Rapid Chemical Processes at Low Temperatures

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V. A. Lishnevskii, B. M. Uzhinov, and G. B. Sergeev

Rapid Chemical Processes at Low Temperatures

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In a previous paper (^{1}) it was shown that at very low temperatures chlorine reacts instantaneously with a whole series of compounds containing a double bond, and that addition products are obtained in practically quantitative yields. The generality of this phenomenon has been tested by us in the present work using as examples other processes important for industry—such as bromination and nitration of olefins, hydrohalogenation of olefins with a double bond at a tertiary carbon atom, and also certain inorganic addition and exchange-substitution reactions.

The experiments were carried out in a vacuum apparatus that made it possible to obtain a rarefaction down to 10^{-6} mm Hg. The starting substances were prepared and purified by methods known in the literature. In addition to chemical methods, in all cases repeated low-temperature distillation in vacuum was used, with only the middle fraction being taken. Moreover, in order to exclude possible traces of impurities with low vapor pressure (especially moisture), the gases for the experiments were taken from a previously condensed state. During the experiments, measures were also taken to exclude the influence of light. The reactions were studied by the thermographic method with differential recording. The heating curves were recorded using an EPP-09 potentiometer with increased and adjustable sensitivity. The required rate and uniformity of heating of the initial mixture with time were achieved by means of an aluminum block (diameter 60 mm, height 180 mm) immersed in a Dewar vessel. A diagram of the reaction vessel and of the thermographic apparatus is given in Fig. 1.

Preliminary experiments established that all the reactions we studied proceed at temperatures above −196°C. This circumstance made it possible to prepare the initial mixtures at the temperature of liquid nitrogen. Definite quantities of the components (0.0009 mole) were carefully, in order to avoid heating of the mixture, frozen in layers into the narrow part (diameter 6 mm, length 13 mm) of the reaction vessel, cooled with liquid nitrogen. The temperature of the mixture during freezing of the components was monitored from the readings of a differential thermocouple. After preparation of the mixture, a block, pre-cooled to the temperature of liquid nitrogen, was placed on the vessel; it then warmed spontaneously at a rate of approximately one degree per minute. The temperature of the block was measured with a copper-constantan thermocouple, the readings of which were recorded by an M-194 microammeter with an accuracy of

±2°. One junction of the differential thermocouple (copper wire diameter 0.15 mm, constantan wire diameter 0.07 mm) was placed in a special hole in the block together with a simple thermocouple; the other junction (sealed into an evacuated capillary about 0.5 mm in diameter) was located approximately at the center of the reaction mixture. Both thermocouples were calibrated against a standard thermocouple. Knowing the temperature of the block and the temperature difference between the junctions of the differential thermocouple, it was possible to determine the temperature of the reaction mixture at the moment of reaction.

The necessary quantities of products for analysis were obtained in a trap cooled with liquid nitrogen. To avoid an explosion, the product was accumulated in small portions by rapidly freezing layers of 0.004 mole of each component, followed by thawing. In this process, the principal part of the substances reacts directly at the moment of rapid freezing of the second component, owing to heating of the mixture during condensation; the unreacted part reacts during thawing. This operation was repeated many times until 3-5 cm^3 of reaction product had been obtained. Since as a result of the reaction only one product is formed, its yield was determined from the change in pressure. The pressure was measured with a membrane manometer. The bromination and hydrohalogenation products were distilled on a column with glass packing, having 19 theoretical plates, using decalin as the "cushion."

The results of the experiments are summarized in Table 1. As an example, Fig. 2 gives the thermogram of the propylene—bromine system. Similar thermograms were also obtained for the other systems. The experiments showed (see Table 1 and Fig. 2) that all the reactions studied, as well as the addition reactions of chlorine at the double bond ([1]), proceed instantaneously at very low temperatures. With very small amounts of starting substances (0.0009 mole of each component at a ratio of 1 : 1 and 0.0018 mole of one of the components at a ratio of 1 : 2), the temperature rises during the reactions reach tens of degrees. The occurrence of rapid (practically explosive) reactions at such low temperatures indicates the small activation energies required for their course and, possibly, a chain mechanism of these reactions. We believe that the lowering of the activation energy in comparison with the gas phase may be achieved through the preliminary formation of molecular complexes as intermediate substances. The existence of such complexes in the case of iodine and olefins at low temperatures has been shown spectroscopically ([2]). The formation of molecular complexes at low temperatures between hydrogen halides and olefins is also known ([3], [4]).

Table 1

Results of thermographic study of low-temperature reactions

No.	System	Ratio of components	Melting point of components, °C: 1st comp.	Melting point of components, °C: 2nd comp.	Reaction temperature (critical), °C	Product	Yield, % of theor.	Product constants: b.p., °C	Product constants: n_D^{20}
1	Isobutylene – bromine	1 : 1	−140	−7	−154	1,2-Dibromo-2-methylpropane	95	59-60/36 mm	1.5105
2	Propylene – bromine	1 : 1	−185	−7	−125	1,2-Dibromopropane	96	54-55/36 mm	1.5198
3	Isobutylene—hydrogen bromide	1 : 1	−140	−112	−145	2-Bromo-2-methylpropane	93	49/747 mm	1.3686
4	Isobutylene—hydrogen bromide	1 : 2	−140	−88	−137	2-Bromo-2-methylpropane	99	71/750 mm	1.4280
5	Propylene—nitrous oxide*	1 : 2	−185	−9	−60	Nitrous oxide			
6	Propylene—nitrous oxide*	1 : 2	−185	−9	−60	Nitrous oxide	100		
7	Nitric oxide—oxygen	2 : 1	−164	−218	−190	Nitrogen dioxide	99		

