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Molecular Organization of Reactants in the Kinetics and Catalysis of Liquid Phase Reactions: XII. Mechanism of the Boron Trifluoride–Catalyzed Curtius Thermal Rearrangement of Benzoyl Azide into Phenyl Isocyanate

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Abstract—The kinetics of the thermal decomposition and rearrangement of benzoyl azide into phenyl isocyanate was studied in *n*-heptane in the presence of boron trifluoride etherate as the catalyst. The apparent activation energy of the noncatalytic reaction is 28.0 kcal/mol, and that of the catalytic reaction is 11.0 kcal/mol. The electronic structure and geometry of various complexes between benzoyl azide and BF_3 were studied using the PBE/TZ2P density functional method, and fragments of the potential energy surface were calculated for the catalytic rearrangement. Comparatively stable 1 : 1 and 1 : 2 complexes between the *syn* conformer of benzoyl azide and the catalyst can form in the system by coordination to the oxygen and nitrogen atoms of the acyl azide group. The heats of formation of these complexes are between –1.7 and –6.4 kcal/mol. The main consequence of the formation of these complexes is that the acyl azide group comes out of the benzene ring plane and thus becomes more reactive. The effective activation energies calculated for the catalytic rearrangement involving complexes of different compositions are 12–15 kcal/mol lower the effective activation energy of the noncatalytic reaction. Information has been obtained about the structure of the transition state of the catalytic reaction, in which a nitrogen molecule is abstracted from benzoyl azide with a synchronous rearrangement of other atoms, resulting in the formation of the ultimate product.

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The Curtius thermal decomposition and rearrangement of acyl azides is among the few phosgene-free routes to isocyanates, which are basic monomers in polyurethane chemistry. This reaction, which obeys a first-order rate law up to 100% conversion, liberating N_2, is rather easy to carry out. Furthermore, it is environmentally safer than commercial isocyanate production by the phosgenation of primary amines. The kinetics of the Curtius rearrangement has been investigated rather well and is systematized in a recent review [1]. The Curtius reaction is low-sensitive to the nature of the solvent. Its activation energy is 25–30 kcal/mol, and the preexponential factor is 10^{12}–10^{14} s^{-1}, which are typical of monomolecular thermal decomposition reactions of organic compounds. A serious limitation to the commercial application of this reaction is that rather high temperatures usually lying between 70 and 90°C are required for the decomposition and rearrangement of acyl azides. It is, therefore, necessary to find catalysts allowing the process to be carried out under milder conditions.

There have been no detailed reports dealing with catalysis in the Curtius rearrangement. This is particularly true for the mechanism of the catalytic conversion of acyl azides into isocyanates. However, the thermal rearrangement of aromatic acyl azides is known to be catalyzed by weak acids [2, 3] and Lewis acids [4, 5].

The noncatalytic conversion of acyl azides into isocyanates under thermolysis conditions has bee investigated in greater detail. In recent years, the mechanism of this reaction has been studied using quantum chemical calculations, whose results have been very informative [6–8]. In particular, it was established that acyl azides, both aliphatic and aromatic, exist as *syn* and *anti* conformers (with respect to the C–N bond). Due to the higher stability of the *syn* conformers and the comparatively high barrier to *syn–anti* isomerization (7–9 kcal/mol), their thermal rearrangement occurs in a single step via a synchronous (concerted) mechanism in which the rearrangement of atoms and bonds takes place simultaneously with the elimination of N_2, resulting in the formation of an isocyanate group from the acyl azide group:

$$R–C(O)–N_3 \longrightarrow R–N=C=O + N_2.$$

The rearrangement of the *anti* conformers is typically a two-step process: initially, the elimination of a nitrogen molecule yields the intermediate biradical acylnitrene,

R–C(O)–N:, and the second step is the monomolecular conversion of this biradical into the corresponding isocyanate. Because of this conformational control and the higher activation barrier in the two-step route, the Curtius thermal rearrangement of acyl azides proceeds entirely via the concerted mechanism through the conversion of the *anti* conformer [6–8].

Here, we report the mechanism of catalysis in the Curtius rearrangement, using benzoyl azide conversion into phenyl isocyanate as the example. This work includes a kinetic study of this reaction and quantum chemical calculation of the electronic structure and geometry of the initial reactants, probable intermediate complexes, transition states, and fragments of the potential energy surface for the catalytic decomposition and rearrangement of benzoyl azide.

EXPERIMENTAL

Benzoyl azide was synthesized by the exchange reaction between benzoyl chloride (reagent grade) and sodium azide recrystallized from water. The reaction was carried out in a water–acetone medium according to the procedure described in [9]. The melting point of the product (whose yield was 55% after recrystallization from acetone) was 27.0°C, in agreement with the literature [4]. Boron trifluoride etherate (Aldrich) was used as received. *n*-Heptane to be used as the solvent in kinetic measurements was purified by a standard procedure, dried over sodium metal, and distilled immediately before use.

