

Regular article

A density functional theory study of N₂O formation from the reaction of NO with pyridine and with acridine

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Abstract. The mechanism of N₂O formation from the reaction of NO with pyridine and with acridine was studied at the UB3LYP/6-311G(d,p) level. According to our results acridine as a char nitrogen model behaves better than pyridine, which is crucial to explain the appearance of the maximum of N₂O formation as experimentally reported. A rationalization is proposed in terms of the destabilization of the intermediate precursor of N₂O with the rise of temperature, and the tendency at higher temperatures to increase the competitiveness of the evolution of this intermediate to yield N₂O compared with its reversion towards the separate reactants.

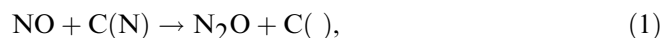
Keywords: Pyridine/acridine – N₂O formation – Density functional calculations – Effect of temperature

Introduction

The minimization of emissions of nitrogen oxides during coal combustion is one of the major environmental problems in relation to the depletion of the ozone layer, the greenhouse effect, the formation of acid rain and the generation of photochemical smog. It is well established that fuel-bound nitrogen is the main source of the N₂O emitted from coal combustion, particularly at low temperatures, as in fluidized-bed reactors [1]. During combustion, the coal nitrogen is split into volatile nitrogen and char nitrogen (char-N), so N₂O can be generated through homogeneous reactions in the gas phase and heterogeneous reactions involving the char [2, 3, 4, 5]. The heterogeneous reaction mechanisms are still not completely understood. A first approach to do it was the identifica-

tion of the nitrogen functionalities present in coal and in char. X-ray photoelectron spectroscopy analyses of coals and chars have shown the presence of pyrrolic, pyridinic and quaternary nitrogen species [6, 7, 8].

Experimental findings have explained the N₂O formation from char-N combustion taking into account the participation of O₂ in the reaction mechanisms [1, 9, 10, 11, 12, 13, 14, 15, 16, 17]. N₂O was also obtained when pyridine was burned in air in a fluidized bed [18]. In the absence of O₂ this nitrogen oxide could also be detected though the amount was low [11, 15, 19] and its has been proposed that NO reacts with char-N to form N₂O [15]



where C(N) and C() are the surface nitrogen species and the carbon-free site, respectively. When the effect of temperature on this process was investigated the maximum N₂O formation was found at about 1,100 K [15, 19].

Semiempirical calculations have found that the NO molecule chemisorbs preferentially on the N atom in the pyridine molecule [as a model C(N) compound] to form C(N)NO complexes [20]. Thus, the N₂O desorption from such C(N)NO species was proposed as a possible origin for the N₂O formation during coal combustion. Density functional theory (DFT) studies on the reaction of NO with different models of a carbonaceous surface have indicated that the NO approach perpendicular to the edge plane of the carbonaceous surface is thermally more favorable for the N atom than for the O atom [21], although the chemisorption of the NO molecule with its bond axis parallel to the edge plane has given the stablest chemisorbed species [21, 22]. The formation of N₂ from the reaction of pyridinic nitrogen models with NO has been found to be a very unfavorable process [21].

We present here a theoretical study of the N₂O formation from the reaction of NO with pyridine and with acridine as model nitrogen compounds, in order to gain greater knowledge of the heterogeneous reaction mech-

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anisms between NO and char-N during coal combustion in the absence of O₂.

Methods

Quantum chemical computations were performed with the Gaussian98 series of programs [23]. Stable species and transition states (TS) were optimized by means of the UB3LYP DFT method [24, 25, 26] with the 6-311G(d,p) basis set [27, 28], using Schlegel's algorithm [29]. No significant spin contamination in the DFT wave function of the located structures was found. Analytical computations of harmonic vibrational frequencies were carried out in order to characterize the critical points located and to evaluate the zero-point vibrational energy (ZPVE).

B3LYP/3-21G intrinsic reaction coordinate calculations starting at each saddle point verified the two minima connected by that TS using the Gonzalez and Schlegel method [30, 31] implemented in Gaussian98 with the default step size.

