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THE HOMOGENEOUS CATALYSIS OF THE ISOTOPE EXCHANGE BETWEEN HYDROGEN AND LIQUID WATER

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SOMMAIRE

Les solutions aqueuses de chlorure de ruthénium (III), de cyanure de cobalt (II) et d'hydroxyde de sodium catalysent l'échange isotopique entre l'hydrogène et l'eau. De l'influence sur la vitesse d'échange de la pression de l'hydrogène et de la concentration du catalyseur, il résulte que l'échange implique, pour le chlorure de ruthénium et l'hydroxyde de sodium, une dissociation hétérolytique, pour le cyanure de cobalt une dissociation homolytique de l'hydrogène. L'hydrogène activé par le cyanure de cobalt et le chlorure de ruthénium est susceptible de réduire ou d'hydrogéner des substrats, tandis que les ions OH ne peuvent accélérer que la réaction d'échange isotopique de l'hydrogène.

The isotope exchange between hydrogen and water is at temperatures up to several hundred centigrades immeasurably slow. To enhance its rate a catalyst is required. A number of solid catalysts for the isotope exchange have been investigated, but relatively little is known about homogeneous catalysts dissolved in the aqueous phase (1).

The catalytic activity of some transition metal complexes (Cu, Ru, Rh, Pd, Ag, Hg) for the reduction of Fe^{III} or $Cr_2O_7^{=}$ by hydrogen has been reported (2–6). It could be expected that these compounds also catalyse the isotope exchange. Co^{II}-cyanide in cyanide solution is known to absorb hydrogen very rapidly (7, 8), to transfer it to other compounds (9) and to accelerate the hydrogen isotope exchange (7). However, the experimental data reported are not sufficient for evaluating the reaction mechanism or estimating the reaction rates. — The catalytic activity of aqueous bases, e. g. sodium or potassium hydroxide, for the hydrogen-water isotope exchange was observed some 25 years ago (10) and confirmed recently in a more elaborate study (11). Moreover, some enzymes have been shown to catalyse the hydrogen isotope exchange (12–14).

In this paper a thorough study of the hydrogen-water isotope exchange (normal water and hydrogen containing 0.2 percent HD) with Ru^{III}- chloride in hydrochloric acid, Co^{II}- cyanide in cyanide solution and several basic systems will be presented. These were chosen because it was anticipated that they might activate the hydrogen by different mechanisms. It is the aim of this study to evaluate the exchange mechanisms, compare the exchange rates, and give suggestions how to improve the homogeneous catalytic systems.

Experiments.

Depending on the pressure the experiments were carried out in a small glas flask or an autoclave connected to a thermostate. To ensure good phase mixing the reaction cells were vigorously shaken by a vibrator driven by an eccentric. Temperature and catalyst concentration were so chosen that the reaction rates did not depend on shaking frequency or amplitude, i.e. that they were not controlled by diffusion processes in the liquid phase or in the gas phase.

The exchange was followed by mass spectrometric analysis of gas samples drawn from the reaction cells at appropriate times (mass spectrometer CEC 21-103 C, Consolidated Electrodynamics Corp., Pasadena, Calif.).

With an excess of the aqueous phase the change of the mole fraction γ of HD in the gas phase with time can be expressed by

$$\frac{\gamma_t - \gamma_\infty}{\gamma_0 - \gamma_\infty} = e^{-k't}$$

(γ_0, γ_t and γ_∞ denote the mole fraction of HD at time $t = 0$, t and ∞).

Correspondingly, if the catalyst did not undergo chemical changes with time, the plots of $\gamma_t - \gamma_\infty$ versus time on semi-log paper yielded straight lines from which the halftimes of the exchange reactions were obtained. These were converted into reaction

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rates (mol/l. sec) referring to 1 liter catalyst solution.

Ruthenium-III-chloride in hydrochloric acid was prepared by reduction of a hydrochloric acid solution of Ru^{IV}-chloride with 700 torr hydrogen at 95 °C. Cobalt-II-cyanide solutions were obtained by mixing Co^{II}-chloride and potassium cyanide solutions in vacuum at 10 °C. To ensure reproducible results the solutions were shaken with 500 torr hydrogen for several hours before starting the exchange experiments. — Sodium methylate in methyl alcohol and sodium acetate in acetic acid were prepared by dissolving metallic sodium in methyl alcohol and acetic acid.