The kinetics of the thermal conversion of benzoyl azide into phenyl isocyanate was studied spectrophotometrically in *n*-heptane between 46 and 86°C (Specord M40 spectrophotometer, quartz cells temperature-controlled with an accuracy of ±0.5°C, optical path length of 1 cm). The reaction was monitored as absorbance at a wavenumber of 40500 cm^{-1}, which corresponded to the maximum difference between the absorbances of the initial reactant and the final product. (The extinction coefficient of benzoyl azide is $\varepsilon_{40500} = 1.7 \times 10^4$ l mol^{-1} cm^{-1}.) The $PhC(O)N_3$ and BF_3 concentrations were $(1–7) \times 10^{-5}$ and 0.02–0.1 mol/l, respectively. The first-order rate constants derived from spectrophotometric data (at concentrations of 10^{-4}–10^{-5} mol/l) and those obtained by manometric determination of the gaseous nitrogen evolution rate (at concentrations of 10^{-1}–10^{-2} mol/l) are in good agreement [1], suggesting that the thermal decomposition of acyl azides takes place via a monomolecular mechanism. In the absence of a catalyst, the first order of the reaction persists up to 100% conversion. In the presence of the catalyst, the reaction is first-order up to 70–80% conversion, depending on the catalyst concentration and temperature. A deviation from the first-order rate law at high conversions was also observed for the Curtius rearrangement in the presence of other Lewis acids [5]. The true causes of this deviation have not been elucidated. This behavior is possibly due to the formation of a complex between the catalyst and the rearrangement product—isocyanate—which, as follows from quantum chemical calculations (see below), is fairly stable.

COMPUTATIONAL METHOD

Quantum chemical calculations were carried out by the density functional method (DFT) using the nonempirical generalized gradient approximation and the PBE functional [10, 11] implemented in the PRIRODA program [12]. One-electron wave functions were expanded in TZ2P augmented basis sets. Geometry optimization was performed for all stable compounds and complexes; saddle point optimization, for transition states. The types of the stationary points found (minimum or saddle point) were determined by calculating the eigenvalues of the matrix of the second derivatives of the energy of the system with respect to the coordinates of the nuclei. Transition states were assigned to a certain transformation by reaction coordinate calculations. We demonstrated in earlier works [7, 8] that the DFT method correctly reproduces the electronic structure and geometry of various aromatic and aliphatic acyl azides, isocyanates, and the corresponding transition states in the noncatalytic Curtius rearrangement. The activation energies and heats of the reactions calculated by the DFT method are in satisfactory agreement with experimental data for liquid-phase processes in spite of the "gas-phase specialization" of these calculations. As in our previous works [7, 8], all electronic energies reported here refer to $T = 0$ K. No zero-point energy correction was applied. It was demonstrated earlier that this correction is extremely small for the objects examined here and that taking it into account will not exert any significant effect on the relative changes in the energy of the system.

RESULTS AND DISCUSSION

The apparent rate constant of the thermal rearrangement of benzoyl azide (k_{app}) depends linearly on the catalyst concentration (c_{Cat}) in the c_{Cat} range examined (Fig. 1). Table 1 lists the rate constants of the noncatalytic reaction (k_0) and k_{app} values at a constant catalyst concentration of $c_{Cat} = 0.1$ mol/l in the temperature range examined. Figure 2 presents the Arrhenius plots of the kinetic data, which suggest that, at the catalyst concentration of 0.1 mol/l, there is a marked decrease in the apparent activation energy: the activation energy of the noncatalytic rearrangement of benzoyl azide in *n*-heptane is 28.0 ± 0.5 kcal/mol, while that of the catalytic rearrangement is 11.0 ± 0.5 kcal/mol.

The higher rate and the lower activation energy of the catalytic reaction are obviously due to the formation of a complex between benzoyl azide and BF_3. Complexes of this type or aromatic acyl azide–BF_3 adducts were postulated by other authors [13], who observed that, at –20°C, the components interact (presumably at the carbonyl group of the acyl azide [13]) and, as a

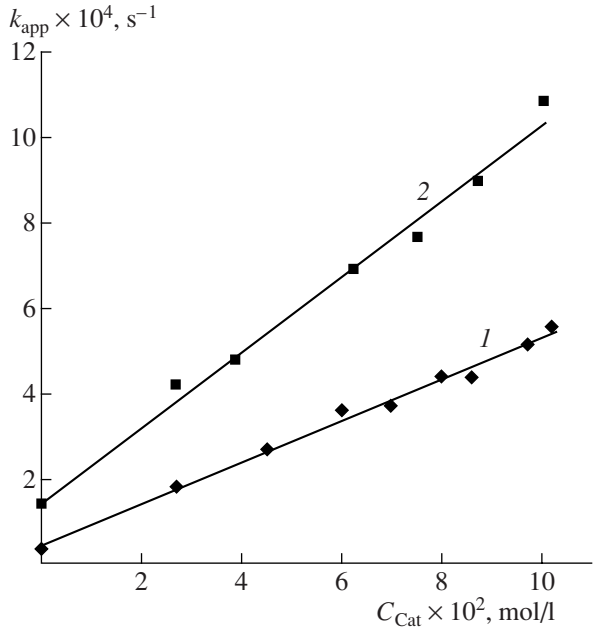


Fig. 1. Apparent rate constant as a function of the catalyst concentration at (*1*) 67.0 and (2) 82.0°C.

