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KINETICS OF ALKANE OXIDATION BY CHROMIC ACID IN AQUEOUS SOLUTIONS OF Ir(IV) CHLORIDE COMPLEXES

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The kinetics of propane and isobutane oxidation by aqueous solutions of chromic acid in the presence of Ir(IV) chloride complexes has been studied. Reaction rate decreases with increasing Cl ion concentration and decreasing acidity. $Ir(H_2O)Cl_5^-$ complexes are by an order of magnitude more active than $IrCl_6^{2-}$.

Изучена кинетика окисления пропана и изобутана водными растворами хромовой кислоты в присутствии хлоридных комплексов Ir(IV). Скорость реакции уменьшается с ростом концентрации Cl-ионов и понижением кислотности среды. Комплексы $Ir(H_2O)Cl_5^-$ на порядок более активны, чем $IrCl_6^{2-}$.

As was found previously, in aqueous solutions Ir(IV) chloride complexes catalyze the oxidation of alkanes (RH) to alkyl chlorides by chromic acid /1/. Here we present the results of kinetic studies of this process to find the most active form of the complex catalyst.

The reaction was performed in a temperature-controlled syringe reactor without a gas phase and followed by sampling the liquid during the experiment for chromatographic analysis of RH and the reaction product /2/. Chromic acid and the iridium complex were taken in excess with respect to RH, thus the change of their concentration in the reaction could be neglected. The variation of [RH] with time corresponds to the first order equation $\ln[RH]_o = \ln[RH]_{in} - kt$ ($[RH]_o$ is the alkane concentration at moment t, $[RH]_{in}$ is the initial hydrocarbon concentration) which was used to estimate the rate constant k. It has been found that the rate is greatly

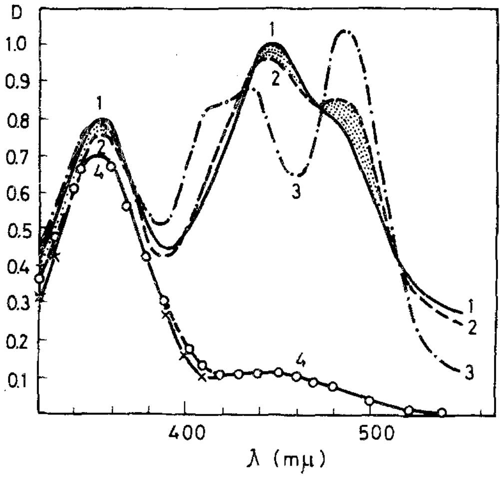

Fig. 1. Spectra of test solutions, depending on the method of catalyst preparation. Starting reagents: 1 – K_3IrCl_6, 3 – K_2IrCl_6 and H_2IrCl_6. [Cat] = = 2.3×10^{-2}, [Cr(VI)] = 5×10^{-2} and [H_2SO_4] = 1.33 mol/l. 1 → 2 – spectrum variation of test solution 1 after the addition of 0-0.6 mol/l NaCl. (Points designate spectra of solutions with [NaCl] = 0.04, 0.1, 0.2 and 0.414 mol/l, respectively). 4 – spectra of Cr(VI), i.e. of the solutions containing all the components except iridium (0 → x for NaCl = 0 → 0.35 mol/l). l = 1.18×10^{-2} cm

dependent on the method of solution preparation. When the starting reagents were H_2IrCl_6 or K_2IrCl_6, the rate was by an order of magnitude lower than for K_3IrCl_6, though Ir(III) oxidation by chromic acid to Ir(IV) started already during mixing the solutions and completed after 1 hr boiling of the mixture before pouring it into the reactor.

To determine the active complex catalyst form, spectra of the test solutions have been studied. In each experiment the mixture spectrum was recorded twice: before RH addition to the system and after completion of reaction, viz. after the complete consumption of dissolved alkane. The catalyst form during the reaction is unchanged, but according to literature data /3/, the Ir(IV) spectrum corresponds to $IrCl_6^{2-}$ in the former case and to $Ir(H_2O)Cl_5^-$ in the latter case (Fig. 1, spectra

3 and 1, respectively). This difference in the catalyst form can be attributed to the faster aquation of Ir(III) as compared with Ir(IV) complexes /4/. Therefore, during oxidation of Ir(III) to Ir(IV) the test solution contains aqua complexes, which, however, have no time to form when K_2IrCl_6 is taken as a starting reagent. It is of interest that when $[Cr(VI)] < 3\,[K_3IrCl_6]$ and hence the test mixture contains Ir(III) complexes and $Ir(H_2O)Cl_5^-$, which in principle can be both the catalyst and the oxidant for a given reaction, the system has but a low activity. Thus the ratio of the rate constants of isobutane oxidation in the systems Cr(VI)–RH (1), Ir(III)–$Ir(H_2O)Cl_5^-$–RH (2), $IrCl_6^{2-}$–Cr(VI)–RH (3) and $Ir(H_2O)Cl_5^-$–Cr(VI)–RH (4) is

