PHYSICAL CHEMISTRY

V. A. SHUSHUNOV and B. Ya. ANDREEV

1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. A. SHUSHUNOV and B. Ya. ANDREEV

KINETIC ISOTOPE EFFECT IN THE REACTION OF HYDROGEN AND TRITIUM WITH OXIDES OF CERTAIN METALS*

(Presented by Academician V. N. Kondrat' ev, 2 IV 1958)

There are only a few works in the literature ([1]-[6]) in which a difference is noted in the rate of topochemical reactions involving hydrogen and deuterium. As far as we know, analogous works using tritium instead of deuterium have not been carried out by anyone up to the present time.

The study of differences in the rates of topochemical reactions involving hydrogen and tritium, as well as the elucidation of the influence of a number of factors on the kinetic isotope effect of such reactions, in our opinion, may yield much of interest. The present work contains the results of an investigation of the influence of isotopy on the rate of reduction by hydrogen and tritium of oxides of a number of metals.

The experiments were carried out under dynamic conditions in an apparatus essentially differing little from that described earlier ([7]). We followed the course of the reaction by the drop in gas pressure, and the isotopic composition of the latter by determining the intensity of its radiation with a Geiger–Müller counter with internal filling. In order to ensure irreversibility of the reaction under investigation, the water vapor formed during the reduction of the oxides was rapidly removed from the reaction vessel and frozen out in a trap cooled with liquid nitrogen.

A mixture of hydrogen and tritium was obtained by chemical decomposition of water. Since the concentration of tritium in the water and in the gas was not more than $2 \cdot 10^{-4}\%$, it may be considered that the gas mixture consisted only of molecules H_2 and HT. Consequently, the isotope effect in the reactions studied pertains to the interaction of only these molecules, and not of H_2 and T_2 molecules.

The metal oxides were prepared by various methods described in widely known handbooks ([8],[9]), and were fractionated by sieving through a screen. In the experiments, as a rule, powder of a definite dispersion was used.

Assuming that the reduction of the oxides proceeds according to first order both with respect to H_2 and with respect to HT, and making certain reasonable

Fig. 1. Reduction of cupric oxide at different initial gas pressures. Oxide charge 1 g, $t = 150°$. Initial gas pressure: 1—50, 2—100, 3—150, 4—200, 5—314, 6—453 mm Hg.

Figure 1: Fig. 1. Reduction of cupric oxide at different initial gas pressures. Oxide charge 1 g, $t = 150°$. Initial gas pressure: 1—50, 2—100, 3—150, 4—200, 5—314, 6—453 mm Hg.

assumptions, we obtained the following equation expressing the dependence of the specific activity (A) of the gas on its pressure (p), valid for a reaction carried out at constant temperature and constant volume of the system:

$$\lg A = \left(\frac{1}{\alpha} - 1\right) \lg p + B. \tag{1}$$

The isotope kinetic effect α is equal to the ratio of the rate constant (k_1) of the reaction of H_2 to the rate constant (k_2) of the reaction of HT with metal oxides; B is a constant characterizing the initial state of the gas.

In all the oxide-reduction reactions studied, a linear dependence of $\lg A$ on $\lg p$ was strictly observed, which confirms the validity of the assumptions we made in deriving equation (1). The nature of this dependence does not change when the initial gas pressure, the size of the charge of the oxide being reduced, or the temperature is changed. This can be seen from Figs. 1 and 2, where several plots for the reaction of cupric oxide with hydrogen have been constructed from the experimental data.

Of course, relation (1) is not applicable in those cases where two or three oxides of the same metal are reduced simultaneously, for example in the reduction of MnO_2 and the Mn_2O_3 formed in the process. Here a linear dependence of $\lg A$ on $\lg p$ will occur only at the very beginning of the reaction, when the second oxide has not yet accumulated in sufficient quantity.

Fig. 1. Reduction of cupric oxide at different initial gas pressures. Oxide charge 1 g, $t = 150°$. Initial gas pressure: 1—50, 2—100, 3—150, 4—200, 5—314, 6—453 mm Hg.

Using relation (1), we constructed plots in the coordinates $\lg A$—$\lg p$, and from the slope of the straight line expressing this dependence we calculated the value of the kinetic isotope effect (α) for each experiment. The results of these determinations are summarized in Table 1.

It should be noted that the value of α does not depend on the initial gas pressure, the size of the charge of the oxides being reduced, or on the method of preparation and the degree of their dispersion. On the contrary, as is evident from

* G. M. Vlasov, Yu. A. Ivanov, and A. L. Buchachenko took part in carrying out the experiments.

