THE MECHANISM OF 2-METHYLBUTENE-2 HYDROHALOGENATION IN SOLID PHASE

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Abstract - Complexes and reactions of 2-methylbutene-2 with hydrohalogen (HCl, HBr) have been studied in solid phase at 80-150 K. It has been found that 2-methylbutene-2 forms with HX complexes of 1:1 and 1:2 composition. Hydrohalogenation proceeds via the rearrangement of complex $2HX \cdot C_5H_{10}$ into complex of the addition product with HX. Kinetic equation depends on the reagents ratio. In excess of HX ($1 \leq HX \cdot C_5H_{10} \leq 10$) reaction can be described by the first order kinetic equation. If the ratio $HX \cdot C_5H_{10}$ is more than 10, reaction is described by polychronous kinetic law. The effective activation energy of solid phase hydrohalogenation does not exceed 20 kJ/mole. The molecular mechanism of hydrohalogenation in solid phase has been proposed.

The mechanism of hydrohalogens addition to multiple bonds in condensed phase has not been fully clarified. Olefins hydrohalogenation is a multistage process. It proceeds via ionic intermediate or molecular complexes. Free radicals take part in hydrohalogenation in the case of hydrogen bromide addition. Usually hydrohalogenation is regarded as an ionic process.^{1,2} The recently obtained data show, however, that reaction, can be accomplished by means of molecular mechanism, without participation of ions or ion pairs.^{3,4}

The low temperature investigations are effective for more detail understanding reaction mechanism. Direct observation of molecular complexes, which are unstable at room temperature, is possible under this conditions. At low temperatures one succeeds in determing the conformation of primary addition products. It has been done, for example, that ethylene chlorination goes in solid state as cis addition.⁵

Hydrohalogens give with olefins in solid state at low temperatures halogenalkanes with 100% yield. At phase transition points explosive processes are obtained. At other temperatures hydrohalogenation proceeds with normal rates. Molecular complexes are formed as a result of reagents codeposition on a cooled by liquid nitrogen surface.^{6,7} These complexes play an important role in low

In the present work study on the kinetic and the mechanism of solid phase hydrohalogenation of 2-methylbutene-2 at 80-150 K has been performed.

EXPERIMENT

The samples used to investigate complex formation and reaction of 2-methylbutene-2 with hydrohalogens in solid state were obtained by codeposition of reagents from gaseous phase on the surface of cooper block. This surface was cooled by liquid nitrogen. Condensation rates were $10^{15}-10^{16}$ molecules/cm².s. Under these conditions molecular beam mode take place, and the gas phase interaction dasn't proceed. The thickness of condensate film was 2-10 μ m. To exclude the interaction between cooper and organic substances or hydrohalogens, inert substance films have been deposited on the block surface before reagents cocondensation.

The solid state processes were studied by means of IR-spectroscopy. The measurment technique has been described in detail in.⁵ Under experimental conditions Lambert-Beer's law holds true for the absorption bands of initial substances as well as reaction products.

The proceeding of hydrohalogenation was registered by the appearance of such bands in the spectrum which answer to those known from literature⁸ for 2-halogen-2-methyl butanes (bands at 1140, 600 and 535 cm⁻¹ for trans- and gauche-2-chloro-2-methylbutane and at 1135, 565 and 498 cm⁻¹ for trans- and gauche-2-bromo-2-methyl butane). Simultaneously with an increase of the intensity of these bands a decrease of the intensity of the bands of 2-methylbutene-2 complexes with hydrohalogens (1662 and 1650 cm⁻¹) was observed, the band intensities of reagents not combined into complexes remained constant (olefin bands at 1680 cm⁻¹, bands of crystalline hydrohalogens).