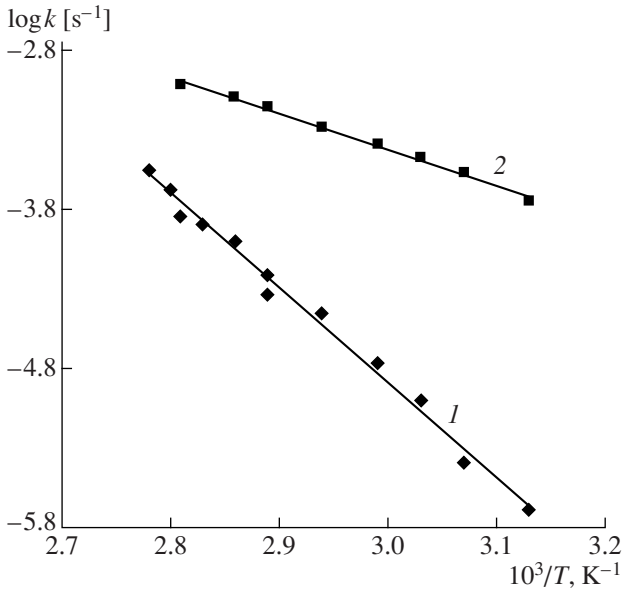


Fig. 2. Arrhenius plots of the rate constants of the (*1*) noncatalytic and (*2*) catalytic reaction.

result, as the temperature is raised, the isocyanate forms much more rapidly than it does in the absence of BF_3. In order to obtain a quantitative estimate of the reactivity of the resulting complex or adduct, we synthesized this species (as was reported in [13], but at $T = 0$°C) in *n*-heptane using a tenfold excess of BF_3 at boron fluoride and benzoyl azide concentrations of 0.4 and 0.04 mol/l, respectively. Samples of the solution at 0°C were diluted to obtain the same benzoyl azide concentration as was used in the kinetic studies of the reaction ($\sim 5 \times 10^{-5}$ mol/l) and was transferred into a spectrophotometric cell for measuring the thermal decomposition rate of the product at the temperatures used in the kinetic experiment. The rate constants that were measured at $T = 53.0$°C ($k = 4 \times 10^{-4}$ s^{-1}) and $T = 77.0$°C ($k = 8 \times 10^{-4}$ s^{-1}) are well above the corresponding rate constants of the noncatalytic reaction (k_0) and fall in the k_{app} range characteristic of the thermal decomposition of benzoyl azide in the presence of excess BF_3 (Table 1, Fig. 1).

The main issue in the mechanism of catalysis in the thermal rearrangement is how the interaction between BF_3 and the acvl azide group activates the latter to accelerate the reaction to a significant extent. The Fourier-transform IR spectra of the reaction system in *n*-heptane at $T = 0$°C turned out to be poorly informative in this respect. For example, the stretching frequencies of the azide and carbonyl groups of benzoyl azide—2135.9 and 1697.4 cm^{-1}—shift only slightly (by 2–5 cm^{-1}) and in opposite ways on passing to the product of benzoyl azide–BF_3 interaction at 0°C, becoming 2133.4 and 1702.0 cm^{-1}, respectively. The mechanism of catalysis in the thermal rearrangement of benzoyl azide and the causes of the acceleration of the reaction and of the decrease in the activation energy were elucidated in this study by quantum chemical calculation of the structures of the initial reactants, the resulting intermediates, and fragments of the potential energy surface (PES). As was noted above, the Curtius rearrangement of the acyl azide proceeds via a con-

Table 1. Rate constants of noncatalytic benzoyl azide rearrangement k_0 and of the same reaction in the presence of 0.1 mol/l BF_3 k_{app} at various temperatures

T, °C	$k_0 \times 10^4$, s^{-1}	$k_{app} \times 10^4$, s^{-1}	$(k_{app} - k_0) \times 10^4$, s^{-1}
46.4	0.02	1.80	1.78
53.0	0.04	2.70	2.64
57.0	0.10	3.40	3.30
62.0	0.17	4.20	4.03
67.0	0.35	5.50	5.15
72.5	0.46*	–	–
73.0	0.60	7.50	6.90
77.0	1.00	8.90	7.90
80.0	1.25*	–	–
82.0	1.40	10.90	9.50
84.0	2.07*	–	–
86.5	2.75*	–	–

* Data from [14]. Because of the narrow temperature range (14°C), the activation energy of the noncatalytic reaction derived from these data (31.2 kcal/mol [14]) is less accurate than the activation energy determined in this study using the totality of rate constant data over a 40°C temperature interval Fig. 2.