The experiments with Ru-chloride and the basic systems were carried out at temperatures between 75 and 115 °C, the experiments with Co-cyanide between 10 and 30 °C.

Results and Discussion.

Ruthenium-III-chloride in hydrocholric acid.

From the linear increase of the reaction rate v with the H_2 pressure and the Ru^{III}-concentration (Fig. 1 and 2) follows the rate law

$$v = k.c_{H_2}.c_{Ru} \qquad (1)$$

with the rate constant (rate referring to c_{H_2} and $c_{Ru} = 1$ m; c = concentrations (*)) $k = 1{,}43$ l/mol. sec at 85 °C in 4 m HCl. The energy of activation calculated from the temperature dependence of the reaction rate is $E = 24 \mp 1$ kcal/mol. The frequency factor A of the Arrhenius equation $k = A.e^{-E/kT}$ is found to be $A = 5.10^{14}$ l/mol.sec. This value is higher by more than a factor of 100 compared with the frequency factors of normal bimolecular reactions.

The steep increase of the exchange rate with the HCl-concentration up to 3 m HCl (Fig. 3) indicates that a higher Ru-III-chloride complex $[RuCl_n]^{(n-3)-}$ is responsible for the catalytic action. The decrease of the reaction rate in very concentrated hydrochloric acid could be caused by the formation of an even higher chloride complex of Ru^{III} with no or smaller catalytic activity or by a decrease of the solubility of hydrogen in concentrated solutions (**) or possibly both.

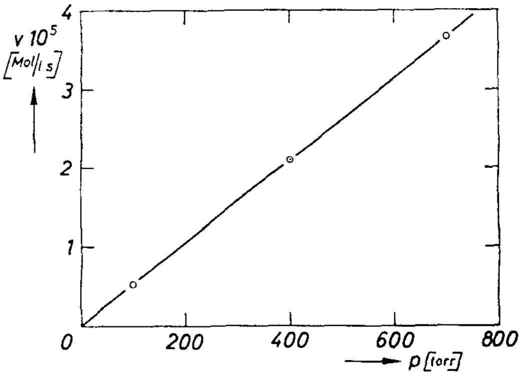

Fig. 1. — Ru^{III}-chloride in hydrochloric acid : effect of H_2-pressure on the exchange rate (0.05 m Ru, 4 m HCl, 85 °C).

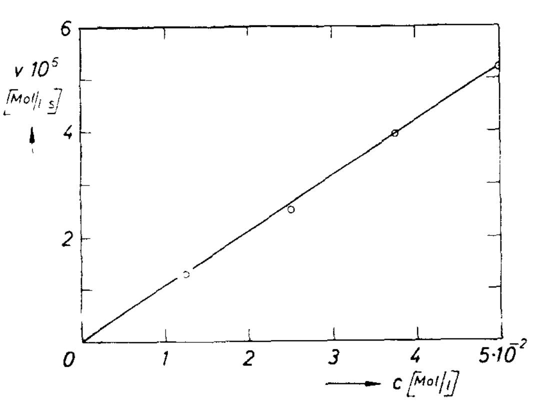

Fig. 2. — Ru^{III}-chloride in hydrochloric acid : effect of Ru-concentration on the exchange rate (4 m HCl, 100 torr H_2, 85 °C).

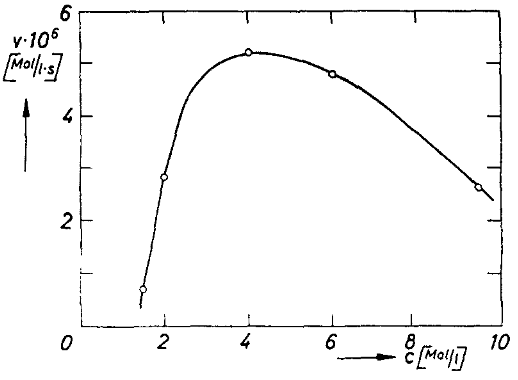

Fig. 3. — Ru^{III}-chloride in hydrochloric acid : effect of HCl-concentration on the exchange rate (0,05 m Ru, 100 torr H_2, 85 °C).