The reaction degree and rate were measured by a decrease in the absorption band intensities for the complexes and an increase in band intensities for the reaction products. When calculating the reaction degree from the bands with a half width of 50-100 cm⁻¹ (γ_{HX} in the complexes) the integral intensities were used; for narrow bands with a half width of the order of 10 cm⁻¹ ($\gamma_{C=C}$ in the complex and γ_{C-X} in the hydrohalogenation product) the optical densities at the maximum of the band were used. It was at first checked that the intensity of these bands did not practically depend on temperature.

Rate constants of the first order at a fixed temperature were calculated from the following formulae:

$$k_1 = \frac{1}{t} \ln \frac{D_0}{D_t}$$
 and $k_1 = \frac{1}{t} \ln \frac{D_{\infty}}{D_{\infty} - D_t}$,

where D_o is the integral intensity or the optical density of the band of the complex, D_t is the same parameter at moment t, D_t^i is the corresponding value for the band of the product, and D_{∞} is the reaction product absorption at 100% degree of conversion. The value of D_{∞} was determined after the samples had been left to stay at 130-150 K for an hour. In these conditions a quantitative yield of addition products is achieved, and their evaporation from the surface of solid films is not observed.

temperature halogenation.

EXPERIMENTAL RESULTS

<u>Complexes of 2-methylbutene-2 with hydrohalogens</u>. Cocondensation of 2-methylbutene-2 with hydrohalogens on a cooled to 80 K surface results in the formation of molecular complexes. Their origination manifests itself in IR spectra by the appearance of new absorption bands not belonging to the initial reagents and the hydrohalogenation products. Typical spectra of reagents and cocondensates are shown in Figs.1 and 2. As seen from the figures, the spectral pattern depends essentially on the ratio of reagents. This dependence indicates a possible formation in the system of the complexes of different composition.



Fig.1. IR-spectra: HC1 - 1, $C_5H_{10} - 2$, mixture of HC1with C_5H_{10} at $HX:C_5H_{10} = R =$ 0.2, T = 80 K - 3 and T =94 K - 4; at R = 5, T = 80 K - 5 and T = 120 K - 6.

In samples with an excess of olefin (HX: $C_5H_{10} = R < 1$) the bands with the maximus at 2520 cm⁻¹ (HCl) and 2206 cm⁻¹ (HBr) are observed. In samples containing an excess of hydrohalogens (R > 1) the maximus of bands are located at 2570 and 2230 cm⁻¹. According to the data,⁶ this dependence between the position of bands and the value of R is associated with the formation of the complexes $HX:C_5H_{10}$ (2520 and 2206 cm⁻¹ bands for \mathcal{V}_{H-X} of the hydrohalogens combined in a complex) and $2HX \cdot C_5H_{10}$ (bands at 2570 and 2230 cm⁻¹). This assignment is confirmed by the fact that the shifts of the maximus of the bands respectively to the hydrohalogen isolated in a inert matrix, ΔV , equal in this case for the lower frequency bands to 323 and 331 cm⁻¹, lie on the curve representing the dependence of ΔV on the clefin ionization potential for the complexes of 1:1 composition. Assignment of the bands at 2570 and 2230 cm^{-1} to complexes of 2:1 composition is in agreement with the $\Delta \mathcal{V}$ H-X values published in literature for complexes of such composition. The difference in the position of the maximus of complexes 1:1 and 2:1 according to the data⁶ is 35-60 cm^{-1} for HCl and various olefins and to 21 cm⁻¹ in the case of HBr complexes with ethylene. In the present work we obtained 50 cm⁻¹ for 2-methylbutene-2 complexes with HCl, and 25 cm⁻¹ for the complexes with HBr.



Fig.2. IR-spectra: HBr - 1, mixture of HBr with $C_{5H_{10}}$ at R = 0.3, T = 80 K - 2 and T = 103 K - 3; at R = 3. T = 80 K - 4.