Table 2. Electronic energies (E) and their differences relative to the reaction products (ΔE) calculated for the stationary points of the PES in the Curtius rearrangement of the *syn* conformer of benzoyl azide*

Reagents, complexes, TSís, and products	$-\Delta E$, au	ΔE, kcal/mol
$PhC(O)N_3$	508.7994	40.4
TS (rearrangement of $PhC(O)N_3$)	508.7445	74.9
$PhNCO + N_2$	508.8638	0
$PhC(O)N_3 + BF_3$	833.1790	42.7
Complex **I**	833.1859	38.3
Complex **II**	833.1883	36.8
Complex **III**	833.1816	41.0
TS (rearrangement of **I**)	833.1427	65.5
TS (rearrangement of **II**)	833.1421	65.8
TS (rearrangement of **III**)	833.1296	73.7
$PhNCO \cdot BF_3 + N_2$	833.2470	0
$PhC(O)N_3 + 2BF_3$	1157.5586	44.0
Complex **IV**	1157.5676	38.3
Complex **V**	1157.5688	37.6
TS (rearrangement of **IV**)	1157.5359	64.5
TS (rearrangement of **V**)	1157.5249	65.1
$PhNCO \cdot 2BF_3 + N_2$	1157.6287	0

* The data for the noncatalytic rearrangement are taken from [7].

certed mechanism involving the *syn* conformer [7, 8]. For this reason, the object of the quantum chemical calculations in this study was the *syn*-$PhC(O)N_3$–BF_3 system.

Table 2 lists the electronic energies (E) of systems of various compositions and the differences between E and the energies of the corresponding products (ΔE) for the stationary points of the PES's of the reactions. It follows from these data that there can be five benzoyl azide–boron trifluoride complexes (1 : 1 and 1 : 2) differing in structure and stability. The boron trifluoride molecules in these complexes can be coordinated to the oxygen or nitrogen atom of the acyl azide group (Fig. 3). The basic geometric parameters of the identified complexes are given in Table 3, and the enthalpies of formation of these complexes (ΔH) are presented in Table 4. The 1 : 1 complexes involving carbonyl oxygen (**I** and **II**) are two isomers, complex **II** being more stable ($\Delta H = -5.9$ kcal/mol). Of the 1 : 2 complexes **IV** and **V**, the latter is more stable ($\Delta H = -6.4$ kcal/mol). As was expected, the least stable complex is the 1 : 1 complex **III** ($\Delta H = -1.7$ kcal/mol), which is formed by a nitrogen atom of the acyl azide group. The existence of this very unstable intermediate, whose enthalpy of formation exceeds the kT value only by a factor of 3, is questionable. Note, however, that complexes **I**–**V** are in equilibrium with one another and their interconversion requires their dissociation into $PhC(O)N_3$ and BF_3, so the barrier to this interconversion is equal to the largest absolute value of the enthalpy of complexation. From the data characterizing the relative stability of the complexes, it cannot be inferred which complex is involved in the catalytic reaction. By reaction coordinate calculations, we determined the rearrangement barriers for all of the intermediates and ascertained that these barriers correspond to the transition states through which the intermediates transform into the rearrangement products. The calculated energy barriers for the conversion of complexes **I**–**V** (Table 4) indicate that, in all cases, the activation energy of the catalytic rearrangement is lower than that of the noncatalytic reaction.

The rearrangement product—phenyl isocyanate—also forms 1 : 1 and 1 : 2 complexes with BF_3, but these complexes are weaker than the benzoyl azide complexes. For the most stable 1 : 1 complex formed by the oxygen atom of RNCO, $\Delta H = -2.3$ kcal/mol; for the 1 : 2 complex, $\Delta H = -3.6$ kcal/mol. The calculated enthalpy of rearrangement depends on the relative stability of the RNCO complexes and ranges between –38.0 and –40.3 kcal/mol, differing only slightly from the enthalpy of the noncatalytic reaction, which is –40.4 kcal/mol [7].

In conclusion of the discussion of complexation in the system, note that, in the temperature range examined, benzoyl azide can interact directly with boron trifluoride etherate without predissociation of the latter (although this would be quite natural).This is particularly likely because the initial concentration of the etherate in our experiments was much higher than the benzoyl azide concentration. Calculations for the model system *syn*-$PhC(O)N_3$–$BF_3 \cdot OMe_2$ in the simplest case of coordination to the carbonyl oxygen atom demonstrated that the formation of a complex is accompanied by the abstraction of the ether molecule from BF_3. This molecule occupies a place near the acyl azide group and serves as a solvating agent. The heat of formation of this complex is $\Delta H = -8.5$ kcal/mol, which is 4.1 kcal/mol higher than the heat of formation of the similar, but unsolvated, complex **I** ($\Delta H = -4.4$ kcal/mol, see Table 4). The basic geometric parameters of the ether-containing complex differ little from the corresponding parameters of the complexes with BF_3 alone (Table 3).

