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CATALYTIC SYNTHESIS OF HYDROGEN IODIDE FROM IODINE AND WATER IN THE PRESENCE OF CARBON MONOXIDE AS REDUCING AGENT

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ABSTRACT. A catalytic synthesis for hydrogen iodide (a co-catalyst source for Reppe reactions) from iodine, water and carbon monoxide is reported. Beside the well known noble metal catalyst (e.g., rhodium, iridium), iron (powder) and iron compounds (e.g., $Fe(CO)_5$, FeI_2) were found to have high and constant activities in the HI formation during reactions performed on recycled catalysts. The induction period observed with iron and iron compounds as catalyst precursor in the first catalytic reaction is completely missing in the advanced ones.

Keywords: Hydrogen iodide, Catalytic synthesis, Co-catalysts, Carbonylations

INTRODUCTION

Hydrogen iodide and alkyl iodides are effective co-catalysts for the carbonylation reactions of alcohols and the hydrocarboxylation reactions of alkenes or alkynes, known under the common name of Reppe reactions [1-10]. As the hydrogen iodide is very corrosive, it is recommended that its use in industrial reactors should be avoided. Fortunately, this is possible, since under the conditions of the Reppe reactions the hydrogen iodide changes into alkyl iodides and these latter ones intervene effectually in the catalytic cycle. In view of avoiding the advanced corrosion processes of the bulky carbonylation reactors, the alkyl iodides (methyl iodide and ethyl iodide) used in the industrial processes must be synthesized separately in low volume reaction vessels. Methyl iodide, the co-catalyst of the carbonylation reaction of methanol to acetic acid can be obtained according to the following chemical reaction [1,7]:

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$$CH_3OH + HI \rightarrow CH_3I + H_2O$$

whereas ethyl iodide, the co-catalyst for the carbonylation reaction of ethanol as well as for the hydrocarboxylation reaction of ethylene to propionic acid can be won according to the reaction [1,7]:

$$CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O$$

The synthesis of hydrogen iodide from elemental iodine and water under the reducing action of carbon monoxide requires the presence of noble metal catalysts, for example salts or complexes of rhodium or iridium [7,11,12] and takes place in accordance with the chemical equation:

$$I_2 + CO + H_2O \rightarrow 2\,HI + CO_2$$

Owing to the fact that the reaction takes place in the liquid phase and that the recovery of rhodium and iridium, very expensive noble metals, raises serious technical difficulties, cheaper transition metals have been tested as catalysts in the synthesis of hydrogen iodide.

EXPERIMENTAL

Elemental iodine (p.a.) and hydrogen iodide (57%) of FLUKA origin have been used. The distilled water and carbon monoxide (99.5%) have been prepared in the "Babes-Bolyai" University (BBU) laboratory. CO has been prepared by means of the catalytic dehydration of the technical formic acid with concentrated sulphuric acid. The gas thus formed has been neutralized by bubbling through a solution of sodium hydroxide and is collected in a gas reservoir, from whence it is compressed in gas cylinders. The absolute methanol (p.a., 99,5%) has been provided by the "Chimopar" Bucharest. The transition metal salts (p.a.) used as catalyst precursors are of Merck and FLUKA origin. $[Rh(CO)_2Cl]_2$ and $Fe(CO)_5$ have been prepared in the BBU laboratory. The basic diagram of the batch-type hydrogen iodide production equipment is represented in Figure 1.

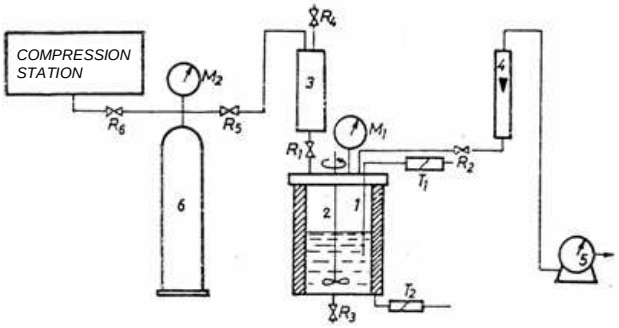

Figure 1. Diagram of the hydrogen iodide preparation (Legend in the text).