The existence of 2-methylbutene-2 hydrohalogen complexes of 1:1 and 2:1 composition in the systems if additionally confirmed by the changes taking place in the $V_{C=C}$ valence vibration region. Observed in the spectra of samples containing hydrohalogens is the appearance of new bands at 1662 cm⁻¹ (R<1) and 1650 cm⁻¹ (R>1), whose position does not depend on the choice of hydrohalogen. These bands have been assigned for the HBr - C_5H_{10} system by the method of isomolar series. The spectra processing results are presented in Fig.3. The intensity of 1662 cm⁻¹ band is maximal at equimolar ratio of reagents; this band is thus associated with valence vibration in the olefin combined into a complex of 1:1 composition. The maximum of 1650 cm⁻¹ band is maximal complexes.



An increase in temperature results in a change in the spectral pattern of cocondensates. When samples with R < 1 are heated to 90-100 K the 2520 and 2206 cm⁻¹ bands shift into high-frequency region and turn into 2570 and 2230 cm⁻¹ bands (see Fig.1,2). These changes are irreversible: cooling to 80 K

does not restore the original pattern of the spectra. The changes observed in the spectra show that disproportionation of the complexes of 1:1 composition is proceeding in accordance with the following scheme:

 $2(HX \cdot C_5H_{10}) \longrightarrow 2HX \cdot C_5H_{10} + C_5H_{10}$

Disproportionation of the complexes of 1:1 combination is confirmed by the changes taking place in the region of $\rangle_{C=C}$ valence vibrations. As seen from Fig.2, heating is accompanied by a decrease in the intensity of the band at 1662 cm⁻¹ (complex 1:1 and a simultaneous increase in the intensity of the bands at 1650 cm⁻¹ (complex 2:1) and 1680 cm⁻¹ (olefin not combined into a complex). The obtained result shows that the ratio of reagents is not the only factor determining the composition of complexes in solid joint condensates. The heating of samples can result in the transformations of complexes. In the given case they can be assumed to be caused by a higher stability of 2:1 complexes in the investigated systems.

Complexes of 1:1 composition disproportionate with a small rate (1-3%/h) already at 80 K, the disproportionation being accelerated with an increase in temperature. The rate of the process grows nonuniformly: for each system there exists a critical temperature at which disproportionation is suddenly sped up -89 K for the system with HCl and 100 K in the case of HBr. The microscopic study of films in reflected polarized light at 600-fold magnification has shown that phase transitions, probably of the glass-crystal type, are taking place in the systems at these temperatures. An increase in the mobility of particles during the phase transition creates favourable conditions for disproportionation to be taking place.

Conditions of interaction and the stereochemistry of solid-phase hydrohalogenation. The rate of conversion of 2-methylbutene-2 complexes with hydrohalogens into addition products depends on the ratio of reagents, R. At R>3 hydrohalogenation is taking place at a considerable rate already in the course of cocondensation of reagents at 80 K. In this case after condensation, along with the bands of reagents and complexes, a number of new bands are present in the spectra, specifically 2670, 1140, 600 and 535 cm⁻¹ for HCl and 2300, 1135, 565 and 498 cm⁻¹ for HBr. The band at 2670 cm⁻¹ is associated with $\gamma_{\rm HCl}$ vibrations in the complex with hydrochlorination product - 2-chloro-2-methyl-butane.⁷ The 600 and 535 cm⁻¹ bands are close to those in the spectra of trans- and gaucheconformers of 2-chloro-2-methyl-butane; their shift by 15-20 cm⁻¹ into the lowfrequency region is also caused by the complex formation with HCl. The band at 1140 cm⁻¹, common for both conformers of the product, does not change with complex formation. The bands appearing in the case of samples with HBr coincide with these observed in the independently obtained HBr condensates with 2-bromo-2-methyl-butane and belong to HBr complexes with gauche- (498 cm⁻¹) and trans(565 cm⁻¹) conformers of the hydrobromination product. The 2300 cm⁻¹ band answers to the valence vibrations of HBr in this complex. The bands of 2-bromine-3-methyl-butane are absent in the spectra; this shows that solid-phase addition of HBr to 2-methylbutene-2 proceeds only in accordance with Markovnikov's rule.

