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Kinetics of Para-Ortho Hydrogen Conversion on Charcoal

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In the previous papers[1] it has been shown that the surface of charcoal is not uniform with respect to the para-ortho hydrogen conversion and the exchange reaction of $H_2 + D_2$. When studying the kinetics of the para-ortho conversion on charcoal we observed two kinds of active centers: centers of the first and centers of the second kind. These centers become poisoned with hydrogen adsorbed at high temperature. The poisoning of the centers of the first kind requires considerably less hydrogen to be adsorbed on the surface than the poisoning of the centers of the second kind. The dependence of the kinetics of the para-ortho conversion on temperature shows that this reaction has a small positive coefficient corresponding to an activation energy of 300 cals. On pure charcoal a positive temperature coefficient was observed when carrying out the reaction both by the static and the dynamic method.

When studying the para-ortho conversion on poisoned charcoal by the static method we observed a positive temperature coefficient, and when using the dynamic method, a negative temperature coefficient.

As has been previously shown, these phenomena may be explained by assuming that the para-ortho conversion has a different reaction order on pure and on poisoned charcoal: on pure charcoal — zero order, and on poisoned charcoal — first order.

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[1] R. Burstein, Acta Physicochimica URSS, 1, 465 (1934); Trans. Farad. Soc., 32, 823 (1936); Acta Physicochimica URSS, 8, 857 (1938).

To check these conclusions, in the experiments described below the reaction order was studied on both pure and poisoned charcoal.

The experiments were made in a way analogous to those described in the previous papers. The outgassing of sugar charcoal was conducted in a quartz vessel at 950° C for not less than 48 hours. In the intervals between the experiments the charcoal was not brought in contact with air.

The time required for the outgassing depends on the nature of the charcoal used and the method of its preparation; the charcoal was therefore considered pure if its activity practically did not change upon further outgassing. All the experiments were carried out with two grams of charcoal at 90° K using the static method. After outgassing the charcoal, a certain amount of hydrogen was collected in the part of the apparatus separated by a stopcock from the tube in which the charcoal was placed whereupon the pressure was measured; then the stopcock was opened and the hydrogen admitted into the apparatus in which the catalyst was placed. Prior to the beginning of adsorption the charcoal was cooled to the temperature of liquid air for 2 hours. The kinetics of the para-ortho conversion were studied by the thermoconductivity method[2] at a pressure of 12—15 mm. The measuring vessel was maintained at 90° K, and the filament was heated to 170° K. The pressure was measured with a manometer to within 0.1—0.2 mm.

The adsorption equilibrium of hydrogen on charcoal was established within one minute. Fig. 1 shows the relation between the quantity of adsorbed hydrogen and pressure. After the establishment of equilibrium the stopcock connected with the tube containing charcoal was closed, and the hydrogen contained in the remaining part of the apparatus was evacuated (if its pressure exceeded 2 mm.). Control experiments showed that during the establishment of adsorption equilibrium the hydrogen which was outside the adsorption vessel was practically unconverted. Therefore, it could be considered that the conversion was confined to the hydrogen adsorbed on charcoal and the hydrogen which remained

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[2] R. Burstein, Acta Physicochimica URSS, 6, 815 (1937).

in the adsorption vessel in the gaseous phase. In a definite time after the beginning of the reaction the vessel with liquid air was removed, the hydrogen was desorbed from charcoal in some seconds, and the amount of converted hydrogen was determined. After carrying out the experiment, the converted hydrogen was evacuated from the apparatus, and the charcoal outgassed at room temperature. Then the experiments were repeated with different pressures. In this way the experiments were carried out at final pressures in the region from 1 to 220 mm. In order to establish the reproducibility of these experiments the charcoal was outgassed again at high temperature, and the relation between the velocity constant and the quantity of hydrogen A was again determined.

