Low Temperature Ortho-Para Hydrogen Conversion-Kinetic Studies

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Rate studies were carried out for the ortho-para hydrogen conversion at liquid nitrogen temperature with a multiple-impregnation nickel on aluminum oxide catalyst. Data were obtained at pressures up to 400 lb./sq. in. gauge over a range of flow rates for three catalysts of different pellet sizes.

For the largest particle, ⅛-in. cylinders, diffusion resistances were significant. Effectiveness factors were evaluated and found to be somewhat less than 0.5 for this relatively active catalyst. After the diffusion resistances were accounted for, the surface rate was correlated on the basis of a *mechanism supposing* molecular hydrogen to be adsorbed on the surface. Separate evaluation of the catalyst for the hydrogen-deuterium exchange reaction suggested that dissociation was not significant at liquid nitrogen temperature.

Interest in para hydrogen has increased owing to its advantageous storage properties. There have been a number of investigations (*3, 4, 7, 8, 11, 14*) of the ortho-para hydrogen reaction, but these have been directed primarily toward finding an active catalyst. In a continuation of this work the authors (*10*) have recently reported the activities of a number of catalysts for the low-temperature reaction. The most active material was found to be a multiple-impregnation nickel on aluminum oxide carrier. As the activity of the catalyst increases, the external and internal (pore) diffusion resistances become increasingly important. For the nickel catalyst these effects had to be considered in order to determine the kinetics of the surface reaction. Experimental rate measurements were made as a function of pressure, flow rate, and catalyst particle size, all at liquid nitrogen temperature (—196°C.), and with a feed corresponding to the equilibrium para hydrogen content of normal hydrogen at 25°C. The results were used to determine the external diffusion resistance, the effectiveness factor of the catalyst particles, and a rate equation for the surface steps.

The pressure range was from 40 to 400 lb./sq. in. gauge. The flow rate was varied from 24 to 197 cc. (0°C. and 1 atm.)/sec. through the reactor. This corresponded to a W/F range of 125 to 2,100 (g. of catalyst) (sec.)/(g. mole). Three catalysts were studied.

1. Nominal, ⅛-in. cylindrical pellets which were ⅛-in. in diam. and 0.138 in. long. The diameter of a sphere whose volume is the same as that of the pellet is 4.03 mm., and this was used as the particle diameter, for this catalyst.
2. Granular particles, 0.420 to 0.589 mm. in size, obtained by crushing and sieving the ⅛-in. pellets. The value of d_p was taken as 0.505 mm.
3. Granular particles 0.105 to 0.149 mm.; d_p = 0.127 mm.

EXPERIMENTAL WORK

The apparatus is shown in Figure 1. Prior to the reactor, electrolytic hydrogen, 1, (numbers refer to Figure 1) flowed through a Deoxo unit, 2, packed with palladium particle to remove oxygen. Then followed three silica gel drying tubes, 3, in series, each constructed of stainless steel pipe ½ in. I.D. and about 10 in. long. The final two silica gel tubes and the reactor, 4, also ½ in. I.D. stainless steel pipe 10 in. long, were immersed in a liquid nitrogen, constant temperature bath, 5. A copper-constantan thermocouple was inserted in the ⅛ in. O.D. stainless steel probe, 6, to measure the reactor temperature. Because of the almost negligible heat of reaction the reactor temperature was not measurably different from the bath temperature which was also measured with a copper-constantan thermocouple.

A sample gas stream, 9, was withdrawn after the reactor for the thermal conductivity cell. The remainder passed through a wet test meter, 7.

The thermal conductivity cell, 10, was a Gow-Mac type 30-S. The analytical system was maintained at 28.3°C. in a constant temperature bath, 12, in accordance with the procedure recommended by Weitzel and White (*12*). The para hydrogen content in the sample stream was determined by passing the sample gas through one side of the cell and normal hydrogen, 8, through the reference side. The normal hydrogen contains the equilibrium amount of para hydrogen at room temperature, which is 25.0% (2). Flow rates through both sides of the cell were measured with soap-film meters, 13, and maintained at 1.0 cc./sec. The cell was operated at a constant current of 140 ma. and the unbalanced electro motive force read with a sensitive potentiometer, 11.