The reaction degree in the course of condensation at large (3-20-fold) excesses of hydrohalogen is considerable: in the case of hydrochlorination it reaches 30-50%, and in the case of hydrobromination - 40-100%.

In the samples of equimolar composition, or in those containing an excess of olefin, no addition is taking place in the course of condensation and when the samples are left to stay at 80 K. Hydrochlorination is accomplished only after heating to 94 K and higher temperatures. The dependence of the temperature of the onset of measurable (3-5%/h) hydrobromination on the ratio of reagents is given below:

R 1.5 1 0.5 T.K 83 85 100

Hydrohalogenation products at R < 1 are mixtures of free gauche- and transconformers of 2-halogen-2-methylbutanes and their complexes with the corresponding hydrohalogens.

The trans-conformer of 2-chlorine-2-methyl butane is unstable in solid phase at low temperatures and is irreversibly transformed into the gauche-conformer:



At 100 K, isomerization proceeds quantitatively during one minute, a decrease in temperature and the complex formation with HCl slows it down.⁷ At 80 K and more than a 10-fold excess of HCl, isomerization can be neglected. In these conditions we observed, as it was shown above, the formation of the trans-conformer of the hydrochlorination product. Trans-2-chloro-2-methyl butane can only be formed as a result of hydrohalogen cis-addition. The obtained result thus indicate the actualization of cis-addition in solid phase. Drawing a similarly unambiguous conclusion with respect to trans-addition proves to be impossible since the second conformer, gauche-2-halogen-2-methyl butane, can appear both as a result of trans- and cis-addition.

<u>Kinetics of 2-methyl butene-2 solid-phase hydrohalogenation</u>. Kinetic measurements have shown that the kinetics of hydrohalogenation in solid phase depends

on the ratio of components in the solid cocondensate at a constant rate of reagents condensation $(10^{15} \text{ molecules/cm}^2 \cdot s)$.

Typical kinetic curves for the accumulation of the complex of addition products with HCl and the consumption of the complex of initial substances in 2-methylbutene-2 hydrochlorination are shown in Fig.4, together with their linearization in the coordinates of the first order kinetic equation. The kinetic equation is seen to describe the process satisfactorily at the degrees



Fig.4. Kinetic curves for the accumulation of C₅H₁₁Cl·HCl - 1 and the consumption of C5H10.2HC1 -2 at R = 9, T = 85 K andtheir linearization in the coordinates of the first order kinetic equation.

50 t min

The kinetics do not correspond to the first order kinetic equation at R>10 for solid-phase hydrochlorination and at R>3 for hydrobromination; kinetic curves are linearized in the coordinates of polychronous kinetics⁹ typical for many solid-phase processes. An example of such linearization in $\lg \eta - t^{0.5}$ coordinates at R = 18 is shown in Fig.5.



Fig.5. Kinetic curves for the assumption of $C_5H_{11}Cl \cdot HCl - 1$ and the consumption of C5H10 2HC1-2 at R = 18, T = 80 K andtheir linearization in the coordinates of polychronous kinetic.

The processing of hydrochlorination kinetic curves at R = 3 - 10 in the coordinates of the first order kinetic equation results in the following values of effective rate constants:

Т, К	80	83	86	90	92
k ₁ •10 ⁵ , s ^{−1}	3.5 <u>+</u> 1	4 <u>+</u> 1	13 <u>+</u> 3	26 <u>+</u> 3	29 <u>+</u> 4

The effective activation energy of hydrochlorination in these conditions amounts to 12 ± 3 kJ/mole, of hydrobromination at $R \le 3 - 4\pm2$ kJ/mole.

