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Isotope heat effect in reactions involving hydrogen evolution on palladium catalyst particles

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Abstract. The heat effect in the reduction of copper(II) by formaldehyde on palladium catalyst particles accompanied by hydrogen evolution depends on the presence of deuterium in the system. In the case of 80% substitution of hydrogen in the system by deuterium the heat effect increases 1·5 times. This fact can not be attributed only to the difference in the energies of the bonds of hydrogen and deuterium in compounds participating in the reaction.

Keywords. Hydrogen; isotope; heat; evolution.

1. Introduction

Reports have recently appeared on sufficient differences in electrolysis of water and heavy water on palladium electrodes (Fleischmann and Pons 1989; Jones *et al* 1989). The purpose of the present investigation was to determine the characteristic properties of hydrogen evolution on palladium particles from aqueous solutions as a result of chemical transformations in the case of substitution of deuterium for hydrogen.

As a model reaction we chose the autocatalytic precipitation of copper from solutions upon reduction with formaldehyde in the presence of metallic palladium particles as a catalyst. Such reactions are widely known in engineering as the reactions of "chemical precipitation" and are used for the metallization of dielectrics. The evolution of hydrogen in this is a side reaction from the point of view of technology:

$$2CH_2O + Cu^{2+} + 4OH^- \xrightarrow{Pd} Cu + H_2 + 2HCOO^- + 2H_2O,$$

or taking into account the fact that formaldehyde is present in alkaline media in the form of anionic methylene glycol,

$$2H_2C\begin{matrix}OH\\O^-\end{matrix} + Cu^{2+} + 2OH^- \xrightarrow{Pd} Cu + H_2 + 2HCOO^- + 2H_2O.$$

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The most likely mechanism for the precipitation is considered to be a coupled electrochemical reduction of copper(II) and oxidation of formaldehyde (Sviridov 1987) occurring on the palladium particle.

Anodic oxidation of formaldehyde:

(i) diffusion of a methylene glycol anion to the palladium surface;
(ii) its dissociative chemosorption $H_2C(OH)O^- \rightleftharpoons HC(OH)O^-_{ads} + H_{ads}$;
(iii) further oxidation $HC(OH)O^- + OH^- \rightarrow HCOO^- + H_2O + \bar{e}$;
(iv) the recombination of the adsorbed hydrogen $2H_{ads} \rightarrow H_2$;
(v) hydrogen desorption.

Cathodic reduction of copper(II):

(i) diffusion of Cu(II) to the catalyst surface;
(ii) adsorption;
(iii) reduction

$$Cu^{2+}_{ads} + 2\bar{e} \rightarrow Cu.$$

The quantity of copper deposited measured by weight does not differ from the quantity of hydrogen eliminated within limits of measuring error (5%).

Hence the main role of the palladium particle is to ensure the transport of an electron from the reducer to the oxidizer. The formation of hydrogen takes place on the metallic palladium particles.

2. Experimental

The chemical precipitation solutions contain (g/l): copper sulphate, pentahydrate – 20; trylon B – 55 (disodium salt of ethylenediamin tetraacetic acid, dihydrate); sodium hydroxide – 40, and formaldehyde solution (40%) – 80 ml/l. The pH of the solution was 12–13.

Dissolution was carried out in the given order. The formaldehyde solution was added ten minutes before the beginning of the reaction. All the reagents were of "chemically pure" and "pure for analysis" grade.

The solutions were prepared using distilled water and heavy water with an isotope content of 90%. The overall degree of deuteration in the system, with allowance for water and protons occurring in the reagents, is about 80%.

A solution containing colloidal palladium particles was prepared by mixing solutions of palladium chloride and tin chloride in hydrochloric acid (GOST 1988). The solution contained 1·0 g/l colloidal particles. Palladium in such suspensions is in the form of particles with dimensions of less than 1 μm.

The experimental procedure is as follows. Formalin was introduced into the solution to be precipitated and, after a ten-minute interval necessary for the conversion of formaldehyde to methylene glycol in alkaline medium, a solution containing colloidal palladium particles (40 ml/l) was introduced.

