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Effect of Donor–Acceptor Interaction on the Kinetics of Gas-phase Chemical Reactions

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We have shown that the reaction $BCl_3+NH_3 \rightarrow Cl_2BNH_2+HCl$ takes place in the gas phase at 70 °C and pressure < 1 Torr at the rate of collision between the molecules; the essential role of donor–acceptor interactions in the dynamics and kinetics of similar reactions is suggested.

Bimolecular donor–acceptor reactions, *i.e.* reactions in which one of the initial molecules is a donor and the other one is an electron-pair acceptor, are widely known in chemistry. Much work on these reactions in the liquid and solid phases has been done. However, the mechanism of donor–acceptor reactions in the gas phase, where it is possible to avoid any environmental influence, has hardly been studied.

The kinetics of some of these reactions in gas-phase addition reactions, giving complexes [1] (adducts) as the only products in which initial molecules are linked by donor–acceptor bonds, has been described in refs. 2 and 3. At present a theory of addition reactions is well formulated. The rate of formation of the adduct in such reactions at sufficiently high pressure is often near to the rate of collision between molecules of the reagents.

There are, however, examples of gas-phase reactions which do not stop at the stage of formation of the adduct.[4] For example, in the reaction of B_2H_6 with $NH_{3-n}(CH_3)_n$, $n=0$–2, the formation of products of the structure $H_2BNH_{2-n}(CH_3)_n$ is shown. The authors conclude that in all these reactions the primary product adduct decomposes giving H_2.

In this communication we present experimental data on the kinetics and products of the simplest donor–acceptor reaction of BCl_3 with NH_3. We also wish to draw attention to the strongest influence of donor–acceptor interaction on the kinetics and dynamics of the reactions between these closed-shell molecules.

No data are known about the kinetics of the reaction of BCl_3 with NH_3 in spite of the fact that the reaction is used for pyrolytic production of boron nitride.

In one series of experiments the reaction was studied in a copper spherical flow reactor, i.d. 3 cm. The reagents, diluted with He, were brought into the reactor separately through thin nozzles. During the reaction a weak variable flow of gases from the reactor passed into the ionization chamber of a mass spectrometer by the shortest way. The experimental technique and procedure is described elsewhere[5] in more detail. The temperature of the reactor was 70 °C; initial concentrations of the reagents were: BCl_3 $(3–15)\times10^{14}$ cm^{-3}, NH_3 $(1–10)\times10^{14}$ cm^{-3}, total pressure 1–9 Torr.† The concentration of BCl_3 usually slightly exceeded that of NH_3.

In these experiments HCl was identified as a product of the reaction by mass spectrometry. At a pressure <2.5 Torr the quantity of HCl produced approached that of reacted NH_3. Between 2,5–9 Torr, with an increase or decrease in total pressure the amplitude of the signal from HCl mass decreased or increased, respectively. The estimated value of the rate constant of the reaction was 5×10^{-11} cm^3 s^{-1} at 1 Torr.

Thus, under the above-mentioned experimental conditions there is a fast ammonolysis reaction at the B–Cl bond, reaction (1), the rate of which depends on total pressure.

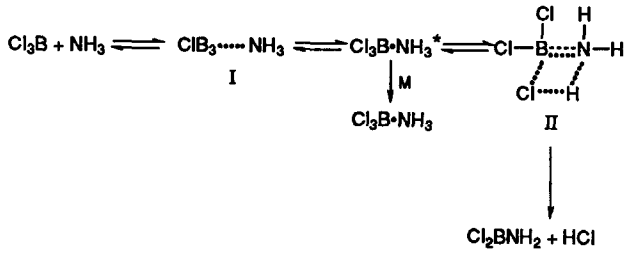
$$BCl_3 + NH_3 \rightarrow Cl_2BNH_2 + HCl \qquad (1)$$

Heterogeneous processes on the wall of the reactor could not be avoided in these experiments. Therefore, we later studied the reaction by a diffusion-flame method, which ensured true homogeneous conditions for the reaction. This method was proposed long ago for measuring the rate constants of fast reactions in the gas phase.[2,6] The application of the method to our experiments is described in full in ref. 7. The method allows us to obtain a value for the rate constant for the disappearance reaction of the nozzle reagent. Thermometric registration of the reaction zone also allowed us to determine the heat of the reaction.

