Full Articles

Thermal isomerization of acetylnitrene: a quantum-chemical study

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The electronic structure and pathways of thermal isomerization of formylnitrene and acetylnitrene were studied by the B3LYP/6-311G(d,p) density functional method and *ab initio* G2(MP2,SVP) computational procedure using the geometries obtained from B3LYP calculations. According to G2 calculations, both nitrenes have singlet ground states while the energies of the corresponding triplet states are 2.8 and 5.7 kcal mol^{-1} higher. For acetylnitrene, the activation barrier to the nitrene → isocyanate isomerization was estimated at 28.9 kcal mol^{-1} (G2). Calculations revealed no pathway for single-step isomerization of nitrene into cyanate in both systems. The formation of methyl cyanate from isocyanate is thermodynamically unfavorable (ΔE = 26.5 kcal mol^{-1}) and requires a high activation barrier (89.4 kcal mol^{-1}) should be overcome. Based on the results obtained, the pathways of transformation of nitrene formed in thermal decomposition of acetyl azide (Curtius rearrangement) were analyzed.

Key words: formylnitrene, acetylnitrene, quantum-chemical calculations, Curtius rearrangement, B3LYP density functional, G2(MP2,SVP) computational scheme.

Thermal transformations of carbonyl azides into isocyanates (Curtius rearrangement)[1—4] provide a source of rich synthetic chemistry. They have long been employed but their mechanisms are still poorly studied from the theoretical standpoint. It is commonly accepted that this reaction involves the formation of acylnitrene (**1**) as an intermediate (Scheme 1).

Attempts to detect singlet carbonylnitrene MeOC(O)N using, *e.g.*, matrix IR spectroscopy[5] were unsuccessful. However, an EPR study of photolysis of azide in organic glass revealed the formation of triplet ethoxycarbonylnitrene EtOC(O)N.[6] The simplest model system CHNO, in which the Curtius rearrangement can occur, was theoretically studied in considerable detail.[7—10] The system is characterized by a rather complex potential energy surface (PES), which has a total of twelve local minima for linear and cyclic isomers of the composition CHNO besides the structures corresponding to different types of fragmentation and the transition states (TS) connecting the minima mentioned above.[7] The PES of the system CHNO was studied by *ab initio* methods,[7,8] using the density functional approach (B3LYP version),[9] and the Gaussian-2 computational scheme.[10] According to calculations, the most stable isomer in this system is isocyanic

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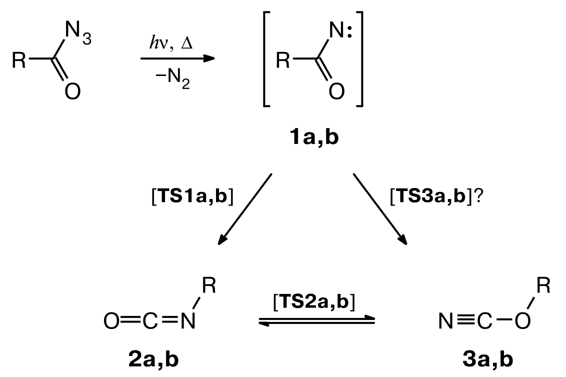
Scheme 1



R = H (**a**), Me (**b**).

acid HNCO (**2a**) followed by cyanic acid HOCN (**3a**). The most accurate calculations[10] gave a value of 25.4 kcal mol^{-1} for the energy difference (ΔE) between **3a** and **2a**. These compounds are followed[10] (in order of increasing energy ΔE) by two acids of the same elemental composition, namely, fulminic acid HCNO (70.1 kcal mol^{-1}) and isofulminic acid HONC (83.8 kcal mol^{-1}); singlet formylnitrene HCON (**1a**) (84.9 kcal mol^{-1}); dissociation products of triplet isocyanic acid (**2a**), namely, $HN(^3\Sigma)$ + $CO(^1\Sigma)$ (86.0 kcal mol^{-1}); triplet formylnitrene (**4a**) (87.8 kcal mol^{-1}); and, finally, by dissociation products of singlet nitrene **1a** (H + $NCO(^2\Pi)$, 105.5 kcal mol^{-1}). The PES of the system CHNO has a number of minima with even higher energies;[9,10] however, the corresponding structures can hardly be involved in the Curtius rearrangement.

