Variation of the isotopic composition of complexing reaction products as a result of isotopically selective excitation of the molecules of one of the reagents

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The possibility of influencing the complexing reaction rate by laser radiation was examined. The variation of the isotopic composition of BCl_3 in the reaction $BCl_3 + N(CH_3)_3 = BCl_3N(CH_3)_3$ was shown experimentally as a result of selective excitation of $^{11}BCl_3$ by CO_2 laser radiation.

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The mechanism of the gas-phase reactions for the formation of stable complexes AB from molecules A and B can be represented by the scheme[1]:

$$\begin{aligned} &\text{I.}\quad A + B = AB^{*} \\ &\text{II.}\quad AB^{*} = A + B \\ &\text{III.}\quad AB^{*} + M = AB + M \end{aligned} \qquad (1)$$

where AB^{++} is the intermediate formation that has an energy sufficient for reverse decay. The stable complex AB is obtained in the process of stabilizing AB^{++} as a result of inelastic collisions with the surrounding molecules M. According to the scheme, the formation rate of AB for the condition that the AB^{++} concentration is stationary is

$$d[AB]/dt = k[A][B], \text{ where } k = k_{I}\, k_{III}\,[M]/(k_{II} + k_{III}\,[M]). \tag{2}$$

It follows from (2) that the formation rate of AB at a given pressure depends on the lifetime of τ_{AB} of AB^{++} ($\tau_{AB} = 1/k_{II}$), which is determined, according to the theory of monomolecular reactions, by the energy excess ΔE above the value necessary for the decay of AB^{++}. The value of τ_{AB} decreases with increasing ΔE. Thus, if some additional energy, such as vibrational energy, is imparted to the molecules A or B before they take part in the reaction, then the complexing process proceeds more slowly with a rate constant $k^{*} = k_{I}k_{III}[M]/(k_{II}^{*} + k_{III}[M]) < k$, since $k_{II}^{*} > k_{II}$. This unique feature of the complexing reaction can be used for the purpose of changing the isotopic composition of the molecules. Thus, when one of the reagents consists of isotopically different molecules, the produced complex will be depleted, as a result of selective excitation of the molecules of one of the isotopes, and the unreacted reagent will be enriched with this isotope.

The enrichment factor can be estimated by using the following simplified reaction scheme:

$$\begin{aligned} &1.\ A + B_1 = \Pi_1 \\ &2.\ A + B_1^{*} = \Pi_1 \\ &3.\ A + B_2 = \Pi_2 \end{aligned} \tag{3}$$

where B_i^{*} is the excited molecule of isotope B_i and Π_i are the reaction products. In this scheme we assumed that the selectivity of the B_1 excitation is complete and that there is no $v - v$ energy exchange between B_1 and B_2.

Defining $[\Pi_i] = b_i^{0} + b_i (i = 1,2)[B_1] = \alpha b_i [B_1] = (1-\alpha)\, b_i$, $k_1 = k_2 = k$, and $k_2 = k^{*}$, where b_i^{0} and b_i are the initial and instantaneous concentrations of the ith isotope and α is the fraction of excited molecules, we have:

$$\frac{ab_1}{ab_2} = \left(1 - \alpha + \alpha\frac{k^{*}}{k}\right)\frac{b_1}{b_2} = \gamma\frac{b_1}{b_2}\,. \tag{4}$$

Assuming that α does not change during the reaction and taking into account that $b_2 = b_2^{0}$ for $b_1 = b_1^{0}$, we obtain

$$\frac{b_1}{b_1^{0}} = \left(\frac{b_2}{b_2^{0}}\right)^{\gamma} \text{ and } \beta = \frac{b_1}{b_2} \Big/ \frac{b_1^{0}}{b_2^{0}} = \left(\frac{b_2^{0}}{b_2}\right)^{1-\gamma}, \tag{5}$$

where β is the separation factor. It can be seen from (5) that β depends not only on the degree of excitation α and the difference in the rate constants k and k^*, but also on the concentration of the unreacted gas, and the more intensely the reaction occurs, the more the unreacted gas is enriched by the isotope B_1.

An experimental study of the complexing reaction in the presence of isotopically selective excitation of one of the reagents was performed for the process $BCl_3 + N(CH_3)_3 = BCl_3N(CH_3)_3$. This reaction was chosen for the following reasons. First, the BCl_3 molecules absorb well the CO_2 laser radiation with a high degree of isotopic selectivity. In addition, preliminary approximate calculations could be made for this reaction by using the kinetic data for the similar and thoroughly studied complexing reaction $BF_3 + N(CH_3)_3 = BF_3N(CH_3)_3$.[2] In addition, for the BCl_3 molecules the rate constants of the $v - T$ relaxation and of the $v - v$ exchange are known for many gases.[3]

The value of β was estimated for the experimental conditions: $P_{N_2} = 1$ Torr, $P = 3\times10^{-3}$ Torr, $P_{N(CH_3)_3} = 2.5\times10^{-3}$ Torr, a 30-W/cm^2 laser radiation intensity of the BCl_3, and $T = 300$ K. We selected small concentrations of the reagents at relatively high nitrogen pressure in order to "suppress" the exchange by the intensive $v - T$ relaxation.[4] In the calculation of k it was assumed $k_I = k_{III} = 10^{-10}$ cm^3/sec and k_{II} was calculated by using the quantum Cassel theory[5] assuming that only one-half of the oscillators participate in the intramolecular energy exchange. The validity of such a calculation was verified in the reaction of BF_3 with $N(CH_3)_3$, for which k_{II} data are available.[2] The quantum energy of the CO_2 laser ($\lambda = 10.6$ μm) was taken as ΔE in the calculation of k^*_{II}. The obtained ratio $k^*/k = 0.32$. We selected a value of 2/3 for α on the basis of the fact that the ν_3 vibration in $^{11}BCl_3$, which absorb the CO_2 laser radiation, is doubly degenerate and that for the indicated laser intensity the radiation absorption occurs in the saturation region.[6] Taking this into account, we estimated the value of $\beta \approx 4$.

The experiments were performed under the aforementioned conditions. The reagents were introduced into a nitrogen stream in a 12-mm-diameter glass tube and the reaction zone was illuminated by the beam (diameter ≈ 8 mm) of an LG-22 cw laser along the tube through the NaCl end window. The unreacted BCl_3 was collected and analyzed for isotopic composition with an IR spectrometer. The value of 1.18 ± 0.03 was obtained for the enrichment factor of the BCl_3 by the $^{11}BCl_3$ isotope. The difference between the calculated and the experimental value of β is apparently attributable primarily to the nonoptimum pressure of the diluent and reagents and also to the inefficient use of the laser radiation.

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