The same dependence on the HCl- and Ru-concentration, the H_2- pressure and the temperature as reported here for the rate of the isotope exchange was found by HALPERN (2) for the rate of reduction of Fe^{III} by hydrogen, also catalysed by Ru-chloride. He gives as frequency factor in 3 m HCl the value $A = 4.10^{14}$ l/mol.sec which compares favourably with the value for the isotope exchange in 4 m HCl given here.

(*) It is assumed that all Ru is in the catalytic active form. The solubility of H_2 at 85 °C in 4 m HCl was estimated from its solubility at 25 °C assuming the same temperature dependence as in pure water.

(**) The solubility of hydrogen in HCl is known up to 4 m HCl only (15).

The agreement of the results of the two hydrogen reactions suggests that the rates of both are controlled by the same reaction step. This step must be the activation of hydrogen by the Ru-chloride because this is the only reaction which both the hydrogen isotope exchange and the reduction of Fe^{III} by hydrogen have in common.

For the activation of hydrogen by Ru-chloride (and other transition metal complexes, e.g. Rh, Pd, Ag, Cu, Hg) HALPERN ($^{2-6}$) proposed a mechanism with heterolytic splitting of the H_2 — molecule into a positive and a negative hydrogen ion. The H^--ion is supposed to be bound by the Ru-complex. So the hydrogen isotope exchange could be described by the following sequence of reactions which is in agreement with the experimental results (*Ru* stands for the hydrogen activating Ru-chloride complex):

$$\begin{array}{lll}
\text{(I)} & Ru + HD & \longrightarrow RuD^- + H^+ \\
\text{(Ia)} & Ru + HD & \longrightarrow RuH^- + D^+ \\
\text{(II)} & RuD^- + H_2O & \longrightarrow RuH^- + HDO \\
\text{(III)} & RuH^- + H^+ & \longrightarrow Ru \quad + H_2
\end{array}$$

The activation of hydrogen (reaction I) is rate determining, the exchange reaction (II) and the recombination of hydrogen (III) follow very quickly. Because in experiments with pure D_2 only little HD is formed it can be concluded that the exchange must be faster thant the recombination of hydrogen.

Co-II-cyanide in potassium cyanide solution.

By mixing Co^{II}-chloride with KCN solutions the Co^{II}- pentacyanide complex of the composition $[Co(CN)_5]^{3-}$ is obtained ($^{7,\,8}$). This complex is formed already at low CN^- concentrations whenever the mole ratio CN : Co is 5 or more. According to

$$2\,Co + H_2 \longrightarrow 2\,CoH$$

(*Co* stands for the pentacyanide complex) it reversibly absorbs hydrogen to yield the Co-hydropentacyanide complex via which the isotope exchange is assumed to proceed (^{7}).

The exchange rate increases approximately with the square of the cobalt concentration (Fig. 4) but only little with the hydrogen pressure ($\sim p^{0,3}$; Fig. 5). This can be be described by the following reaction steps with reaction (III), the recombination of hydrogen, controlling the rate of exchange:

$$\begin{array}{lll}
\text{(I)} & 2\,Co + HD & \longrightarrow CoD + CoH \\
\text{(II)} & CoD + H_2O & \longrightarrow CoH + HDO \\
\text{(III)} & 2\,CoH & \longrightarrow 2\,Co + H_2
\end{array}$$

Consequently, the rate v is expressed by

$$v = kc^2_{CoH} \qquad (2)$$

Due to the slow recombination of hydrogen according to reaction (III) almost all cobalt is in the form of Co-hydrocyanide. Therefore, its concentration and consequently the exchange rate can increase only little with hydrogen pressure.

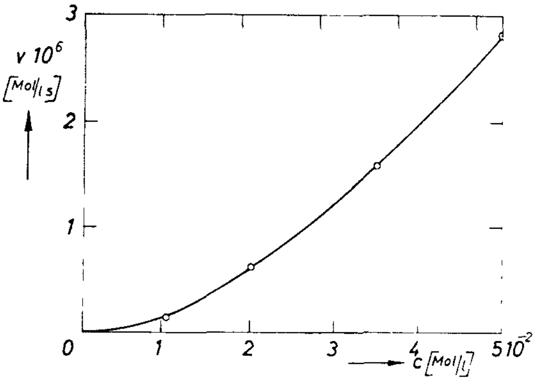

Fig. 4. — Co^{II}-cyanide in cyanide solution: effect of Co-concentration on the exchange rate (0.5 m KCN, 100 torr H_2, 30 °C).

