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# Mechanism and structural aspects of thermal Curtius rearrangement. Quantum chemical study

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The electronic and geometric structures of formyl, acetyl, and benzoyl azides were studied and fragments of the potential surfaces for the thermal Curtius rearrangement of these azides into the corresponding isocyanates were calculated by density functional theory at the PBE/TZ2P level. Acyl azides adopt two stable, conformations *syn* and *anti*, with respect to the C—N bond. The *syn* conformers are more stable than their *anti* analogs. The activation energies of the *syn*—*anti* isomerization in the series under study are 9.4, 7.0, and 9.2 kcal mol$^{-1}$, respectively, and the activation energies of the reverse reaction are 8.5, 6.1, and 2.5 kcal mol$^{-1}$. The rearrangement of *syn*-acyl azides is a one-step process, in which elimination of $N_2$ occurs synchronously with the rearrangement of atoms and bonds to form isocyanates. The activation energies of the rearrangements of *syn*-$HC(O)N_3$, *syn*-$MeC(O)N_3$, and *syn*-$PhC(O)N_3$ are 28.0, 32.9, and 34.5 kcal mol$^{-1}$, respectively. The rearrangement of the *anti* conformers of the above-mentioned azides involves the formation of singlet acylnitrene. The activation energies of the latter process are 34.6, 32.9, and 32.3 kcal mol$^{-1}$, respectively. The activation energies of the rearrangement of acylnitrenes into isocyanates are 20.9, 18.9, and 13.6 kcal mol$^{-1}$, respectively. The energy characteristics of the process and the structural data for the starting compounds, final products, and transition states provide evidence that the thermal Curtius rearrangement occurs predominantly by a concerted mechanism.

**Key words:** acyl azides, acylnitrenes, isocyanates, thermal Curtius rearrangement, quantum chemical calculations, reaction mechanism.

The thermal rearrangement of acyl azides into isocyanates (Scheme 1) was discovered[1] by Curtius more than 100 years ago and this reaction has found application in preparative organic chemistry. The Curtius rearrangement has not gained acceptance in the industrial production of isocyanates and has given way to more-recently developed phosgenation of primary amines.[2] However, present-day ecological requirements for chemical engineering associated, in particular, with the undesirable use of highly toxic phosgene have stimulated considerable recent interest in the Curtius rearrangement, which is one of the simplest procedures for the phosgene-free synthesis of isocyanates as the main monomers in polyurethane chemistry.

**Scheme 1**

$$R—C(O)—N_3 \longrightarrow R—N{=}C{=}O + N_2$$

The kinetic aspect of the Curtius rearrangement has been studied in-depth. Recently, the main features of this reactions have been considered in detail.[3] Thermal decomposition of acyl azides at moderate temperatures (60—80 °C) affords isocyanates in almost 100% yield. The reaction is described by a simple first-order kinetic equation, its rate constant is little sensitive to changes in the nature of the medium. The activation energies are 25—32 (decomposition of $ArC(O)N_3$) and 25—27 kcal mol$^{-1}$ (decomposition of $AlkC(O)N_3$), and the preexponential factors vary in the range of $10^{12}$—$10^{14}$ s$^{-1}$ typical of monomolecular thermal decomposition of organic compounds.[4]

Some principal details of the reaction mechanism are being widely debated. The key question is whether the Curtius rearrangement involves many steps or it is a one-step process in which the formation of isocyanate occurs through the rearrangement of the azide group with simultaneous elimination of the nitrogen molecule (so-called

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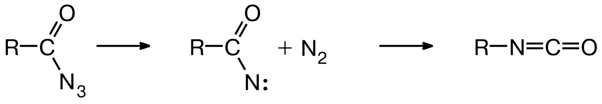
synchronous or concerted reaction mechanism[3]). The assumption that the thermal Curtius rearrangement can afford biradicals, *viz.*, carbonylnitrenes, as intermediates (Scheme 2) was made by analogy with the photochemical rearrangement of acyl azides. The formation of such intermediates in the latter reaction,[5] as well as the formation of so-called "rigid" nitrenes in the course of decomposition of aryl and alkyl azides $RN_3$,[6] are beyond doubt. Another question is whether the generation of carbonylnitrenes is involved in the pathway of the thermal or even photochemical rearrangement of acyl azides into isocyanates or their formation (although in small amounts) and further transformations occur synchronously with the main process.

**Scheme 2**



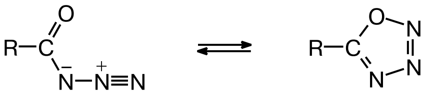
Nitrenes (both singlet and triplet) are highly reactive and are generally identified according to their reaction products. Nitrenes RN: (R = Alk or Ar) are involved in such reactions as hydrogen abstraction from solvents, insertion into C—H bonds, addition to C=C bonds, recombination giving rise to azo compounds (for ArN:), *etc.*[6] Generally, these reactions proceed rapidly. For example, recombination of nitrenes ArN: is a diffusion-controlled process with a rate constant of about $10^9$ L mol$^{-1}$ s$^{-1}$, whereas the rate constants for hydrogen abstraction are in the range of $10^2$—$10^3$ L mol$^{-1}$ s$^{-1}$.[7,8] Carbonylnitrenes, which are generated by photochemical decomposition of acyl azides, cannot undergo recombination, but they are rather active in other reactions.[6] The by-products of the Curtius rearrangement were unambiguously identified only in the case of decomposition, both photochemical and thermal, of ethoxycarbonyl azide (ethyl azidoformate, $EtOC(O)N_3$).[9] Thermal decomposition of this azide in *trans*-decalin is the only example where the corresponding acylnitrene was detected experimentally by chemical polarization of nuclei based on signals for the protons (emission instead of absorption) of the N—H bond of amide produced by intramolecular recombination of the corresponding radical pair.[10] The signal was not observed in the case of thermolysis of benzoyl azide in *trans*-decalin performed under the same conditions.[3]

The fact that the rearrangement of acyl azides into isocyanates can occur synchronously with generation of acylnitrenes is indirectly evidenced by the data on decomposition of $Bu^tC(O)N_3$.[11] Low-temperature (−10 °C) photolysis afforded the corresponding isocyanate in the same yield (~40%) regardless of the nature of the solvent capable of serving as a trap for nitrenes. Thermolysis at 28 °C did not give reaction products of nitrenes with a solvent at all. It is unlikely that the difference of ~40 °C would eliminate trapping of acylnitrenes, if they were generated during thermolysis. Hence it follows that the thermal rearrangement of acyl azide into isocyanate does not necessarily involve the intermediate formation of acylnitrene.

