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Theoretical study of the reaction of ketylenyl and nitrogen dioxide radicals ($\text{HCCO} + \text{NO}_2$)

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Abstract

Portions of potential energy surface containing low-energy pathways of $\text{HCCO} + \text{NO}_2$ reaction were constructed using the G3B3 method. These show that only two separate reaction pathways are possible leading to $\text{HCNO} + \text{CO}_2$ and $\text{HCO} + \text{NO} + \text{CO}$. Selectivity between product channels (CO_2 vs. CO) occurs very early on the attractive entrance channels. The absence of an entrance barrier is consistent with available rate constants showing their negative dependence on temperature. The product distribution estimated in this Letter is in agreement with recent experimental results of Meyer and Hershberger [J.P. Meyer, J.F. Hershberger, J. Phys. Chem. A, 109 (2005) 4772].

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1. Introduction

The ketylenyl radical (HCCO) is a predominant product of the oxidation of acetylene over a wide range of temperatures [1–3].



During hydrocarbon combustion under fuel-rich conditions, the chemical flux through the ketylenyl radical is therefore expected to be one of the largest of all the small C-containing radicals [4]. The HCCO radical takes part significantly in the removal of NO in NO_x -reburning strategies [5–8] in which nitric oxide, formed in stationary combustion systems, is removed by small radicals such as HCCO , CH , CH_2 , CH_3 , and C_2H , that are generated under fuel-rich conditions in a second combustion stage after the primary combustion zone.

The kinetics of the reaction between ketylenyl and nitric oxide has therefore attracted the attention of several groups [9–16]. The absolute rate coefficient of $\text{HCCO} + \text{NO}$ has

been determined experimentally over the range of temperature 296–802 K [9,14], and both its magnitude and temperature dependence were reproduced by theoretical evaluation [15]. It appears, both from the recent rate constant determinations showing a pronounced negative temperature dependence [14] and from the product distribution, that the $\text{HCCO} + \text{NO}$ reaction should have a smaller contribution to the natural NO_x -reburning than previously accepted [8,17]. Though it is still expected to be important in view of its production of HCNO : the subsequent reactions of which may either regenerate NO or yield HCN, the latter leading to removal of NO. It is therefore of importance to examine other potential reburning reactions that could complement the $\text{HCCO} + \text{NO}$ reaction in NO_x -reburning. The reaction between ketylenyl and nitrogen dioxide ($\text{HCCO} + \text{NO}_2$) is an obvious process that may be influential in NO_x -reburning in the temperature range below about 1400 K under fuel-rich conditions provided its products are directly involved in the reburning scheme or may be easily converted to those that are involved.

The rate constant of the $\text{HCCO} + \text{NO}_2$ reaction has recently been investigated over an extended temperature range using a laser-photofragment/laser-induced fluorescence technique [18] and earlier, at a single temperature,

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using far-infrared magnetic resonance [19]. According to Carl et al. [18] its rate coefficient exhibits a negative temperature dependence in the range of 293–769 K:

$$k(T)(\text{HCCO} + \text{NO}_2) = (2.3 \pm 0.4) \times 10^{-11} \times \exp(340 \pm 40)K/T \text{ cm}^{-3} \text{ s}^{-1}. \quad (2)$$

The corresponding Arrhenius A -factor is about 1.4 times larger than that of the $\text{HCCO} + \text{NO}$ reaction [14]. During the preparation of this manuscript a second kinetic study of $\text{HCCO} + \text{NO}_2$ over an extended temperature range has appeared in the literature [1]. These authors reported rate constants over the temperature range 295–430 K of $k = (2.43 \pm 0.26) \times 10^{-11} \exp((171 \pm 37)K/T)$, that corresponds to a fraction of 0.7 at room temperature of that reported by Carl et al. [14], but with a similar Arrhenius A -factor and also a negative temperature dependence. In the same study, the products HCNO , CO_2 and CO were quantitatively detected. No evidence was found for the production of HNCO , HNO , HCN , *trans*- HONO and NCO , though the authors caution that IR line strengths for HNO and HNCO are unknown. From these observations, product branching fractions were deduced as 0.40 ± 0.05 to $\text{HCNO} + \text{CO}_2$ and 0.60 ± 0.05 to $\text{HCO} + \text{NO} + \text{CO}$.