As for the activation parameters, it is noteworthy that the activation energies of the "gas-phase" Curtius rearrangement calculated by the DFT method using the PBE/TZ2P density functional do not differ significantly from the data of the liquid-phase experiment (see the detailed discussion in our earlier work [7]). For example, for benzoyl azide rearrangement, the calculated activation energy of the noncatalytic reaction is E_a = 34.5 kcal/mol [7] and the observed activation energy of

the reaction in *n*-heptane is 28.0 kcal/mol. Therefore, it is quite correct to draw a comparison between the activation energy values calculated for the noncatalytic reaction and for the conversion of the catalytic complexes into the corresponding products, at least at the semiquantitative level. As is clear from Table 4, the calculated activation energy of the rearrangement of most of the complexes is 5–8 kcal/mol lower than the activation energy of the noncatalytic reaction. The only exception is the reaction involving the least stable complex **III**. Figure 4 plots the typical potential energy profile for the catalytic Curtius rearrangement, using the reaction involving complex **I** as the example. Table 4 lists the effective activation energies of the conversion of **I**–**IV** into the products ($E_{eff} = E_a + \Delta H_{com}$). These quantities can be compared with experimental data since the apparent rate constant is the product of the equilibrium constant of the formation of the catalytic complex and the rate constant of the monomolecular conversion of this complex. It the data for the reaction involving the weakest complex **III**, in which boron trifluoride is coordinated to a nitrogen atom, are ignored for the above reasons, than it will be clear from Table 4 that E_{eff} for the catalytic reaction is lower than E_{eff} for the noncatalytic reaction by a large value of 12–15 kcal/mol. The experimental difference between these E_{eff} values, determined in this study for particular catalytic rearrangement conditions (Fig. 2), is 17 kcal/mol and is in agreement with the value predicted by the quantum chemical calculations.

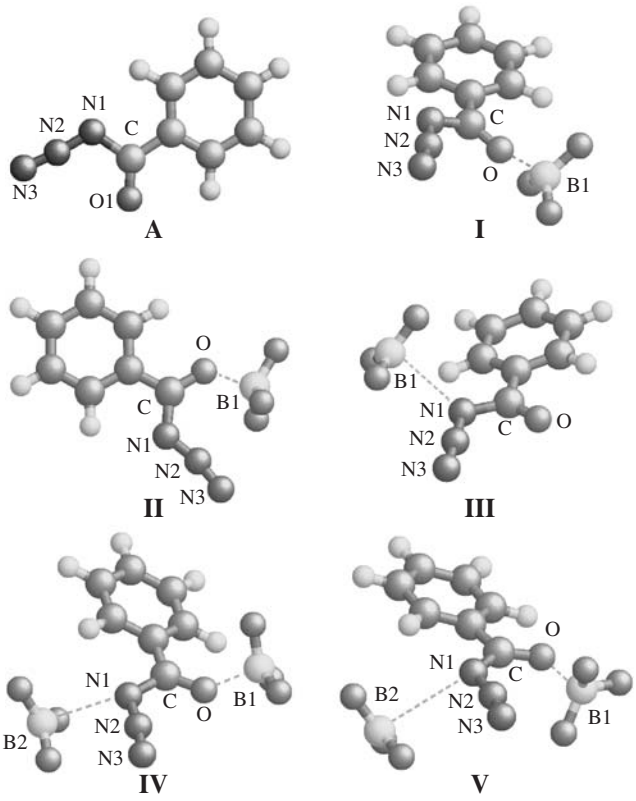


Fig. 3. *syn*-Conformer of benzoyl azide (**A**) and its 1 : 1 and 1 : 2 complexes with BF_3 (**I**–**V**).

In the light of the above experimental and theoretical activation parameters, which are in satisfactory agreement, the following natural question arises: what structural changes in the acyl azide molecule upon the formation of a complex with BF_3 are responsible for the acceleration of the reaction with this great decrease in the effective activation energy in the presence of the catalyst? By way of example, Fig. 5 shows diagrams presenting the main geometric parameters for the *syn*-conformer of $PhC(O)N_3$ and for the transition state of

Table 3. Geometric parameters of *syn*-benzoyl azide and its complexes with BF_3*

Bond, angle	Interatomic distances (Å) and bond angles (deg) in the acyl (**A**) and its complexes						
	A	**I**	**II**	**III**	**IV**	**V**	**I** · OMe_2
O–B1	–	1.759	1.667	–	1.779	1.675	1.694
C–O	1.218	1.250	1.257	1.216	1.248	1.255	1.255
C–N1	1.445	1.405	1.381	1.456	1.412	1.386	1.396
N1–N2	1.242	1.252	1.255	1.247	1.256	1.258	1.253
N1–B2	–	–	–	2.827	2.948	3.245	–
N2–N3	1.138	1.133	1.131	1.136	1.132	1.30	1.132
C–N1–N2	115.2	115.7	123.6	113.8	114.8	122.7	115.7
N1–C–O	123.0	118.9	127.8	122.3	118.7	127.6	118.9
N1–N2–N3	174.6	172.2	167.4	175.7	172.9	167.8	171.7
C2–C6–O–N1	0.2 (83.7)	17.0 (78.8)	0.0 (75.0)	9.9 (77.8)	20.2 (73.6)	8.3 (75.8)	19.2

* The geometric parameters of benzoyl azide (**A**) are taken from [8]. The parenthesized numbers in the last row are the C2–C6–O–N1 angles in the transition states.