A statistical thermodynamics treatment was also carried out to calculate ΔH , ΔS and ΔG at 1 atm and 298, 1,100 and 1,500 K within the ideal gas, the rigid rotor and the harmonic oscillator approximations [32].

Results and discussion

We present first the results obtained for the formation of N₂O from the reaction of NO with pyridine and then the corresponding results from the reaction of NO with acridine. The relative electronic energies without and with ZPVE of the different structures located for these two processes are collected in Table 1. The optimized geometries of those structures are displayed in Fig. 1. The corresponding absolute energies and ZPVE correc-

tions are listed in Table 2. Unless otherwise stated, we give in the text UB3LYP/6-311G(d,p) energies including the ZPVE correction.

Initially the interaction between NO and pyridine gives rise to a complex C 1.5 kcal/mol stabler than the separate reactants. From C the system evolves through TSC-1 13.4 kcal/mol less stable than the reactants to give the intermediate I1 0.3 kcal/mol above TSC-1 (when the ZPVE is not included I1 is 0.1 kcal/mol under TSC-1). TSC-1 is the TS for the attack of the lone pair of the pyridinic N atom to the N atom of NO wherein the N–N distance is 1.553 Å, while at I1 it is 1.470 Å. I1 evolves to I2, 67.4 kcal/mol above the reactants, through TS1-2 with an energy barrier of 66.4 kcal/mol. At this stage the NNO moiety goes out of the plane, and as the N–N distance shortens the two C–N bonds stretch and the new C–C bond giving rise to the five-membered ring starts to form (Fig. 1). I2 renders I3, 43.1 kcal/mol less stable than the reactants, through a TS, TS2-3, for the breaking of one of the C–N bonds with an energy barrier of 6.1 kcal/mol. The rate-determining TS is thus TS1-2, which is 6.6 kcal/mol less stable than TS2-3. Finally this intermediate evolves through TS3-P for the rupture of the remaining C–N bond with an energy barrier of 15.7 kcal/mol to give the products, N₂O and a cyclopentadienyl radical, 27.2 kcal/mol above the reactants.

The reaction of NO with acridine to form N₂O and a fluorenyl radical proceeds through a mechanism analogous to that for pyridine. The initial complex Ca is 1.3 kcal/mol stabler than the reactants. TS1-2a and TS2-3a are 7.4 and 15.1 kcal/mol less stable, respectively, than TS1-2 and TS2-3. Therefore, in contrast with the case of pyridine, for acridine the rate-determining TS is TS2-3a, which is 1.1 kcal/mol less stable than TS1-2a. The intermediate I2a is also 19.3 kcal/mol less stable

Table 1. Relative UB3LYP/6-311G(d,p) electronic energies without (ΔE_{elec}) and with the zero-point vibrational energies (ZPVEs) ($\Delta E_{\text{elec}} + \text{ZPVE}$), enthalpies (ΔH), entropy contributions ($-T\Delta S$) and Gibbs free energies (ΔG) in kilocalories per mole of chemically important structures located for the N₂O formation from the reaction of NO with pyridine and with acridine at 298, 1,100 and 1500 K