Calculations with inclusion of electron correlation[8,9] showed that singlet formylnitrene is characterized by a rather high energy; however, this compound can exist as a kinetically independent intermediate. The singlet and triplet states of formylnitrene have close energies. Different methods give both singlet[8,10] and triplet[9,11] states as the ground state of **1a**. According to recent most rigorous calculations, the singlet—triplet splitting, ΔE_{ST}, for formylnitrene varies from −3.5 kcal mol^{-1} (CASPT2/cc-pVTZ)[11] to +2.9 kcal mol^{-1} (G2)[10]. Such a small energy difference between these terms means that singlet formylnitrene initially formed during, *e.g.*, thermal decomposition of azide can convert to the triplet state, thus making the rearrangement into isocyanate energetically unfavorable. Besides, the reaction involving a biradical triplet intermediate must result in a broad spectrum of products, whereas the Curtius rearrangement is usually characterized by a high yield of isocyanate.[2] According to calculations,[10] the rearrangement of **1a** into **2a** requires the overcoming of a barrier of nearly 29 kcal mol^{-1}. It should be noted that all earlier studies of the system CHNO [7—10] revealed no transition state **TS3a** corresponding to a single-step rearrangement of nitrene **1a** into cyanate **3a**. The most probable two-step mechanism of formation of **3a** involves the sequence of transformations **1a** → **2a** → **3a** (see Scheme 1)

No Curtius rearrangement was experimentally observed for the system $HC(O)N_3$, as well as no theoretical studies of this reaction for more complex acyl azides have been reported as yet. At the same time, this reaction is widely used in synthetic chemistry for the preparation of isocyanates containing saturated aliphatic or aromatic substituents.[12] Acetylnitrene MeC(O)N provides an example of the simplest system, in which the Curtius rearrangement is observed experimentally.[13] The earlier quantum-chemical studies of the PES of the system MeCNO were limited to calculations of the ground-state geometry and spectral characteristics of methyl isocyanate **2b** [14,15] and methyl cyanate **3b**,[16,17] and to consideration of the mechanism of trimerization of **3b**.[18]

In this work, we studied the fragments of the PES of the system MeC(O)N, corresponding to singlet acetylnitrene (**1b**) and to the most stable isomers of this compound, namely, triplet methyl isocyanate (**2b**), methyl cyanate (**3b**), and acetylnitrene (**4b**) and to the transition states **TS1b—TS3b** of the transformations **1—3** (see Scheme 1). The geometric parameters and vibrational frequencies were calculated by the B3LYP method,[19] while the energies were obtained using the G2(MP2,SVP) computational scheme.[20] To evaluate the effect of the Me group on the transformation energies, we also calculated the energies of the stationary points **1a—3a** and **4a** and of the transition states **TS1a** and **TS2a** for the simplest system CHNO using the G2(MP2,SVP)//B3LYP computational scheme.

Calculation Procedure

Quantum-chemical calculations of the PES fragments, including vibrational frequency calculations, were carried out using both the restricted and unrestricted versions of the B3LYP [19] density functional method using the 6-311G(d,p) basis set. The energies of the stationary points corresponding to the reagents, products, and transtion states were calculated using the G2(MP2,SVP) version[20] of the Gaussian-2 quantum-chemical computational scheme.[21] The G2(MP2,SVP) calculations are an approximation to the QCISD(T)/6-311G+(3df,2pd) energy calculations and the geometries and vibrational frequencies obtained from B3LYP/6-311G(d,p) calculations were used. The zero-point vibrational energy correction, *ZPE*, was calculated using a scale factor of 0.9806, as recommended[22] for the B3LYP calculations. The characters of the stationary points located (the minimum or the saddle point) were determined by calculating the eigenvalues of the Hessian matrix. The correspondence between a particular transition state and a given transformation was established using the intrinsic reaction coordinate (IRC) method.[23] Thermodynamic functions were calculated in the framework of the "harmonic oscillator—rigid rotator" model.

