Gradient line reaction path of ammonia addition to formaldehyde

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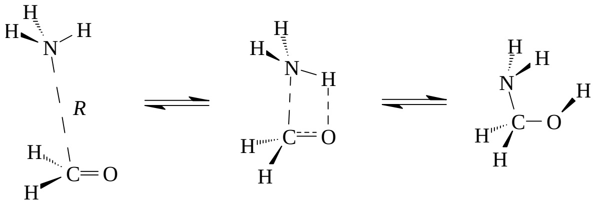
The gradient line reaction path of the gas phase ammonia addition to formaldehyde has been calculated by using the RHF/6-31G and MP2(full)/6-311++G** methods and it has been shown that two successive transition state structures lie on the path.**

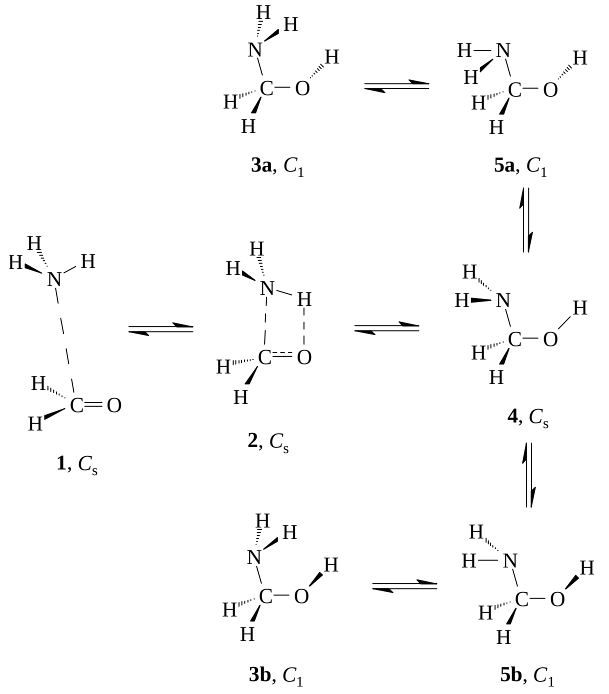
Nucleophilic carbonyl additions are one of the most fundamental reactions in chemistry and biochemistry.[1,2] Therefore, elucidation of the pathways of such reactions on the corresponding potential energy surfaces (PES) plays an important role in a study of their detailed mechanism.[2–7] In this respect, ammonia addition to formaldehyde in the gas phase is a convenient molecular model with which to study all interactions governing the system along a reaction path and therefore this system was investigated rather well by theoretical methods.[2,8–11] Earlier, Scheiner *et al.*,[8] using *ab initio* methods, predicted that NH_3 formed a weak pre-reaction complex **1** with a $N\cdot\cdot C$ distance (R) of 2.6 Å at the beginning part of the reaction pathway.



1 **2** **3**

SCF/3-21G calculations on **1** subsequently performed by Williams[10] gave $R = 2.8$ Å. However, SCF/6-31G* and MP2/6-31G* calculations predicted strong repulsion between NH_3 and H_2CO within the range of $R \geq 2.5$ Å,[10] in disagreement with earlier results.[8,9] Recent *ab initio* calculations[11] at the MP2/6-311G(2d) level predicted a low-energy complex **1** bounded at $R = 3.00$ Å.

Transition state **2** and product structures **3** for ammonia addition to formaldehyde have been well studied by *ab initio* SCF/3-21G calculations.[9,10] However, a continuous reaction pathway for NH_3 addition to H_2CO on the corresponding PES has not been constructed up to now and without this pathway one can not obtain a correct reaction mechanism.[12] Here *ab initio* RHF/6-31G** and MP2(full)/6-311++G** calculations[13,14] for the gradient line reaction path[12] of the gas phase ammonia addition to formaldehyde are reported. The calculations show that the reaction follows a more complicated pathway **1** $\rightleftarrows$ **2** $\rightleftarrows$ **4** $\rightleftarrows$ **5a**,**b** $\rightleftarrows$ **3a**,**b** rather than **1** $\rightleftarrows$ **2** $\rightleftarrows$ **3**. This implies that the system during the reaction firstly passes through two successive transition state structures **2** and **4**, then at point **4** it changes its direction of movement and arrives at two equivalent (mirror image forms) products **5a** and **5b**. Only from **5a** and **5b** can the system pass to two conformers **3a** and **3b** by internal rotation around the C–N bond.



