Physical Chemistry

1960

SovietRxiv

Abstract

Full Text

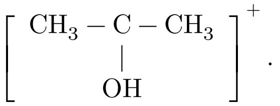
Physical Chemistry

B. A. Kuznetsov and N. D. Elkina

On the Mechanism of the Heterogeneous Exchange of Acetone and H_2O in the Gas Phase

(Presented by Academician V. N. Kondrat’ ev, 24 II 1960)

In a preceding work it was shown (^{1}) that the exchange of gaseous HBr with acetone occurs upon collision of HBr molecules arriving from the gas phase with acetone adsorbed on the wall. Owing to the acidic properties of HBr, protonolysis of acetone on the wall is probably possible in such a way that not one proton, but the entire HBr molecule, is added. In this case there is formed on the surface a so-called ion pair, which is an analogue of the ion formed in the liquid phase:



$$\left[\begin{array}{c} CH_3 - C - CH_3 \\ | \\ OH \end{array}\right]^+ .$$

Further, Br becomes capable of splitting off H from the CH_3 group within the complex

$$CH_3 - C(= O \cdots H - Br) - C(H_2) - H \longrightarrow CH_3 - C(OH) = CH_2 + HBr.$$

The reverse cycle of the process described leads to exchange.

To test these assumptions and to elucidate the general regularities of the exchange of compounds possessing an unshared pair and hydrogen at one atom with acetone, which has chemically active hydrogen, we undertook a study of the kinetics and mechanism of the isotopic exchange of acetone with H_2O and NH_3.

Experiments on the exchange of NH_3 with acetone-d_6, by the method described earlier (^{1}), in the temperature range from 20 to 250° at $P_{NH_3} = 140$ mm and $P_{ac} = 70$ mm showed that the exchange reaction does not occur within 2-3 hours. From this we conclude that a mechanism analogous to the liquid-phase mechanism with an ion pair on the wall and a transition complex

$$CH_3 - C(= O \cdots H - NH_2) - C(H_2) - H$$

Figure 1

Figure 1: Figure 1

is very unfavorable, since H in the CH_3 group probably cannot be the site of the primary attack of NH_3.

The exchange of acetone and H_2O was studied with the aid of tritium. In view of the fact that we could arbitrarily increase the sensitivity of the method by taking the corresponding specific activity of the initial water ($\rho_{\mathrm{HTO}} = 4.52 \cdot 10^6$ imp/min·mm), we succeeded in observing a very slow exchange (1000 times slower than the exchange of HBr with acetone) of HTO with acetone and in determining its kinetic regularities. As will be shown, the exchange of HTO and acetone proceeds according to laws different from those discussed above. The experiments were carried out in a vacuum apparatus in a quartz vessel of volume 1.5 liters, previously

treated with chromic mixture and thoroughly washed with distilled water. The amount of the admitted mixture was determined by a mercury manometer using a microcathetometer. After the reaction, the mixture was frozen out and diluted with acetone 50–100 times. The resulting mixture of acetone with water (the amount of which was about 1.5 ml) was separated in the following way. Dibutyl ether and 2–3 drops of water were added. The mixture was shaken, separated by means of a separatory funnel, and the solution of acetone in dibutyl ether was dried with Al_2O_3. Then the washing operation with water was repeated once more, after which the acetone was distilled off from a flask with a dephlegmator. Special experiments showed that no exchange occurs during the separation process.

The tritium content in acetone was determined with an internal-filling counter. The pressure of acetone in the counter was determined with an accuracy of up to 0.01 mm Hg. The tritium content in water was determined from the specific activity of hydrogen obtained by reduction of the initial HTO over Mg in a vacuum apparatus at $470°C$. The exchange rate was calculated from the formulas:

$$Rf_1 = \frac{1}{t}\frac{nAmB}{nA+mB}\ln\left(1-\frac{\rho_a}{\rho}\right), \tag{1}$$

$$Rf_1 = \frac{1}{t}\frac{\rho_a nA}{\rho} \tag{2}$$

for small percentages of exchange.