Species	ΔE_{elec}	$\Delta E_{\text{elec}} + \text{ZPVE}$	298 K			1,100 K			1,500 K		
			ΔH	$-T\Delta S$	ΔG	ΔH	$-T\Delta S$	ΔG	ΔH	$-T\Delta S$	ΔG
NO + pyridine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	-2.0	-1.5	-1.1	6.1	5.0	1.3	18.3	19.6	2.5	23.6	26.1
TSC-1	12.6	13.4	12.4	11.2	23.6	13.3	39.7	53.0	13.8	53.6	67.4
I1	12.5	13.7	13.0	10.9	23.9	15.4	35.9	51.3	16.7	47.4	64.1
TS1-2	81.1	80.1	79.3	10.9	90.2	81.0	37.2	118.2	81.7	50.0	131.7
I2	67.3	67.4	66.6	11.0	77.6	69.6	35.5	105.1	71.0	46.8	117.8
TS2-3	74.3	73.5	72.6	10.9	83.5	74.3	37.6	111.9	74.9	50.5	125.4
I3	42.2	43.1	42.6	9.8	52.4	45.0	32.0	77.0	46.3	42.1	88.4
TS3-P	59.5	58.8	58.4	9.7	68.1	60.0	32.8	92.8	60.5	44.0	104.5
N ₂ O + cyclopentadienyl radical	29.7	27.2	27.6	-1.5	26.1	29.1	-7.8	21.3	29.3	-11.8	17.5
NO + acridine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca	-1.7	-1.3	-0.8	6.1	5.3	1.6	18.1	19.7	2.8	23.4	26.2
TSC-1a	16.2	16.6	15.9	10.8	26.7	16.9	38.4	55.3	17.4	51.8	69.2
I1a	13.6	15.0	14.4	10.9	25.3	16.7	36.6	53.3	17.9	48.5	66.4
TS1-2a	89.0	87.5	86.9	11.0	97.9	88.7	37.1	125.8	89.4	49.8	139.2
I2a	87.8	86.7	86.4	10.5	96.9	89.7	32.8	122.5	91.3	42.9	134.2
TS2-3a	90.0	88.6	88.1	10.8	98.9	90.0	36.5	126.5	90.6	49.0	139.6
I3a	55.2	56.0	55.6	10.1	65.7	58.0	33.1	91.1	59.3	43.6	102.9
TS3-Pa	61.9	61.3	60.9	9.7	70.6	62.3	33.5	95.8	62.8	45.0	107.8
N ₂ O + fluorenyl radical	6.1	5.7	5.6	-0.6	5.0	5.9	-3.0	2.9	6.0	-4.1	1.9