Turning back to the kinetics of thermal decomposition of acyl azides, it should be noted that elimination of the nitrogen molecule rather than the rearrangement of intermediate acylnitrene, even in the event that this intermediate is generated during the reaction, is always the rate-determining step of the rearrangement.[3] This follows from the fact that the rate constants and activation parameters determined in studies of the kinetics by the manometric method (based on the rate of elimination of $N_2$) are exactly equal to those determined by the spectrophotometric method (based on the change in the absorbance of the starting acyl azide, final isocyanate, or urethane, which was produced in an alcoholic medium).

Studies by IR spectroscopy showed[12] that the acyl azide group has the so-called open rather than cyclic structure. According to the results of *ab initio* calculations,[13] the open form is in tautomeric equilibrium with the cyclic form (Scheme 3), formyl and acetyl azides being more stable than their cyclic tautomers, *viz.*, oxatriazoles, by 20—30 kcal mol$^{-1}$ (depending on the calculation method or the basis set, HF/6-31G, MP2, or MP4-SDQ).

**Scheme 3**



It is worthwhile to invoke the results of *ab initio* quantum chemical calculations published in the literature[14—24] for the consideration of the structures and stability of acylnitrenes as probable intermediates of the Curtius rearrangement. Most studies have been carried out in connection with research on isomerization and decomposition of HCNO as the simplest organic molecule that plays an important role in combustion and utilization of $NO_x$. Fragments of the potential energy surface for isomerization of HCNO were studied in sufficient detail.[14—19] More than ten relatively stable structures were found. Among them, HNCO (isocyanic acid) is most stable. The next in order are HCNO (fulminic acid), HONC (isofulminic acid), and HOCN (cyanic acid). Data on the enthalpies of isomerization and the activation energies of the rearrangements and decomposition of particular structures are available. On the whole, the results of most studies are in qualitative agreement with each other (the data on the geometry are in quantitative agreement) regardless of the parametrization of the calculation methods. The data on stability of acylnitrenes as probable intermediates of isomerization are rather contradictory. According to the results of the study,[15] formylnitrene (both singlet and triplet) is unstable and undergoes spontaneous rearrangement into HNCO, whereas the results of other studies[14,16,19,21,24] provided evidence that there is the activation barrier between HC(O)N: or MeC(O)N: and the corresponding isocyanates, the height of this barrier being dependent on the quantum chemical method used.

In spite of substantial progress in understanding isomerization processes of the simplest systems, such as HCNO or MeCNO, the possibilities of quantum chemistry for studying the mechanism of the thermal Curtius rearrangement are far from being exhausted. Among the problems, which have virtually not been examined by modern quantum chemical methods, two problems are of considerable importance. First, it is of interest to investigate the electronic and geometric structures of the starting alkyl- and arylacyl azides (the only publication[13] was devoted to the structures and charge distribution in $HC(O)N_3$ and $MeC(O)N_3$). Second, it is important to perform calculations of the potential energy surface for the thermal rearrangement of the above-mentioned acyl azides into isocyanates, which can provide new evidence on the reaction mechanism and the structures of the transition states and intermediates, if the latter are generated during the reaction. It should be noted that the free energy surfaces for the Curtius rearrangement and some typical bimolecular reactions involving the corresponding acylnitrenes (reactions with propane, ethylene, and methanol) have been calculated by quantum chemical methods only recently[24] using acetyl azide and methoxycarbonyl azide as examples.

In the present study, we performed quantum chemical calculations of the structures of a series of acyl azides and the derived isocyanates and obtained data on the reaction enthalpies, activation energies, and structures of intermediates and transition states (TS), which gave an insight into certain debated aspects of the reaction mechanism under consideration.

## Calculation procedure

Theoretical studies were carried out by density functional theory (DFT) using the nonempirical generalized gradient approximation and the PBE functional[25,26] implemented in the PRIRODA program.[27] One-electron wavefunctions were expanded in the extended atomic basis sets TZ2P of the contracted Gaussian functions {311/1} for the H atom and {611111/411/11} for the C, N, and O atoms. Optimization was performed for all stable compounds and saddle points. The character of the stationary points (minimum or saddle point) was determined by calculating the eigenvectors of the matrix of second derivatives of the energy with respect to the coordinates of nuclei. The transition states were assigned to particular transformations by calculating the reaction coordinate. All the energies reported in the present study refer to $T = 0$ K; the zero-point energy correction was not applied. Preliminarily, we have demonstrated that this correction is very small in our calculations and the inclusion of this correction has virtually no effect on the relative changes in the energy of the system.

## Results and Discussion

**Geometric and electronic structures of acyl azides and isocyanates.** We calculated the geometric and electronic structures of three model acyl azides, *viz.*, formyl azide ($HC(O)N_3$, **1**), acetyl azide ($MeC(O)N_3$, **2**), and benzoyl azide ($PhC(O)N_3$, **3**). The calculations demonstrated that the acyl azides under study can exist as two stable conformers, *syn* and *anti*, with respect to the C—N(1) bond. In all cases, the *syn* conformers are more stable than the corresponding *anti* analogs. For $HC(O)N_3$ (**1**) and $MeC(O)N_3$ (**2**), the enthalpy of *anti—syn* isomerization is rather low (–0.9 kcal $mol^{-1}$), whereas the enthalpy for $PhC(O)N_3$ (**3**) is –6.7 kcal $mol^{-1}$. This means that acyl azides exist predominantly as *syn* conformers. The same conclusion follows from the already mentioned publication,[24] where the possibility of the existence of analogous conformers of $MeC(O)N_3$ and $MeOC(O)N_3$ was established by calculations of fragments of the free energy surface ($\Delta G$) for the Curtius rearrangement with the use of the DFT and CBS-QB3 methods. According to these data, the *syn* conformer of $MeC(O)N_3$ is 4.5—4.8 kcal $mol^{-1}$ more stable than the *anti* conformer. The profiles of the potential energy surface (PES) for isomerization of the compounds under study are shown in Fig. 1. The activation barriers of the *syn—anti* isomerization in a series of acyl azides **1—3** are 9.4, 7.0, and 9.2 kcal $mol^{-1}$, and the barriers of the reverse reaction are 8.5, 6.1, and 2.5 kcal $mol^{-1}$, respectively (Table 1). As demonstrated below, the existence of acyl azides in different conformational states determines the possibility of radically different pathways of their thermal rearrangement into the corresponding isocyanates **4—6**.