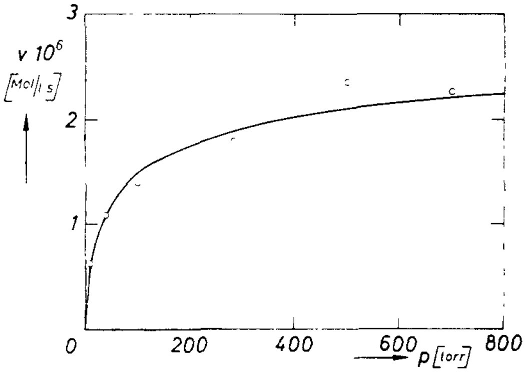

Fig. 5. — Co^{II}-cyanide solution: effect of H_2-pressure on the exchange rate (0.05 m Co, 0.5 m KCN, 30 °C).

In accordance with the assumption of the rate determining step the exchange rate increases with added electrolytes (KCN, KCl, NaOH; Fig. 6) because reactions between ions with charges of equal sign are known to be accelerated by addition of any electrolyte (^{16}).

As in the case of the Ru-catalysed exchange here too only little HD is formed in the D_2 — H_2O exchange proving that the exchange reaction (II) is faster than the recombination of hydrogen (III).

The rate constant as defined by (2) at 30 °C is about 1.10^{-3} l/mol.sec, assuming that at a hydrogen pressure of 100 torr about 80 percent of the cobalt are in the form of the hydrocyanide complex. With the measured energy of activation $E = 7{,}0 \mp 1$ kcal/mol the frequency factor of the Arrhenius equation follows to be $A = 1.10^2$ l/mol.sec. This extremely low value is again in agreement with the assumption that the rate controlling step of the exchange is a reaction of two ions with multiple charge of equal sign (16).

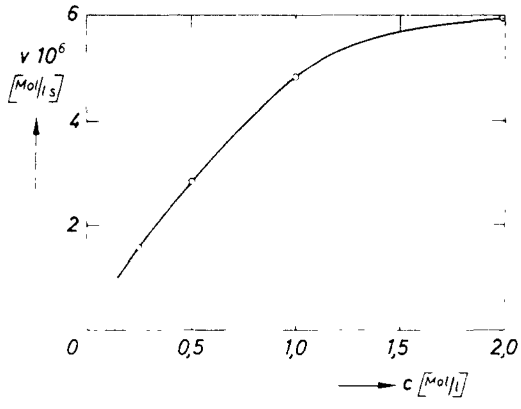

Fig. 6. — Co^{II}-cyanide in cyanide solution: effect of KCN-concentration on the exchange rate (0.05 m Co, 100 torr H_2, 30 °C.)

Basic Systems.

The investigations on the base catalysed hydrogen isotope exchange in water by WILMARTH (11) were extended to higher base concentration and to higher hydrogen pressure, and to other basic systems.

In aqueous sodium hydroxide the exchange rate is proportional to the OH^- ion concentration up to about 1 *m* and proportional to the hydrogen pressure up to at least 100 at (Fig. 7 and 8). Within these limitations the rate law is expressed by

$$v = kc_{OH}\cdot c_{H_2} \qquad (3)$$

with the rate constant at 115 °C $k = 2.10^{-2}$ l/mol.sec. The energy of activation is $E = 24 \mp 2$ kcal/mol. From these data the frequency factor $A = 8.10^{11}$ l/mol.sec is calculated. This is within the range of the frequency factors of normal bimolecular reactions. — The same value was reported by WILMARTH (11) for the p-H_2 conversion, catalysed by OH^- ions in water.