The equipment consisted of an autoclave (1) of 200 cm^3 volume, manufactured from corrosion-resisting Hast-Alloy C, fitted with a magnetic stirrer (2) and a heating system steered by a heat regulator with a chromel-coppel T_2 thermocouple. The temperature of the reaction vessel was measured by an iron-constantan thermocouple T_1. The valves R_1, R_2 and R_3 were also made of Hast-Alloy C. The autoclave pressure has been measured by means of manometer M_1, equipped with a separating Teflon membrane. As carbon monoxide source a gas cylinder (6) of 40 l has been used, equipped with the manometer M_2 containing the CO compressed at 150 bar. The pressure vessel (3) made of Hast-Alloy C, directly linked to the autoclave through valve R_1 is used for the injection of the solution composed of elemental iodine, water, hydrogen iodide (57% aqueous solution) and catalyst. After the introduction of the reaction mixture, the air was removed by means of repeated purging with CO. Then the heating was started and on reaching the running temperature, by means of the inlet valve R_1 and the evacuation valve R_2 for the CO, the pressure was adjusted to the desired value. The gas output was measured by the rotameter (4) and the wet gas meter (5). The moment of determining the operating pressure counts as the time $t_0 = 0$ at the time-dependent inspection of the reaction. The kinetic measurements have been carried out at constant temperature and pressure. The gas output flow rate has been kept between 4-6 l/h.

The reaction has been followed by monitoring the decrease of the elemental iodine concentration and the increase of the hydrogen iodide concentration against time. The variation of the composition of the solution contained in the autoclave has been determined on the basis of the samples taken through valve R_3 at definite time intervals. The volume of a sample was approximately of 0.5-1 cm^3. The concentration of the elemental iodine has been volumetrically measured by titration with a 0,1 N solution of $Na_2S_2O_3$ in the presence of starch.

The actual concentration of the hydrogen iodide has been obtained by means of titration with a 0,1 N solution of sodium hydroxide in the presence of phenolphthalein. Because the free iodine disturbs the titration of the hydrogen iodide, the iodine has been extracted in advance with carbon tetrachloride. On the basis of the instantaneous values of the concentration of the free iodine $[I_2]$ and of those of the hydrogen iodide [HI] respectively, and taking into consideration their initial concentrations $[I_2]_0$ and $[HI]_0$, their momentary conversions have been calculated (X_{iodine} and X_{HI}) according to the relations:

$$X_{iodine} = ([I_2]_0 - [I_2])/[I_2]_0; \qquad X_{HI} = ([HI] - [HI]_0)/2[I_2]_0$$

The conversion curves obtained by the graphical representation of X = f(t) served for the study on the reproducibility of the process and for the study on the influence of the reaction parameters upon the conversion. It has been furthermore inquired into the possibility of reusing the catalytically active species in more catalytic cycles.

RESULTS AND DISCUSSION

Figure 2 presents the conversion curves obtained as a result of the use of the $[Rh(CO)_2Cl]_2$ (curve 19) and the $Co(CH_3COO)_2 \cdot 4H_2O$ (curve 20) as catalyst precursors.

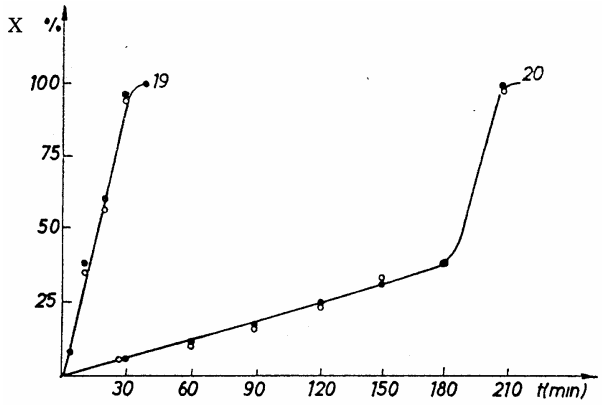

Figure 2. Conversion curves of hydrogen iodide synthesis in two significant experiments: (19)-catalyst $[Rh(CO)_2Cl]_2$, [Rh] = 3,4 10^{-3} mol/l, P = 10 bar; (20)-catalyst $Co(CH_3COO)_2 \cdot 4H_2O$, [Co] = 0,175 mol/l, P = 50 bar. Conditions: $[I_2]_0$ = 0,71 mol/l, $[H_2O]_0$ = 3,33 mol/l, $[HI]_0$ = 1,933 mol/l, T = 130 °C; (●)- calculated from the consumption of I_2, (○)-calculated from the increase of the HI concentration.

In case of these experiments the actual conversions have been calculated as well as from the elemental iodine consumption as from the increase of the hydrogen iodide concentration. It follows from these diagrams that the conversion values determined on the basis of the two variants lies on the same curve, within the limit of experimental errors. However, the values calculated from the increase of the HI concentration are systematically somewhat lower than those calculated from the decrease of the elemental iodine concentration, but the differences are insignificant. The minor systematic error is probably owing to the loss of HI occurring as a result of the extraction of iodine from the aqueous solution with carbon tetrachloride. Subsequently, the calculation of conversion in most experiments has been performed only by means of determining the iodine consumption.