In this context, we set out to determine the possible products of the reaction $\text{HCCO} + \text{NO}_2$. Portions of the potential energy surface containing the reaction channel leading to the formation of possible products have thus been constructed making use of high level quantum chemical methods.

2. Computational methods

We attempt to identify the probable product channels making use of quantum chemical calculations. All calculations were performed using the GAUSSIAN 03 suite of programs [20]. Optimizations of the stationary-point geometries (reactants, products and transition structures) were conducted using density functional theory (DFT) with the popular hybrid functional, B3LYP, in conjunction with 6-311++G(d,p) basis set. The harmonic vibrational frequencies and the zero-point energies (ZPE) were also computed at B3LYP/6-311++G(d,p). The zero-point energies were scaled down by the factor of 0.9806. To confirm that a transition structure connects the right reactants and products, the intrinsic reaction coordinate (IRC) path was calculated at B3LYP/6-311++G(d,p) level. The single-point electronic energy of each optimized geometry was recalculated.

Table 1
Calculated relative energy (kcal/mol) for various fragments in the $\text{HCCO} + \text{NO}_2$ reaction using different levels of theory

	B3LYP 6-311++G(d,p)	G2M	G3B3		Exptl.
			0 K	298 K	
HCCO + NO ₂	0.0	0.0	0.0	0	0
HCNO + CO ₂ (9)	−98.4	−104.7	−105.2	−105.2	−100
HOCNO + CO (10)	−51.3	−62.4	−61.2	−61.1	
HCO(CO) + NO(11)	−42.5	−46.4	−44.0	−43.9	
HCO + CO + NO(12)	−38.9	−51.1	−46.0	−44.7	−44
H + 2(CO) + NO(13)	−18.7	−38.4	−31.6	−29.1	
HONO + CCO	24.8	20.0	21.7	21.6	
HCCO-NO + O	30.5	25.9	27.7	27.5	
HCNO ₂ (t) + CO	22.1	14.9	15.5	15.3	
HCNO ₂ (s) + CO	16.1	2.7	5.4	5.2	
CNO + OH + CO	29.2	21.8	26.1	27.6	
HOCO + CNO	3.8	−0.4	3.6	3.6	
OCCNO + OH	3.9	10.3	6.9	7.3	
OCCNOO + H	53.1	50.6	51.4	51.7	
M1	−51.3	−58.6	−58.0	−59.3	
M2 _{trans}	−44.3	−52.5	−51.8	−52.5	
M2 _{cis}	−44.2	−51.2	−50.4	−51.3	
M3	−28.8	−32.3	−31.9	−33.1	
M4	−45.6	−56.6	−55.7	−60.9	
M5	−55.1	−69.3	−66.9	−67.6	
M6	−83.0	−90.2	−91.1	−92.2	
M7	−56.1	−61.4	−61.0	−61.8	
TS1-2	24.2	17.5	16.7	−16.2	
TS1-3	−6.1	−9.5	−9.5	−10.9	
TS1-4	−41.4	−49.5	−48.9	−50.6	
TS2-5	−34.0	−41.8	−40.3	−41.3	
TS4-9	−39.8	−45.8	−46.5	−47.9	
TS3-6	−11.9	−16.2	−16.9	−18.3	
TS6-7	−15.3	−16.3	−17.6	−18.7	
TS7-10	−42.6	−52.1	−51.0	−51.7	
TS11-12	−32.7	−40.0	−35.9	−35.5	
TS12-13	−17.5	−35.1	−29.7	−28.1	

lated using the coupled-cluster CCSD(T)/6-311++G(d,p) method, followed by extrapolating to CCSD(T)/6-311++G(3df,2p) level using MP2/6-311++G(3df,2p) energy following an additive scheme:

$$\begin{aligned} \text{G2M} = & \text{CCSD(T)}/6\text{-}311++\text{G(d,p)} + [\text{MP2}/6\text{-}311 \\ & + +\text{G(3df,2p)} - \text{MP2}/6\text{-}311 + +\text{G(d,p)}] + 0.9806 \\ & * \text{ZPE(B3LYP)} \end{aligned}$$

which was known as the G2M(CC,MP2) approach [21]. In addition, the G3B3 approach [22] was also used. It is expected that both the G3B3 and G2M(CC,MP2) techniques can reproduce relative energies within the chemical accuracy, e.g., a deviation of about 1 or 2 kcal/mol as compared to experimental data [23–26]. The calculated reaction enthalpies are presented in Table 1, which shows that for minima and transition structures, the G2M values agree well with those of G3B3, but the G3B3 values for fragments are in better agreement with available experimental data. Therefore, we have chosen the G3B3 values for the following discussion, unless mentioned otherwise.

3. Results and discussion

3.1. Some thermochemical parameters of HCCO

The ketylenyl radical has been the subject of several experimental and theoretical studies [23–31]. Its geometry, electronic structure and vibrational frequencies have been well established. Some of its basic thermochemical parameters have also been determined experimentally including heat of formation (ΔH_f) [28], and electron affinity (EA) [25,26]. As a preliminary calibration for the method employed, we have first evaluated a few parameters of HCCO. Table 2 lists the calculated values for ΔH_f , EA, IE, PA (proton affinity), and BDE (bond dissociation energy) using B3LYP and G3B3 quantum chemical methods. As seen in Table 2, the values computed at both methods agree well with each other and also with the available experimental data. However, the G3B3 values are in closer agreement

with experiment, i.e., a deviation of about 1 kcal/mol. These results convince us to use the G3B3 energy scheme to construct the potential energy surface.

Earlier EA and ΔH_f for HCCO measured by Oakes et al. [25] amount to 2.350 ± 0.020 eV and 42.4 ± 2.1 kcal/mol, respectively, using negative ion photoelectron spectroscopy. They were re-measured by the Neumark's group [24,26] using fast radical beam photofragment translational spectroscopy; namely $\text{EA} = 2.338 \pm 0.008$ and $\Delta H_f = 42.2 \pm 0.7$ kcal/mol, in excellent agreement with the former values. Our calculations at the G3B3 level predict $\text{EA} = 2.30$ eV and $\Delta H_f = 41.3$ kcal/mol, resulting in a deviation of only 1 kcal/mol from experiment. In addition, we computed BDE(C–H) of ketene to be 105.7 kcal/mol, in excellent agreement with the value of 105.9 ± 2.1 kcal/mol derived by experiment [25,32]. To our best knowledge, both IE and PA for ketylenyl radical have not been determined experimentally yet. Our G3B3 calculations predict $\text{IE} = 10.02$ eV and $\text{PA} = 197.3$ kcal/mol, with a probable error of ± 1 kcal/mol, i.e., a similar error can be expected as the cases of EA and ΔH_f .

3.2. Potential energy surface

As far as we are aware, there are no previous quantum chemical calculations on the (HCCO + NO₂) system, whose potential energy surface constructed using the G3B3 method is presented in Fig. 1. At the first step of the reaction, the C-atom with an unpaired electron of HCCO can add onto either the central N or the O end of NO₂ leading to the adducts **M1** and **M2**, respectively. These additions occur on the singlet surface and are barrierless as a result of combination of two unpaired electrons to form a single chemical bond with high exothermicity. The **M1** is 58.0 kcal/mol below the initial reactants and has a C_s point group.