The main geometric parameters of the *syn* and *anti* conformers, except for the mutual arrangement of the C=O and N(1)—N(2)—N(3) fragments with respect to the C—N(1) bond, differ only slightly, if at all. The acyl azide group has the same structure for R = H, Me, and Ph. The bond lengths and bond angles in the *syn* conformers of $HC(O)N_3$ and $MeC(O)N_3$ calculated at the PBE/TZ2P level agree well with the results obtained by other methods.[13,24]

Experimental data on the geometric structures of acyl azides are lacking in the literature. However, the structure of methyl azide $MeN_3$ was studied by electron diffraction (ED) and microwave spectroscopy (MWS). These data make it possible to estimate the reliability of the calcu-

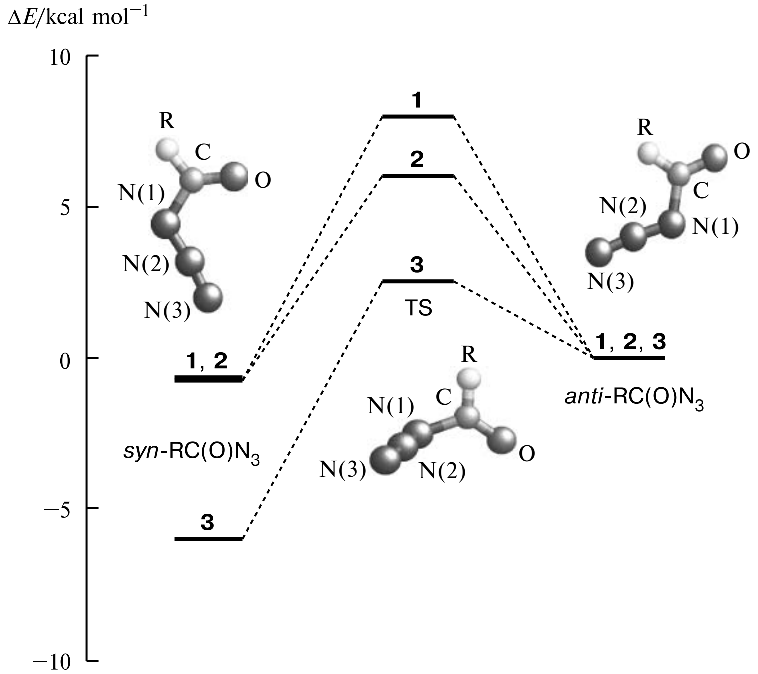


**Fig. 1.** Profiles of the potential energy surface for *syn—anti* isomerization of acyl azides $HC(O)N_3$ (**1**), $MeC(O)N_3$ (**2**), and $PhC(O)N_3$ (**3**).

lated bond lengths and bond angles in the azide group in the compounds under consideration. According to the results of ED[28,29] and MWS,[30] the C—N(1), N(1)—N(2), and N(2)—N(3) bond lengths in $MeN_3$ are 1.46—1.47, 1.22—1.24, and 1.12—1.13 Å, respectively. The corresponding calculated parameters for acyl azides (Fig. 2) are 1.43—1.45, 1.24—1.25, and 1.14 Å, respectively. The experimental and calculated C—N(1)—N(2) bond angle in $MeN_3$ is 117—120° and 115—120°, respectively. Earlier,[28—30] it has been postulated that the N(1)—N(2)—N(3) group is linear. However, the calculations show that this group is slightly nonlinear (the N(1)—N(2)—N(3) angle in the *syn* and *anti* conformers of **1—3** varies in the range of 172—175° depending on the group R).

The data on the geometric structures of isocyanates RNCO (R = H (**4**), Me (**5**), or Ph (**6**)), which are the final products of the thermal rearrangement of acyl azides **1—3**, are also presented in Fig. 2. In Table 2, the results of calculations at the PBE/TZ2P level are compared with the data published in the literature. The geometric and electronic structures of isocyanates were studied in more detail both experimentally[31—34] and theoretically with the use of *ab initio*[14—21] and semiempirical methods.[35] This is associated primarily with an interest in the mechanism of the reaction of isocyanates with alcohols, which lies at the basis of the processes for the synthesis of urethanes and other polymerization reactions with the use of these monomers. As can be seen from Table 2, the experimental data are in good agreement with most results of calculations by *ab initio* methods with different basis sets. The only exceptions (which refer to certain geometric parameters) are earlier calculations[15] with the use of the STO-3G and 4-31G basis sets.

**Table 1.** Electronic energies of the *syn* and *anti* conformers of acyl azides **1—3** ($E$), their differences relative to the *syn* conformer (reaction enthalpies, $\Delta H$), and the activation energies of the forward and reverse isomerization reactions of acyl azides ($E_a$) (TS is the transition state)

| Acyl azide, TS | R = H (**1**) | | R = Me (**2**) | | R = Ph (**3**) | |
|---|---|---|---|---|---|---|
| | $-E$/a.u. | $\Delta H$ ($E_a$) /kcal mol$^{-1}$ | $-E$/a.u. | $\Delta H$ ($E_a$) /kcal mol$^{-1}$ | $-E$/a.u. | $\Delta H$ ($E_a$) /kcal mol$^{-1}$ |
| *syn*-$RC(O)N_3$ | 277.9410 | 0 | 317.2247 | 0 | 508.7994 | 0 |
| *anti*-$RC(O)N_3$ | 277.9396 | 0.9 | 317.2232 | 0.9 | 508.7887 | 6.7 |
| TS(*syn*→*anti*) | 277.9260 | (9.4) | 317.2135 | (7.0) | 508.7847 | (9.2) |
| TS(*anti*→*syn*) | 277.9260 | (8.5) | 317.2135 | (6.1) | 508.7847 | (2.5) |