The cell was calibrated by preparing mixtures of known para-hydrogen content. The composition of the gas at equilibrium at —196°C. is 50.26% (*2, 15*). This equi-

TABLE 1. EXPERIMENTAL DATA AND RATE CONSTANTS

Mass of catalyst, g.	Pressure, lb./sq. in. gauge	Flow rate, cc./sec. (0°C. and 1 atm.)	$y_{g2} - y_{g1}$	(W/F)*	$(1/K_{ov})$*	$(1/k_F)$*	$(k_p \times 10^4)$†
Catalyst: ⅛-in. cylinders (⅛-in. × 0.138 in., d_p = 4.03 mm.)							
2.55	40	30.1	0.1290	1,880	2,640	260	4.20
		67.7	0.0726	839	2,490	190	4.35
		141	0.0386	403	2,470	140	4.29
	100	26.7	0.1531	2,120	2,280	270	4.97
		58.6	0.0916	969	2,160	200	5.10
	400	28.7	0.1786	1,980	1,610	270	7.46
		78.5	0.0980	724	1,480	180	7.69
Catalyst: granular particles (average d_p = 0.505 mm.)							
1.13	100	24.2	0.1761	1,040	873	**	11.5
		147	0.0465	171	844		11.8
	400	35.8	0.1800	701	562		17.8
		77.1	0.0985	325	659		15.2
Catalyst: granular particles (average d_p = 0.127 mm.)							
0.739	100	40.6	0.0878	404	947	††	10.6
	400	68.5	0.0881	240	564		17.7

* Units are (g. of cat.) (sec.)/g. mole.
† Units are g. mole/(g. of cat.) (sec.).
** Values of $1/k_F$ are 5 to 9.
†† Values of $1/k_F$ are 0.5 to 0.7.

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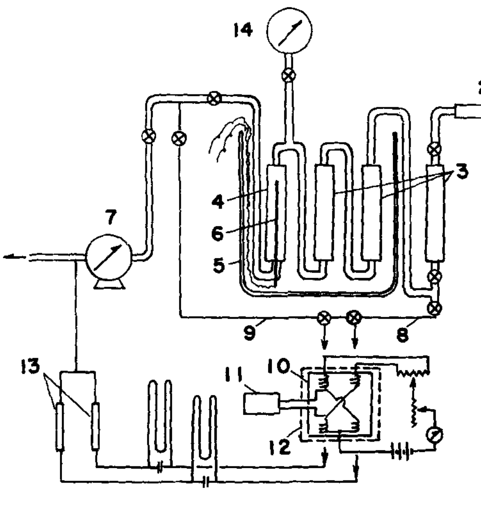

Fig. 1. Schematic drawing of equipment.

librium gas was obtained by the use of an active catalyst in the reactor and the reduction of the flow rate until the effluent concentration did not change. This gas was then mixed at measured flow rates with normal hydrogen to obtain a gas with any desired para content between 25.0 and 50.26%. The relationship between the electro motive force of the cell and the per cent para hydrogen was linear.

The pressure on the system was measured with a bourdon tube gauge, 14, and the total flow rate determined by adding the wet test meter and soap-film meter readings.

The catalysts were prepared by soaking gamma alumina powder in nickel nitrate solution. This was done in ten successive stages in order to distribute the nickel atoms over as much of the surface as possible. The catalyst contained approximately 5.0 wt. % nickel (as oxide).

After each impregnation the catalyst was dried for 4 hr. at 450°C. In the tenth impregnation dried powder was pelleted into ⅛-in. cylindrical particles with a press to a density of 1.91 g./cc. For the granular catalysts the pellets were crushed and sieved.

A sample of catalyst, from 0.7 to 2.5 g., was supported in the reactor by a stainless steel screen upon which was placed a layer of glass wool approximately 1 cm. in depth. A similar thickness of glass wool was placed on top of the catalyst layer. The catalyst was reduced to nickel by passing hydrogen through the reactor, maintained at 400°C., for 12 hr. Cooling the reactor by placing it in the liquid nitrogen bath with a flow of hydrogen over the catalyst readied the system for operation. The surface area of the catalyst was measured to be 155 sq. m./g. in a B.E.T. nitrogen apparatus.