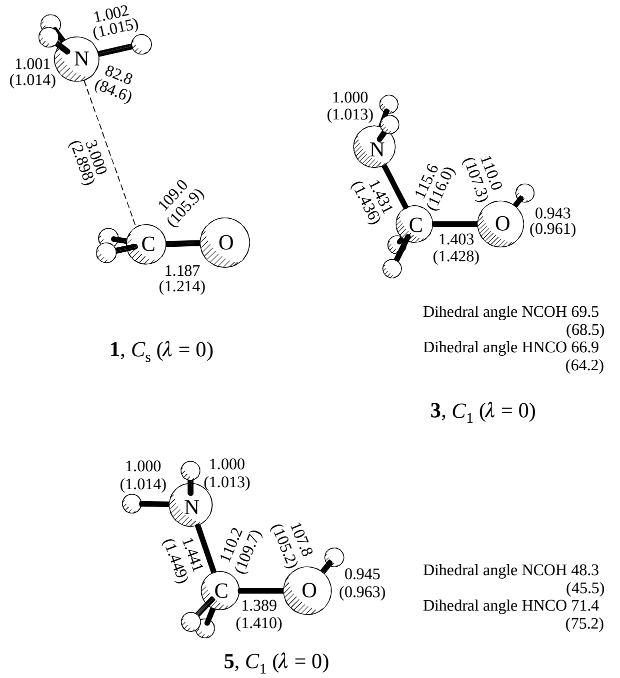
3a, C_1 **5a**, C_1 **1**, C_s **2**, C_s **4**, C_s **3b**, C_1 **5b**, C_1

Table 1 Total energy (E_{tot} in hartree),[a] relative energy (ΔE in kcal mol^{-1}),[b] the number of negative hessian eigenvalues (λ), zero point energy (ZPE in hartree), relative energy with including ZPE (ΔE_{ZPE} in kcal mol^{-1}), the imaginary or the smallest positive frequency ($i\nu/\nu_1$ in cm^{-1}) predicted by RHF/6-31G** and MP2(full)/6-311++G** (in parentheses) methods for structures **1**–**4** of $NH_3\cdot\cdot H_2CO$ and NH_3 and H_2CO molecules.

Structure	E_{tot}	ΔE	λ	ZPE	ΔE_{ZPE}	$i\nu/\nu_1$
1, C_s	–170.07067	0	0	0.06805	0	49.3
	(–170.71960)	(0)	(0)	(0.06396)	(0)	(33.3)
2, C_s	–169.99585	46.9	1	0.06964	47.9	i1812.1
	(–170.66524)	(34.1)	(1)	(0.06496)	(34.7)	(i1460.6)
3, C_1	–170.08532	–9.2	0	0.07521	–4.7	307.3
	(–170.73641)	(–10.5)	(0)	(0.07102)	(–6.1)	(322.4)
4, C_s	–170.08120	–5.9	1	0.07424	–4.1	i292.9
	(–170.73279)	(–8.3)	(1)	(0.06994)	(–5.6)	(i294.4)
5, C_1	–170.08437	–6.1	0	0.07524	–2.7	279.7
	(–170.73553)	(–8.3)	(0)	(0.07001)	(–4.5)	(262.5)
NH_3, C_{3v}	–56.19554	0	0	0.03681	0	1140.9
	(–56.43468)	(0)	(0)	(0.03486)	(0)	(1072.1)
H_2CO, C_{2v}	–113.86974	0	0	0.02898	0	1335.6
	(–114.27923)	(0)	(0)	(0.02698)	(0)	(1208.2)

[a] 1 hartree = 2625.4497 kJ mol^{-1}. [b] 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