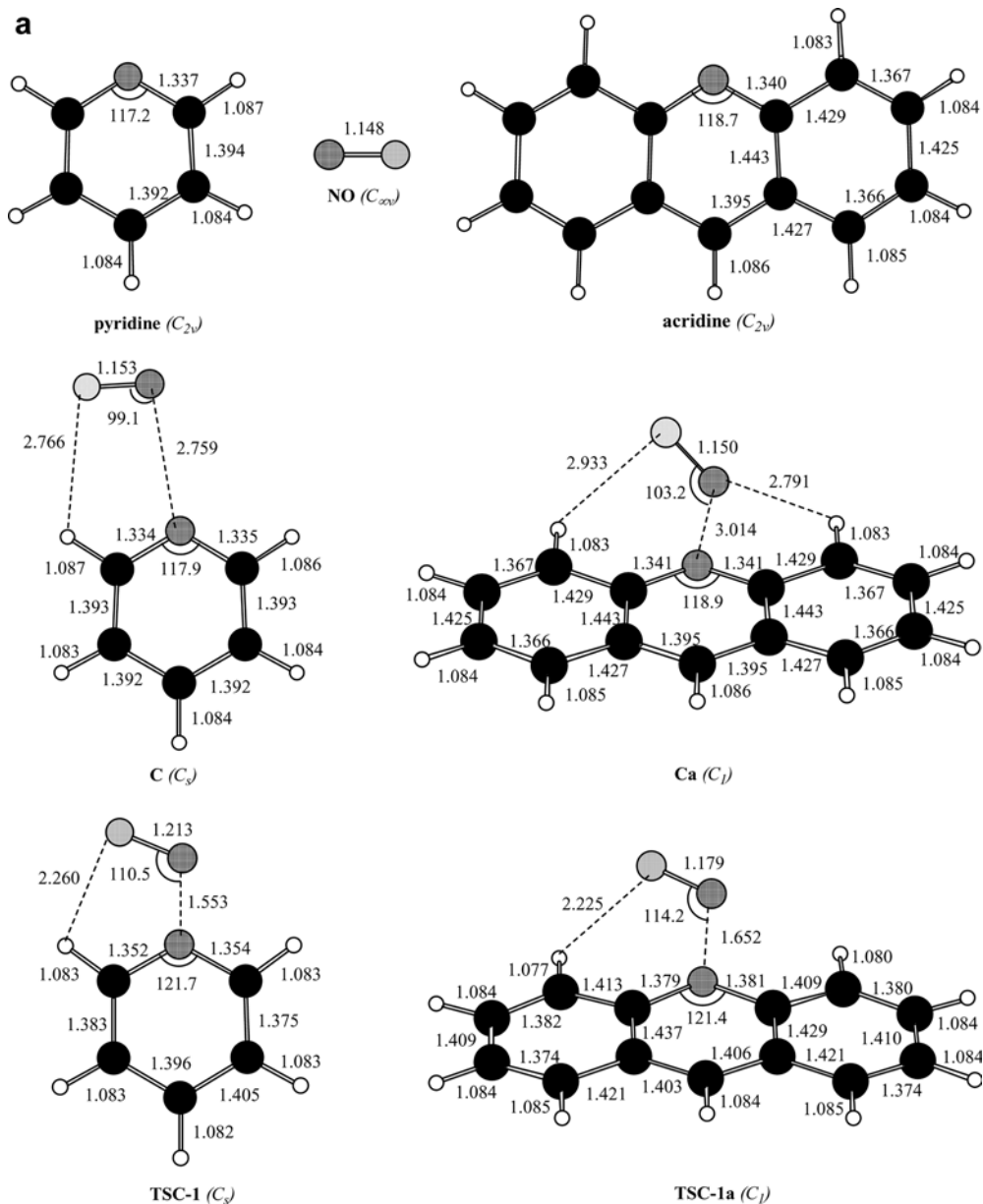


Fig. 1. UB3TYP/6-311G(d,p) optimized geometries located for the N_2O formation from the reaction of NO with pyridine and with acridine. Distances are given in angstroms and bond angles in degrees

than I2. The endoergicity of the process (5.7 kcal/mol) is smaller for acridine than for pyridine.

In order to compare our results with experiment we included the thermal energy and entropy for three different temperatures (298, 1,100 and 1,500 K). The thermodynamic magnitudes obtained for the two processes are shown in Table 1. The corresponding Gibbs energy profiles are displayed in Figs. 2 and 3. Unless otherwise indicated, the Gibbs energies will be reported in this section.

The initial complexes C and Ca disappear from the Gibbs energy profile and become less stable than the separate reactants. When including thermal energy and entropy the intermediates become less stable and the endoergicity of the processes diminishes with the rise of temperature. Given that both processes are disfavored by entropy, the energy barriers increase with tempera-

ture considerably more than the mean energy available to the reactants. In the case of pyridine TS1-2 is less stable than TS2-3 at the three temperatures considered by us and the difference in energy tends to remain constant with increasing temperature. In contrast, for acridine TS1-2a is 1 kcal/mol stabler than TS2-3a at 298 K, but the energy difference between these two TSs tends clearly to diminish as the temperature rises. This behavior of the acridine model permits the rationalization of the experimental findings, showing its better suitability for modeling char-N. In effect, at higher temperatures the energy barrier for I2a formation increases but its evolution into N_2O and a fluorenyl radical becomes comparatively more favored with respect to its decomposition into the initial reactants with increasing temperature (according to our results the rate constant for I2a reversion into I1a is 5 times