Fig. 2. Reduction of cupric oxide at different temperatures. Oxide charge 1 g. 1 and 5—125, 2 and 6—150, 3 and 7—175, 4 and 8—200.

Figure 2: Fig. 2. Reduction of cupric oxide at different temperatures. Oxide charge 1 g. 1 and 5—125, 2 and 6—150, 3 and 7—175, 4 and 8—200.

Table 1, the value of this effect depends to a large extent on the temperature and on the nature of the oxides being reduced.

All the oxides whose reduction we studied can be divided into two groups. The first group includes oxides that react with hydrogen at a higher rate than with tritium. In this case the value of the kinetic isotope effect (α), i.e., the ratio k_1/k_2, is greater than unity. For these reactions we conventionally considered α to be positive. As is seen from Table 1, the reduction of Ag_2O, Cu_2O, CuO, HgO, PbO_2, MnO_2, and, at high temperature, Fe_2O_3 is characterized by a positive value of the kinetic isotope effect.

The second group includes oxides that react with hydrogen at a lower rate than with tritium. In this case the value of the kinetic isotope effect (α) is less than unity, and we conventionally considered it negative. This group of oxides includes Mn_3O_4, Mn_2O_3, NiO, CoO, Fe_3O_4, and Fe_2O_3. The reduction of ferric oxide proceeds with a negative kinetic isotope effect only at temperatures up to 320°, while at higher temperatures α becomes positive.

Fig. 2. Reduction of cupric oxide at different temperatures. Oxide charge 1 g. 1 and 5—125, 2 and 6—150, 3 and 7—175, 4 and 8—200.

In studying the kinetic isotope effect in the reaction of reduction of metal oxides by hydrogen and tritium, attention must be paid

attention to the possibility of isotopic exchange under these conditions:

$$\mathrm{HT} + \mathrm{H_2O} leftarrows \mathrm{HTO} + \mathrm{H_2}. \tag{I}$$

This reaction can be catalyzed both by oxides and by the metals formed upon their reduction. Experiments specially carried out by us showed that oxides of the first group and the corresponding metals catalyze reaction (I) very weakly. The rate of isotopic exchange under the conditions of our experiments is very small in comparison with the rate of reduction of the oxides of the first group by hydrogen and tritium. For the second group of oxides, on the contrary, catalysis of reaction (I) by both the oxides themselves and the pure metals is very characteristic. Therefore, in this case our results had to be treated with a certain caution.

Fig. 3. Reduction of CuO at 180° by hydrogen *(1)* and deuterium *(2)* and of MnO_2 at 200° by hydrogen *(3)* and deuterium *(4)*. Initial gas pressure 200 mm Hg.

Fig. 3. Reduction of CuO at 180° by hydrogen (1) and deuterium (2) and of MnO_2 at 200° by hydrogen (3) and deuterium (4). Initial gas pressure 200 mm Hg.

Figure 3: Fig. 3. Reduction of CuO at 180° by hydrogen (1) and deuterium (2) and of MnO_2 at 200° by hydrogen (3) and deuterium (4). Initial gas pressure 200 mm Hg.

Fig. 4. Reduction of NiO at 180° by hydrogen (1) and deuterium (2) and of Fe_3O_4 at 280° by hydrogen (3) and deuterium (4). Initial gas pressure for NiO 200 mm Hg, for Fe_3O_4 150 mm Hg.

Figure 4: Fig. 4. Reduction of NiO at 180° by hydrogen (1) and deuterium (2) and of Fe_3O_4 at 280° by hydrogen (3) and deuterium (4). Initial gas pressure for NiO 200 mm Hg, for Fe_3O_4 150 mm Hg.

Fig. 4. Reduction of NiO at 180° by hydrogen *(1)* and deuterium *(2)* and of Fe_3O_4 at 280° by hydrogen *(3)* and deuterium *(4)*. Initial gas pressure for NiO 200 mm Hg, for Fe_3O_4 150 mm Hg.

However, the procedure of our experiments made it possible rapidly to remove from the reaction zone the water vapor formed during the reduction of metal oxides, which very strongly lowered the reaction rate. Thus it may be considered that reaction (I) did not play a decisive role in our experiments.

This supposition is very convincingly confirmed by experiments we carried out on the reduction of metal oxides by hydrogen and deuterium*. It turned out that reduction of the oxides of the first group by hydrogen proceeds considerably (by a factor of 1.4–1.8) faster than by deuterium. Conversely, reduction of the oxides of the second group by hydrogen proceeds considerably more slowly (by a factor of 1.4–1.6) than by deuterium. Figures 3 and 4 show several kinetic curves that clearly illustrate this regularity.

