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# KINETICS AND SELECTIVITY OF THE OXIDATION OF ALKANES IN $Cl_2-H_2O$ AND $Cl_2-Hg^{2+}-H_2O$ SOLUTIONS

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Relative oxidation rate constants of several normal, iso-, cyclo- and methylcycloalkanes have been measured in $Cl_2-H_2O$ and $Cl_2-Hg^{2+}-H_2O$ solutions at 343 K. The selectivity of C–H bond dissociation in both systems is the same. HOCl is assumed to be the active species for the two systems.

В растворах $Cl_2-H_2O$ и $Cl_2-Hg^{2+}-H_2O$ при 343 К измерены относительные константы скорости окисления ряда нормальных, изо-, цикло- и метилциклоалканов; селективность расщепления С–Н связи в обеих системах одинакова. Заключено, что активной частицей в обеих системах является кислота HOCl.

Aqueous chlorine solutions are known to oxidize alkanes (RH) to form chloroalkanes /1/. We have established that the oxidation of RH is enhanced by $Hg^{2+}$ ions being the acceptors of $Cl^-$. Active species can be polarized chlorine, e.g. as the adduct $Cl^{\delta+}-Cl^{\delta-}..Hg^{2+}$. However, taking into account the concepts on the role of bridged ligands in the oxidation of alkanes /2, 3/, the more probable active species is HOCl formed in the reaction /4/

$$Cl + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (1)$$

To establish the structure of reactants, we have studied the oxidation kinetics and selectivity of alkanes of various structures in competing reactions using the syringe-reactor method applied previously to study the reaction of alkanes in aqueous solutions with OH radicals /5/ and also with $MnO_4^-$, $HMnO_4$, $SO_4^-$ and other oxidants /3/.

Theree systems have been studied:

I. $Cl_2-H_2O$ having commensurable concentrations of $Cl_2$ and HOCl /4/;

II. $Cl_2-Hg^{2+}-H_2O$ in which due to the reaction

$$Cl_2 + Hg^{2+} + H_2O \rightarrow HOCl + H^+ + HgCl^+ \qquad (2)$$

the HOCl concentrations are about twice as high as in I, and $Cl_2$ is practically absent /4/;

III. Individual measurements were made in the $HOCl-H_2O$ system; the solutions of HOCl were prepared like in Ref. /6/ and did not contain $Cl_2$.

The reactions are of the first order with respect to RH and, apparently, HOCl:

$$-\frac{d[R^iH]}{dt} = k^i[R^iH]\,[HOCl] \tag{3}$$

The rate ratio for the two substrates $R^AH$ and $R^BH$ being under simultaneous study, permits to eliminate the concentration of reactant and leads to the equation to determine the $k^A/k^B$ ratio:

$$\lg\,[R^AH] = (k^A/k^B)\lg\,[R^BH] + \text{const.} \tag{4}$$

For the three systems the oxidation selectivity is the same within the experimental accuracy, and the absolute oxidation rates are approximately equal (Table 1).

In the $Cl_2-Hg^{2+}-H_2O$ system the first-order rate constant was slightly higher and the scatter in the kinetic data was lower than in the $Cl_2-H_2O$ solutions. Apparently, these effects can be attributed to the low concentration of $Cl_2$ in the $Cl_2-Hg^{2+}-H_2O$ system. Consequently, on the one hand, the HOCl concentration and the reaction rate increase, and on the other hand, owing to the absence of a gas bubble in the syringe-reactor, the reproducibility of the results is improved. Since the concentration of $Cl_2$ in the $Cl_2-Hg^{2+}-H_2O$ system is significantly lower, whereas the reaction rate is higher, it can be concluded that the radical-chain chlorination

$$RH + \dot{Cl} \rightarrow \dot{R} + HCl, \qquad \dot{H} + Cl_2 \rightarrow RCl + \dot{Cl} \tag{5}$$

does not take place under our conditions.

The results indicate that in systems I, II and III the immediate reactant is HOCl.

Alkaline additions inhibit reactions in the $H_2O-Cl_2$ system, which permits to conclude that the $OCl^-$ anion is much less active in the oxidation of alkanes than the HOCl acid. According to our data, the $MnO_4^-$ anion is approximately $10^3$ times less active in the oxidation of alkanes in aqueous solutions than $HMnO_4$.

