RHODIUM(III) COMPLEXES WITH O-ALKYL-S-ALKYL THIOCARBONATES AS CATALYSTS FOR THE HOMOGENEOUS HYDROGENATION OF UNSATURATED COMPOUNDS

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Catalytic activity was found for Rh^{3+} complexes with O-alkyl-S-alkyl thiocarbonates in the homogeneous hydrogenation of unsaturated compounds. Cyclic voltamperometry was used to detect the formation of rhodium hydride intermediates during the hydrogenation of alkenes in the presence of these complexes.

Homogeneous catalysts derived from rhodium complexes with ligands stabilizing the lower oxidations of a metal such as tertiary phosphines and phosphites, carbonyls, and sulfoxides are commonly used for the hydrogenation of unsaturated compounds [1]. Rhodium complexes with organosulfur compounds containing a thioester fragment have been studied less extensively. This circumstance is largely related to the low stability of the Rh^+ intermediates formed in solution due to the weak π-electron-withdrawing properties of the sulfur atom [2]. Thus, interest is found in compounds, which contain functional groups in addition to sulfur capable of delocalizing the excess electron density of the central ion in its lower oxidation state and enhancing the stability of the corresponding intermediates.

In the present work, we studied the catalytic activity of Rh^{3+} complexes with O-alkyl-S-alkyl thiocarbonates (L) with the general formula $RhCl_3L_3$, where L = ROC(O)SR′, R = i-Pr, i-Bu, C_7H_{15}, Ph, and R′ = Me, Et, Pr, Bu, and i-Bu in the homogeneous hydrogenation of unsaturated compounds.

EXPERIMENTAL

The preparation and purification of the O-alkyl-S-alkyl thiocarbonates were carried out by reported methods [3]. The Rh^{3+} complexes with these ligands were obtained by procedures analogous to those described by Kochetkova and Sveshnikova [4]. The composition of the complexes and their purity were monitored using elemental analysis, molecular mass data, electronic, IR, and PMR spectroscopy. The solvents (DMF, DEPA, and DMAA) were purified by common procedures [5].

The hydrogenation was carried out in a 10-ml cell maintained at constant temperature, atmospheric pressure, and 25-75°C. The reaction rate was evaluated relative to hydrogen absorption. The products were analyzed by gas-liquid chromatography. The samples of 1-hexene, 1-nonene, cinnamic alcohol, and allyl alcohol were distilled prior to use. Maleic acid was recrystallized twice from ethanol. The apparatus and procedure for the electrochemical studies were described in our previous work [6].

RESULTS AND DISCUSSION

Figure 1 gives characteristic curves for hydrogen absorption in the hydrogenation of maleic acid and 1-hexene in DMF in the presence of Rh^{3+} complexes with O-alkyl-S-alkyl thiocarbonates. The corresponding curves for the other compounds are analogous in form. Special experiments showed that the higher rate of hydrogen absorption at the reaction onset is related to additional consumption for the reduction of the Rh^{3+} complexes to Rh^+ complexes in the initial segment of the curves. The Rh^+ complexes display catalytic activity. In all cases, only the double bond is hydrogenated, while the functional groups are not affected. The reaction rate constants are given in Table 1.

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TABLE 1. Reaction Rate Constants for Unsaturated Compounds in the Presence of Rh^{3+} Complexes with O-Alkyl-S-alkyl Thiocarbonates

Ligand	k_2, liter/mole·sec				
	1-nonene	1-hexene	maleic acid*	cinnamic alcohol	allyl alcohol
$C_7H_{15}OC(O)SBu$	0,73±0,10	0,98±0,15	0,56±0,06	0,71±0,09	0,62±0,11
i-PrOC(O)SMe	–	–	0,36±0,05	–	–
i-BuOC(O)SBu	–	–	0,61±0,08	0,84±0,12	0,75±0,09
i-BuOC(O)SEt	0,68±0,12	0,91±0,13	0,30±0,05	–	–
i-BuOC(O)SPr	0,81±0,15	0,98±0,16	0,41±0,06	–	–

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*At 75°C.

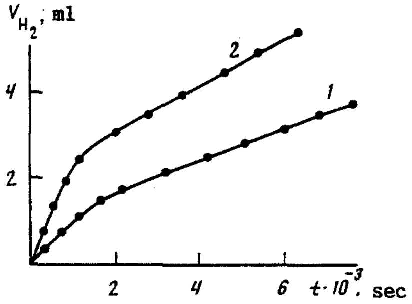

Fig. 1. Hydrogen absorption curves in the hydrogenation of 0.035 mole/liter solutions of maleic acid (1) and 1-hexene (2) in DMF in the presence of $3.5 \cdot 10^{-3}$ mole/liter $RhCl_3(i\text{-}BuOC(O)SBu)_3$ at 55°C.