There are three possible pathways starting from the nitro-compound **M1**: (i) a ring-closure to **M4** via **TS1-4**, which has a very low barrier height of 9.1 kcal/mol; (ii) a 1,3-H-shift to **M3** via **TS1-3**, which faces a barrier height of 48.5 kcal/mol; (iii) a rearrangement to the nitrite **M2** via **TS1-2**, which is very tight. This step is prohibited by a large barrier, up to 74.7 kcal/mol. In an earlier study for the CH₃ + NO₂ reaction, a similar barrier height of 69 kcal/mol computed at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ level was also found [33]. It is clear that the two latter steps cannot compete with the former via **TS1-4**, in such a way that they are not expected to play any important role in forming final products. A lifetime of ~ 2 ps is estimated using the RRKM theory, for **M1** which, once formed, will rearrange rapidly to **M4** under low and moderate pressures ($P \leq 1$ atm). The isomer **M4** lies 55.7 kcal/mol below the initial reactants and has a C_s point group. This can either isomerise back to **M1** via **TS1-4**, or decompose directly to final products HCNO + CO₂ via **TS4-9**. The barrier heights are 6.8 and 9.2 kcal/mol for the former and latter channel, respectively. Therefore, the

Table 2
Calculated thermochemical parameters of ketylenyl radical using the (U)B3LYP/6-311++G(d,p) and G3B3 methods

Parameter	B3LYP	G3B3	Exptl.
ΔH_f (0 K) (kcal/mol)	43.4	40.7	42.0 ± 0.7^a
ΔH_f (298 K) (kcal/mol)	43.7	41.3	42.2 ± 0.7^b 42.4 ± 2.1^c
EA (eV)	2.31	2.30	2.350 ± 0.022^c 2.338 ± 0.008^d
IE (eV)	10.00	10.02	
PA (kcal/mol)	194.3	197.2	
BDE ₂₉₈ (kcal/mol) (H–HCCO)	103.4	105.7	105.9 ± 2.1^c

Experimental data were given for the purpose of comparison.

^a Ref. [24].

^b Ref. [26].

^c Ref. [25].

^d Ref. [32].