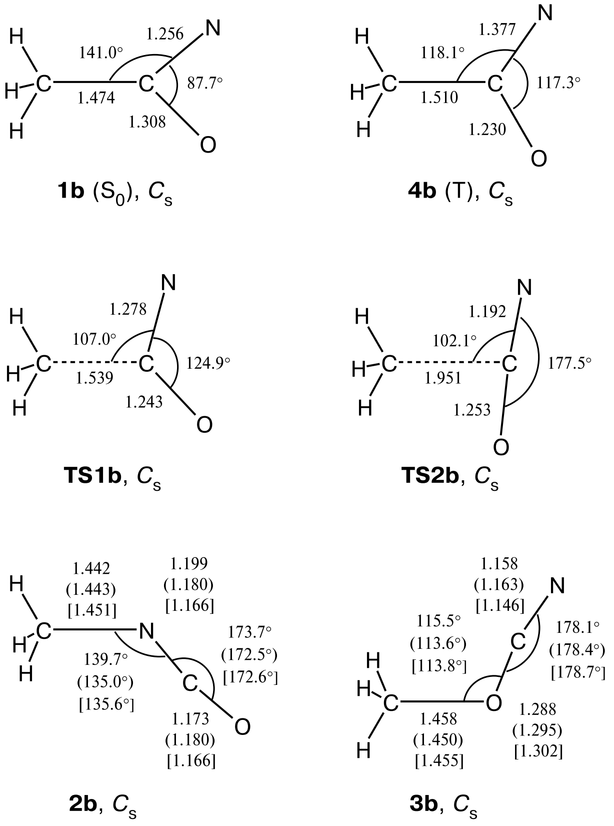
Calculations were carried out using the GAUSSIAN-98 program.[24]

Results and Discussion

The parameters of the structures corresponding to the stationary points of the PES of the systems CHNO **1a—4a** and **TS2a** obtained from B3LYP/6-311G(d,p) calculations coincide with the published data[9] and are in good agreement with the results of MP2/6-31G(d) calculations.[10]

It should be noted that the geometric parameters obtained from B3LYP and MP2 [10] calculations for the transition states **TS1a** and **TS2a** differ to a somewhat greater extent compared to the results obtained for the minima **1a—4a**.

The structures and geometric parameters of the methyl-substituted isomers **1b—4b** and transition states **TS1b** and **TS2b** are shown in Fig. 1. Topologically, the MeCNO PES fragment studied in this work is identical to that reported earlier for the system HCNO. In both cases, no pathway of single-step nitrene isomerization into cyanate was revealed. According to the IRC calculations, the transition state **TS2a** corresponds to 1,3-proton migration (*i.e.*, isocyanate → cyanate rearrangement) rather than a single-step nitrene → cyanate rearrangement suggested earlier.[9] Thus, cyanate **3b** can be formed from nitrene **1b** only *via* the two-step mechanism **1b** → **TS1b** → **2b** → → **TS2b** → **3b**.



1b (S$_0$), C_s **4b** (T), C_s

TS1b, C_s **TS2b**, C_s

2b, C_s **3b**, C_s

Fig. 1. Geometric parameters (interatomic distances/Å, angles/deg) of the stationary points of the PES of the system MeCNO calculated in the B3LYP/6-311G(d,p) approximation. The structure numbers are followed by the symmetry groups. The results of MP2/cc-pVTZ (for **2b**)[15] and CCSD/6-311++G(d,p) (for **3b**)[17] calculations are given in parentheses and the microwave spectroscopy data taken from Ref. 25 for **2b** and from Ref. 26 for **3b** are given in brackets.

The singlet carbonylnitrene **1b** (S$_0$) is characterized by a very short, nearly double bond C=N (1.256 Å) and a nearly "sesqui-"bond C—O (1.308 Å), which is a consequence of redistribution of the electron density in the NCO fragment. This is also indicated by the small angle O—C—N (87.7°, see Fig. 1). This feature of singlet carbonylnitrene, which was first noticed for formylnitrene[8] **1a** (O—C—N angle is 94.1°), was interpreted as an indication of a cyclic structure of **1a** with an elongated O—N bond. B3LYP calculations showed that the O—N distance in the singlet nitrenes is somewhat shortened from 1.791 Å in **1a** [9] to 1.777 Å in **1b**, which points to stabilization of the species. A trend toward shortening of the O—N bond is also typical of more complex phenyl-substituted carbonylnitrenes.[27] Similarly to formylnitrene, transition of acetylnitrene **1b** to the triplet state is accompanied by an increase in the O—C—N angle and by ring opening. Introduction of a Me group has little effect on the geometry of the NCO fragments of isocyanate **2** and cyanate **3**.

The structural parameters of the NCO fragment of the transition state **TS1** remain virtually unchanged upon replacement of the migrating H atom by the Me group. The C—O bond is slightly elongated from 1.240 Å (**TS1a**) to 1.243 Å (**TS1b**), the C—N bond is shortened from 1.281 Å (**TS1a**) to 1.278 Å (**TS1b**), and the angle N—C—O decreases from 125.9° to 124.9°. At the same time, the geometry of **TS2** changes to a greater extent. Namely, the C—O bond is shortened from 1.265 Å (**TS2a**) to 1.253 Å (**TS2b**), while the angle N—C—O decreases from 187.8° to 177.5° (*i.e.*, the NCO fragment is now bent in the opposite direction).