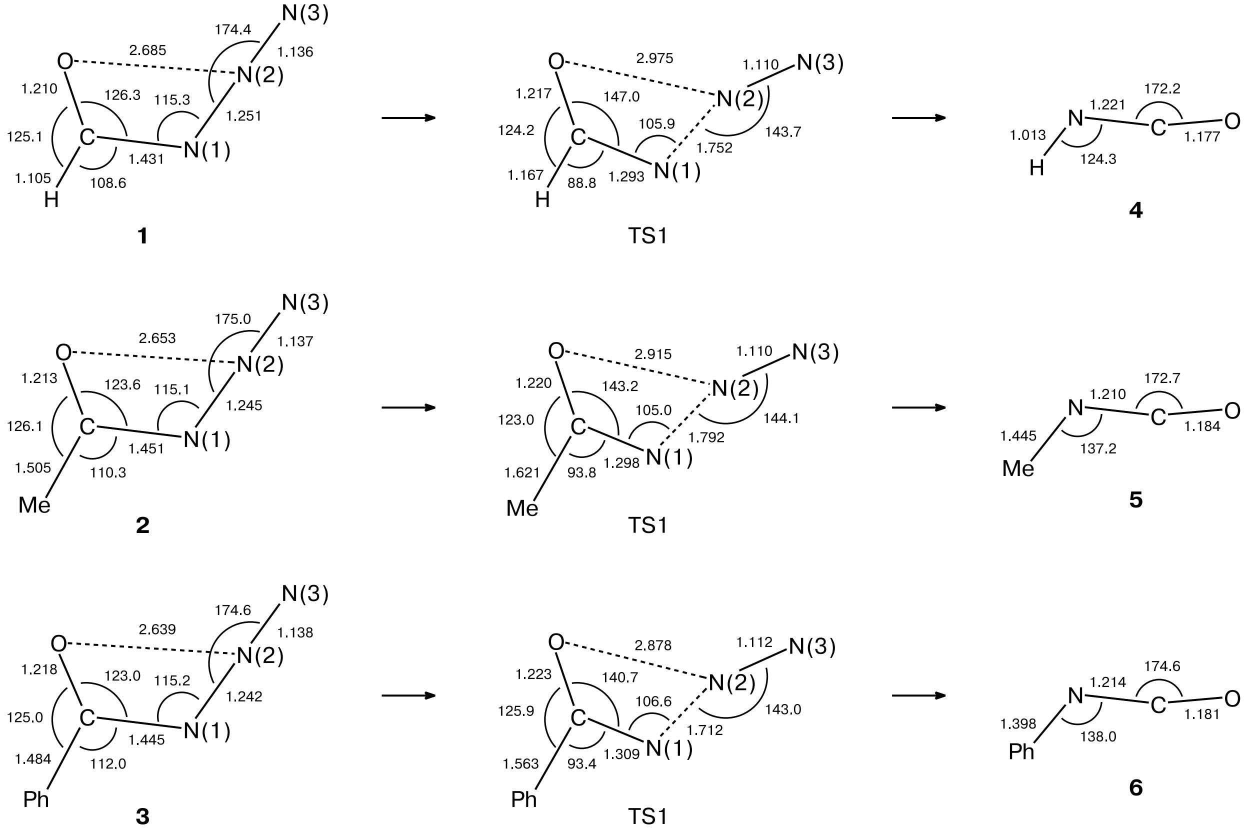


**Fig. 2.** Geometric structures of the *syn* conformers of HC(O)$N_3$ (**1**), MeC(O)$N_3$ (**2**), and PhC(O)$N_3$ (**3**) and the corresponding transition states TS1 of their rearrangement into isocyanates HNCO (**4**), MeNCO (**5**), and PhNCO (**6**). Here and in Fig. 4, the bond lengths (Å) are given; the bond angles (deg) are presented above the arcs.

**Fragments of the potential surface for the Curtius rearrangement and structures of transition states.** The main results of calculations of fragments of potential energy surfaces for the transformation of acyl azides into isocyanates is that the reaction can, in principle, proceed by two mechanisms, *viz.*, by a concerted mechanism involving the rearrangement of atoms and bonds in acyl azide simultaneously with elimination of the nitrogen molecule and by a stepwise mechanism involving the formation of acylnitrene as an intermediate. As can be seen from Fig. 3, the rearrangement of *syn*-acyl azides follows the former pathway, whereas the rearrangement of the *anti* conformers occurs by a stepwise mechanism, which is consistent with the results of the study,[24] where the free energy of the rearrangement of acetyl azide was calculated. The total electronic energies and their differences, which we calculated for stationary points on the potential energy surface for the Curtius rearrangement (starting reagents, final products, intermediates, and transition states), are presented in Table 3. The values of $\Delta E$ are given relative to the most stable state (RNCO + $N_2$).

The reliability of the calculated enthalpies of the reactions under consideration can be judged by comparing the results of calculations with experimental data. In the only published study,[36] the thermal effect of the rearrangement of acryloyl azide $CH_2$=CHC(O)$N_3$ into vinyl isocyanate $CH_2$=CHNCO in the liquid state (−47.1 kcal $mol^{-1}$) was measured by DSC. The calculated $\Delta H$ for the rearrangement of *syn*-HC(O)$N_3$, -MeC(O)$N_3$, and -PhC(O)$N_3$ are −51.7, −37.9, and −40.4 kcal $mol^{-1}$, respectively. The absolute enthalpies of the rearrangement of the *anti* isomers are larger than the enthalpies of isomerization of acyl azides. It can be seen that the difference between the calculated values of $\Delta H$ and the experimental value is small and the agreement is quite satisfactory.