Table 4. Calculated values of the heat of formation of complexes ($-\Delta H_{com}$), the activation energy of the rate-limiting step (E_a), and the effective activation energy ($E_{eff} = E_a + \Delta H_{com}$) for the catalytic rearrangement of the *syn*-conformer of benzoyl azide

Reaction	$-\Delta H_{com}$, kcal/mol	E_a, kcal/mol	E_{eff}, kcal/mol
$PhC(O)N_3 \longrightarrow PhNCO + N_2$	–	34.5*	34.5
$PhC(O)N_3 + BF_3 \longleftrightarrow$ **I** $\longrightarrow PhNCO \cdot BF_3 + N_2$	4.4	27.2	22.8
$PhC(O)N_3 + BF_3 \longleftrightarrow$ **II** $\longrightarrow PhNCO \cdot BF_3 + N_2$	5.9	29.0	23.1
$PhC(O)N_3 + BF_3 \longleftrightarrow$ **III** $\longrightarrow PhNCO \cdot BF_3 + N_2$	1.7	32.7	31.0
$PhC(O)N_3 + 2BF_3 \longleftrightarrow$ **IV** $\longrightarrow PhNCO \cdot 2BF_3 + N_2$	5.7	26.2	20.5
$PhC(O)N_3 + 2BF_3 \longleftrightarrow$ **V** $\longrightarrow PhNCO \cdot 2BF_3 + N_2$	6.4	27.5	21.1

* Data from [7].

its catalytic rearrangement into phenyl isocyanate [7]. These data are compared with the data obtained in this study for the reactions involving complexes **I** and **II** resulting from the interaction between BF_3 and the carbonyl group of the acyl azide. The most pronounced manifestation of the effect of complex formation is that the elongation of the N1–N2 bond in the transition state (TS) of the catalytic reaction is larger than in the case of the noncatalytic reaction, particularly for the more stable complex **II**. In the acyl azide, the length of this bond is 1.242 Å; in complexes **I** and **II**, 1.252 and 1.255 Å, respectively; in the TS of the noncatalytic reaction, 1.712 Å; in the TS's of the catalytic reactions involving **I** and **II**, 1.727 and 1.771 Å, respectively. The lengthening of the N1–N2 interatomic distance, which rakes place synchronously with the movement of other atoms during the rearrangement, must make the main contribution to the reaction coordinate. Most of the geo-

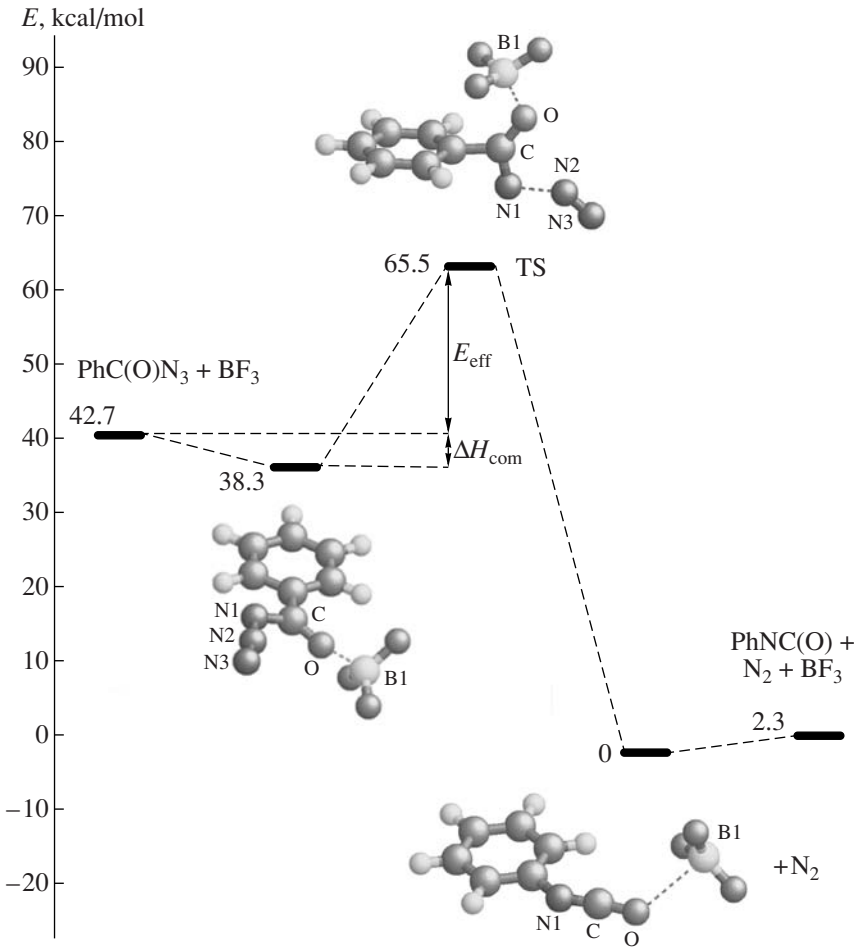


Fig. 4. Typical potential energy profile for the catalytic reaction exemplified by the rearrangement of complex **I**.