Fig. 1. Dependence of the exchange rate on the pressure of acetone $(1,3)$ at $P_{\mathrm{H_2O}} = 15$ mm and of water $(2,4)$ at $P\ = 5$ mm, in an empty vessel $(1,2)$ and in a vessel with packing $(3,4)$

Fig. 2 and Fig. 3 graphs

Figure 2: Fig. 2 and Fig. 3 graphs

These formulas were obtained from the previously derived (1) at $\rho_a, \rho\ , \rho \ll 1$, $k = 1|1|$; $\rho_a/\rho \ll |2|$, where in the initial formula $\rho_a = A^*/nA$ is the relative isotope content, i.e. $\rho_a = [T]\ /6A$. Since the intensity of β-radiation is proportional to the amount of tritium $I = \lambda[T]$, λ is the decay constant, and formulas (1), (2) contain only ratios of different values of I, there is no need in the calculation to find the true tritium concentrations.

Thus, $n\rho_a$ is the specific activity of acetone at time t; $m\rho$ is the initial specific activity of water; Rf_1 is the exchange rate multiplied by the kinetic isotope effect; A, B are the concentrations of acetone and H_2O; n, m are the numbers of hydrogen atoms in the molecule of acetone and H_2O; $\rho = \frac{\rho\ Bm}{nA+mB}$ is the average specific activity of the hydrogen atoms of the system.

The study of the reaction orders in an empty quartz vessel at a temperature of 180° showed (Fig. 1) an almost complete absence of dependence of the reaction rate on the concentration of the reacting substances within certain limits (acetone from 3 to 80, H_2O from 4 to 20 mm). When the temperature is increased, the character of the dependence of the rate on the pressure of the reacting substances is preserved. The temperature dependence has a complex character (Fig. 2). At 180–250°, $E = 1.5$ kcal/mole; at $t = 350°$, E increases to 25 kcal/mole. Higher temperatures were not used because of possible cracking of acetone. Next, the dependence of Rf_1 on s/v was studied. When the size of the vessel is changed, the rate increases proportionally to s/v. When using

when quartz chips were used as the packing, the geometric quantity S/v was increased 16-fold. The rate, however, increased 100-fold, which may be explained by the different properties of fused and crushed quartz (2). We assumed that the exchange of acetone and water occurs with the participation of hydroxyl groups on the surface, which serve as an intermediate link in the transfer of hydrogen isotopes. To test this hypothesis, a study was made of the rates of hydrogen exchange of surface hydroxyl groups with water and acetone. The surface of the vessel was preliminarily treated three times with HTO vapor for 24 hours at $t = 300$–$350°$. The experiments were carried out after thorough evacuation of H_2O for 4–5 hours at 300°. Water vapor was admitted into the vessel for a definite time, and after freezing out its specific

Fig. 2. Dependence of the exchange rate on temperature: 1 —in an empty vessel, 2 —in a vessel with packing

Fig. 3. Dependence of the rate of exchange of acetone (1) and H_2O (2) with surface hydroxyls on the fraction of the exchanged surface

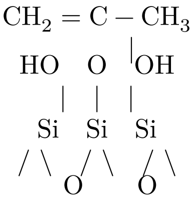
activity was determined. The operation was repeated several times with an increasing period of exposure of H_2O vapor in the vessel until the activity passing from the surface became negligibly small. The exchange rate was calculated from formula (1), with the value mB taken as equal to 1.5 mm Hg (found experimentally from the total activity retained on the surface). In calculating the rate in each subsequent experiment, the change in the specific activity of the SiOH groups was taken into account in such a way that Rf_1 for the individual substance had to remain constant. The total activity retained on the wall was $3.4 \cdot 10^6$ imp/min, which corresponded to $30\,\mu\text{mol/m}^2$ of geometric surface ($S = 0.95\,\text{m}^2$). The limiting concentration of SiOH groups on the surface is $11\,\mu\text{mol/m}^2$. Consequently, the surface studied by us is equal to $\simeq 3\,\text{m}^2$.

It was found that there is a certain continuous distribution of SiOH groups with respect to exchange rates. Moreover, the greater part of the surface exchanges comparatively slowly. The maximum rate, obtained by extrapolation to $\tau = 0$, is $Rf_{1\,\text{max}} = 0.2$ mm Hg/min. The minimum rate is $Rf_{1\,\text{min}} = 0.002$ mm Hg/min. ($t = 180^\circ$). Such a difference in rates is caused by $\Delta E = 2$ kcal/mol.