According to RHF/6-31G** and MP2(full)/6-311++G** calculations, structures **1**, **3** and **5** correspond to minima ($\lambda = 0$, hereafter λ denotes the number of the negative hessian eigenvalues) and **2** and **4** to saddle points ($\lambda = 1$) on the $NH_3\cdots H_2CO$ PES. Geometrical and energy parameters of **1**–**5** calculated by *ab initio* methods are presented in Figures 1 and 2 and Table 1. As can be seen from Figures 1 and 2, the geometries of **1**, **2** and **3** are in excellent agreement with data obtained earlier.[10,11] The energy barrier of reaction **1** $\rightleftarrows$ **2** $\rightleftarrows$ **4** $\rightleftarrows$ **5a**,**b** equals 46.9 and 34.1 kcal mol^{-1} calculated by the RHF/6-31G** and MP2(full)/6-311++G** methods, respectively. The second value is close to 36.7 kcal mol^{-1} obtained by the RHF/3-21G calculations.[10] The important feature of the path is that the system descends from saddle point **2** directly to the neighbouring saddle point **4** along the unique gradient line (steepest descent line). At point **4** the system changes its direction of motion and transfers the first gradient line to the orthogonal one corresponding to the internal rotation of the OH group around the C–O bond with a calculated rotational energy barrier of 2.0 (RHF/6-31G**) and 1.7 [MP2(full)/6-



1, C_s ($\lambda = 0$)

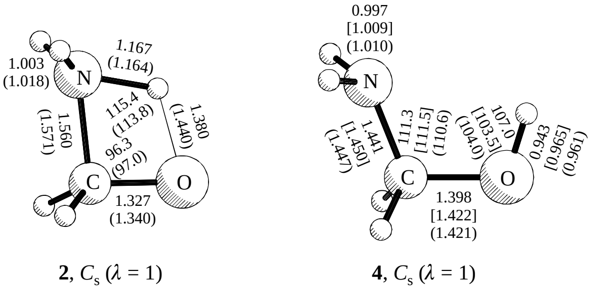
3, C_1 ($\lambda = 0$)

5, C_1 ($\lambda = 0$)

Figure 1 Geometrical parameters of structures **1**, **3** and **5** corresponding to minima ($\lambda = 0$) on the $NH_3\cdots H_2CO$ PES calculated by the RHF/6-31G** and MP2(full)/6-311++G** (in parentheses). Bond lengths and angles are given in angströms and degrees, respectively.

311++G**] kcal mol^{-1} and along two parts of the last line passes to minima **5a** and **5b**. From **5a** and **5b** the system proceeds to minima **3a** and **3b** by internal rotation around the C–N bond. Total energy smoothly decreases and the C_s point group of the system (mirror plane containing three atoms N, C and O) conserves along the gradient lines from **2** to **4**. All hessian eigenvectors and eigenvalues correlate along this line: the transition vector of **2** transforms into the hessian eigenvector of the smallest positive eigenvalue at **4**, the eigenvector of the smallest positive hessian eigenvalue at **2** transforms into transition vector at **4**. This pathway differs slightly from that calculated by Williams.[10] The difference, it seems, is due to the fact that Williams did not study a continuous reaction path from **2** to **3** on the PES.

Thus, according to *ab initio* calculations performed, the $NH_3\cdots H_2CO$ PES topology in the configuration region of the nucleophilic addition reaction $\mathbf{1} \rightleftarrows \mathbf{2} \rightleftarrows \mathbf{4} \rightleftarrows \mathbf{5a,b}$ is rather complicated. To elucidate the behaviour of all gradient lines on the PES in reaction region and compare those with the gradient line reaction path, a two-dimensional analytic function $V(R,\varphi)$ consisting of eleven ($i = 11$) gaussian functions $V(R,\varphi) = \Sigma a_i \exp[-(R - R_i)^2 - (\varphi - \varphi_i)^2]$ was constructed. Values R and φ define the N–C distance and the rotation angle of OH around the C–O bond, respectively. Constants a_i, R_i and φ_i are chosen so that the location, λ, and relative energies of stationary points **1**, **2**, **4** and **5a**,**b** on $V(R,\varphi)$ are close to those on the $NH_3\cdots H_2CO$ PES. As can be seen from the map of $V(R,\varphi)$ presented in Figure 3, all gradient lines originate or disappear only at stationary points ($\nabla E = 0$) or pass to infinity.[12] Gradient lines can not originate or disappear at regular points ($\nabla E \neq 0$). There exists a unique gradient line which goes from minimum **1** and passes *via* the first saddle point **2** and then further enters neighbouring saddle point **4**. Only one gradient line corresponding to the internal rotation of the OH group around the C–O bond in **5** connects minima **5a** to **5b** and passes *via* saddle point **4**.