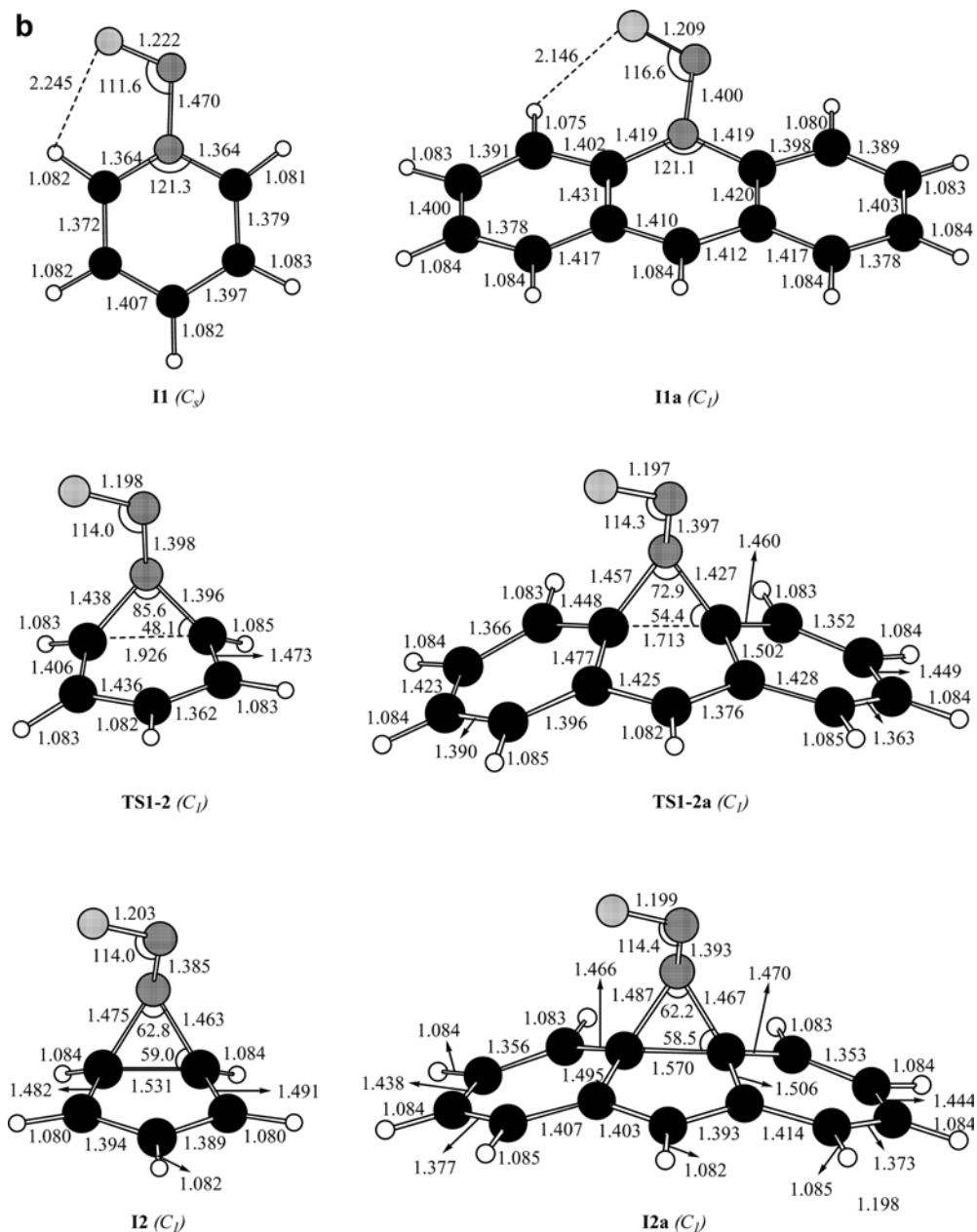


Fig. 1. (Continued)

larger than that for its evolution into I3a at 298 K and only 1.1 times larger at 1,500 K). As a consequence, the action of these two opposite factors would explain the appearance of the maximum N_2O concentration at a given temperature [15, 19]. In agreement with experimental findings [11, 15, 19] the value corresponding to this peak of the N_2O concentration is low owing to the magnitude of the energy barrier for the process.

In summary, acridine seems to model char-N better than pyridine, making possible the interpretation of the appearance of the maximum N_2O formation at about 1,100 K. According to our analysis this peak of the concentration is caused by the effect of two opposite tendencies: the formation of the intermediate precursor

of N_2O is disfavored by higher temperatures, whereas the evolution of this intermediate into the final products becomes relatively favored by increasing the temperature.