$$k_1 : k_2 : k_3 : k_4 = 0.3 : 0.7 : 10 : 100$$

(The results have been obtained at $[Ir(III)] = [Ir(IV)] = 2.3 \times 10^{-2}$, $[Cr(VI)] = 5 \times 10^{-2}$, $[H_2SO_4] = 1.33$ and $[RH] \sim 10^{-4}$ mol/l, $T = 97.5\ ^{\circ}C$). It can be seen that the active catalyst form in the Ir(IV)–Cr(VI)–RH system is the $Ir(H_2O)Cl_5^-$ complex. It increases the rate of RH oxidation by chromic acid by 2.5 orders of magnitude and is by an order of magnitude more active than $IrCl_6^{2-}$ in the same conditions. These results indicate that even in the presence of a strong oxidant in the system, the alkane should be preactivated, so that RH oxidation will occur at an appreciable rate (compare systems 1, 3 and 4). It can be supposed that iridium complexes, which catalyze the oxidation, perform this activation through an electrophilic attack of Ir(IV) on the C–H bond electrons, and apparently through the formation of an alkyl Ir(IV) complex as an intermediate. Redox potentials, E_0, for $IrCl_6^{2-}/IrCl_6^{3-}$, trans-$Ir(H_2O)_2Cl_4$/trans-$Ir(H_2O)_2Cl_4^-$ and 1,2,3-$Ir(H_2O)_3Cl_3^+$/ /1,2,3-$Ir(H_2O)_3Cl_3$ are equal to 1.017 /5/, 1.22 and 1.30 V /6/, respectively. As is seen, the substitution of Cl^- by H_2O enhances the electrophilic properties of Ir(IV) and apparently promotes alkane activation. Therefore, $Ir(H_2O)Cl_5^-$ is a more active catalyst for RH oxidation than $IrCl_6^-$.

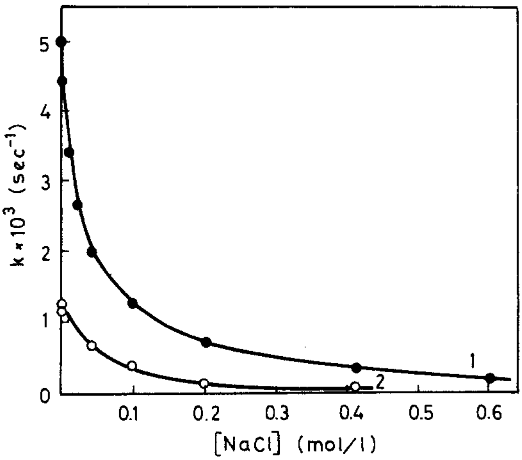

Fig. 2. Rate of isobutane and propane oxidation (curves 1 and 2, respectively) vs. the concentration of NaCl added to system 4. $[K_3IrCl_6] = 2.3 \times 10^{-2}$, $[Cr(VI)] = 5 \times 10^{-2}$, $[H_2SO_4] = 1.33$ and $[RH] \sim 10^{-4}$ mol/l, T = 97.5 °C

The rate of alkane oxidation in systems 3 and 4 linearly increases with increasing acidity ($[H_2SO_4] = 0.1$-1.33 mol/l). It is likely that the main reason for this dependence is the fact that chromic acid possesses strong oxidizing properties only in acidic media:

$$HCrO_4^- + 7H^+ + 3e = Cr^{3+} + 4H_2O, \; E_o = 1.35 \text{ V} \qquad (5)$$

In addition, the spectra of test solutions of system 4 show that with decreasing acidity the catalyst form changes ($Ir(H_2O)Cl_5^-$ transforms into $Ir(OH)Cl_5^{2-}$) and the increase in the negative charge by one unit weakens electrophilic properties of Ir(IV).

The addition of Cl ions to system 4 sharply decreases the rate of alkane oxidation (Fig. 2). The substitution of NaCl by $NaNO_3$ does not change the rate, i.e. the ionic strength within this range does not influence the reaction rate. As is demonstrated by the spectra of the same solutions (Fig. 1), during the 1-hr boiling in mixture preparation and during the reaction time of alkane oxidation $Ir(H_2O)Cl_5^-$ cannot transform into the less active $IrCl_6^{2-}$ form. Only at the maximum concentration of NaCl used in the experiments do the $IrCl_6^{2-}$ bands become noticeable, i. e. does $Ir(H_2O)Cl_5^-$ partially transform into $IrCl_6^{2-}$.

The addition of NaCl decreases the rate of alkane oxidation in system 3, i. e. when K_2IrCl_6 is taken as starting reagent, the form of $IrCl_6^{2-}$ catalyst is not changed by $[Cl^-]$. As is illustrated by the $IrCl_6^{3-}$ complexes in Ref. /7/, the rate constant of Cl^- substitution by H_2O decreases with increasing competing Cl^- ligand concentration in the solution. It is likely that, for the same reason, RH activation via complex formation with Ir(IV) will be hindered by the increase of $[Cl^-]$ due to the competing influence of Cl^- ions.

The decrease of RH oxidation rate with increasing [NaCl] may be due to changes in the oxidizing properties of chromic acid. After Cl^- addition to the system, the equilibrium $H^+ + Cl^- + HCrO_4^- = ClCrO_3^- + H_2O$ is attained and $ClCrO_3^-$ is known to possess a decreased oxidizing power /8/. As is illustrated by the $Ir(III)-Ir(H_2O)Cl_5^- -RH$ and $Ir(H_2O)Cl_5^- -Cr(VI)-RH$ systems, it is seen that in the presence of the most active catalyst form in the solution the rate of RH oxidation is determined by the oxidizing properties of the oxidant.

The apparent activation energy of isobutane and propane oxidation is $E_{eff} \sim 32$ kcal/mol ($[K_3IrCl_6] = 2.3 \times 10^{-2}$, $[Cr(VI)] = 5 \times 10^{-2}$, $[H_2SO_4] = 1.33$ and $[RH] \sim 10^{-4}$ mol/l, T = 77.5-97.5 °C).

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