The B3LYP and G2 calculated energies of the stationary points of the systems HCNO and MeCNO are listed in Table 1 (see also the energy profile in Fig. 2). In both systems, the most stable structure is isocyanate **2**. The relative energies, ΔE, of isomers in the unsubstituted system HCNO, estimated in this work at the G2(MP2,SVP) level are in good agreement with the results of conventional G2 calculations.[10] The small difference between the energies of the transition state **TS1** (see Table 1) can be explained by different structural parameters obtained from the MP2 and B3LYP calculations.

Introduction of the Me group stabilizes the singlet nitrene relative to the other structures (see Table 1). The stabilization effect is most pronounced

Table 1. Total energies[a] (E/a.u.) and the total energy differences (ΔE and $\Delta E(T)$/kcal mol^{-1}) and the Gibbs free energy differences (ΔG/kcal mol^{-1}) calculated for $T = 0$ and 298 K by the B3LYP/6-311G(d,p) and G2(MP2,SVP)//B3LYP/6-311G(d,p) methods at the stationary points of the PES of the systems CHNO and MeCNO

Structure	$-E$		ΔE			$\Delta E(T)$		ΔG	
	G2(MP2,SVP)	B3LYP[c]	G2[d]	G2(MP2,SVP)	B3LYP	G2(MP2,SVP)[b]	B3LYP	G2(MP2,SVP)[b]	B3LYP
1a (S)	168.31819	168.56551	0	0.0	0.0[c]	0.0	0.0	0.0	0.0
2a	168.45341	168.71204	−84.9	−84.9	−92.0[c]	−84.8	−91.9	−84.3	−91.4
3a	168.41343	168.66632	−59.5	−59.8	−63.3[c]	−59.6	−63.1	−59.4	−62.9
TS1a	168.28098	168.54235	29.9	23.4	14.5	23.2	14.4	23.4	14.6
TS2a	168.31087	168.56437	3.1	4.6	0.7[c]	4.7	0.8	4.9	1.0
4a (T)	168.31365	168.57990	2.9	2.8	−9.0[c]	2.9	−9.0	2.2	−9.7
1b (S)	207.55871	207.88230		0.0	0	0.0	0.0	0	0
2b	207.66445	208.00012		−66.4	−73.9	−66.3	−73.8	−66.8	−74.4
3b	207.62203	207.95148		−39.7	−43.4	−39.8	−43.4	−39.7	−43.4
TS1b	207.51230	207.85977		29.1	14.1	28.9	13.9	29.3	14.3
TS2b	207.52179	207.85180		23.2	19.1	23.1	19.1	22.9	18.9
4b (T)	207.54966	207.89043		5.7	−5.1	5.7	−5.1	4.7	−6.1

[a] Calculated for 0 K with inclusion of *ZPE* correction.

[b] The correction obtained from B3LYP calculations for $p = 1$ atm and $T = 298$ K was used.

[c] Data taken from Ref. 9.

[d] Data taken from Ref. 10.

(18—20 kcal mol^{-1}) when the energy of **1b** (S) is compared to those of isocyanate, cyanate, and transition state **TS2**. Stabilization of **1b** (S) relative to the triplet **1b** (T) and **TS1** is much less pronounced (1—5 kcal mol^{-1}). The estimates of the singlet-triplet splitting are virtually independent of the computational method employed (*cf.* −5.1 and 5.7 kcal mol^{-1} found for **1b** from B3LYP and G2 calculations, respectively). Since the G2 estimate is more accurate, a singlet ground state of acetylnitrene can be suggested. A consequence of stabilization of the singlet acetylnitrene **1b** is a decrease in the exothermicity of its transformations into isocyanate **2b** by 18.1 (B3LYP)—18.5 kcal mol^{-1} (G2). Since replacement of the H atom by the Me group simultaneously stabilizes both the singlet nitrene and the transition state **TS1**, it has a little effect on the activation barrier, E_a, to the isomerization of **1** into isocyanate **2** (−0.5 kcal mol^{-1} for B3LYP and 5.7 kcal mol^{-1} for G2 calculations). The activation energy, E_a, for nitrene isomerization **1b** → **2b** at 298 K was calculated to be 13.9 (B3LYP) and 28.9 kcal mol^{-1} (G2). This allows the possibility of detection of carbonylnitrene **1b** formed in thermal decomposition of acetyl azide to be estimated. Unfortunately, no experimental data on the kinetics of this reaction are available. Information on the decomposition kinetics of other carbonyl azides undergoing the Curtius rearrangement are also scarce. Thermal decomposition of azides is performed in the temperature range 293—423 K (the recommended temperature is 353 K [12]). We estimated the energy E_a for monomolecular decomposition of azide assuming that the reaction obeys a first-order kinetics and is characterized by a "normal" pre-exponential factor of 10^{-13} s^{-1} [28] and a semi-conversion time of the order of 1 h. The results obtained lie between 22.2 and 32.0 kcal mol^{-1}, which corresponds to the outermost points of the temperature range 293—423 K. Both these values exceed the estimate obtained from B3LYP calculations (E_a = 13.9 kcal mol^{-1}). Assuming this order of the first and the second activation barrier heights, the decomposition of azide should be followed by fast isomerization of the nitrene formed into isocyanate. In this case, no accumu-