Preliminary runs were made without catalyst in the reactor. These data showed no conversion, indicating that the stainless steel and glass wool had no catalytic action. In the catalyst evaluation work (*10*) runs made with copper and hydrogenized palladium on aluminum oxide showed zero conversion, suggesting also that aluminum oxide was not an active catalyst.

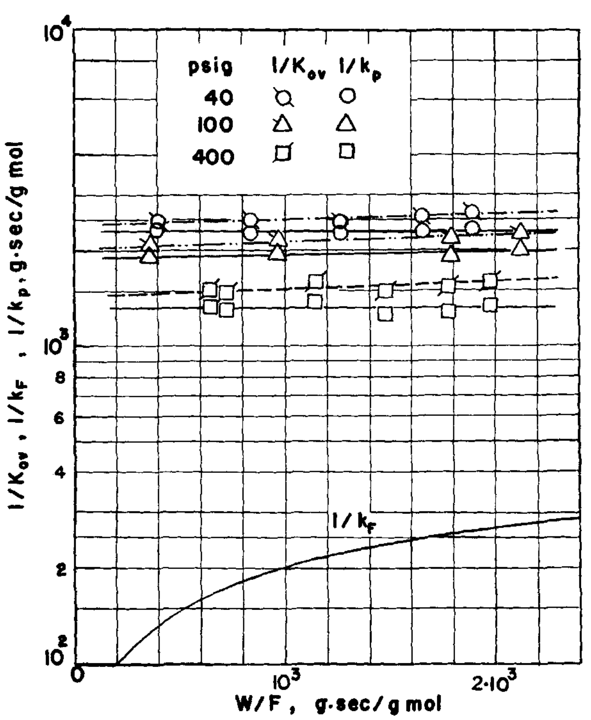

Fig. 3. Importance of diffusion on reaction rate (⅛-in. catalyst).

RESULTS

Table 1 illustrates the results for the three catalysts. The first five columns report the experimental measurements of composition, flow rate, pressure, and mass of catalyst. From this information a rate constant based upon the overall driving force in the gas phase was first evaluated. This quantity K_{ov} is a function of external and pore diffusion resistances, pressure, and the specific reaction rate of the reaction on the catalyst surface. For the steady state flow system the relation between the average rate for the catalyst pellet and the gas composition is

$$\bar{r}\,dW = F\,dy_g \qquad (1)$$

Suppose the rate of the surface processes can be represented by a first-order equation at constant pressure. Then the rate per pellet can be expressed in terms of K_{ov} and the overall driving force in the bulk gas stream:

$$\bar{r} = K_{ov}\,(y_{eq} - y_g) \qquad (2)$$

The value of y_{eq} is 0.5026, the equilibrium para hydrogen mole fraction at the reaction temperature (−196°C.). The quantity y_g is the actual mole fraction of para hydrogen in the gas. If one combines Equations (1) and (2) and integrates between the entrance (y_{g1} = 0.250) and exit (y_{g2}) of the reactor, the result is

$$\frac{1}{K_{ov}} = \frac{W/F}{\ln\dfrac{y_{eq} - y_{g1}}{y_{eq} - y_{g2}}} \qquad (3)$$

Figure 2 shows all the data plotted as W/F vs. the logarithmic term. Values of $1/K_{ov}$ are presented in column 6 of Table 1. At each pressure the data describe a linear relationship in Figure 2. In the next section it is shown that external diffusion resistances are negligible for the two smaller catalyst particles and small for the ⅛-in. pellet. Hence it is concluded from Figure 2 that the surface rate, at constant pressure, is first order. The next step is the separation of the external and pore-diffusion resistances from that of the reaction on the catalyst surface.

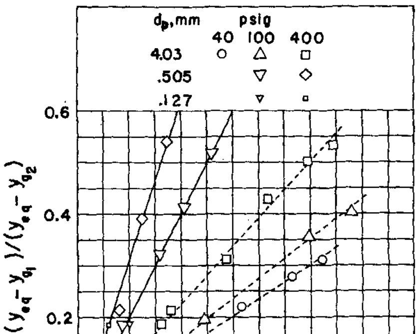

Fig. 2. Catalyst size vs. rate data.