Fig. 1

Figure 1: Fig. 1

No.	Systems	Ratio of components	Melting point of components, °C: 1st comp.	Melting point of components, °C: 2nd comp.	Reaction temperature (critical), °C	Product	Yield, % of theor.	Product constants: b.p., °C	Product constants: n_D^{20}
8	Nitric oxide—chlorine	2 : 1	−164	−102	−115	Nitrosyl chloride and bromine	100		
9	Hydrogen bromide — chlorine	2 : 1	−88	−102	−102	Nitrosyl chloride and bromine			

* The nitration products of isobutylene and propylene were not analyzed. An attempt to obtain nitration products of isobutylene upon heating in a frozen layer mixture (0.08 mole of isobutylene and 0.06 mole of nitrous oxide) led to a powerful explosion.

Table 1 also shows that addition reactions at the double bond under the conditions studied are, moreover, characterized by a directed and complete course, as a result of which practically one product is obtained in quantitative yield. It should be noted that each system is characterized by its own critical temperature, at which the rapid reaction occurs. Below the critical temperatures the reactions practically do not proceed. The critical temperatures for the systems studied, as is seen from Table 1, lie mainly in the range from −190 to −100°C.

Fig. 1. Diagram of the reaction vessel and thermographic apparatus: 1 —reaction vessel (volume = 80 cm^3); 2 —aluminum block; 3 —Dewar vessel; 4 —simple thermocouple; 5 —differential thermocouple; 6 —piston; 7 —capillary containing the junction of the differential thermocouple; K —switch; R_2 —resistance box of the KMS-6 type (increasing and adjusting the sensitivity of the potentiometer by additional shunting of the rheochord); E —dry cell; R_3 —high-resistance variable resistor (zero setting).

Fig. 2

Figure 2: Fig. 2

Fig. 2. Heating curve of the propylene-bromine system (differential recording). Ratio of components 1 : 1 (0.0009 mole of each component). Maximum overheating = 60°.

These temperatures are reproduced from experiment to experiment within 2-15 degrees. Table 1 gives the average values of 4-5 experiments. Comparing the critical temperatures of the systems with the melting temperatures of the constituent components, one may distinguish: systems whose critical temperatures lie below the melting temperatures of both components (isobutylene—bromine) or near the melting temperature of the component with the lower melting point (isobutylene—hydrogen chloride, isobutylene—hydrogen bromide, hydrogen bromide—chlorine), and systems whose critical temperatures lie between the melting temperatures of the individual components (propylene—bromine, isobutylene—nitrogen dioxide, propylene—nitrogen dioxide).

In the case of the reaction of nitric oxide with chlorine, the critical temperature is above the boiling temperature of nitric oxide (−152°), but below the melting temperature of chlorine.

The existence of critical temperatures may be connected with the fact that the reactions proceed at the moment of, or near, phase transitions. In systems of the first type, the critical temperatures are probably associated with the tempe-

melting temperatures of the mixture. Since, in layer-by-layer freezing-on of the components of a rapid reaction, dissolution of one component in the other must apparently precede the reaction, the critical temperatures in systems of the second type may be determined either by processes of dissolution and complex formation or by the melting temperatures of molecular complexes. In the general case, the melting temperatures of molecular complexes may differ greatly from the melting temperatures of the constituent components ([3]). It may also be noted that reactions with isobutylene proceed at lower temperatures than the corresponding reactions with propylene, which is probably connected with the more polar structure of the isobutylene molecule. The fact that, in the case of hydrogen halides and isobutylene, products of normal addition are obtained apparently indicates the ionic character of the addition reactions at the double bond.

Thus, using the systems studied as examples, a new phenomenon has been discovered: the practically instantaneous occurrence of addition and exchange-substitution reactions at very low temperatures in the condensed phase. In the gas phase, at room and moderately higher temperatures (up to 150°), such reactions either do not proceed at all or proceed slowly, being catalyzed by the walls of the vessel ([5–7]).

The observed phenomenon cannot be explained by an increase in the concentration of substances in the condensed phase, but is apparently the result of the specific character of the condensed state and, possibly, of low temperatures.

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1. V. A. Lishnevskii, G. B. Sergeev, DAN, **128**, 767 (1959).
2. S. Freed, K. M. Sansier, J. Am. Chem. Soc., **74**, 1273 (1952).
3. Cook, L. Lupien, W. G. Schneider, Canad. J. Chem., **34**, 957 (1956).
4. O. Maass, C. H. Wright, J. Am. Chem. Soc., **46**, 2664 (1924).
5. H. P. A. Groll, G. Hearn et al., Ind. and Eng. Chem., **31**, 1239 (1939).
6. R. G. W. Norrish, J. Chem. Soc., **123**, 3006 (1923).
7. G. B. Kistiakowsky, C. H. Stauffer, J. Am. Chem. Soc., **59**, 165 (1937).

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