In view of studying the reproducibility of the hydrogen iodide synthesis many experiments in identical conditions have been conducted. Figure 3 illustrates the conversion curves obtained for two experiments performed in the presence of $Fe(CO)_5$ under identical conditions.

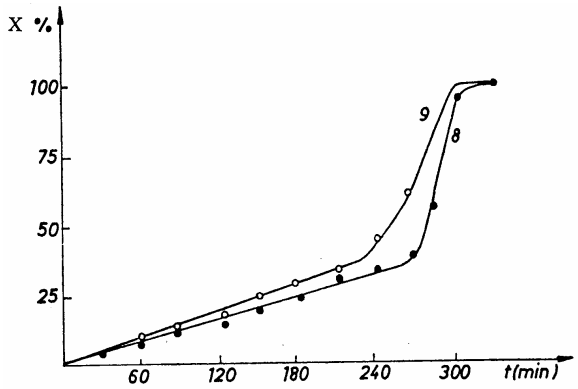

Figure 3. Conversion curves for two HI syntheses catalyzed by $Fe(CO)_5$ carried out under identical conditions P = 50 bar, T = 130 °C, [Fe] = 0,175 mol/l, $[I_2]_0$ = 0,71 mol/l, $[HI]_0$ = 1,933 mol/l, $[H_2O]_0$ = 3,33 mol/l.

The rate of the conversion curves displayed an acceptable reproducibility merely for the first phase, which being slow, was also called the induction period of the reaction. In the rapid phase, as the speed was considerably higher, the density of the experimental data was reduced and the conversion determination errors were higher. From the combinations of cheaper transition metals only those of Fe and Co have displayed catalytic activity in the reaction of hydrogen iodide formation from elemental iodine

and water in the presence of CO. Figure 4 represents the conversion curves obtained as a result of the use of different compounds of iron and cobalt as catalysts and the conversion curve obtained with the $[Rh(CO)_2Cl]_2$ catalyst (curve 19) which was considered the reference curve.

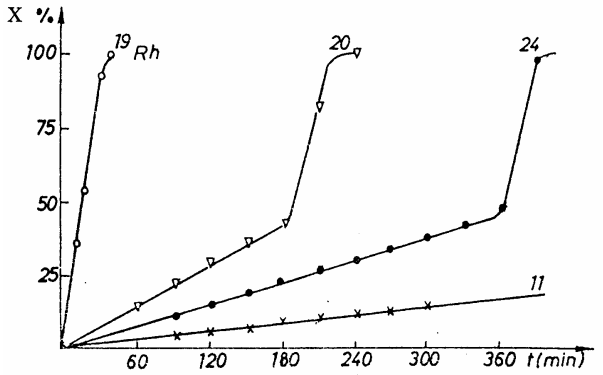

Figure 4: Diagrams X = f(t) for HI synthesis in the absence and presence of transition metal compounds. (11)-without catalyst, P = 50 bar; (19)-$[Rh(CO)_2Cl]_2$, [Rh] = $3.4 \cdot 10^{-3}$ mol/l, P = 10 bar; (20)-$Co(CH_3COO)_2 \cdot 4H_2O$, (24)-$FeSO_4 \cdot 7H_2O$, [Fe] = [Co] = 0,175 mol/l, P = 50 bar; T = 130 °C, $[I_2]_0$ = 0,71 mol/l, $[HI]_0$ = 1,933 mol/l, $[H_2O]_0$ = 3,33 mol/l.

The experiments (20) and (24) reveal that the reaction had an auto-acceleration character. Thus, the first slow stage corresponds to the phase of formation of a catalytically active species from the utilized precursor catalyst. The formation of the active catalyst is immediately followed by the rapid reduction of elemental iodine to hydrogen iodide. It follows from the analysis of the conversion curves (20) and (24) that the catalytic activity of the Fe and Co compounds is close, the incline of the two curves is in the rapid phase similar. However, the time necessary for the formation of the effective catalysts from the precursors differs. The formation of the catalytically active species from cobalt acetate occurs more rapidly than that from ferrous sulphate. Nevertheless, in both cases one can observe the auto-acceleration which is owing to the formation of the catalytically active species from the precursor initially employed.

The temporal sequence of the reaction in the presence of the iron catalyst is dependent on the nature of the compound utilized as a precursor. Figure 5 illustrates the conversion curves obtained with different iron compounds used as catalyst precursors.

