *tert*-pentyl alcohol in a yield up to 93% (20 °C, $[RSO_2OOH]_0 = 5 \cdot 10^{-2}$ mol L^{-1}). In the case of 2,2,4-trimethylpentane, we found only 2,2,4-trimethylpentan-4-ol in 66% yield (20 °C, $[RSO_2OOH]_0 = 0.38$ mol L^{-1}). Thus, the weakest C—H bond undergoes hydroxylation. Similar results were observed for the oxidation of various hydrocarbons by carboxylic peracids.[7—10] The oxidation of ethers by caboxylic peracids gave virtually only the products of oxidation at the C—H bonds in the α-position to the ether group.[11] Alcohols are oxidized by peracetic acid in the presence of NaBr to the corresponding carbonyl compounds.[12] Most likely, the appearance of the latter is preceded by attack at the α-C—H bond with the formation of geminal diol and subsequent abstraction of water. It is assumed that only the α-C—H bond of nitro-substituted alkanes is attacked. Based on the above-mentioned facts, we calculated the partial rate constant of oxidation of one C—H bond (k_2^{CH}) by the equation $k_2^{CH} = k_2/n$, where n is the number of the most reactive C—H bonds in the oxidized substrate (for decane, n = 16; for cyclohexane, n = 12; for 2,2,4-trimethylpentane, n = 1; *etc.*).

As can be seen from the data in Table 1, the reactivity of the substrates in the reaction with *n*-decanepersulfonic acid decreases in the following sequence: cyclohexanol > isopropyl alcohol > ethanol > 1-octanol > 2,3-dimethylbutane > 3-methylhexane > 2,4-dimethylpentane > 1,4-*cis*-dimethylcyclohexane > 2,2,4-trimethylpentane > 1,4-*trans*-dimethylcyclohexane > 3,3-dimethylpentane > 1-nitropropane > 2-nitropropane > cyclohexane ≥ hexane ≥ heptane > cyclohexane-d_{12} > nitromethane ≥ chloroform.

Thus, the lowest reactivity is observed for linear hydrocarbons. As in the case of carboxylic peracids,[9] linear hydrocarbons are oxidized by persulfonic acid more slowly than cyclic hydrocarbons. Tertiary C—H bonds are hydroxylated ~30—100 times more rapidly than secondary bonds. For *p*-nitropersulfonic acid, this value reaches 500.[9] Comparison of hydrocarbons containing tertiary C—H bonds shows that 3-methylhexane is approximately 3 times more reactive with respect to RSO_2OOH than 2,2,4-trimethylpentane. Comparison of the rate constants of oxidation of epimers of 1,4-dimethylcyclohexane gives the ratio $k_{cis}/k_{trans} = 1.5$. This value agrees well with the results obtained for carboxylic peracid for which it amounts to 1.9[10] and 1.6.[13]

The kinetic isotope effect (KIE) of the reaction was measured for deuterated cyclohexane (see Table 1). The KIE value $k_2^{CH}/k_2^{CD} = 2.2 \pm 0.3$ (323—343 K) indicates that the reaction of RSO_2OOH with R'H includes the cleavage of the C—H bond of hydrocarbon as the rate-limiting stage. According to the obtained data, the reactivity of hydrocarbons increases when electron-donor substituents are introduced. For example, 1,4-*trans*-dimethylcyclohexane is oxidized approximately 18 times and cyclohexanol at most 1000 times more rapidly than cyclohexane. Note that the ratio of the rate constants of oxidation of toluene to benzene by *n*-decanepersulfonic acid is equal to 19, and that of phenol to benzene is 10000.[14] The presence of electron-acceptor substituents (NO_2 and Cl) retards the oxidation: the rate constant of the reaction of *n*-octanol with *n*-decanepersulfonic acid is approximately 30 times higher than that for nitropropane and 2500 times higher than that for chloroform (see Table 1).

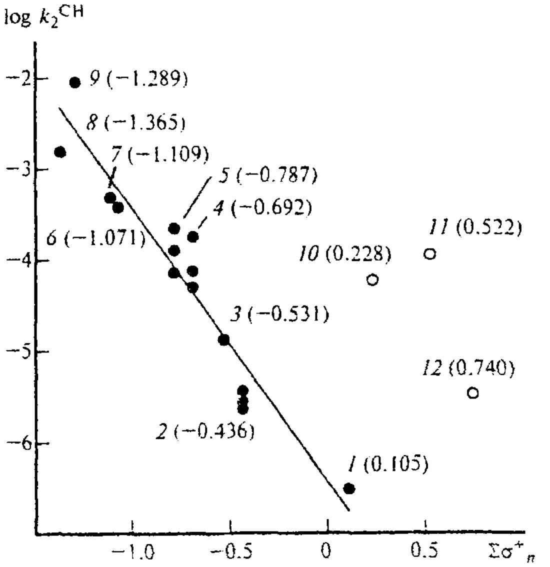

Fig. 1. Correlation of the partial rate constants of oxidation of hydrocarbons and alcohols by *n*-decanepersulfonic acid with the $\Sigma\sigma^+_n$ constants (values in parentheses) of substituents (according to Okamoto—Brown) at 323 K: *1*, chloroform; *2*, *n*-heptane, *n*-hexane, and *n*-decane; *3*, 3,3-dimethylpentane; *4*, 1,4-*trans*-dimethylcyclohexane, 1,4-*cis*-dimethylcyclohexane, and 3-methylhexane; *5*, 2,2,4-trimethylpentane, 2,4-dimethylpentane, and 2,3-dimethylbutane; *6*, 1-octanol; *7*, ethanol; *8*, isopropyl alcohol; *9*, cyclohexanol; *10*, 2-nitropropane; *11*, 1-nitropropane; and *12*, nitromethane.

Analysis of the data in Table 1 shows that the dependence of k_2^{CH} on the structure of alkanes and alcohols under study is described by the Okamoto—Brown equation common for these compounds (Fig. 1)

$$\log k_2^{CH} = -(6.4 \pm 0.2) - (3.0 \pm 0.3) \cdot \Sigma\sigma^+_n \ (323\ \mathrm{K}).$$

The $\Sigma\sigma^+_n$ values were taken from the handbook.[15] The negative value of the ρ coefficient (−3.0) indicates that the reaction proceeds *via* the electrophilic mechanism.[16] The data for nitro compounds do not obey this equation, which can indicate a different reaction mechanism.

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