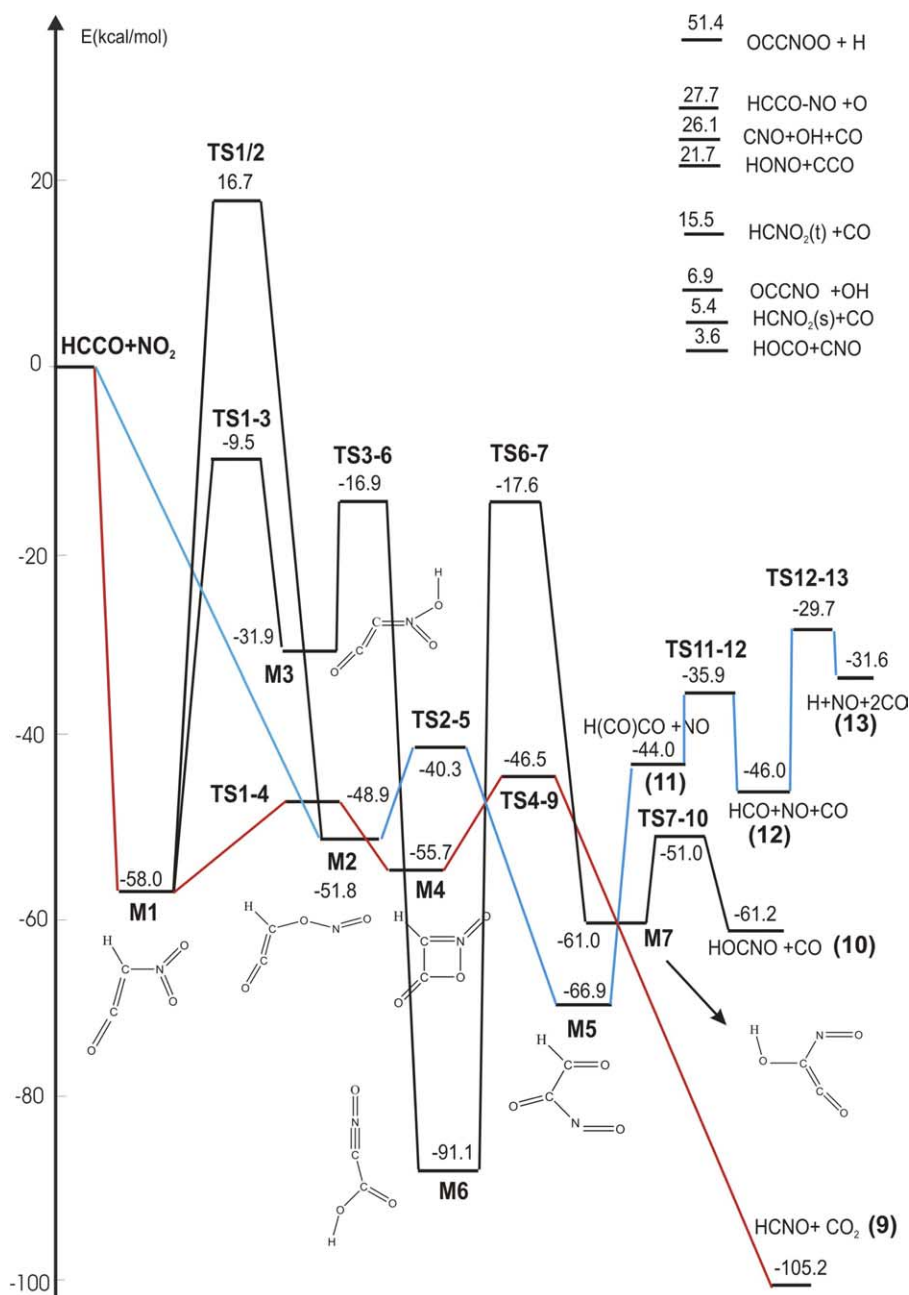


Fig. 1. Portion of the potential energy surface for HCCO + NO₂ reaction constructed using the G3B3 method.

rearrangement of **M4** back to **M1** is slightly more favoured than its dissociation into the final products. That results in a marginal prolongation of the lifetime of **M1**, from ~2 to ~3 ps (for geometries, see Figs. 2 and 3).

The isomer **M3**, being 31.9 kcal/mol below the initial reactants, once formed, undergoes a 1,3-OH migration to **M6** via **TS3-6**. This step is characterized by a barrier height of 15.0 kcal/mol. The isomer **M6** has a C_s symmetry and lies in a deep well with an internal energy of 91.1 kcal/mol relative to the initial reactants. If **M6** is produced as an intermediate in this reaction, it might be trapped as a final product under a high pressure upon loss of its internal energy by colliding with a bath gas. **M6** could proceed by further rearrangement to **M7** via **TS6-7** by a 1,2-OH migra-

tion. This step is energy-demanding with a high barrier of 73.5 kcal/mol. The intermediate **M7**, having very high internal energy of 61 kcal/mol, if formed, will rapidly dissociate to final products HOCNO + CO via **TS7-10** with a barrier height of only 10.0 kcal/mol.

The structure **M2t**, being a *trans*-form of **M2**, formed from addition of HCCO to NO₂ at the first step, lies 51.8 kcal/mol lower in energy than the initial reactants and has no symmetry. The *cis*-form **M2c** is another conformer of **M2** and lies 1.4 kcal/mol higher. Thus, **M2**, once formed, will rapidly rearrange into **M5** via **TS2-5** by a 1,3-NO migration and a barrier height of 11.5 kcal/mol. Using the RRKM theory [34], a lifetime for **M2** was estimated to be about 1.5 ps, slightly shorter than that of 2 ps for **M1**.

Hence, a re-dissociation of **M2** back to the initial reactants is neither predicted, nor a stabilization of **M2** under reaction conditions of $P \leq 1$ atm and $T \leq 1500$ K. The structure **M5** is 66.9 kcal/mol lower in energy than the initial reactants. It can dissociate to $\text{HC(=O)CO} + \text{NO}$ without an exit barrier, or could rearrange back to **M2** via **TS2-5**, but this step faces a higher barrier and **TS2-5** is also tighter. Therefore, the $\text{M5} \rightarrow \text{HC(=O)CO} + \text{NO}$ step is kinetically and thermodynamically more favoured than the $\text{M5} \rightarrow \text{TS2-5} \rightarrow \text{M2}$ step. The intermediate product HC(=O)CO containing a high internal energy of 44 kcal/mol will decompose rapidly into $\text{HCO} + \text{CO}$ via a **TS11-12** with a barrier of 8.1 kcal/mol, followed by a direct dissociation of HCO to final products $\text{H} + \text{CO}$, if HCO possesses enough internal energy to overcome a barrier height of 16.3 kcal/mol.