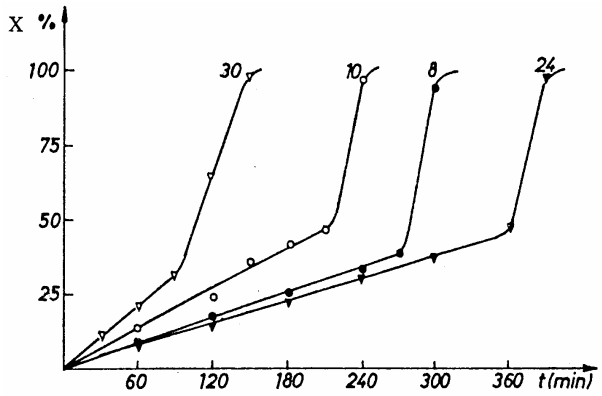

Figure 5. Representations X = f(t) obtained for the HI synthesis as a result of the use of iron compounds as catalyst precursors. (8)-$Fe(CO)_5$, (10)- Fe powder, (24)-$FeSO_4 \cdot 7H_2O$, (30)-FeI_2; P= 50 bar, T = 130 °C, $[I_2]_0$ = 0,71 mol/l, $[HI]_0$ = 1,933 mol/l, $[H_2O]_0$ = 3,33 mol/l.

It follows from the diagram that from the different tested iron compounds, the catalytically active species were formed the most rapidly from iron iodide and iron powder. The presence of SO_4^{2-} anion seems to be disturbing the catalytic process (curve 24).

Furthermore, it has been suggested that one should temporally examine the HI syntheses in the presence of catalysts preformed from FeI_2 or iron powder in a previous experiment. Due to the injection of the stoichiometric quantity of methanol at the boiling temperature of iodomethane (43 °C), the hydrogen iodide previously formed was transformed in methyl iodide, which gets distilled from the system. Once again the I_2 solution and the stoichiometric quantity of water were injected in the autoclave. After several purging with CO, the reaction mixture was warmed up at 130 °C and the working pressure was set with CO at 10 bar. Figure 6 comparatively presents the conversion curves obtained under identical conditions for the $[Rh(CO)_2Cl]_2$ catalyst (curve 19) and an iron catalyst preformed in a former experiment (curve 32). In this case representations X = f(t) no longer have an inflexion point. As anticipated, the slow phase, the stage of formation of the active species from the precursor, is missing. Accordingly, the active species once formed from the iron precursor maintains its catalytic activity. Furthermore, it does not get deactivated even during the synthesis of the methyl iodide which takes place at atmospheric pressure and in the absence of the CO atmosphere.

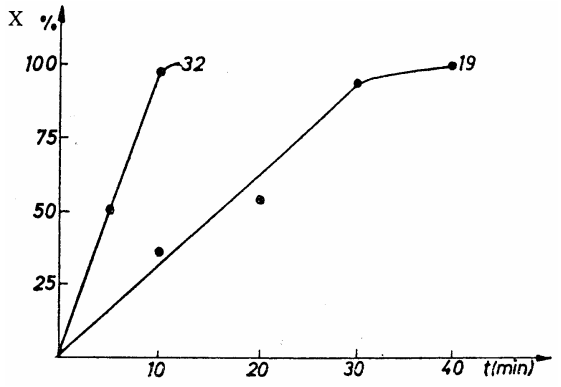

Figure 6. Comparison of the activity of the recycled iron catalyst to that of the rhodium under the following concentration ratios: [Fe]:[Rh] = 50, (19)-$[Rh(CO)_2Cl]_2$, (32)- catalyst preformed from FeI_2, P= 10 bar, T = 130 °C, $[I_2]_0$ = 0,71 mol/l, $[HI]_0$ = 1,933 mol/l, $[H_2O]_0$ = 3,33 mol/l.

Figure 6 shows, that under a concentration ratio of [Fe]/[Rh] = 50, the preformed iron catalyst is more effective than that of rhodium. On calculating the reaction speeds from the slope of the two curves, it is found that the rate of reaction is 3 times higher in the case of the preformed iron catalyst. Accordingly, at an iron concentration of 16,5 ·[Rh] it is possible to effect a performance similar to that of the rhodium catalyst.

CONCLUSIONS

Hydrogen iodide can be prepared under favorable conditions from elemental iodine, water and carbon monoxide in the presence of adequate catalysts. Thus, rhodium and iron salts or other type of compounds of these metals can thereby function as catalysts. During the catalytic synthesis of HI on recycled iron catalysts, the catalytically active species formed from iron powder or iron iodide (FeI_2) becomes more effective due to the absence of the induction period initially observed and maintains an increased activity throughout more catalytic cycles.

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