Calculations of the activation energies for different pathways of the rearrangement of acyl azides show that the one-step concerted rearrangement into the corresponding isocyanates is more preferable than the rearrangement proceeding through the formation of acylnitrene as an intermediate. The activation barriers of the concerted rearrangement of the *syn*-acyl azides ($E_{a,1}$), which were calculated in the gas-phase approximation (Table 4), differ only slightly from the experimental values, which refer to the liquid-phase process. For example, the activation energies of the thermal rearrangement of MeC(O)$N_3$ and PhC(O)$N_3$ (data on the kinetics of the

**Table 2.** Calculated and experimental (MWS and ED data) bond lengths ($d$) and bond angles ($\omega$) in isocyanates **4—6**

| $d$/Å | | | $\omega$/deg | | Calculation method | Refs |
|---|---|---|---|---|---|---|
| R—N | N=C | C=O | R—N—C | N—C—O | | |
| HNCO (**4**) ($E$ = −168.5733 a.u.) | | | | | | |
| 1.013 | 1.221 | 1.177 | 124.3 | 172.2 | PBE/TZ2P | [a] |
| 0.993 | 1.199 | 1.148 | 125.0 | 174.2 | RHF/6-31G** | 14 |
| 1.006 | 1.212 | 1.165 | 125.4 | 172.9 | B3LYP/6-311G(d.p) | 16 |
| 1.002 | 1.217 | 1.172 | 124.6 | 171.3 | MP2/TZP | 17 |
| 1.012 | 1.229 | 1.177 | 121.2 | 172.5 | CCSD/DZ(d.p) | 18 |
| 1.008 | 1.224 | 1.184 | 125.8 | 171.7 | MP2/6-31G(d) | 19 |
| 1.036 | 1.246 | 1.183 | 114.6 | 169.7 | RHF/STO-3G | 15 |
| 0.976 | 1.170 | 1.177 | 157.8 | 176.3 | RHF/4-31G | 15 |
| 0.987 | 1.207 | 1.171 | 128.1 | 180.0[b] | MWS | 31 |
| 0.986 | 1.209 | 1.166 | 128.0 | 180.0[b] | MWS | 32 |
| MeNCO (**5**) ($E$ = −207.8351 a.u.) | | | | | | |
| 1.445 | 1.210 | 1.184 | 137.2 | 172.7 | PBE/TZ2P | [a] |
| 1.143 | 1.210 | 1.180 | 135.0 | 172.5 | MP2/cc-pVTZ | 20 |
| 1.442 | 1.199 | 1.173 | 139.7 | 173.7 | B3LYP/6-311G(d.p) | 21 |
| 1.451 | 1.214 | 1.166 | 135.6 | 172.6 | MWS | 33 |
| 1.450 | 1.202 | 1.168 | 140.4 | 180.0[b] | ED | 34 |
| PhNCO (**6**) ($E$ = −399.4137 a.u.) | | | | | | |
| 1.398 | 1.214 | 1.181 | 138.0 | 174.6 | PBE/TZ2P | [a] |

[a] Data from the present study.

[b] On the assumption that the N=C=O groups are linear.

**Table 3.** Electronic energies ($E$) and their differences ($\Delta E$) (relative to the state RNCO + $N_2$) calculated for stationary points on the potential energy surface (PES) for the Curtius rearrangement

| Stationary point PES | R = H | | R = Me | | R = Ph | |
|---|---|---|---|---|---|---|
| | $-E$/a.u. | $\Delta E$ /kcal mol$^{-1}$ | $-E$/a.u. | $\Delta E$ /kcal mol$^{-1}$ | $-E$/a.u. | $\Delta E$ /kcal mol$^{-1}$ |
| *syn*-RC(O)$N_3$ | 277.9410 | 51.7 | 317.2247 | 37.9 | 508.7994 | 40.4 |
| TS1 | 277.8964 | 79.7 | 317.1723 | 70.8 | 508.7445 | 74.9 |
| *anti*-RC(O)$N_3$ | 277.9396 | 52.6 | 317.2232 | 38.9 | 508.7887 | 47.1 |
| TS2 | 277.8844 | 87.2 | 317.1707 | 71.8 | 508.7372 | 79.4 |
| RC(O)N: + $N_2$ | 277.8861 | 86.1 | 317.1791 | 66.6 | 508.7481 | 72.6 |
| TS3 + $N_2$ | 277.8529 | 107.0 | 317.1489 | 85.5 | 508.7265 | 86.2 |
| RNCO + $N_2$ | 278.0234 | 0 | 317.2852 | 0 | 508.8638 | 0 |

rearrangement of HC(O)$N_3$ are lacking in the literature because the latter compound, being very unstable, was not isolated so far) in inert heptane are 27.0 and 31.2 kcal mol$^{-1}$, respectively. In donor-acceptor and polar solvents, the activation energies of decomposition of acyl azides are only 3—5 kcal mol$^{-1}$ lower than those in an inert medium.[3] A comparison of the calculated activation energies for the concerted rearrangement of *syn*-acyl azides (see Table 4) with the energy barriers separating *anti*-acyl azides and the corresponding isocyanates (see Table 3 and Fig. 3) shows that the latter (54.4, 46.6, and 39.1 kcal mol$^{-1}$ for R = H, Me, and Ph, respectively) are much higher than the former. This fact, along with the fact that the calculated values of $E_{a,1}$ are similar to the experimental activation energies of the thermal rearrangement of acyl azides, is also evidence for the concerted reaction mechanism.

The structure of the transition state of the concerted rearrangement of *syn*-acyl azides (see Fig. 2, TS1) is of interest. The N(1)...N(2) distance, which is a characteristic structural parameter indicative of the migration of the nitrogen atom in the course of the rearrangement, is 1.7—1.8 Å. This distance is much longer than those in the starting acyl azides (1.24—1.25 Å; see Fig. 2, structures **1—3**). In the transition state, the O...N(2) interatomic distance is 0.3 Å longer than that in the starting

