PHYSICAL CHEMISTRY

B. A. KUZNETSOV

1960

SovietRxiv

Fig. 1. Diagram of the apparatus for studying exchange: 1 —gas cuvette; 2 —reaction vessel; 3, 4, 5, 6 —vessels for storing the substance

Figure 1: Fig. 1. Diagram of the apparatus for studying exchange: 1 —gas cuvette; 2 —reaction vessel; 3, 4, 5, 6 —vessels for storing the substance

Abstract

Full Text

PHYSICAL CHEMISTRY

B. A. KUZNETSOV

STUDY OF THE HYDROGEN EXCHANGE OF ACETONE AND DBr IN THE GAS PHASE BY MEANS OF INFRARED SPECTRA

(Presented by Academician N. N. Semenov, November 13, 1959)

The study of reactions by means of isotopes and, in particular, the study of exchange reactions as models of ordinary chemical reactions has brought many successes to chemical kinetics. However, these successes are connected mainly with the study of liquid-phase reactions. The exchange reaction in the gas phase and, in particular, hydrogen exchange is at present a little-studied field, which cannot but hinder other investigations using hydrogen isotopes.

It is known that compounds belonging to the class of substances having an unshared electron pair and a hydrogen atom attached to one atom (of the type ROH, HHal, RNH_2) exchange with one another rapidly in the gas phase ([1,2]). In the present work an attempt was made to study such a combination of substances in which one substance has an unshared pair—HBr, H_2O—and the other has chemically active hydrogen (acetone).

Fig. 1. Diagram of the apparatus for studying exchange: 1 —gas cuvette; 2 —reaction vessel; 3, 4, 5, 6 —vessels for storing the substance

The exchange of acetone and DBr was studied in a vacuum apparatus, the diagram of which is shown in Fig. 1. The reaction was carried out in molybdenum and quartz vessels 2, placed in a furnace. After the reaction the mixture was passed into cuvette 1, where the deuterium content of all components of the mixture was analyzed. The vessel and cuvette were thermostatted. Special experiments showed that exchange in the cuvette during the time of analysis could be neglected. The extent of exchange was measured from the intensity of bands in the following regions: 2400 cm^{-1} (HBr), 1872 cm^{-1} (DBr), 3000 cm^{-1} (CH), and 2100 cm^{-1} (CD). The values of deuterium content obtained from different measurements were averaged.

The apparatus was calibrated for DBr and HBr with allowance for the dependence of band intensity on the total pressure, and also for acetone with known deuterium content. Samples containing from 5 to 90% D (at intervals of 5-10%) were prepared by exchange of acetone with heavy water (93.6% D) with addition of NaOD (pH 12).

Preliminary calculations of the deuterium content were carried out by a formula obtained from the expression for the isotope equilibrium constant. The equilibrium constant was taken equal to 0.85 (^{3,4}). The isotopic composition of the deuterium-containing acetones obtained was checked by analysis on an MS-4 mass spectrometer. The analysis gave good agreement with the theoretically expected results. Fully deuterated acetone was obtained by eightfold exchange. Each exchange operation was carried out over 10 days. Acetone sepa-

was freed from water by distillation. Drying was carried out with specially prepared Al_2O_3 (^{5}). After drying, a second distillation was performed. The absence of traces of water was determined with the aid of the double salt of potassium iodide and lead.

DBr was synthesized by decomposition of PBr_5 with heavy water in vacuum. Drying was carried out with PBr_5. The purity of the DBr obtained was determined from the vapor pressure at the melting temperature. The deuterium content of all products was determined on a mass spectrometer in the form of hydrogen, which was obtained by a special procedure (^{6}). The rate of exchange was calculated from the formula derived by us, in which the primary isotope effect is taken into account.

If one uses the notation adopted by S. Z. Roginskii (^{7}), namely: denote by R the rate of exchange of nonisotopic molecules proceeding irreversibly, and introduce an additional allowance for the isotope effect, denoting by Rf_1 the initial rate of exchange

$$\mathrm{AX}_n + \mathrm{BX}^*_m \rightleftarrows \mathrm{AX}_{n-1}\mathrm{X}^* + \mathrm{BX}^*_{m-1}\mathrm{X},$$

and by Rf_2 the initial rate of the reverse exchange

$$\mathrm{AX}^*_n + \mathrm{BX}_m \rightleftarrows \mathrm{AX}^*_{n-1}\mathrm{X} + \mathrm{BX}_{m-1}\mathrm{X}^*,$$

then the following differential equation can be written for the rate of accumulation of the heavy isotope in AX_n, taking into account the fractions of the isotope-exchange rate in the total exchange rate

$$d\dot{A}/dt = Rf_1(1-\rho_a)\rho_b - Rf_2(1-\rho_b)\rho_a,$$

where $\dot{A}, \dot{B}$ are the amounts of isotope X^*, respectively, in AX_n and BX_m; $\rho_a = \dot{A}/nA$; $\rho_b = \dot{B}/mB$; A, B are the concentrations of the substances $\mathrm{AX}_n, \mathrm{BX}_m$.