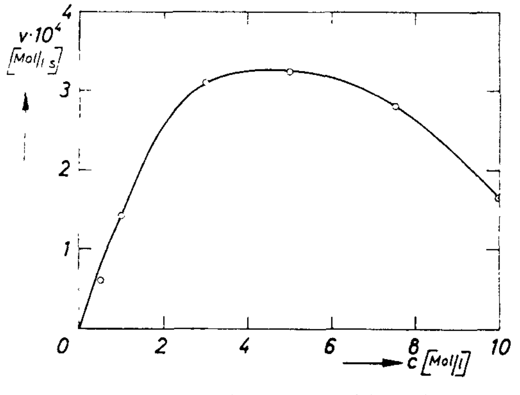

Fig. 7. — Sodium hydroxide: effect of NaOH-concentration on the exchange rate (100 at H_2, 115 °C).

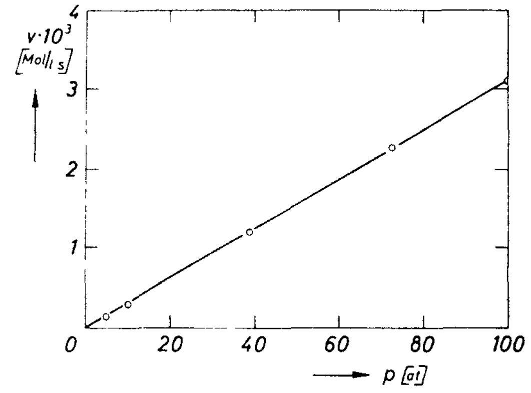

Fig. 8. — Sodium hydroxide: effect of H_2-pressure on the exchange rate (3 m NaOH, 115 °C).

In methyl alcohol OH^- and CH_3O^- ions have the same catalytic activity for the exchange reaction. The energy of activation is the same as in water. But due to the higher solubility of hydrogen the exchange proceeds in methyl alcohol about three times faster than in water under equal experimental conditions.

In accordance with the rate law (3) the rate controlling step of the base catalysed exchange is the reaction of hydrogen with a hydroxide ion forming a transition state schematically described by $(HDOH)^-$:

$$\text{(I)} \qquad HD + OH^- \longrightarrow (HDOH)^-.$$

It can be imagined that the exchange proceeds via one of the following decay reactions of the transition state

$$\text{(II }a) \qquad (HDOH)^- \longrightarrow H_2 + OD^-$$
$$\text{(III }a) \qquad OD^- + H_2O \longrightarrow OH^- + HDO$$

or

$$\text{(II }b) \qquad (HDOH^-) \longrightarrow H^- + HDO$$
$$\text{(III }b) \qquad H^- + H_2O \longrightarrow H_2 + OH^-$$

or

$$\text{(III }c) \quad (HDOH)^- + H_2O \longrightarrow HDO + H_2 + OH^-$$

Mechanism (II*a*) is not possible for the exchange catalysed by CH_3O^- ions (*) which has the same rate as the OH^- catalysed exchange in methyl alcohol. Therefore, it very likely can be excluded also for the OH^- ion catalysed exchange in water.

In mechanisms (II*b*) and (II*c*) the polarisation of hydrogen by OH^- must be assumed. This leads

(*) $CH_3O^- + HD \rightarrow (CH_3OHD)^- \rightarrow CH_3O^- + HD$.

in (II*b*) to the formation of an H^- ion (heterolytic scission of hydrogen). For this process an energy of activation of 20-22 kcal/mol was calculated ([1, 11]) under the assumption that the H^- ion reaches *momentary hydration equilibrium before it reacts* with water.

If the H^- ions were formed and had a lifetime long enough for reaching hydratation equilibrium it also should initiate other hydrogen reactions. But no base catalysed reductions or hydrogenations could be observed under the conditions of the isotope exchange experiments. Therefore, mechanism (II *b*) *including the intermediate formation of an hydrogen anion is doubted.*

This leaves mechanism (II *c*) which schematically was proposed by Wirtz and Bonhoeffer ([10]). Here, too, heterolytic scission of hydrogen is assumed, but *it occurs only when the polarised hydrogen can react with water*

$$HO^- \cdot\cdot (\overset{(+)}{D}\overset{(-)}{H}) + HOH \rightarrow HOD + H_2 + OH^-).$$

This process formally includes a triple collision; but due to the strong hydratation of OH^- ions it can be treated as a normal bimolecular reaction. — The decrease of the exchange rate in concentrated base (Fig. 7) might be partly due to the weaker hydratation of the OH^- ions (*).