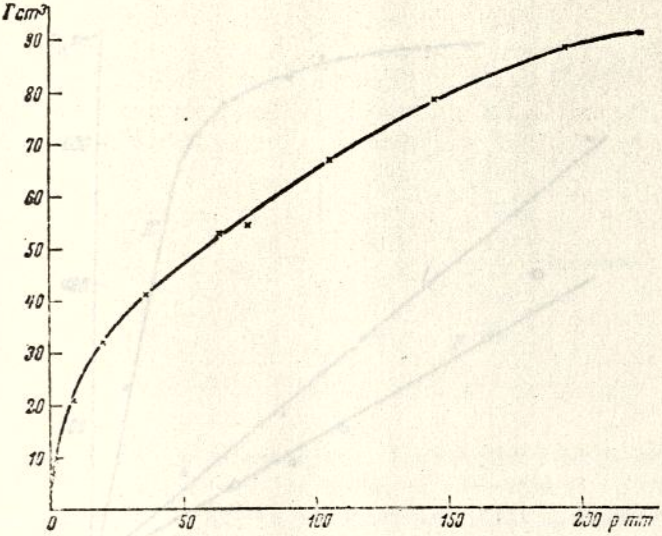

Fig. 1.

The results of two series of such experiments carried out with a month interval are shown in Table 1 and Fig. 2 (*I* and *II*). In this figure, on the abscissae are plotted the amounts of hydrogen,

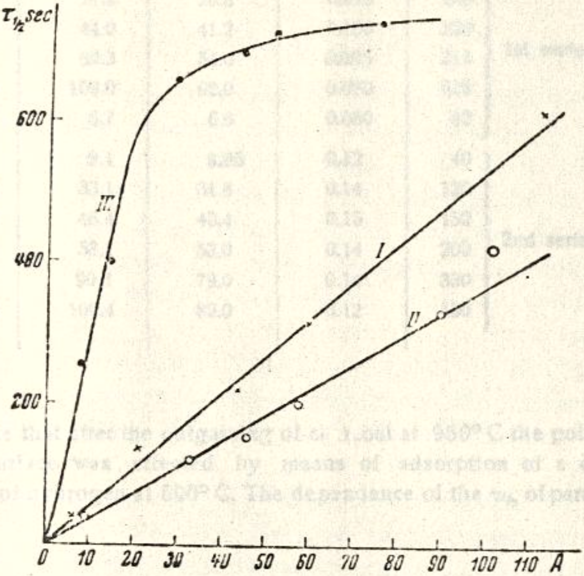

Fig. 2.

and on the ordinates, $\tau_{1/2}$. In the interval between the two series the charcoal was subjected to outgassing at 950° C.

In Table 1 p is the final pressure, A — amount of hydrogen in cm.^{3} taking part in the reaction, v — velocity of reaction, $\tau_{1/2}$ — time of half conversion, Γ — amount of adsorbed hydrogen.

As shown by these data, the outgassing conducted during one month somewhat increased the reaction velocity but the relation between the reaction velocity and the quantity of hydrogen remained the same. Experiments with poisoned charcoal were conducted in a manner analogous to those with pure charcoal with the only

Table 1

p mm.	A cm.³	Γ cm.³	v cm.³/sec.	$\tau_{1/2}$ sec.	
1	6.4	6.35	0.080	40	1st series
8.8	21.5	20.8	0.075	140	
36.4	44.0	41.2	0.100	220	
75.0	60.3	54.6	0.095	315	
222.0	109.0	92.0	0.090	618	
1.2	6.7	6.6	0.080	42	
2	9.1	8.95	0.12	40	2nd series
20.9	33.1	31.8	0.14	120	
39.2	46.4	43.4	0.15	152	
64.8	58.1	53.0	0.14	200	
144.8	90.1	79.0	0.14	330	
194.4	100.4	89.0	0.12	430	

difference that after the outgassing of charcoal at 950° C the poisoning of its surface was effected by means of adsorption of a definite amount of hydrogen at 500° C. The dependence of the $\tau_{1/2}$ of para-ortho