External Diffusion

Similar to Equation (2) in terms of y_g, the average rate per catalyst particle may be expressed in terms of the mole fraction of para hydrogen at the outer surface of the pellet y_s. This expression is

$$\bar{r} = k_p\,(y_{eq} - y_s) \qquad (4)$$

It includes the effect of pore diffusion but not external diffusion. The rate of external diffusion to the outer surface of the pellet is related to the mass transfer coefficient k_f by the equation

$$\bar{r} = \frac{4\pi R^2 k_f\, P(y_s - y_g)}{\rho_p\,(4/3)\,\pi R^3} \qquad (5)$$

Combining Equations (2), (4), and (5) one gets

$$\frac{1}{K_{ov}} = \frac{1}{k_p} + \frac{1}{k_F} \qquad (6)$$

$$k_F = \frac{3k_f P}{R\,\rho_p} \qquad (7)$$

The mass transfer coefficient may be predicted from available correlations for mass transfer in packed beds. In this study the following dimensionless correlation (9), applicable at Reynolds numbers less than 100, was used:

$$N_{sh} = \frac{k_f M d_p P}{D_{H_2}\,\rho_g} = 2 + 1.45\,(N_{Sc})^{1/3}\,(N_{Re})^{1/2} \qquad (8)$$

The last two columns of Table 1 show $1/k_F$ results computed from Equation (7) and k_p from Equation (6). The k_F values for the two catalysts consisting of granular powders were so large that $1/k_F$ amounted to but 5 to 9 (for the 0.505-mm. particles) and 0.5 to 0.7 (for the 0.127-mm. catalyst). In both cases these quantities were negligible with respect to $1/k_p$. Hence external diffusion was significant only for the ⅛-in. catalyst, where the resistance was from 6 to 17% of the total, as suggested by comparing $1/k_F$ and $1/K_{ov}$ values from Table 1. These results are shown in Figure 3, where $1/K_{ov}$, $1/k_p$, and $1/k_F$ are plotted vs. W/F.

Pore (Internal Diffusion)

The rate constant k_p must be corrected for the effect of pore-diffusion resistance before the kinetics of the surface reaction can be studied. The significance of pore diffusion depends upon the form of the surface rate equation, so the two processes cannot be analyzed separately. The procedure is: propose a kinetic expression for the surface reaction, then use this and the data on different size catalyst particles to determine both the significance of pore diffusion (effectiveness factor) and the validity of the kinetic equation.

It has already been found (from the linear curves in Figure 2) that the rate, at constant pressure, is first order with respect to para hydrogen concentration. Hence only surface-rate expressions with a kinetic term of the form $p_o - p_p/K$ are suitable. The expression of this type that best fits the data is derived from the form

$$r = \frac{k_c\,(p_o - p_p/K)}{1 + K_o p_o + K_p p_p} \qquad (9)$$

Equation (9) is obtained from the Langmuir-Hougen concepts on the supposition that molecular ortho hydrogen is adsorbed on a single catalyst site, that the controlling process is a conversion to para hydrogen on the surface, and that the para hydrogen desorbs into the gas phase. Ortho and para hydrogen are similar; they differ only by the direction of the electron spin associated with the hydrogen atom. Cunningham, et al. (*4*) have indicated that the difference in heats of vaporization is but 4.3 cal./g. mole. Although no heat of adsorption data appear to be available, it is logical to suppose that heats of adsorption and adsorption equilibrium constants are nearly equal. With this assumption Equation (9) becomes

$$r = \frac{k_c\,(p_o - p_p/K)}{1 + K_{Ad}\,P} \qquad (10)$$

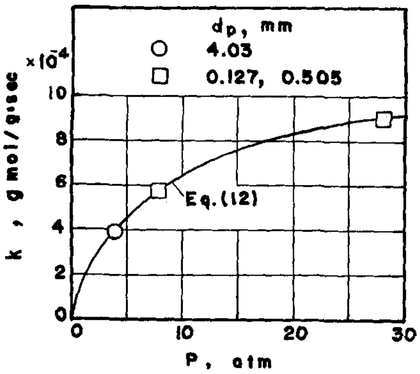

Fig. 4. Correlation of rate data.