The kinetics of the reaction were studied at 72 °C. By varying reagent flows data were obtained which evidenced the bimolecular character of the reaction. These experiments were performed at 1 Torr (mainly He). At variable NH_3 flow the concentration of BCl_3 was 4×10^{14} cm^{-3}; the NH_3 flow varied threefold, but its concentration did not exceed 10^{12} cm^{-3} near the nozzle (3 mm away from the nozzle tip where the first point of the temperature profile was taken). At variable BCl_3 flow the concentration was varied fourfold, the maximum value being 4×10^{14} cm^{-3}. The NH_3 concentration in these experiments was within the above-mentioned limits.

A considerable and abrupt decrease in the rate constant for the reaction at increasing total pressure was observed; this is shown in Fig. 1. Also, we see that even the minimum value of the rate constant is only 200 times less than the collision factor (4×10^{-10} cm^3 s^{-1}) between BCl_3 and NH_3 molecules.

The preliminary value of the heat of the reaction was estimated at 1 Torr to be 60–80 kJ mol^{-1}.



† 1 Torr = (101325/760) Pa ≈ 133.322 Pa.

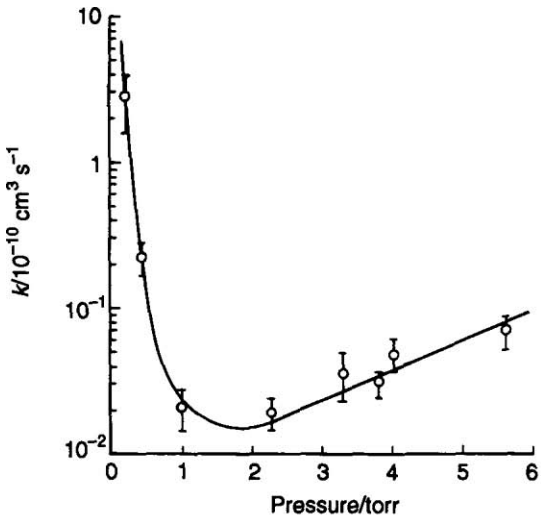


Fig. 1 Rate constant dependence on total pressure. BCl_3 concentration at different pressure (in units 10^{14} cm^{-3}):0.2 Torr, 1.4; 0.42 Torr, 3.3; 1 Torr, 4.3; 2.28 Torr, 3.3; 3.3 Torr, 3.5; 3.8 Torr, 2.5; 4.1 Torr, 3.45; 5.55 Torr, 3.75. Average calculated concentration of NH_3 in the reactor was $(0.8–2) \times 10^{13}$ cm^{-3}.

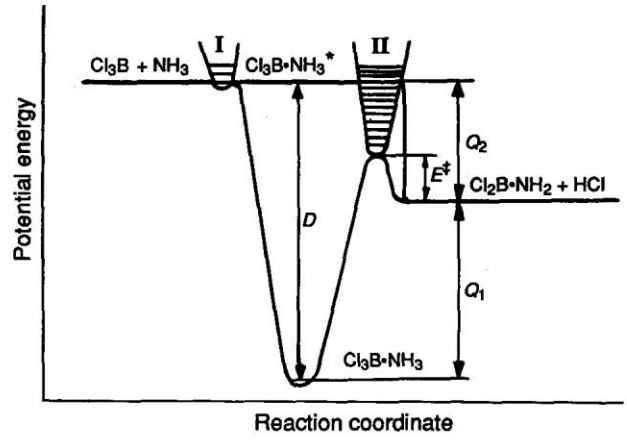


Fig. 2 Energy diagram of the reaction. D energy of B–N bond in adduct $Cl_3B{\cdot}NH_3$; Q_1 and $E^‡$ heat and activation barrier of the reaction of elimination of HCl from the thermolized adduct; Q_2 heat of reaction (1).

The dependence of the rate constant upon the pressure suggests that it is an effective one, which in its turn is indicative of a complex reaction mechanism.

Scheme 1, which is an appropriate description of the unimolecular decomposition of chemically-activated particles,[8] helps to explain the experimental facts.