The metal precipitation reaction on palladium particles under the given conditions is characterized by an induction period of more than 500 s, after which a sudden acceleration of the reaction takes place. The process is accompanied by the violent evolution of hydrogen and is completed in 1200 s.

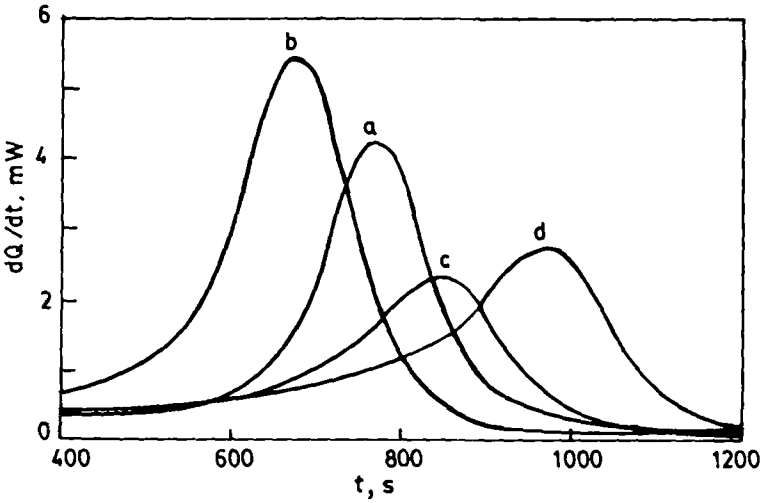

Figure 1. The rate of heat evolution dQ/dt in milliwatts in the process of heat evolution on palladium particles. Curve a – protium system; curve b – the system deuterated by 80%. Thermal effects $Q_1 = 1{\cdot}40$ cal/g, $Q_2 = 2{\cdot}04$ cal/g. The time interval after the introduction of formalin is 10 min. Time is reckoned from the introduction of palladium. Curves c and d – the analogous situation for the protium and deuterated system. The solution is kept for 60 min after the introduction of formalin.

The reaction was conducted directly in the DSC (Setaram, France) differential scanning calorimeter under isothermal conditions at 24°C. The measuring cell volume was 1 ml. The accuracy of determination of the integral heat effect is 0·02 cal/g.

The results are presented in figure 1 as a plot of heat evolution in the reaction versus the duration of the process. Curves a and b relate to solutions prepared using water and heavy water, respectively. It is seen that the overall thermal effect of the reaction is 1·4 cal/g, and it increases to 2·04 cal/g or 1·46 times when using heavy water as the medium.

Curves c and d relate to a solution allowed to stand for 1 h instead of 10 min before the addition of palladium. The thermal effect increases from 0·76 cal/g to 1·21 cal/g or 1·59 times when carrying out the reaction in D_2O.

The overall degree of deuteration in the given experiments was 80%. The decrease of the degree of deuteration to 20% decreases the effect approximately by a factor of 4.

It is seen that the peak of the isothermal DSC curve shows a shift. It is surprising that the peak shifts to lower values when the copper solution for electrolysis is aged for 10 min. The shift is in the opposite direction when ageing time is 60 min.

3. Discussion

Thus, the heat effect in the reaction of chemical precipitation of copper on palladium colloidal particles accompanied by hydrogen evolution depends on the presence of deuterium in the system. It turns out that in the case of substitution of hydrogen in the system by deuterium to the extent of 80%, the heat effect of the reaction increases approximately 1·5 times.

The present report discusses the reaction in a closed system, which implies no

additional introduction of energy in the course of investigation, and hence mistakes related to this circumstance are ruled out. The kinetics of the conversion involving a marked induction period also enables one to carry out correctly an experiment on study of heat evolution in the course of chemical transformation proper.

The dissociation heats are (Kikoin 1976): for $H_2 - 4{\cdot}48\,eV$, for $D_2 - 4{\cdot}55\,eV$. Apparently, the observed effect can not be attributed only to the difference in the energies of the bonds of hydrogen and deuterium in compounds participating in the reactions.

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