The form of the curves and the similarity of the k_2 values to the corresponding values for Rh^{3+} complexes with dialkyl sulfides [7] indicate that the hydrogenation reaction occurs through the reduction of Rh^{3+} complexes to Rh^{+} complexes by hydrogen, the oxidative addition of the latter, and the reductive elimination of the reaction products. Such a scheme is typical for the homogeneous hydrogenation of unsaturated compounds in the presence of rhodium catalysts.

The rhodium hydride complex formed in the catalytic cycle was detected by cyclic voltamperometry. Figure 2 gives the cyclic voltamperogram for the rhodium complex with O-heptyl-S-butyl thiocarbonate in the presence of 1-nonene before and after flushing with hydrogen. The additional signal recorded at less negative potentials corresponds to the electrochemical reduction of the hydride complex. The intensity of this peak decreases over time (Fig. 3). The rate constant for decomposition of the intermediate is $(1.9 \pm 0.2) \cdot 10^{-3}$ sec^{-1}.

In contrast to Rh^{3+} complexes with dialkyl sulfides, the thiocarbonate complexes display high stability during the hydrogenation reaction, are stable upon storage, and retain their activity upon repeated use. As noted above, thioesters have weak π-electron-withdrawing properties and do not efficiently stabilize the lower oxidation states of metals. Thus, rhodium complexes with dialkyl sulfides decompose in solution upon the hydrogenation of terminal alkenes such as 1-nonene and 1-hexene, cinnamic alcohol, and allyl alcohol. The distribution of excess electron density of the central ion over the delocalized σ,π-electron system of the ligand, which enhances the stability of the Rh^{+} intermediates, becomes possible due to the presence of the keto group along with the electron-donor sulfur atom in the thiocarbonate molecules. The steric hindrance created by the bulky thiocarbonate molecules also enhances the stability of the complexes by preventing the disproportionation of the Rh^{+} compounds, which is one of the main reasons for the separation of metallic rhodium during the hydrogenation reaction [7]. Greatest stability among the dialkyl sulfide complexes is found for the complexes with tertiary and secondary alkyl groups.

We should note that the catalytic activity of these complexes is only slightly altered upon going from DMF to DEPA and DMAA. The hydrogenation in alcohols such as ethanol, methanol, and 2-propanol is accompanied by the rapid decomposition of the complexes and separation of metallic rhodium. The reaction virtually does not proceed in acetone, 2-butanone, and acetonitrile. This failure is apparently related to the lower basicity of the solvents [8]

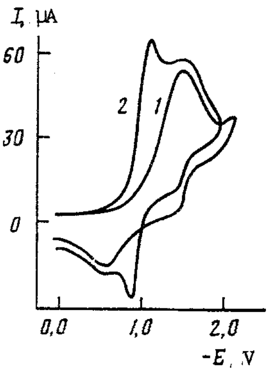

Fig. 2

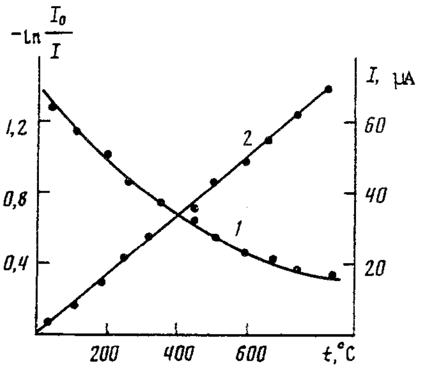

Fig. 3

Fig. 2. Cyclic voltamperograms of $3.5 \cdot 10^{-3}$ mole/liter $RhCl_3(C_7H_{15}O$-$C(O)SBu)_3$ in DMF in the presence of $3.5 \cdot 10^{-2}$ mole/liter 1-nonene before (1) and after hydrogen flushing (2) at 25°C.

Fig. 3. Kinetic curve for the decomposition of the intermediate in the system containing $3.5 \cdot 10^{-3}$ mole/liter $RhCl_3(C_7H_{15}OC(O)SBu)_3$, $3.5 \cdot 10^{-2}$ mole/liter 1-nonene, and H_2 in DMF (1) and its semilog transformation (2) at 25°C.

and higher stability of the complexes since dissociation of the ligands precedes the penetration of the substrate molecules into the coordination sphere. In addition, the rate of the rearrangement of the coordination sphere from octahedral to square planar in the reduction of Rh^{3+} complexes to Rh^{+} compounds also depends on the donor properties of the solvent [9].

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