The energy of activation E for the base catalysed exchange depends on the proton affinity of the base; in the strong basic system NH_2^-/NH_3 E is only about 10 kcal/mol ([17]); from the low exchange rate in the very weak basic acetate/acetic acid system a value of E of at least 35 kcal/mol is calculated here.

General Discussion.

For comparison Table 1 shows the rates, the energies of activation, and the frequency factors of the hydrogen isotope exchange catalysed by the three homogeneous systems investigated here, and by the homogeneous amide/ammonia system ([17]) and by a heterogeneous platinum charcoal catalyst ([18]) (weight ratio Pt: C = 0.1). All data refer to a hydrogen pressure of 1 at and of 1 litre solution or suspension with 0.01 mol of catalyst.

TABLE I

Rates v, energy of activation E, and frequency factor A of the hydrogen isotope exchange with several catalyst systems. Hydrogen pressure 1 at, 1 litre solution or suspension with 0,01 mol catalyst:

Catalyst	Température	*v*[mol/l.s]	E[kal/mol]	A[l/mol.s]
—	—	—	—	—
Ru-chloride in 4 m HCl	85 °C	8×10^{-6}	$23{,}8 \pm 0{,}5$	5×10^{14}
Co-cyanide in 0,5 m KCN	30 °C	9×10^{-8}	$7{,}0 \pm 1$	1×10^{2}
Sodium hydroxide in water	115 °C	$1{,}5 \times 10^{-7}$	$24{,}0 \pm 2$	8×10^{11}
Potassium amide in ammonia	— 53 °C	$\sim 2 \times 10^{-5}$	~ 10	$\sim 6 \times 10^{11}$
Pt on charcoal in water	30 °C	1×10^{-4}	5,8	—

It is seen that platinium on charcoal is by far the most effective catalyst for the hydrogen isotope exchange with liquid water. The relatively poor catalytic activity of the homogeneous aqueous systems is due to the high energy of activation or to the low frequency factor of the rate determining steps.

As shown before the energy of activation of the isotope exchange in the basic systems depends on their basicity. Since the OH^- ion is the strongest base stable in water (stronger bases will react with water: $B^- + H_2O \rightarrow BH + OH^-$), no better basic aqueous systems will be found. However, by changing the medium, e. g. ammonia instead of water, the stronger base NH_2^- with higher exchange rate is available.

With all transition metal complexes so far investigated [Cu, Ru, Rh, Pd, Ag, Hg ([2-6])] which activate hydrogen by heterolytic scission, the energy of activation of the reduction of Fe^{III} or $Cr_2O_7^=$ by hydrogen is more than 20 kcal/mol. The same energy of activation can be expected for the hydrogen isotope exchange catalysed by the above complexes. — It can be anticipated that a combination of one of the transition metal ions with a base system might improve the catalytic activity of both. For they both split the hydrogen heterolytically but attack it in different ways: the base combines with the H^+ ion, the transition metal with the H^- ion. Therefore, in the concerted attack of a base B and a transition metal complex M on a hydrogen molecule its scission should occur easier:

$$M + H_2 + B \longrightarrow MH^- + HB^+$$

To avoid the necessity of triple collisions a tight combination between M and B by complex formation would be desirable . — A hint in this direction is given by Halpern ([6]) who found that Cu^{II} complexed with acetate or propionate catalyses the reduction

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(*) In 10 m NaOH the mol ratio of H_2O and NaOH is only 5, causing incomplete hydratation of the ions. — Decrease of H_2 solubility and of dissociation of NaOH in concentrated solution will, of course, contribute to the decrease of the exchange rate. Unfortunately, data on these are not available.

of $Cr_2O_7^{=}$ by hydrogen about 100 times better than fully hydrated Cu ions.

The low frequency factor of the rate determining step of the Co-cyanide catalysed exchange was explained by the high ionic charge of the two reacting Co-hydropentacyanide ions. Therefore, one could expect an increase in exchange rate by lowering the charge of the catalyst ion. This could perhaps be done by replacing one or two cyanide ions by uncharged complex forming molecules, e. g. carbon monoxide.

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