Equation (10) may be rewritten in terms of the mole fractions of para hydrogen, in the gas phase, at the surface and at equilibrium:

$$r = k\left(1 + \frac{1}{K}\right)(y_{eq} - y) \qquad (11)$$

where

$$k = \frac{k_c\,P}{1 + K_{Ad}P} \qquad (12)$$

At constant pressure Equation (11) is a first-order kinetic equation which satisfies the linear plot of the data shown in Figure 2.

If adsorption or desorption was assumed to be controlling, Equation (11) could be written the same way, but k would not be independent of composition at a given pressure; that is Equation (12) would become

$$k = \frac{k_c'P}{1 + K_{Ad}\left(1 + \dfrac{1}{K}\right)Py} \quad \text{(adsorption controlling)} \qquad (13)$$

$$k = \frac{k_c''P}{1 + K_{Ad}\,(1 + K)\,P(1 - y)} \quad \text{(desorption controlling)} \qquad (14)$$

Therefore, neither adsorption nor desorption processes could be assumed controlling if one wished to obtain a satisfactory rate equation.

Equation (11) can be used to express the rate of reaction, per unit mass of catalyst, at any point within the catalyst particle. Further the heat of reaction is so low [measured as 320 cal./g. mole by von Elbe and Simon (*1*)] that it is valid to assume that no temperature gradients exist within the particle. Under these conditions the Wheeler (*13*) effectiveness-factor concept is valid and Equation (11) may be written in terms of the surface mole fraction y_s and the average rate per pellet:

$$\bar{r} = k\,(1 + 1/K)\,E\,(y_{eq} - y_s) \qquad (15)$$

If Equation (4) is to be consistent with the proposed surface-rate expression [Equation (10)], Equation (15) shows that the following relationship exists between k_p and k:

$$k_p = k\,(1 + 1/K)\,E \qquad (16)$$

If the effectiveness factor can be determined, Equation (16) and the k_p data in Table 1 may be used to determine k. This latter quantity is the surface rate constant and is not affected by diffusional resistances. The values of k_p shown in Table 1 are essentially the same at equal pressures for both sizes of powdered catalyst. For these catalysts then the pore-diffusion resistance was negligible, and k may be calculated from Equation (16) by taking $E = 1$. The values of k so calculated are the same for all three catalyst sizes and are shown for 100 and 400 lb./sq. in. gauge in Table 2.

This information is sufficient to determine the effectiveness factor and the effective diffusivity for the ⅛-in. catalyst pellets. First E is obtained from Equation (16) by using average values of the k_p data for a given pressure (shown in Table 1). The effectiveness factor is related to the Thiele modulus m (*13*) by the expression

$$E = 3\,\frac{m \coth m - 1}{m^2} \qquad (17)$$

and m is the following function of the effective diffusivity:

$$m = R\sqrt{\frac{k(1 + 1/K)M\,\rho_p}{D_e\,\rho_g}} \qquad (18)$$

From these two equations effective diffusivities were computed and presented in Table 2 along with the effectiveness factors. It is interesting to note that the E values are less than 0.5 for this relatively active catalyst. The factor increases at lower pressures because the reaction rate decreases. The effective diffusivity is compared with the molecular diffusivity of hydrogen (*5*) in the last columns of Table 2. The diffusibility D_e/D_{H_2} is approximately 0.16. This quantity is a measure of the geometry of the pores in the ⅛-in. pellet. The macro void fraction

TABLE 2. COMPUTED RATE CONSTANTS AND EFFECTIVENESS FACTORS

Pressure lb./sq. in. gauge	Rate constants, g. mole/(g. of cat.) (sec.)		⅛-in. catalyst		D_{H_2},†	
	k	k_p (for ⅛-in. cat.)*	E	D_e, sq. cm./sec.	sq. cm./sec.	D_e/D_{H_2}
100	5.73×10^{-4}	5.12×10^{-4}	0.449	0.00245	0.0180	0.14
400	8.90×10^{-4}	7.60×10^{-4}	0.429	0.000888	0.00496	0.18

* Average value from Table 1.
† From Jost (5).

is estimated to be about 0.4, and for this condition the diffusibility value seems to be reasonable (*6*). However diffusibilities are normally determined from diffusion studies through the catalyst pellet. Further investigation is needed to explore the relationship between this type of diffusion and that occurring in micro and macro pores under reaction conditions.