These experiments convincingly prove the existence of a change in the sign of the kinetic isotope effect in reactions of hydrogen isotopes with metal oxides, depending on their nature and on the conditions under which the process is carried out.

It further turned out that the dependence of a on temperature obeys the Arrhenius law. From the temperature coefficient a we calculated the difference in the values of the activation energies for the reduction of metal oxides by hydrogen (E_1) and tritium (E_2) (Table 2).

As is seen from Table 1, the nature of the oxides of the first group has a rather strong influence on $E_1 - E_2$, whereas for the second group of oxides this influence is quite insignificant. For oxides of the first group $E_1 < E_2$, and the value of a decreases with increasing temperature; for oxides of the second group $E_1 > E_2$, and the value of a increases with increasing temperature.

In the case of the reduction of silver oxide and iron oxide we observed an unusual dependence of a on temperature. During the reduction of silver oxide—the value of α with increasing temperature first increases, which is unusual for the first group of oxides, and then decreases. In the region of relatively low temperatures the reduction of ferric oxide proceeds with a negative value of α, and starting from 320° with a positive one. These two anomalous cases are

Table 1

Ag_2O	Ag_2O	Cu_2O	Cu_2O	CuO	CuO	HgO	HgO	PbO_2	PbO_2	MnO_2	MnO_2
t, °C	α	t, °C	α	t, °C	α	t, °C	α	t, °C	α	t, °C	α
20	1.38	80	4.76	80	8.00	120	2.54	140	1.55	100	2.18
40	1.56	100	3.85	100	6.60	200	2.11	160	1.48	120	1.92
60	1.72	120	3.03	125	4.17	300	1.74	180	1.42	140	1.75
70	1.67	160	2.50	140	3.33	380	1.53	200	1.38	160	1.56
80	1.58	180	2.08	150	2.94					180	1.46
90	1.51			175	2.33					200	1.30
				200	2.00					220	1.23

Mn_3O_4	Mn_3O_4	Mn_2O_3	Mn_2O_3	NiO	NiO	CoO	CoO	Fe_3O_4	Fe_3O_4	Fe_2O_3	Fe_2O_3
t, °C	α	t, °C	α	t, °C	α	t, °C	α	t, °C	α	t, °C	α
300	0.50	220	0.68	150	0.30	160	0.30	280	0.47	240	0.54
360	0.56			175	0.33	180	0.32	320	0.51	260	0.58
400	0.59			200	0.40	200	0.33	340	0.53	280	0.73
460	9.64			225	0.42	220	0.37	360	0.55	300	0.85
500	0.68			250	0.45	240	0.40	380	0.57	320	1.00
						260	0.41			340	1.10
						280	0.43			380	1.21
										400	1.25

Table 2

Oxide	Cu_2O	CuO	HgO	PbO_2	MnO_2
$(E_2 - E_1)$, kcal	2.6	3.9	1.0	0.9	1.8
Oxide	NiO	CoO	Mn_3O_4	Fe_3O_4	
$(E_1 - E_2)$, kcal	1.4	1.5	1.4	1.4	

---

* Deuterium contained 2-4% hydrogen.

probably due to a change in the mechanism of reduction of the oxides with increasing temperature.

Research Institute of Chemistry
at Gorky State University
named after N. I. Lobachevsky

Received
27 III 1958

REFERENCES CITED

[1] J. Higuchi, J. Kawana, J. Chem. Soc. Japan, Pure Chem. Sect. **71**, 624 (1950); Chem. Abstr., **45**, 7461 (1951). [2] H. Svec, F. Duke, *Study of Kinetics of the Reactions between Uranium, H_2, HD and D_2*. Oak Ridge, Tenn., 1955. [3] H. W. Melville, E. K. Rideal, Proc. Roy. Soc. A. **153**, 77 (1936). [4] J. Higuchi, Bull. Inst. Phys. Chem. Res. (Tokyo) **21**, 843 (1942); Chem. Abstr., **42**, 5318 (1948). [5] F. Ishikawa, K. Mikai, Bull. Inst. Phys. Chem. Res. (Tokyo), **22**, 665 (1943); Chem. Abstr., **41**, 5778 (1947). [6] H. A. Smith, J. C. Posey, J. Am. Chem. Soc., **79**, 1310 (1957). [7] V. A. Shushunov, B. G. Zateev, ZhFKh, **30**, 321 (1956). [8] Yu. V. Karyakin, *Pure Chemical Reagents*, 1947. [9] G. Brauer, *Handbook of Preparative Inorganic Chemistry*, IL, 1956.

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