In summary, a combination of the C-atom of HCCO with the N atom in NO_2 via the adduct **M1** entirely leads to CO_2 product, whereas combination with an O atom in NO_2 via the adduct **M2** produces almost exclusively CO

product. An inter-conversion between **M1** and **M2** via **TS1-2**, which is located at 16.7 kcal/mol above the initial reactants, is negligible since this step faces a very large barrier of ~ 70 kcal/mol. As a result, there are two major product channels: (i) $\text{HCCO} + \text{NO}_2 \rightarrow \text{M1} \rightarrow \text{M4} \rightarrow \text{HCNO} + \text{CO}_2$ and (ii) $\text{HCCO} + \text{NO}_2 \rightarrow \text{M2} \rightarrow \text{M5} \rightarrow \text{HCO} + \text{NO} + \text{CO}$ (or $\text{H} + \text{NO} + 2\text{CO}$).

3.3. Product distribution

Because there is no entrance-channel adiabatic barrier to this reaction, calculation of the overall rate constant and its temperature dependence requires a variational approach, which is beyond the scope of the present Letter. The observed negative temperature dependence for the $\text{HCCO} + \text{NO}_2$ reaction is consistent with the attractive entrance channels given in this Letter where the variational transition states, at the position of a maximum of free energy of activation, move closer to the initial adducts and become tighter with increasing temperature. This phenomenon is

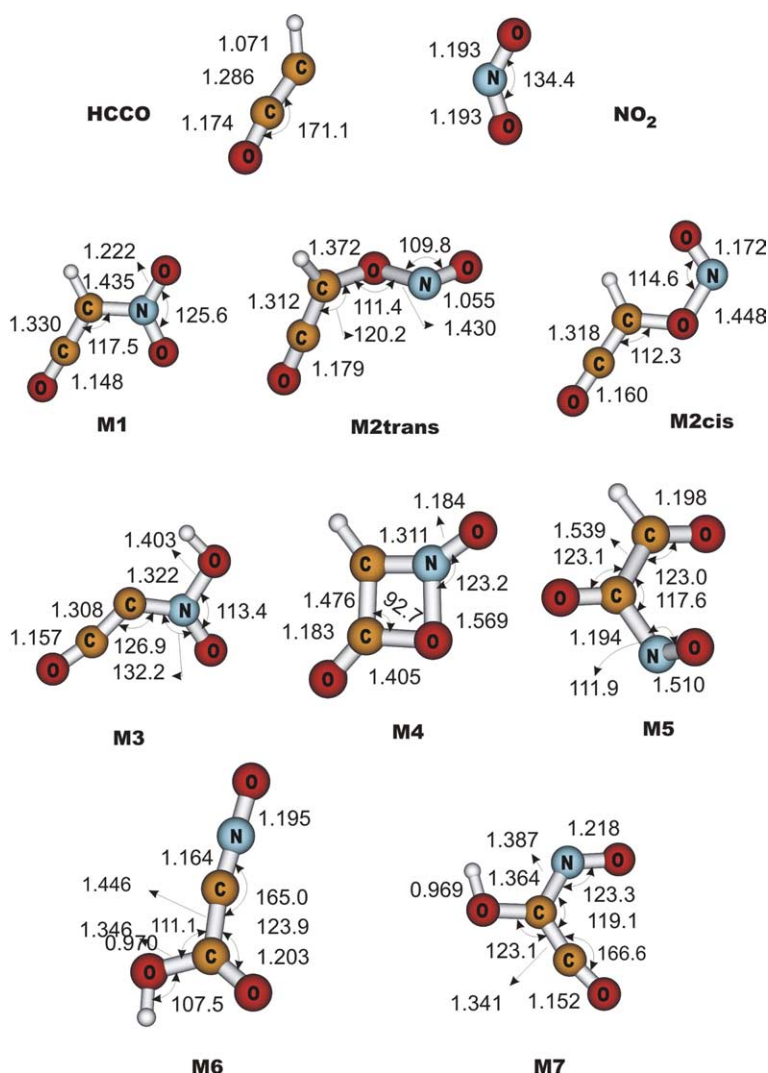


Fig. 2. Optimized geometries for reactants and intermediates in the $\text{HCCO} + \text{NO}_2$ reaction. Bond lengths are given in Å and bond angles in degree.