Experiments on the exchange of acetone with surface hydroxyls were carried out in an analogous manner. In Fig. 3, curve 1 shows the dependence of the exchange rate on the fraction of the exchanged surface. The latter was determined by us as the ratio of the activity removed from the surface at a given moment t to the total deposited activity. It is seen from Fig. 3 that during the experiment the rate falls, and only part of the surface exchanges comparatively rapidly.

Thus, if H_2O has access to all SiOH groups(3), acetone has access only to a fraction of them. After the exchange of the surface with acetone had practically ceased ($\delta s = 0.24$), in the same experiment the rate of exchange of the remaining unexchanged hydroxyls with water was determined (the experimental points are denoted by triangles). On the basis of the coincidence of the rates of exchange of H_2O with surface hydroxyls at identical δs with preliminary acetone exchange and without it, we conclude that the more reactive SiOH groups are such both with respect to water and to acetone. Analyzing the curve in Fig. 3, we find that at $\tau \to 0$ or $\delta s \to 0$, $Rf_{1\text{-max}} = 3.0 \cdot 10^{-4}$ mole/l • h. This value is close to the value that we found for the exchange of acetone with H_2O in their simultaneous presence (Fig. 1). Thus, the rate of exchange of H_2O with hydroxyls exceeds the rate of exchange of H_2O and acetone in their simultaneous presence, while the rate of exchange of acetone with surface hydroxyls is equal to or lower than this value.

Thus, on the basis of the material presented, the entire process of exchange of acetone and H_2O can be explained as follows. Acetone forms a chemisorbed compound, which may result from the opening of Si–O–Si groups, forming an enolate (analogous to the alcoholate)(4), with its subsequent removal after reaction with a neighboring SiOH group exchanged for tritium.



Since the process of exchange of H_2O with SiOH groups is not rate-limiting, zero order should be observed for H_2O. The increase in the exchange rate in the presence of H_2O should be explained by the fact that adsorbed water enters into exchange with chemisorbed acetone in accordance with the fraction of occupied surface (0.01), simultaneously increasing the rate of desorption of chemisorbed acetone. If it is assumed that adsorbed water reacts with acetone at a rate $Rf_1 = 3.0 \cdot 10^{-4}$ mole/l•h, then the weak dependence on the pressure of H_2O can be explained by replacement of the weakly active SiOH groups by more active OH groups of water. The temperature dependence of the rate of exchange of H_2O and acetone confirms our hypothesis concerning the participation of SiOSi groups. Dehydration of the surface and an increase in the number of SiOSi groups are observed precisely in the temperature region(5) where we have a sharp increase in the exchange rate ($t = 300°$). After preliminary dehydration of the surface at 600°, the rate at 180° increases somewhat. To explain the zero order with respect to acetone, or the weak dependence, it should be assumed that the limiting stage in the range $P = 5$–80 mm Hg of acetone is the desorption of chemisorbed acetone. This assumption is also supported by preliminary data on the dependence of the initial rate of exchange of acetone with groups on acetone pressure (zero order at 180°) and on temperature (the activation energy in the range 180–200° coincides with the activation energy for exchange of H_2O and acetone in their simultaneous presence).

Thus, the exchange of acetone and H_2O proceeds through chemisorbed acetone compounds with the participation of surface hydroxyls and adsorbed water.

Moscow State University
named after M. V. Lomonosov

Received
19 II 1960

REFERENCES CITED

1. B. A. Kuznetsov, *DAN*, **131**, No. 3 (1960).
2. S. P. Zhdanov, A. V. Kiselev, *ZhFKh*, **31**, 2213 (1957).
3. V. A. Nikitin, A. I. Sidorov, A. V. Karyakin, *ZhFKh*, **30**, 117 (1956).

4. A. I. Sidorov, *ZhFKh*, **30**, 996 (1956).
5. S. P. Zhdanov, *DAN*, **123**, 716 (1956); W. Stöber, *Koll. Zs.*, **145**, 17 (1956).

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