According to Refs /2, 3/, the oxidation of alkanes in aqueous media by a strong oxidant $LM^n$, where $M^n$ is an electron acceptor and L is a bridged ligand-base, starts with loosening of the C–H bond:

$$RH + LM^n \rightarrow R\,.\,.\,.\,H\,.\,.\,.\,LM^n \rightarrow \text{products} \tag{6}$$

Table 1

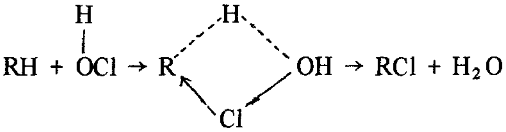
Oxidation selectivities of alkanes in solutions of $Cl_2-H_2O$ and $Cl_2-Hg^{2+}-H_2O$ at 343 K

| RH | $k/k^{n-C_5H_{12}}$ | |
|---|---|---|
| | $Cl_2-H_2O$ | $Cl_2-Hg^{2+}-H_2O$ |
| $C_2H_6$ | | 0.06±0.03 |
| $C_3H_8$ | 0.47±0.09 | 0.42±0.06 |
| $n-C_4H_{10}$ | 0.8±0.1 | 0.71±0.05 |
| $n-C_5H_{12}$ | 1.0 | 1.0 |
| $n-C_6H_{14}$ | 1.3±0.1 | 1.35±0.05 |
| $i-C_4H_{10}$ | 1.5±0.3 | 1.5±0.2 |
| $i-C_5H_{12}$[a] | 1.9±0.3 | 1.6±0.2 |
| $c-C_5H_{10}$[b] | 2.0±0.5 | 2.0±0.4 |
| $c-C_6H_{12}$ | 2.6±0.9 | 2.5±0.5 |
| $c-C_6D_{12}$ | 0.9±0.3 | 0.9±0.2 |
| $c-C_7H_{14}$ | 4.9±2.0 | 4.7±1.2 |
| $CH_3-c-C_6H_{11}$[c] | 3.9±1.9 | 3.2±0.9 |
| $c-C_6H_{12}/c-C_5H_{10}$ | 1.3±0.1 | 1.25±0.05 |
| $c-C_5H_{10}/c-C_6D_{12}$[d] | 2.3±0.1 | 2.35±0.05 |
| $c-C_6H_{12}/c-C_6D_{12}$ | 3.0±0.4 | 2.9±0.2 |

[a] 2-Methylbutane; [b] For cyclopentane k values are approximately equal to 2 × $10^{-2}$ in systems I and III; [c] Methylcyclohexane; [d] In system III this ratio is 2.4

The ratio of rate constants $c-C_6H_{12}/c-C_5H_{10}$ and the kinetic isotope effect (KIE) $c-C_6H_{12}/c-C_6D_{12}$ can be used as tests for a bridged ligand. Thus, for the OH-bridge, the KIE value lies within 2.8–3.0 and the $c-C_6H_{12}/c-C_5H_{10}$ ratio is between 1.3 and 2.1 /3/. The KIE = 3.0 and $c-C_6H_{12}/c-C_5H_{10}$ = 1.3 obtained for the systems examined (Table 1) satisfy these limits. Selectivity data confirm that the immediate reactant in both $Cl_2-H_2O$ and $Cl_2-Hg^{2+}-H_2O$ is HOCl.

All data obtained indicate that the reaction involves a transfer of an H atom (or $H^+$ and $e^-$) to the OH group of reactant and seems to be accompanied by a simultaneous intramolecular attack of the Cl atom on the carbon:



(7)

The selectivity to the products, ways of stabilization and the intermediate reaction geometries require further investigation.

## EXPERIMENTAL

The oxidation kinetics of alkanes was studied by the syringe-reactor method /7/ in the absence of a gas phase. Gaseous chlorine was introduced into the reactor filled by a solution of $H_2SO_4$ (1.0 M) or $H_2SO_4$ (1.2 M), $Hg^{2+}$ (0.05–0.14 M). The gas phase was completely removed by pressing the piston upon saturating the solution (4 $cm^3$, 343 K) by chlorine. The initial concentration of $Cl_2$ in the solution was about $10^{-2}$ M. Then 1–3 $cm^3$ solution of two alkanes ($R^AH$ and $R^BH$) ($H_2SO_4$ – 1.0 M, $RH \leqslant 10^{-4}$ M), was introduced into the syringe-reactor. The decrease in [RH] was followed by gas chromatography /5/.

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