Reports of the Academy of Sciences of the USSR

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1958

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1958. Volume 119, No. 4

PHYSICAL CHEMISTRY

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ON THE THERMAL IONIZATION OF HYDROGEN AND HYDROCARBONS IN THE PRESENCE OF METALLIC CATALYSTS

It is known that gases adsorbed by heated metallic surfaces, or dissolved in a metal, are ionized and impart to the metal surface a stable and reproducible electrochemical potential characteristic of each of them (see, for example, (1)). It has been established that the charge of metallic surfaces can be removed by pumping off the gas; it can also be removed by carrying out chemical reactions, for example by burning hydrogen with oxygen. It has been established that adsorption and desorption of gases by a metal are accompanied by a change in its electrochemical potential.

Our experiments were aimed at the direct detection of the appearance of charged particles in the gas phase in the presence of metallic surfaces possessing catalytic properties (for the apparatus see Fig. 1). Disk electrodes a and a' made of the same metal that could serve as a catalyst were screwed onto rods b and b', sealed into the carefully ground ends of the main bell-jar tube. To the ends of these rods an electrostatic voltmeter v, or another instrument sufficiently sensitive for measuring weak electric currents, was connected. The tube diameter was 3.8 cm, its length 70 cm. A small electric furnace g, 8 cm long, made it possible to heat to 520° the electrodes located in the tube, as well as the gas around them. During heating of the furnace the free ends of the tube remained cold. It was shown that no current passed along the walls, since, first, when the length of the cold part of the tube was varied in different apparatuses the results did not change and, second, the current strength depended on the nature of the electrodes (see below). The distance between the electrodes was 20 mm. The temperature was measured with a thermometer d of molybdenum glass, with a scale up to 510°, whose lower part rested on the upper disk electrode and was fastened by clamps to rod b. The use of molybdenum glass made it possible to conduct experiments in the temperature range 20–510°. With quartz glass, diffusion of hydrogen ions was observed upon heating.

Fig. 1. Diagram of the apparatus

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Fig. 2

Figure 2: Fig. 2

Before the experiments the apparatus was evacuated to 10^{-4} mm Hg. In experiments with saturated vapors of organic liquids, the latter were placed in tube *e*, where they were degassed and subsequently frozen for the time during which a vacuum was being created in the apparatus. The liquids were heated to 25°, and then their vapors were transferred into the tube. After the pressure had equalized, the discharge tube was disconnected (stopcock *zh*), and during a gradual increase in temperature the discharge rate of the electrostatic voltmeter *v*, type S-91, charged to 150 V, was measured; the wires from the electrodes were connected to it without external resistance. The time

was measured with a good stopwatch. From the rate of discharge of the voltmeter one could judge the degree of ionization of the gas and vapors present in the interelectrode space. Experiments with hydrogen were carried out at 1 atm.; the hydrogen was electrolytic and had been purified. The electrodes were made of palladium, aluminum, and copper; the surface area of each of them was 6 cm^2. Palladium was first saturated with hydrogen. The greatest current was observed when the palladium was saturated with hydrogen.

The results of the ionization experiments are presented in the form of curves, in which the abscissa is the time τ—the reciprocal of the rate of discharge of the voltmeter—and the ordinate is the temperature. The greater the ionization, the farther to the left and the lower the curve lies.

The results for hydrogen in the presence of palladium, aluminum, and copper electrodes are given in Fig. 2a, which shows that a noticeable increase in the number of ions begins below 100°. It is very important that the ionization of hydrogen as the temperature is raised depends on the material of the electrodes and is in all cases reproducible and reversible—the heating curve coincides with the cooling curve. The ionizing ability can be characterized, for example, by the temperature at which the reciprocal discharge rate is equal to 60 sec. The smaller this quantity (t_{60}), the greater the ionizing ability. In the presence of palladium electrodes this temperature is very low for hydrogen, $t_{60} = 90°$; with palladium and aluminum electrodes, $t_{60} = 100°$. In the presence of copper electrodes, $t_{60} = 135°$.

Fig. 2. *a*—Hydrogen. Electrodes: 1—Pd/Pd, 2—Pd/Al, 3—Cu/Cu; *b*—Cyclohexane. Electrodes: 1—Pd/Pd, 2—Pd/Al, 3—Al/Al. Benzene. Electrodes: 4—Al/Al.

Fig. 3. *a*—*n*-heptane. Repeated experiments. Electrodes: Pd/Pd; *b*

Fig. 3

Figure 3: Fig. 3

—*n*-heptane. Electrodes: 1, 2—Al/Al, 3—C/Al; *v*—1—*n*-heptane, 2—2,2,4-trimethylpentane. Electrodes: Cu/Cu.