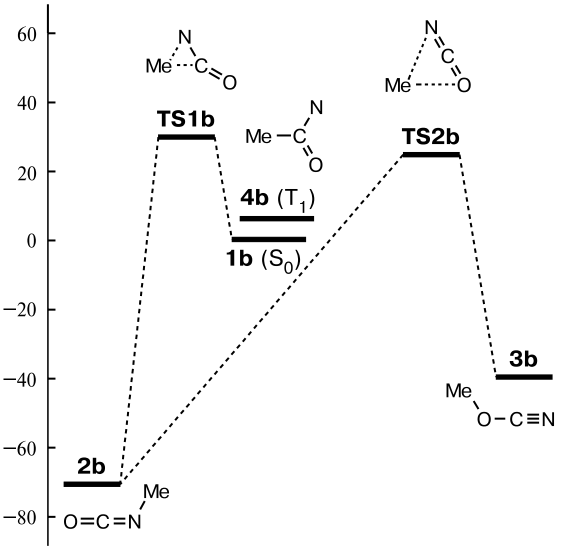


Fig. 2. Energy profile of the PES of the system MeCNO obtained from G2(MP2,SVP)//B3LYP calculations.

lation of nitrene will occur and detection of nitrene as a kinetically independent species is hardly probable. Based on the larger value (E_a = 28.9 kcal mol^{-1}, G2 calculations), the semi-conversion time of the reaction **1b** → **2b** will exceed 10 h in the case of azide decomposition at low temperatures (below 353 K) and the probability of detecting nitrene **1b** (stabilized in, *e.g.*, a low-temperature matrix) or products of its chemical trapping increases dramatically.

Replacement of the hydrogen atom by the Me group has virtually no effect on the activation energy for isomerization **2b** → **3b**, which is characterized by an extremely high barrier of 92.9 (B3LYP) and 89.4 kcal mol^{-1} (G2) and will not occur under standard conditions for the Curtius rearrangement. As follows from our calculations, the activation barrier to the reverse reaction is also rather high, namely, 62.5 (B3LYP) and 62.9 kcal mol^{-1} (G2). Experiments showed that methyl cyanate in the condensed phase is highly sensitive to various impurities and undergoes a fast isomerization into isocyanate and/or decomposition,[29] and polymerization.[29] According to our calculations, cyanate **3b** is stable toward monomolecular rearrangement into **2b** and will not undergo transformation into the more stable isomer **2b** [2] in the absence of impurities, which act as catalysts. The absence of cyanate among the Curtius rearrangement products confirms the impossibility of single-step formation of cyanate from nitrene in thermal reactions.

Passage from formylnitrene to acetylnitrene is accompanied by stabilization of the singlet state with respect to the triplet state. According to the most rigorous G2 calculations, acetylnitrene has a singlet ground state, while the energy of the nearest triplet state is 5.7 kcal mol^{-1} higher. The barrier to isomerization of acetylnitrene into isocyanate predicted by calculations is 13.9 (B3LYP) and 28.9 kcal mol^{-1} (G2). Both systems revealed no possibility for single-step nitrene → cyanate isomerization to occur. The most probable mechanism of the formation of **3b** involves the isomerization **2b** → **TS2b** → **3b**. This process is themodynamically unfavorable, requires the overcoming of a high activation barrier, and does not occur in thermal reactions. As a consequence, acetylnitrene transformations should result in isocyanate as the only product.

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