In samples with hydrohalogen deficiency (R < 1) the addition is actualized with a measurable rate only after a sample is heated to 94 K (HCl) and 100 K (HBr), i.e. after the disproportionation of 1:1 complexes and the formation of 2:1 complexes in the system. Observed in this case is the accumulation of hydrohalogenation products and a cymbate decrease in the content of 2:1 complexes. The process is described by an equation of the first order, but the rate constants here are lower than with R > 1:

T, K9499101103105 $k_1 \cdot 10^5$, s^{-1} 5 ± 2 26 ± 2 40 ± 3 80 ± 5 93 ± 8 (R = 1)

The effective activation energy at R = 1 in the case of hydrochlorination amounts to 20 ± 3 kJ/mole, hydrobromination - 8 ± 2 kJ/mole. The mechanism of olefins hydrohalogenation in solid phase. Results of the work make it possible to suggest the following scheme of transformations taking place in the solid condensates of 2-methylbutene-2 with hydrohalogens

 $2(HX \cdot C_5H_{10}) \xrightarrow{-C_5H_{10}} 2HX \cdot C_5H_{10} \xrightarrow{-C_5H_{11}X \cdot HX} \xrightarrow{-C_5H_{11}X \cdot HX} \xrightarrow{-C_5H_{11}X + HX}$

Realization of reactions from the complexes 2:1 is proved by hydrohalogenation taking place with a noticeable rate only in the samples containing 2:1 complexes. In agreement with this is also the formation of halogen alkane complexes with hydrohalogens as a result of reaction. For hydrohalogenation to be taking place in the systems containing only 1:1 complexes these must previously disproportionated. Let us now examine in greater detail the stage of 2:1 complex being converted into a complex of the addition product with hydrohalogens.

According to the concepts expounded in literature, ¹⁻⁴ the transformation of an olefin complex with HX, in the absence of external initiation, can follow the ionic or the molecular mechanism. The ionic mechanism concepts do not agree with the low activation energies observed in experiment. Indeed, the activation energies of ionic hydrohalogenation in liquid phase, even in polar solvents strongly solvating the ions, usually amounts to some scores of kJ/mole.¹⁰ A low molecular mobility in solid samples must hinder the effective solvation of ions, as in the case of the ionic mechanism one should have expected even higher activation energy values and very low reaction rates at temperatures of about 80 K. However, hydrohalogenation is taking place in the sample of 2:1 composition at 80 K with a measurable rate, the activation energies are not high. These data allow the ionic mechanism of solid-phase addition to be excluded. Transformation of the complexes of hydrohalogens with 2-methylbutene-2 into the complexes of addition products are realized in solid phase, in our opinion, without the formation of ions, following the molecular mechanism similar to the mechanism previously proposed for a liquid-phase process.⁴ The molecular mechanism presupposes the transformation of a complex into a product via a sixmembered transition state, which for cis-addition has the form of



The cyclic structure of transition states leading to the products of transaddition has been dealt with in.¹¹ Low energies of cyclic systems and, therefore, low activation energies of the corresponding reactions are determined, in our opinion, by the stabilization produced by donor-acceptor interactions. This stabilization is facilitated by the extension of bonds taking place in hydrohalogen molecules when the transition states are formed, which results in a decrease in the energy of lower vacant molecular orbitals in HX molecules and in the intensification of their acceptor properties. Extended molecules occupy an intermediate place between the ordinary unperturbed molecules and the separated atoms whose overall affinity to the electron is several times (in this case more than 3 times) higher than the affinity of the corresponding molecules. In our opinion, this effect leads to the situation when the energy of donoracceptor interactions in cyclic systems containing extended molecules can become much greater than in the initial complexes and compensate the energy of bonds extension. Similar stabilization also seems to be possible in other addition processes with the participation of molecules having the properties of donors and acceptors. Investigation of the kinetic regularities of solid-phase ethylene chlorination has actually shown that here too the molecular mechanism with a cyclic transition state is the most probable.⁵ This is probably a common mechanism of solid-phase halogenation and hydrohalogenation.