The solution of this equation in general form leads to the formula

$$Rf_1 = -\frac{mnAB}{tq(\rho_{a_2} - \rho_{a_1})(nA + mB)} \ln \left(\frac{(\rho_{a_1} - \rho_{a_2})(\rho_{a_0} - \rho_{a_1})}{(\rho_a - \rho_{a_1})(\rho_{a_0} - \rho_{a_2})} \right),$$

where

$$\rho_{a1,2} = p/2q \pm \sqrt{(p/2q)^2 + \rho/q}; \qquad q = (k-1)nA/(nA+mB);$$

$$p = (k-1)(\bar{\rho} - mB/(nA+mB)) - 1;$$

$k = f_2/f_1$ is the isotope equilibrium constant; m, n are the numbers of equivalent exchanging atoms in the molecules AX_n and BX_m; $\bar{\rho}$ is the deuterium content

Table 1

Equilibrium constant k for acetone with DBr and acetone-d_6 with HBr at 218° *

$\frac{I_0 - I}{I_0}$ by CH band	D, % by CH band	D, % by CD band	D, % mean	k	exchange t, min	Direction of reaction
0.260	53.9	53.9	53.9	2.42	66	Direct exchange
0.221	62.0	48.0**	53.9	2.42	180	Direct
0.232	60.4	48.6	53.0	2.42	120	Direct
0.246	57.1	53.5	55.6	2.42	150	Reverse
0.236	56.4	56.4	56.4	2.28	255	Reverse
0.213	60.5	48.7	53.1	2.24	120	Reverse
				2.3 ± 0.1		

* Total deuterium content in direct exchange is 0.432 and in reverse exchange 0.465.

** The overestimation of the percentage of D by the CH band and underestimation by the CD band occurs as a result of partial condensation of acetone on the wall. Our data make it possible to take this phenomenon into account.

of the entire system; ρ_{a_0} is the initial deuterium content of component AX_n. This equation gives, with sufficient accuracy, the constant Rf_1, independently of the extent of exchange.

As is seen from the formula obtained, calculation of the reaction rate requires knowledge of the equilibrium constant. We obtained an equilibrium constant k

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

at 218°, which was found to be 2.3±0.1. The experimental data are summarized in Table 1. The constant 2.3 is close to the value 1.98 calculated theoretically from the vibrational frequencies of acetone-d_6.* The calculated value of the ratio of the statistical sums is $(Q_2/Q_1)^{1/6} = 4.168$, and the experimental value is 4.6, taking into account $(Q_2/Q_1)_{\mathrm{HBr}} = 2.01$ (8).

To study the reaction mechanism of the exchange, the order of the reaction with respect to each of the components was determined at 218° in quartz and molybdenum vessels.* The kinetic curves are shown in Fig. 2. The first order with respect to acetone and DBr is evident from Fig. 3.

Fig. 2. Kinetic curves of the exchange of acetone and DBr (1–4) and of acetone-d_6 and HBr (5) at 218°.
1 –P = 35 mm, $P_{\mathrm{DBr}} = 420$ mm;
2 –P = 70 mm, $P_{\mathrm{DBr}} = 420$ mm;
3 –P = 70 mm, $P_{\mathrm{DBr}} = 280$ mm;
4 –P = 70 mm, $P_{\mathrm{DBr}} = 140$ mm;
5 –$P_{\text{-}d_6} = 70$ mm, $P_{\mathrm{HBr}} = 420$ mm.

Next, the dependence of the reaction rate on the ratio s/v was studied. The reaction rate in a vessel with packing increases proportionally to s/v. (For $s/v = 0.9$ cm^{-1} we obtain $Rf_1 = 21$ mm Hg/min; for $s/v = 5.9$ cm^{-1}, $Rf_1 = 125$ mm Hg/min at $t = 218°$, P = 70 mm Hg, $P_{\mathrm{DBr}} = 420$ mm Hg.)

Fig. 3. 1 –dependence of the exchange rate on acetone pressure, $t = 218°$, $P_{\mathrm{DBr}} = 420$ mm;
2 –dependence of the exchange rate on DBr pressure, $t = 218°$, P = 70 mm.

Fig. 4. Temperature dependence of the exchange reaction rate, $s/v = 0.7$ cm^{-1}, P = 45 mm, $P_{\mathrm{DBr}} = 270$ mm.