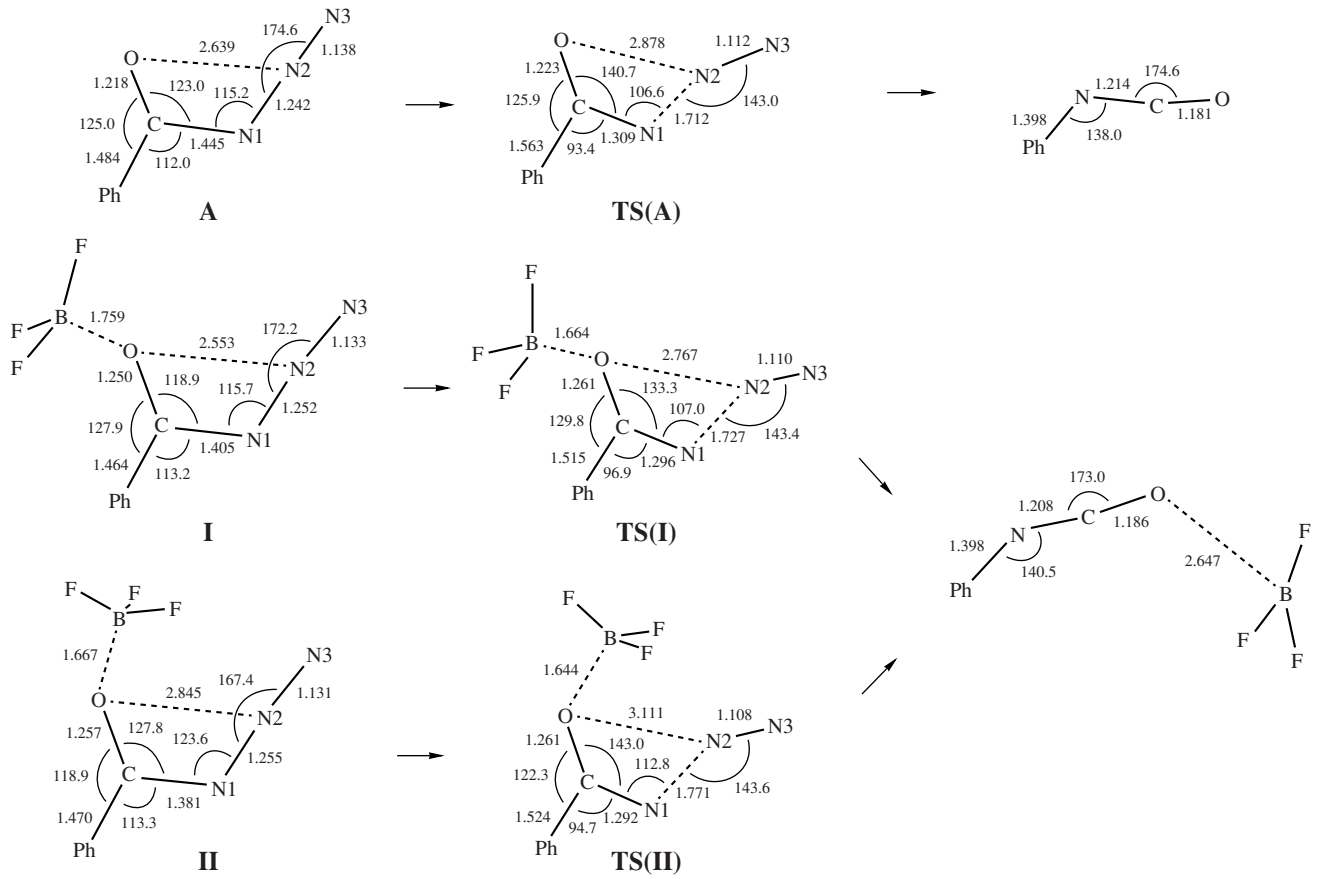
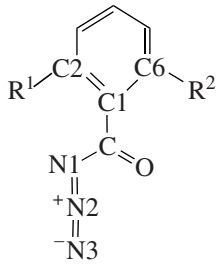


Fig. 5. Geometry of the *syn*-conformer of benzoyl azide (**A**), complexes **I** and **II**, the corresponding TS's, and the rearrangement product.

metric parameters of the complexes are closer to the corresponding parameters of the transition states than the parameters of the azide not bonded with BF_3 (Fig. 5).