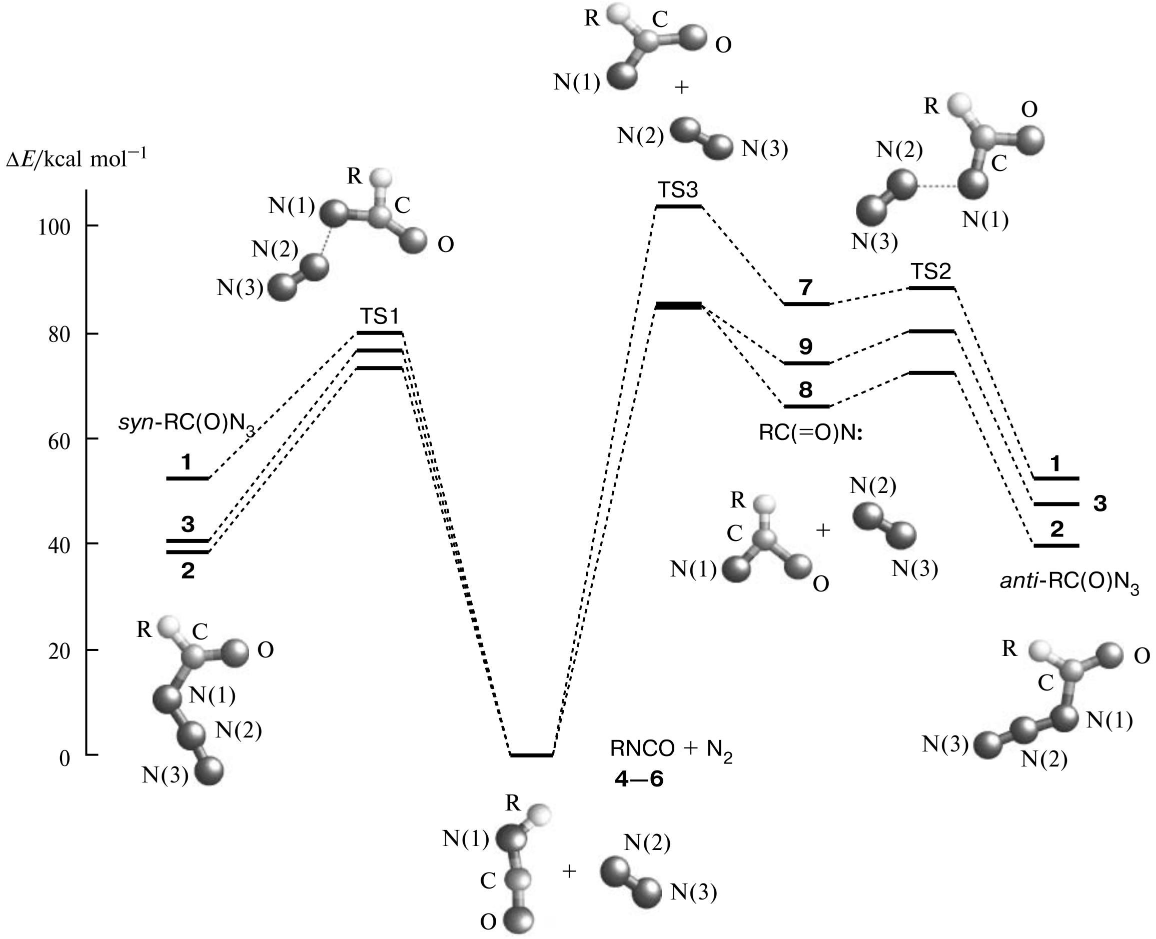


**Fig. 3.** Profiles of the potential energy surface for the rearrangement of the *syn* and *anti* conformers of $HC(O)N_3$ (**1**), $MeC(O)N_3$ (**2**), and $PhC(O)N_3$ (**3**) into the corresponding isocyanates.

**Table 4.** Calculated activation energies ($E_a$) of the reactions and intermediate steps of the rearrangement of acyl azides

| Reaction, step | TS | $E_a$/kcal mol$^{-1}$ | | |
|---|---|---|---|---|
| | | R = H | R = Me | R = Ph |
| *syn*-$RC(O)N_3 \rightarrow$<br>$\rightarrow RNCO + N_2$ | TS1 | 28.0 | 32.9 | 34.5 |
| *anti*-$RC(O)N_3 \rightarrow$<br>$\rightarrow RC(O)N: + N_2$ | TS2 | 34.6 | 32.9 | 32.3 |
| $RC(O)N: \rightarrow RNCO$ | TS3 | 20.9 | 18.9 | 13.6 |

*Note.* The activation energies $E_{a,1}$, $E_{a,2}$, and $E_{a,3}$ correspond to the reactions proceeding through the transition states TS1, TS2, and TS3, respectively.

molecule. The N(2)—N(3) bond length changes from 1.136—1.138 to 1.110—1.112 Å and approaches the bond length in the $N_2$ molecule (1.103 Å). As a result of gradual elimination of the nitrogen molecule in the course of rearrangement, reorganization of the remaining portion of the molecule starts already in the transition state so that the reaction follows the pathway giving rise to the final product. The C—N(1) bond is shortened and becomes similar to that in the isocyanate molecule. The R—C—N(1) angle in the transition state substantially decreases (to 89—94° *vs.* 109—112° in acyl azides), due to which the group R and the N(1) atom approach each other.

Based on the geometry of the transition state of the concerted rearrangement, it can be stated that the molar volume of TS is larger than that of the starting *syn*-acyl azide, *i.e.*, $\Delta V^{\neq} > 0$. Hence it follows that the rate of the Curtius rearrangement should become lower with increasing external pressure analogously to that observed in typical monomolecular reactions, which are not accompanied by strong charge separation.[37] Actually, in experimental studies of the influence of high pressure on the rate of thermal rearrangement of benzoyl azide, $\Delta V^{\neq}$ were estimated to be +2.0 cm$^3$ mol$^{-1}$ in aqueous ethanol and +5.0 cm$^3$ mol$^{-1}$ in ligroin.[38] As can be seen from Table 5, the formation of activated complexes is not accompanied by a substantial charge redistribution, resulting in small

**Table 5.** Atomic charge (*q*) distribution and dipole moments (μ) in *syn*-acyl azides **1—3** and the corresponding transition states TS1

| $RC(O)N_3$, TS | *q* | | | | | | μ/D |
|---|---|---|---|---|---|---|---|
| | R | C | O | N(1) | N(2) | N(3) | |
| *syn*-$HC(O)N_3$ (**1**) | 0.066 | 0.135 | −0.226 | −0.110 | 0.173 | −0.037 | 1.70 |
| TS1 | 0.099 | 0.091 | −0.240 | −0.115 | 0.117 | 0.048 | 1.57 |
| *syn*-$MeC(O)N_3$ (**2**) | 0.071 | 0.172 | −0.238 | −0.115 | 0.164 | −0.054 | 2.53 |
| TS1 | 0.109 | 0.122 | −0.263 | −0.115 | 0.110 | 0.037 | 2.04 |
| *syn*-$PhC(O)N_3$ (**3**) | 0.082 | 0.156 | −0.239 | −0.101 | 0.160 | −0.058 | 3.50 |
| TS1 | 0.148 | 0.105 | −0.271 | −0.123 | 0.113 | 0.028 | 3.02 |

differences between their dipole moments and the dipole moments of the starting *syn*-acyl azides. Consequently, the contribution of the solvating component to $\Delta V^{\neq}$ would be insignificant, as well as the reaction rate would be little affected by the nature of the medium, which is consistent with experimental data.