Table 2

p mm.	A cm.³	Γ cm.³	v cm.³/sec.	$\tau_{1/2}$ sec.	K
1.4	7.84	7.73	0.015	256	0.0019
4.0	14.3	14.0	0.018	396	0.0012
14.5	28.72	27.6	0.021	660	0.00073
35.0	43.99	41.6	0.03	696	0.00068
44.8	50.8	46.0	0.032	708	0.00063
106	75.1	67.0	0.047	720	0.00063

conversion upon the amount of hydrogen is shown in Table 2 and Fig. 2 (*III*). In Table 2 K is the velocity constant of the reaction.

In these experiments the quantity of adsorbed hydrogen at 500° was equal to 0.2 cm.^{3} per 1 gm. of charcoal.

Discussion of results

As shown by the data quoted above, on pure charcoal the conversion velocity practically does not depend on the hydrogen concentration with seventeenfold change of the latter. This fact is an evidence that on the surface of pure charcoal the reaction primarily proceeds on active centers of the first kind. These centers reach saturation already at small pressures, and therefore the increase of the hydrogen concentration does not influence the velocity of reaction, *i. e.*, in this case the reaction takes place according to the zero order. Thus, in order that the reaction should take place, the hydrogen adsorbed throughout the surface of the charcoal must diffuse towards the active centers of the first kind.

On poisoned charcoal, at small concentrations, the reaction velocity increases little with the rise of hydrogen concentration, and at large ones, the reaction velocity increases in proportion to the concentration.

The increase of the velocity constant (Table 2) at low concentrations must probably be accounted for by the inhomogeneity of the surface; it is possible that here a certain number of centers of the first kind have remained unpoisoned. In the region of high concentrations the reaction of para-ortho conversion on poisoned charcoal has the reaction order near to unity. Rummel[3], in measuring the dependence of the velocity constant of para-ortho conversion on pressure, found that this reaction at pressures above 7 mm. has the first order.

The data obtained in the experiments of Rummel are in good agreement with our data for poisoned charcoal. It seems that

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[3] Rummel, Z. physik. Chem., A 167. 221 (1933).

in Rummel's experiments the charcoal was insufficiently outgassed.

Comparing the data previously obtained by us for the temperature relation of the velocity of para-ortho conversion with the data representing the dependence of the reaction velocity on the concentration, we may draw the following conclusions. When studying the kinetics of the para-ortho conversion on poisoned charcoal by the static method, we obtained a positive coefficient corresponding to an energy of activation of 350 cals. It should be noted that the experiments made by the static method were carried out at low temperatures under conditions when practically the whole of the hydrogen taking part in the reaction was in an adsorbed state, *i. e.*, we measured the true energy of activation. When the kinetics of the para-ortho conversion is studied by the dynamic method, under conditions when the adsorption varies with temperature, a negative temperature coefficient is observed corresponding to an apparent activation energy equal to 1300 cals.

Taking into consideration that the para-ortho conversion on poisoned charcoal proceeds approximately according to the first order, it is easy to connect the results obtained by the static and the dynamic methods.

Since the heat of adsorption of hydrogen on charcoal is 1600 cals., the true activation energy is $\epsilon = 1600 - 1300 = 300$ cals.

The agreement between the two methods is, therefore, fairly good. It should be noted, however, that the values given here for the heat of adsorption refer to outgassed charcoal, and, therefore, these conclusions are correct if the adsorption heat does not change markedly upon poisoning.

On the surface of pure charcoal the para-ortho conversion has a positive temperature coefficient corresponding to an activation energy equal to 300 cals. whether the reaction is studied by the static or the dynamic method.

As shown by the data quoted above the para-ortho conversion on pure charcoal follows the zero order. In this case, as is known, the true activation energy is accessible to observation in spite of the fact that the amount of adsorbed hydrogen varies with temperature, since on pure charcoal the reaction proceeds mainly on the centers of the first kind which become saturated at low values of adsorption.

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