Hydrohalogenation mechanisms in solid phase and in non-polar solvents are, in our opinion, similar. In both cases the conditions for effective ion and ion pair stabilization in the systems are absent. The complex formation also proceeds in a similar way: the recently obtained data¹² show that, both in the liquid and the solid phase, hydrohalogens form 2:1 and 1:1 complexes with olefins. The concept of the same mechanism of halogenation in liquid and solid phases agrees with the fact that in both cases the same number of molecules two hydrohalogen molecules and one olefin molecule - take part in the transition state. This follows from the kinetic equations in liquid phase (the second order with respect to HX, the first with respect to the complex of 2:1 composition). The specificity of solid phase associated with a limited molecular mobility manifests itself in kinetic deviations taking place under certain conditions, in particular when there is a large excess of hydrohalogens, from the kinetic law of the first order and in the appearance of kinetic equations characteristic for polychronous kinetics.

The data obtained in the present work make it possible to render more specific some general features of the molecular addition reactions. In the works devoted to liquid-phase processes we assumed the rearrangement of complexes 2:1 into products to be accomplished with a low activation energy.⁴ Direct measurement of this quantity in liquid phase proved to be impossible because of the existence of a whole number of equilibrium processes of complex formation. In solid phase the equilibriums are shifted towards the most stable, in the conditions of experiment, complexes, which made it possible to determine the activation energy of the transformation of those complexes. The obtained values have confirmed the previously made assumptions (2 - 20 kJ/mole).

The existence of rapidly attained equilibrium in liquid phase did not make it possible to ascertain before the nature of primary products of molecular halogenation. The data obtained in the present work show that at the first stage of the process the complexes of halogen derivatives with hydrohalogens are probably formed.

Investigations in solid phase have made it possible to define the stereochemistry of primary addition products for such processes where, in distinction to the best studied in this respect cycloalkene hydrohalogen systems, there are no steric hindrances for the formation of cis-addition products, associated with the specific structure of initial molecules. Cis-addition proved to be taking place in this case. This fact can be compared with the previously noted molecular cis-addition of chlorine to ethylene.⁵ We believe that molecular cisaddition of halogens and hydrohalogens, in the conditions when no additional steric hindrance for the formation of one of the stereoisomers of the product exist, is a general regularity.

It can thus be concluded that the molecular mechanism is in good agreement with the whole totality of data on the kinetics and the reaction products and is common for the processes of halogen and hydrohalogen addition in solid phase and non-polar media.

REFERENCES

- 1. Ingold C.K., Structure and Mechanism in Organic Chemistry, Second Edition, Cornell University press, Ithaca and London, 1969, Ch.XIII.
- 2. Fahey R.C., McPherson C.A., J. Amer. Chem. Soc., 1971, v.93, p.2445.
- 3. Haugh M.J., Dalton D.R., J. Amer. Chem. Soc., 1975, v.97, p.5674.
- 4. Sergeev G.B., Stepanov N.S., Leenson I.A. et al., Tetrahedron, 1982, v.38,

5862

p.2585.

- Sergeev G.B., Smirnov V.V., Shilina M.I., Dokl. Akad. Nauk SSSR, 1984, v.274, p.123.
- 6. Kimel'feld Ya.M., Molecular Interactions, v.3, Wiley Sons, 1982, p.343.
- 7. Sergeev G.B., Smirnov V.V. et al., Vest. Mosk. Gos. Univ., Ser.2 (Khim.), 1985, v.26, p.53, 181.
- 8. Hayashi M., Michiro M., J. Chem. Soc. Japan, Pure Chem., 1958, v.79, p.50.
- 9. Syutkin V.M., Tolkatchev V.A., Radiat. Phys. Chem., 1982, v.20, p.281.
- 10. Reichardt C., Losungsmittel-Effekte in der Organischen Chemie, Verlag Chemie, 1969.
- 11. Sergeev G.B., Smirnov V.V., Molecular halogenation of olefins. Moscow, Moscow State University, 1985.
- 12. Sergeev G.B., Smirnov V.V., Rostovshchikova T.N., Mashyanov M.N., Zh. Obshch. Khim., 1985, v.55, p.1137.