The most important result of this study of the structure of the complexes is that the acyl azide group comes out of the benzene ring plane when forming a complex with BF_3 (Table 3). Earlier [8], we studied the structure of *ortho*-substituted derivatives of benzoyl azide with the general formula



where R^1 = H, R^2 = H (**1**); R^1 = H, R^2 = CH_3 (**2**); R^1 = H, R^2 = *iso*-C_3H_7 (**3**); R^1 = H, R^2 = *tert*-C_4H_9 (**4**); R^1 = CH_3, R^2 = CH_3 (**5**); R^1 = H, R^2 = OH (**6**). In that study, we established a correlation between the reactivity of these compounds and the dihedral angle C2–C6–O–N1 in the aromatic acyl azide. This angle is a quantitative measure of the acyl azide group coming out of the benzene ring plane under the action of the *ortho* substituent. Figure 6, taken from an earlier study [8], demonstrates that the fact that the rate constants of rearrangement of the *ortho*-alkylbenzoyl azides are 1.5–2 orders of magnitude larger than that of the unsubstituted compound is due to the breaking of the resonance conjugation between the acyl azide group and the benzene ring. When a hydroxyl group is in the *ortho* position, the planar structure of the molecule is stabilized by an intramolecular hydrogen bond. As a consequence, the reactivity of this acyl azide is lower almost by two orders of magnitude. A decrease in the activation energy of the rearrangement also takes place as the C2–C6–O–N1 angle in the series of *ortho*-alkyl-substituted derivatives of benzoyl azide increases [8].

It follows from Table 3 that, in all complexes with BF_3 except **II**, the acyl azide group is out of the benzene ring plane.[1] The values of the C2–C6–O–N1 angle in complexes **I** and **III**–**V** are indicated by arrows in Fig. 6. Clearly, the reactions involving the complexes

[1] Complexes **I** and **II** form by boron trifluoride coordination to different lone pairs of the carbonyl oxygen atom. Complex **II** is more planar (Fig. 3) because of the weaker steric hindrance. Accordingly, the acyl azide group of this complex does not come out of the benzene ring plane.

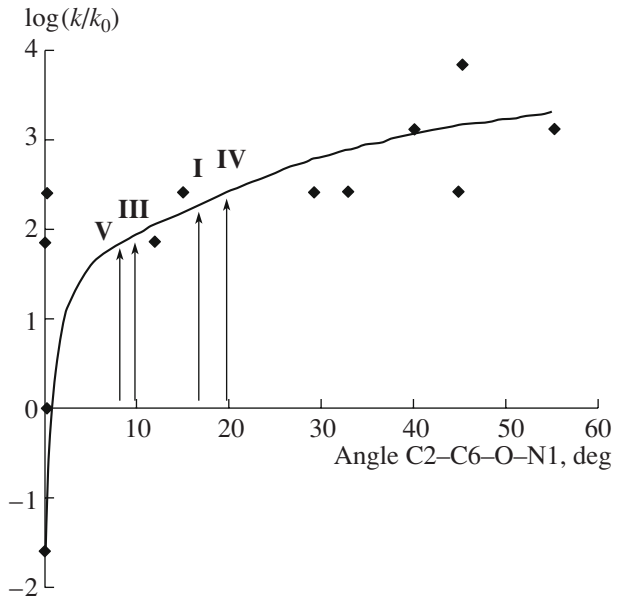


Fig. 6. Reactivity of *ortho*-substituted derivatives of benzoyl azide relative to the reactivity of the unsubstituted compound as a function of the dihedral angle C2–C6–O–N1 in the *syn* conformer, which is a measure of the acyl azide group coming out of the benzene ring plane). The data are taken from [8]. The arrows show the data obtained in this study for complexes **I** and **III**–**V**.

must proceed two order of magnitude more rapidly than the noncatalytic rearrangement of benzoyl azide. In the framework of this interpretation of the results, the catalytic action of boron trifluoride in the Curtius rearrangement is based on the phenomenon that can be called *induced ortho effect*. This effect takes place only in reactions of aromatic acyl azides, and the absence of reports concerning the Lewis acid catalysis of the Curtius rearrangement of alkylacyl azides seems quite natural in the light of the above data. The rate constants of the thermal rearrangement of acetyl azide, $MeC(O)N_3$, in *n*-heptane at 77.0°C in the absence of BF_3 and in the presence of 0.1 mol/l BF_3 were measured to be 1×10^{-3} and 0.6×10^{-3} s^{-1}, respectively. Therefore, under the same conditions as were used in benzoyl azide rearrangement in this study, boron trifluoride does not accelerate the reaction but even slows it down slightly. This effect is most likely due to the polymolecular solvation of the acyl azide by boron trifluoride etherate (which serves as a component of the medium), and it needs a more detailed investigation, which beyond the scope of this work.

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