In spite of the fact that the stepwise transformation of the *anti* conformers of acyl azides into isocyanates is the minor pathway of the Curtius rearrangement, the data on the energy characteristics of this process and the structures of intermediates and the corresponding transition states are of interest. Moreover, the acylnitrenes by themselves (formylnitrene to a larger degree and acetylnitrene to a smaller degree) and their thermal transformations (predominantly beyond the scope of the problem of the mechanism of the Curtius rearrangement) have been studied by quantum chemical methods many times.[14—24]

Our data on the relative stabilities of singlet formyl nitrene (**7**) and acetyl nitrene (**8**) and the transition states of their monomolecular rearrangement into the corresponding isocyanates are given in Table 6. These results are compared with the published data obtained with the use of different calculation methods. The relative positions of stationary points on the potential energy surfaces for the rearrangement of acylnitrenes are adequately described by all methods. The only exceptions are the data on the activation energy of the rearrangement of formylnitrene, which were obtained with the inclusion of configuration interactions.[14]

The data on the geometric structures of singlet acylnitrenes **7—9** and the transition states of their formation from *anti*-acyl azides **1—3** and the transformations into isocyanates (TS2 and TS3, respectively) are presented in Fig. 4. It is noteworthy that the N(1)...N(2) bond in the transition state TS2 is more elongated (by ~0.2 Å) compared to this bond in the transition state TS1 of the rearrangement of the *syn* conformers (see Fig. 2). The geometry of the transition state TS2 strongly differs from that of the transition state TS1 of the concerted rearrangement. The formation of acylnitrenes **7—9** from *anti*-acyl azides **1—3** is accompanied by substantial changes in the C—O and C—N bond lengths, the O—C—N(1) angle approaching 90°. The further rearrangement of acylnitrene, which occurs through the transition state TS3, is accompanied by an increase in the O—C—N(1) bond angle and elongation of the R—C and C—N(1) bonds with the result that the group R and the nitrogen atom approach each other,

**Table 6.** Electronic energy differences (Δ*E*) of HNCO (**4**) and TS3 relative to formylnitrene HC(O)N: (**7**) and the differences of MeNCO (**5**) and TS3 relative to acetylnitrene MeC(O)N: (**8**) according to the results of calculations by different methods[a]

| Structure | Δ*E*/kcal $mol^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | PBE/TZ2P[b] | G2 [19] | G2(MP2,SVP) [21] | B3LYP [21] | B3LYP [16] | MRD-CI [14] |
| **7** | 0 | 0 | 0 | — | 0 | 0 |
| TS3 | 20.9 | 29.9 | 23.4 | — | 14.5 | 2.9 |
| **4** | −86.1 | −84.9 | −84.9 | — | −92.0 | −81.8 |
| **8** | 0 | — | 0 | 0 | — | — |
| TS3 | 18.9 | — | 29.1 | 14.1 | — | — |
| **5** | −66.6 | — | −66.4 | −73.9 | — | — |

[a] According to the results of the study,[24] the free energy differences (at 298 K) for MeNCO and TS3 relative to MeC(O)N: are −61.1 and 25.9 kcal $mol^{-1}$ (calculated by the B3LYP/6-311+G**//B3LYP/6-31G* method) and −61.9 and 27.3 kcal $mol^{-1}$, respectively (calculated by the CBS-QB3 method).

[b] Data from the present study.