The temperature dependence of the exchange reaction rate was determined. As can be seen from Fig. 4, the Arrhenius law is well obeyed in the interval 32-218°C. For $s/v = 0.9$ cm^{-1}, the exchange rate can be expressed by the equation

Fig. 4

Figure 4: Fig. 4

$$Rf_1 = 1.3 \cdot 10^{-19} e^{-5300/RT} \text{ [acetone] [DBr] molecules/sec.}$$

It should be assumed that the reaction proceeds between adsorbed

* N. D. Elkina took part in obtaining these data.

on the wall, and acetone molecules impinging from the gas phase. A calculation of the pre-exponential factor made under this assumption, with an estimate of the degree of coverage and of the heat of adsorption, gives a value of 10^{-19}.

In fact, equating the exchange rate on the surface to the formally calculated volume rate, we obtain

$$\frac{s}{v} \frac{n_1 \bar{v}}{4} \theta e^{-E_{\text{true}}/RT} = k_0 n_1 n_2 e^{-E_{\text{eff}}/RT};$$

s/v is the ratio of surface area to volume, in cm^{-1}; $\bar{v}$ is the velocity of DBr molecules in cm/sec; θ is the degree of coverage; n_1, n_2 are the concentrations, respectively, of DBr and acetone in the volume; θ is the heat of adsorption of acetone.

From the equality obtained it follows that

$$k_0 = \frac{s}{v} \frac{\bar{v}}{4n_2} \theta e^{-Q/RT} \simeq 10^{-15} e^{-Q/RT},$$

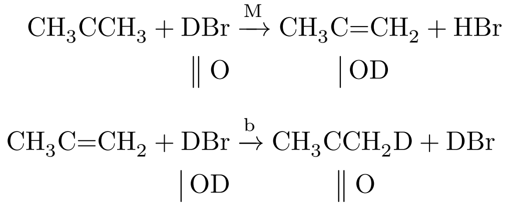
for $\theta \sim e^{Q/RT}$ and $E_{\text{eff}} = E_{\text{true}} - Q$. If $Q = 9$ kcal is taken, which may be estimated from the increment of the heat of adsorption for two CH_3 groups (^{9}), then the pre-exponential factor at $t = 218°$ will be equal to 10^{-19}, and $E_{\text{true}} = 14$ kcal/mole.

The number of collisions between DBr molecules adsorbed on the wall and acetone molecules impinging from the gas phase is 1-2 orders of magnitude smaller than for the mechanism considered. The contribution to the overall exchange rate due to such collisions will accordingly be a small fraction. A reaction in the adsorbed layer should have a pre-exponential factor of 10^{-27}, and is therefore excluded (^{10}).

Under our conditions P/P_s for acetone varies from 0.001 to 0.1, and correspondingly the degree of coverage from 0.01 to 0.5; i.e., we are not working in the region of film formation on the surface, where the reaction follows the laws of the liquid phase (^{11}).

It should be supposed that the proton transfer leading to exchange occurs in double collisions and is facilitated on the wall. The observed reaction should be assigned to the acid-base type, since the properties of HBr as a proton donor appear here. The reaction cannot proceed through the formation of ions on the surface, as follows from the work of N. M. Chirkov on the study of surface electrical conductivity at small P/P_s of hydrogen bromide (^{11}).

Thus, the scheme of the process on the wall is represented as follows:



$$CH_3\underset{\|\,O}{C}CH_3 + DBr \xrightarrow{M} CH_3\underset{|\,OD}{C}{=}CH_2 + HBr$$

$$CH_3\underset{|\,OD}{C}{=}CH_2 + DBr \xrightarrow{b} CH_3\underset{\|\,O}{C}CH_2D + DBr$$

It also follows from the present work that the enolization of ketones in the gas phase is a slower process than the reaction on the wall.

Moscow State University
named after M. V. Lomonosov

Received
13 XI 1959

CITED LITERATURE

1. A. I. Brodskii, *Izv. AN SSSR, OKhN*, 1949, No. 1, 3.
2. H. Kwart, L. P. Kuhn, E. L. Bannister, *J. Am. Chem. Soc.*, **76**, 5998 (1954).
3. A. I. Brodskii, *ZhFKh*, **9**, 75 (1937).
4. R. Klar, *Zs. phys. Chem.*, B26, 335 (1934).
5. F. M. Y. Jonson, *J. Am. Chem. Soc.*, **34**, 94 (1912).
6. R. Viallard et al., *Chim. analyt.*, **36**, 4, 102 (1954).
7. S. Z. Roginskii, *Theoretical Foundations of Isotopic Methods for Studying Chemical Reactions*, Moscow, 1956, p. 133.
8. H. S. Urey, *J. Chem. Soc.*, 1947, 562.
9. A. A. Isirikyan, A. V. Kiselev, B. A. Frolov, *ZhFKh*, **33**, No. 2, 389 (1959).
10. S. Glasstone, K. Laidler, G. Eyring, *Theory of Absolute Reaction Rates*, Moscow, 1948, p. 365.

11. N. M. Chirkov, Doctoral dissertation, Institute of Physical Chemistry, Academy of Sciences of the USSR, 1956.

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