2, C_s ($\lambda = 1$)

4, C_s ($\lambda = 1$)

Figure 2 Geometrical parameters of transition state structures **2** and **4** corresponding to saddle points ($\lambda = 1$) on the $NH_3\cdots H_2CO$ PES calculated by the RHF/6-31G** and MP2(full)/6-311++G** (in parentheses). Bond lengths and angles are given in angströms and degrees, respectively.

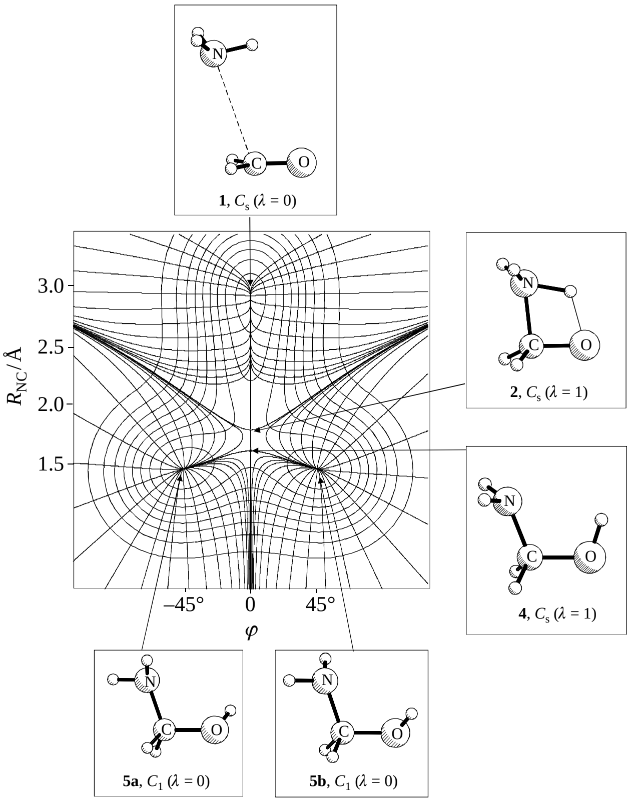


Figure 3 Two-dimensional map of $V(R,\varphi)$ approximating the $NH_3\cdots H_2CO$ PES in reaction region of NH_3 addition to formaldehyde. Closed thin lines denote equipotential lines, thin lines orthogonal to equipotential lines are gradient lines (orthogonal trajectories). Gradient line reaction path consists of two lines $\mathbf{1} \rightleftarrows \mathbf{2} \rightleftarrows \mathbf{4}$ and $\mathbf{5a} \rightleftarrows \mathbf{4} \rightleftarrows \mathbf{5b}$ from which the first corresponds to addition reaction and the second to internal rotation of OH group around C–O bond. R_{NC} denotes the N–C distance and φ is the rotational angle. Angle $\varphi = 0°$ corresponds to eclipsed conformation **4**.

Thus, the gradient line reaction path of NH_3 nucleophilic addition to H_2CO consists of two different gradient lines, one of which passes two successive saddle points **2** and **4** and further goes to infinity avoiding any minima and the other connects two minima **5a** and **5b** passing *via* saddle point **4** and corresponds to the internal rotation in **5**.

The authors thank the Ministry of General and Professional Education of the Russian Federation (grant no. 95-0-9.1-70) for financial support of the present work.

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Received: Moscow, 13th March 1997
Cambridge, 2nd April 1997; Com. 7/01775H