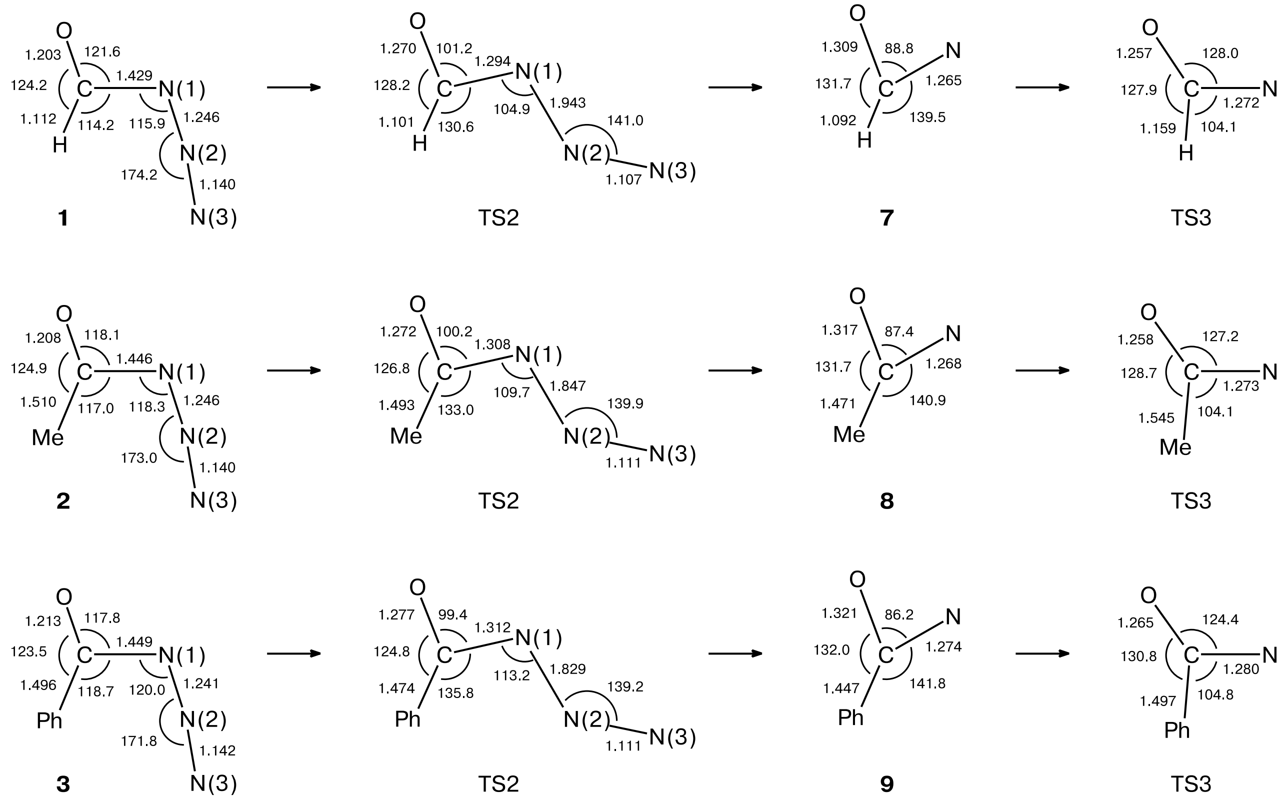


**Fig. 4.** Geometric structures of the *anti* conformers of $HC(O)N_3$ (**1**), $MeC(O)N_3$ (**2**), and $PhC(O)N_3$ (**3**), the transition states TS2 of their decomposition giving rise to acylnitrenes **7**—**9**, and the transition states TS3 of the rearrangement of acylnitrenes **7**—**9** into the corresponding isocyanates.

thus facilitating the pathway giving rise to the final isocyanate.

The data on the structures of singlet acylnitrenes are compared with the published data obtained with the use of different quantum chemical methods (Table 7). The main characteristic feature of singlet acylnitrenes is the small O—C—N angle. According to the results of all calculations (with the only exception[14]), this angle is slightly smaller than 90°. Because of this, some authors believe[14,16,19] that singlet acylnitrenes are structurally similar to oxazirenes containing the three-membered OCN ring. However, it should be noted that the O—N distance is too long (according to our data and the results obtained by other authors,[16,19,23,24] this distance is ~1.7—1.8 Å) to be identified with the N—O covalent bond in the strained three-membered ring. Hence it follows that the structures of singlet acylnitrenes can at best be considered as quasi-oxazirenes. In the present study, the structures of triplet acylnitrenes, as well as their rearrangement (which, apparently, can occur in the case of photochemical decomposition of acyl azides), were not studied in detail. In the note to Table 7, only the electronic energies of the corresponding structures are given. From these energies it follows that the triplet state on the potential energy surface calculated at the PBE/TZ2P level is higher than the singlet state. For acylnitrenes with R = H, Me, or Ph, the singlet-triplet splitting is $-1.0$, $-4.5$, and $-2.3$ kcal $mol^{-1}$, respectively.

Although the so-called concerted and stepwise (nitrene) mechanisms of thermal decomposition of acyl azides have been always considered in the literature as alternative pathways of the thermal Curtius rearrangement, the results obtained in the present study argued against that. Due to ability of acyl azides to exist as two conformers (*syn* and *anti*), their thermal rearrangement can follow both pathways, which do not formally exclude one another. However, due to a substantially lower activation energy of the concerted mechanism characteristic of *syn*-acyl azides compared to the barrier, which is necessary to overcome in the reaction of the *anti* conformer (which involves the formation of singlet acylnitrene and its subsequent transformation into isocyanate), the thermal Curtius rearrangement occurs virtually completely by the former mechanism. The fact that the equilibrium of isomerization of acyl azides is substantially shifted to the more stable *syn* conformer explains why by-products characteristic of the reactions with acylnitrenes were never detected in experiments on thermal decomposition of

**Table 7.** Bond lengths (*d*) and bond angles (ω) in singlet acylnitrenes **7—9** calculated by different methods[a]

| *d*/Å | | | ω/deg | | Calculation method | Refs |
|---|---|---|---|---|---|---|
| R—C | C—O | C—N | O—C—N | R—C—O | | |
| HCON: (**7**) ($E = -168.4360$ a.u.) | | | | | | |
| 1.092 | 1.309 | 1.265 | 88.8 | 131.7 | PBE/TZ2P | [b] |
| 1.072 | 1.307 | 1.247 | 94.1 | 128.7 | CASSCF/6-31G** | 14 |
| 1.086 | 1.300 | 1.255 | 89.0 | 131.6 | B3LYP/6-311G(d,p) | 16 |
| 1.082 | 1.342 | 1.254 | 83.3 | 171.3 | MP2/6-31G(d) | 19 |
| 1.076 | 1.307 | 1.260 | 90.0 | 131.0 | CCSD(T)/cc-pVTZ | 23 |
| 1.088 | 1.305 | 1.260 | 88.2 | 131.6 | B3LYP/6-31 G* | 23 |
| MeCON: (**8**) ($E = -207.7290$ a.u.) | | | | | | |
| 1.471 | 1.317 | 1.268 | 87.4 | 137.4 | PBE/TZ2P | [b] |
| 1.474 | 1.308 | 1.256 | 87.7 | 131.3 | B3LYP/6-311G(d,p) | 21 |
| 1.480 | 1.310 | 1.260 | 86.8 | — | B3LYP/6-311+G** | 24 |
| PhCON: (**9**) ($E = -399.2980$ a.u.) | | | | | | |
| 1.447 | 1.321 | 1.274 | 86.2 | 132.0 | PBE/TZ2P | [b] |
| 1.451 | 1.316 | 1.267 | 85.9 | 131.7 | B3LYP/6-31G* | 22 |

[a] For triplet acylnitrenes **7—9**, $E = -168.4344$, $-207.7218$, and $-399.2943$ a.u., respectively. The energies of singlet-triplet splitting are $-1.0$, $-4.5$, and $-2.3$ kcal mol$^{-1}$ for R = H, Me, and Ph, respectively.

[b] Data from the present study.

usual alkyl- and arylacyl azides. The photochemical Curtius rearrangement, which can, apparently, involve the formation of triplet acylnitrenes, was another matter, but this reaction and the triplet potential energy surface for thermal decomposition of acyl azides are beyond the scope of the present investigation.

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