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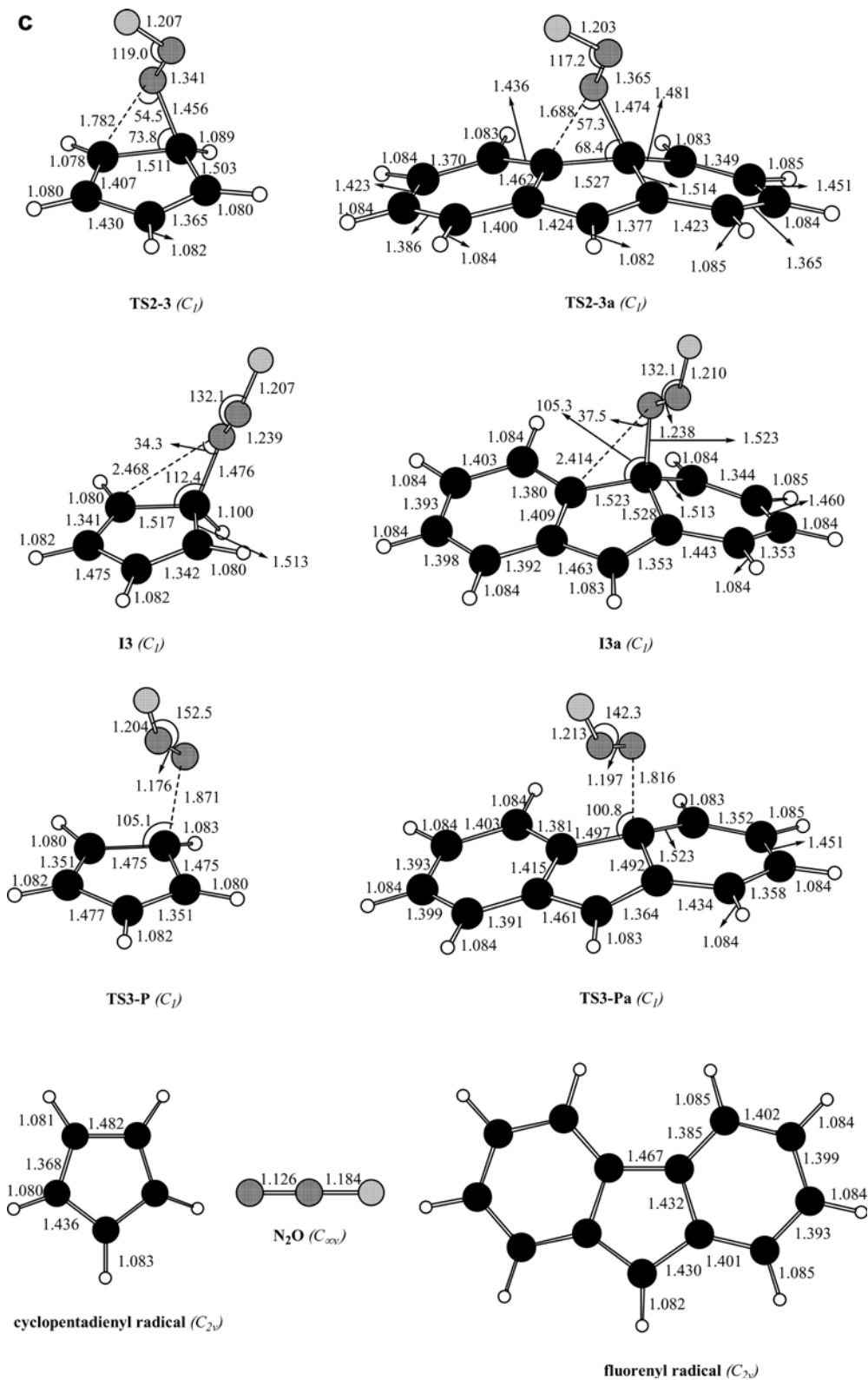


Fig. 1. (Continued)

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Table 2. UB3LYP/6-311G(d,p) absolute energies (in hartrees) and ZPVE corrections (in kilocalories per mole) for chemically important structures located for the N₂O formation from the reaction of NO with pyridine and with acridine

Species	Absolute energy	ZPVE
NO + pyridine	-378.273576	58.3
C	-378.276723	58.8
TSC-1	-378.253566	59.1
I1	-378.253719	59.5
TS1-2	-378.144297	57.3
I2	-378.166346	58.4
TS2-3	-378.155217	57.5
I3	-378.206344	59.2
TS3-P	-378.178757	57.6
N ₂ O + cyclopentadienyl radical	-378.226268	55.8
NO + acridine	-685.625243	116.8
Ca	-685.627906	117.2
TSC-1a	-685.599402	117.2
I1a	-685.603520	118.2
TS1-2a	-685.483417	115.3
I2a	-685.485269	115.7
TS2-3a	-685.481793	115.4
I3a	-685.537322	117.6
TS3-Pa	-685.526663	116.2
N ₂ O + fluorenyl radical	-685.615572	116.4