Surface-Rate Equation

Table 2 gives k at 100 and 400 lb./sq. in. gauge. A third value may be calculated from the k_p data in Table 1 for the ⅛-in. pellet at 40 lb./sq. in. gauge. The effective diffusivity is estimated by assuming the ratio $D_e/D_{H_2} = 0.16$. Then the effectiveness factor k and m are determined by a trial-and-error solution of Equations (16) to (18). The result is $k = 3.95 \times 10^{-4}$ g. moles/(g. of cat.) (sec.).

In accordance with Equation (12) a plot of $1/k$ vs. $1/P$ should be a straight line with a slope equal to $1/k_c$ and on intercept of K_{Ad}/k_c, leading to values of k_c and K_{Ad} of 1.50×10^{-4} g. mole/(g. of cat.) (sec.) (atm.) and 0.13 atm.$^{-1}$.

Figure 4 is a plot of the final expression for k, Equation (12), and shows the experimental points at the three pressures. With these results the rate equation for the surface processes is, in accordance with Equation (10)

$$r = \frac{1.5 \times 10^{-4}}{1 + 0.13\,P}\left(p_o - \frac{1}{K}\,p_p\right) \qquad (19)$$

CONCLUSION

It should be mentioned that dissociation of hydrogen at the catalyst surface has been proposed by numerous investigators as the mechanism of the ortho-para conversion at room temperature. To test this possibility the hydrogen and deuterium exchange reaction was studied with the ⅛-in. nickel catalyst. No reaction was observed at liquid nitrogen temperature, and this was considered to be evidence that dissociation of hydrogen did not occur. The mechanism leading to Equation (10) supposes that the hydrogen molecule is adsorbed on the catalyst on a single site without dissociation. The relationship between catalytic activity and the magnetic properties of the catalyst is discussed in a separate paper (*10*).

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NOTATION

D_e = effective diffusivity of hydrogen in the catalyst, sq. cm./sec.
D_{H_2} = bulk (molecular) diffusivity of hydrogen, sq. cm./sec.
d_p = diameter of spherical particle having the same volume as catalyst particle, cm.
E = effectiveness factor of catalyst particle
F = flow rate in reactor, g. moles/sec.
k = reaction rate constant for surface reaction, defined by Equation (12), g. mole/(g. of cat.) (sec.)
k_c = specific reaction rate for the surface reaction, defined by Equation (10), g. mole/(g. of cat.) (sec.) (atm.)
k_f = mass transfer coefficient from the gas stream to the outer surface of the catalyst particle, g. mole/(sq.cm.) (sec.) (atm.)
k_r = mass transfer coefficient per unit mass of catalyst, defined by Equation (7), g. mole/(g. of cat.) (sec.)
k_p = reaction rate constant for the catalyst particle, g. mole/(g. of cat.) (sec.)
K = thermodynamic equilibrium constant for the ortho-para conversion, K = 1.01 at −196°C.
K_{Ad} = adsorption equilibrium constant, atm.$^{-1}$, K_o and K_p apply to ortho and para hydrogen
K_{ov} = reaction rate constant in terms of the overall driving force, g. mole/(g. of cat.) (sec.)
M = molecular weight of hydrogen
m = Thiele modulus, defined by Equation (18)
N_{Re} = modified Reynolds number, $(d_p u \rho_g)/(\mu)$
N_{Sc} = Schmidt number, $\mu/(\rho_g D_{H_2})$, or 0.78 for hydrogen at −196°C.
N_{Sh} = Sherwood number, $(k_f M d_p P)/(D_{H_2}\rho_g)$
p = partial pressure, atm.
P = total pressure, atm.
r = rate of reaction; rate of production of para hydrogen, g. mole/(g. of cat.) (sec.), $\bar{r}$ is the average rate for the entire catalyst particle expressed in the same units as r
R = radius of spherical particle having the same volume as the actual catalyst particle, cm.
W = mass of catalyst, g.
y = mole fraction of para hydrogen in the gas at any point on the catalyst surface; subscripts *s*, *g*., eq. designate the outer surface of the catalyst particle, the main gas phase, and the equilibrium value at a given temperature.
μ = viscosity of hydrogen, 348×10^{-7} poises at −196°C.
ρ_g = density of gas, g./cc.
ρ_p = density of catalyst particle, g./cc.

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