Similarly, we investigated the ionization of hydrocarbon vapors of different structures: *n*-heptane, 2,2,4-trimethylpentane, cyclohexane, benzene, decalin, tetralin, and also the cyclic ketone—cyclohexanone, with different electrodes (see Figs. 3 and 4). It was shown that ionization occurs in all these cases. Experiments with hydrocarbons were reproducible, except in cases where hysteresis was observed (see below); several irreproducible curves for *n*-heptane with palladium elec-

electrodes (see Fig. 3a and Table 1). Table 1 gives, for comparison, t_{60} for all the hydrocarbons taken, and also for hydrogen, where the pressure was higher (1 atm.). The sign ↑ denotes heating, the sign ↓ cooling; the absence of such signs denotes superposition of the heating and cooling curves, i.e., reversibility of the process, or absence of hysteresis. Curves without hysteresis are in the majority. Hysteresis was observed for decalin and tetralin and, in some cases, for *n*-heptane. For *n*-heptane with aluminum electrodes, filling the cup of the lower electrode with activated palm-wood charcoal leads to a noticeable, though small, increase in ionization—the curve shifts to the left; in this case the process becomes reversible. The lower curves of Fig. 4b with tetralin and Pd were obtained in a repeated experiment, performed immediately after the first; the ionization proved greater than in the first experiment. Thus, ionization in a gas in the presence of metals is noticeable already at low temperatures, for example for hydrogen—below 100°. This is not volume thermal ionization of hydrogen, which, as is known, occurs at high temperatures because the ionization potential of hydrogen is high.

Table 1

Electrode I	Electrode II	Substance in the gas phase	t_{60}
Pd	Pd	Hydrogen	90
Pd	Pd	*n*-Heptane	135—145
Pd	Pd	Cyclohexane	125
Pd	Pd	Decalin	200↑—165↓
Pd	Pd	Tetralin	155↑—125↓
Pd	Al	Cyclohexanone	95
Pd	Al	Hydrogen	100
Pd	Al	Cyclohexanone	280
Cu	Cu	Hydrogen	135
Cu	Cu	*n*-Heptane	175
Cu	Cu	Isooctane	155

Electrode I	Electrode II	Substance in the gas phase	t_{60}
Al	Al	*n*-Heptane	260
Al	Al	Cyclohexane	385
Al	Al	Benzene	400
Al	Al	Decalin	260↑–200↓
Al	Al	Cyclohexanone	145

The observed ionization depends strongly on the material of the electrodes. Consequently, it occurs on the metal surface. In addition, such ionization depends on the nature of the gas (see Table 1). It follows from this that it occurs in a layer of molecules adsorbed on the metal. The already known physical surface effects cannot explain the observed facts, since the Richardson effect, thermionic emission, and the ejection of secondary electrons upon bombardment of surfaces occur at considerably higher temperatures. Ionization which, as is known, is observed in surface chemical and adsorption processes also cannot serve as an explanation here, since it should weaken with time and cease when the surface becomes filled. In the present case, however, no weakening of the current strength with time is observed (in the experiment with H_2 and Pd electrodes at 360°, the current strength remained constant for 45 min.). The fact that the ionization was the greater, the more strongly the Pd electrode had previously been saturated with hydrogen, also argues against the supposition that the ionization occurs at the expense of an adsorption process. Thus, we are dealing with a new effect—thermal ionization of adsorbed molecules with the emission of ions into the gas at low temperature.

At the electrode, electrons rapidly pass into the metal, and consequently, under these conditions there is no equilibrium in ionization. Since the process is stationary, the current strength is determined by the rate of ionization of the adsorbed molecules. The height of the energy barrier for ionization in the adsorbed layer will be lower than in the gas, since from the ionization potential of the molecules in the gas I one must subtract the work function Φ_0. Indeed, the observed ionization decreases in the series

$$\mathrm{Pd} > \mathrm{Cu} > \mathrm{C} > \mathrm{Al} \tag{1}$$

(see Table 1 and the experiments with carbon), and in the same order Φ_0 decreases for these solids.

substances,—according to the summary (^{2}), for Pd, Cu, C, Al, Φ_0 is equal, respectively, to 4.82; 4.47; 4.39; 3.74 V. However, the indicated lowering is still insufficient to explain the observed effect, since, for example, for H_2, $I = 15.4$ V, and for Pd $\Phi_0 = 4.82$ V; the difference, 10.6 V (i.e., $\sim$ 240 kcal), is still very large. Since the rates of processes, in addition to the height of the energy barrier, are determined by the entropy factor, it should be concluded that in the observed processes the entropy factor is very large.

Figure 4

Figure 4: Figure 4

Fig. 4. **a** –Decahydronaphthalene. Electrodes: **1, 2** –Pd/Pd, **3, 4** –Al/Al. **b** –Tetrahydronaphthalene. Electrodes: **1** –Pd/Pd, **2** –Pd/Pd, repeat experiment. **c** –Cyclohexanone. Electrodes: **1** –Pd/Pd, **2** –Al/Al.

Hysteresis for tetralin and decalin may occur as a result of the presence of a steric factor: because of the complexity of these molecules, when electrons strike ions the electrons do not immediately fall back to the place from which they were detached, and therefore recombination is delayed.

It is very important that series (1) is parallel to the series of catalytic activity of metals in the reaction of hydrogenation and dehydrogenation. The phenomenon found occurs in the same temperature intervals as the indicated catalytic reactions.

The new effect, whose existence has been proved here, is important for catalysis. It is not described in existing electronic theories of catalysis. However, there is no doubt that in the development of the theory of catalysis it should be taken into account. The investigation will be continued.

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Received
26 XII 1957

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Note: Figure translations are in progress. See original paper for figures.