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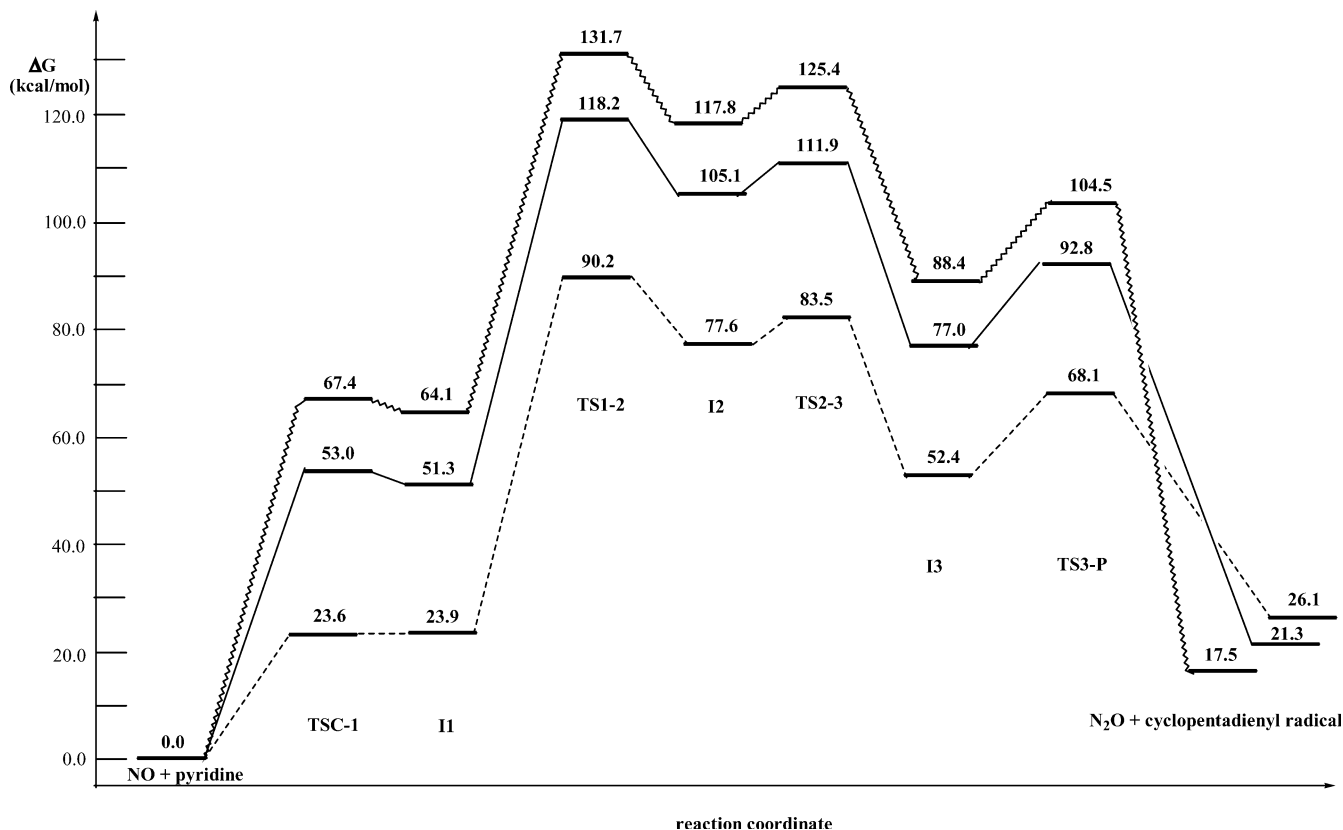


Fig. 2. ΔG profiles at 298 K (dashed line), 1,100 K (continuous line) and 1,500 K (wavy line) for the N₂O formation from the reaction of NO with pyridine