In the first stage of the reaction the active molecule $Cl_3B{\cdot}NH_3^*$ is formed, BCl_3 and NH_3 being linked by a donor–acceptor bond. Activated complex **I** belongs to the category of loose complexes and its formation requires hardly any activation energy. Because of the large B–N distance in this complex (7 Å according to ref. 9) a number of encounters between BCl_3 and NH_3 may exceed the number of collisions, if we make this calculation according to the gas-kinetic parameters of the molecules.

Transformation of the active molecule can proceed in three ways: back decomposition, elimination of hydrogen chloride and deactivation, giving a stable adduct. We suggest that noticeable back decomposition of the active molecule takes place in all our experiments. If this were not so the reaction rate would not depend on pressure and would be equal to a number of encounter collisions between reagents. At 0.2 Torr the rate constant (1.8×10^{-10} cm^{-3} s^{-1}) approached the number of collisions. Here back decomposition and loss of HCl seem to be of approximately equal efficiency. Stabilization of the active molecule at low pressure hardly took place. Such a conclusion can be drawn because the yield of HCl and the quantity of reacted NH_3 were similar. The falling dependence of reaction rate constant (Fig. 1) observed in this region argues for a shift of the process to back decomposition of the active adduct with increasing pressure. A rise in the rate constant from 1–2 Torr and simultaneous decrease in HCl yield can also be considered as the beginning of formation of a stable adduct in the reaction.

Fig. 2 illustrates the change in potential energy of the reagents during the reaction. Values D, Q_1, Q_2 and $E^‡$, the meaning of which are clear from the diagram, are not known for the reaction of BCl_3 with NH_3. Only for Q_2 have we obtained a preliminary value of 60–80 kJ mol^{-1}. Approximately the same value can be estimated if we take into consideration the figures from refs. 2,7 and 10. The absence of activation energy in the reaction of elimination of HCl in our experiments gives reason to consider Q_2 to be the upper limit for the activation barrier $E.^‡$ But $E^‡$ can, in our opinion, be appreciably less than Q_2. Indeed, according to the RRKM theory the value of the rate constant for decomposition of active molecules depends strongly upon the excess of energy above a critical value. At 0.2 Torr as noted above, back decomposition and decomposition with HCl elimination are probably of similar efficiency. This should be possible when the excess of energy in complex **II** above $E^‡$ is appreciably larger than in complex **I** above D because the four-centre complex **II** is much more tight than linear complex **I** and the fewer active degrees of freedom in complex **II** should be compensated by a greater excess of energy.

The drop in rate constant dependence has much in common with a similar dependence observed by Rabinovitch and co-workers in studies of reactions of chemically-activated alkyl radicals. The fall in rate constant of monomolecular decomposition of activated radicals with pressure increase has been explained by the authors on the grounds that deactivation of active radicals proceeds by means of weak collisions (see ref. 8, chapters 8 and 10). They have shown that the greater the number of collisions required for deactivation, the stronger the decrease in the rate constant. As this takes place the change of rate constant is most pronounced as the pressure approaches the low pressure limit. The reason is the decrease in average energy of the active particles with increasing pressure when such a deactivation takes place. We believe that in our reaction the deactivating collisions are also weak. Under these conditions the observed fall in rate constant in the low-presure region may be due to the different dependence of the rate constant of the forward and back decomposition on pressure because of the difference between the structures of the activated complexes. The linear complex **I** should be much less sensitive to changes of excess energy above the critical value than the four-centre complex **II**. Therefore, increase in pressure will shift the process to back decomposition of active adduct and will therefore decrease the rate of consumption of the nozzle reagent.

In conclusion, we have demonstrated fast reactions (with the rate of collisions), in which the initial and final substances are closed-shell molecules. On the basis of the experimental results obtained we can conclude that the reaction proceeds without any energetic difficulties because of the influence of strong donor–acceptor interactions on the dynamics of the reactions. The transfer of a lone pair of electrons from a nitrogen to a boron atom is followed, on the one hand, by the formation of an excited adduct, and, on the other hand, by the redistribution of charges in the adduct. The shift of charges is so effective that the activation barrier, usually very high in the case of four-centre activated

complex, becomes considerably lower. As a result the excited adduct decomposes into two molecules passing over the activation barrier.

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