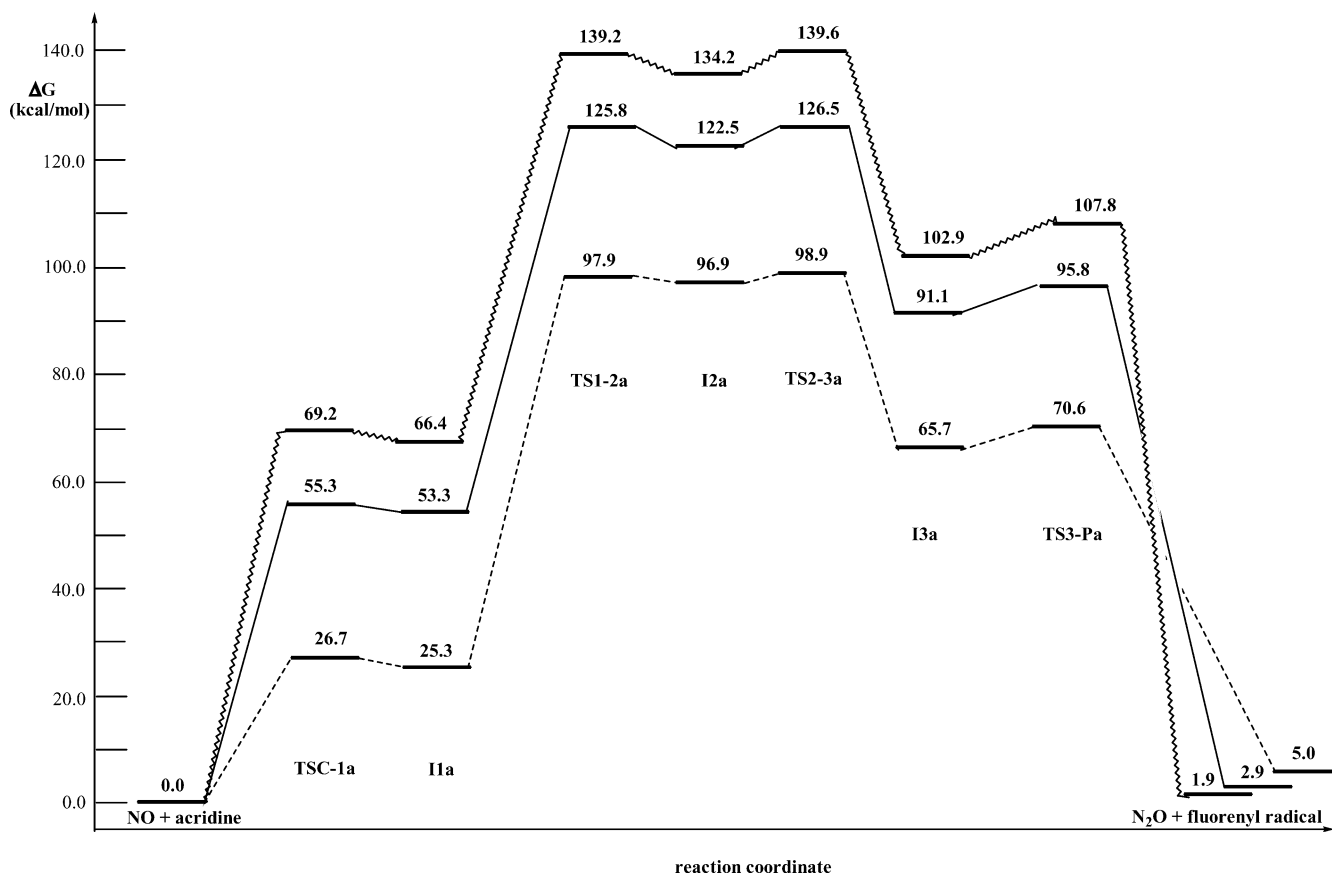


Fig. 3. ΔG profiles at 298 K (*dashed line*), 1,100 K (*continuous line*) and 1,500 K (*wavy line*) for the N_2O formation from the reaction of NO with acridine

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