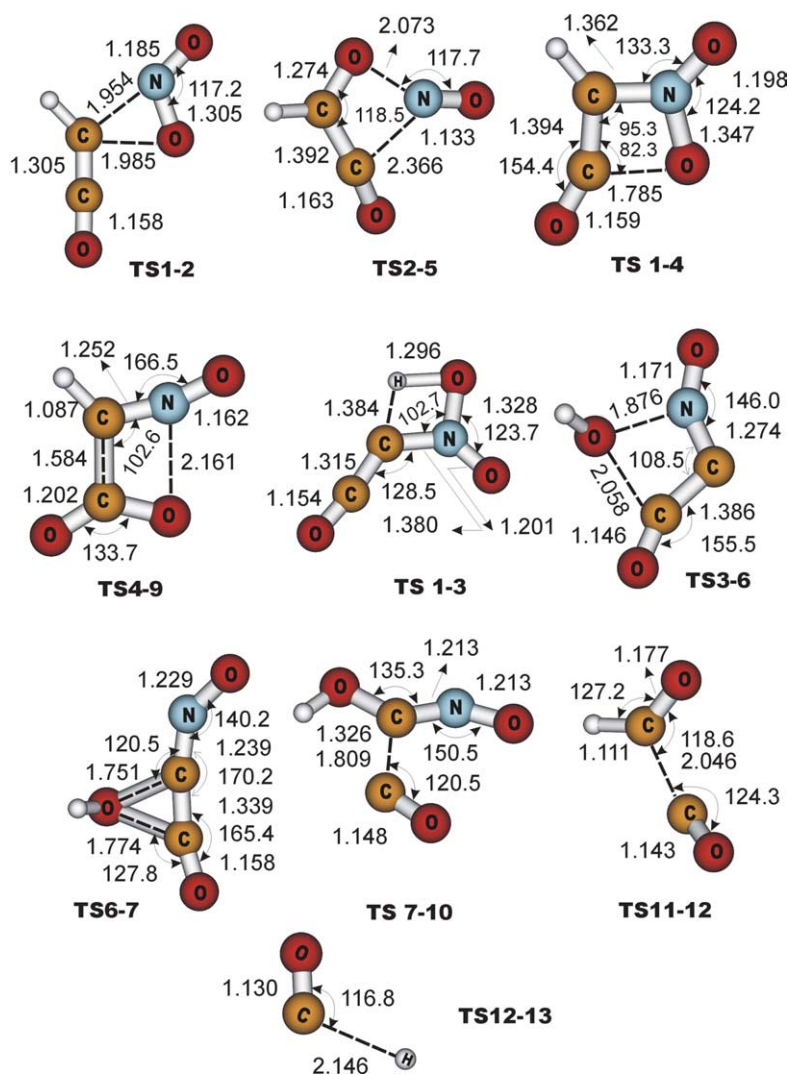


Fig. 3. Optimized geometries for the transition structures in the HCCO + NO₂ reaction. Bond lengths are given in angstrom and bond angles in degree.

also observed for the HCCO + NO reaction and described theoretically by Tokmakov et al. [15]. Since this behaviour is not described by a simple function of temperature extrapolation of rate constants beyond the experimental temperature range must be done with caution. A negative temperature dependence can also occur if there is significant re-dissociation of the initially-formed complex. Here however, this is not the case due to their very short lifetimes, which also excludes any pressure dependence for this reaction.

As discussed above, despite the large number of possible product channels, it is clear from the potential energy surface given in Fig. 1 that only two pathways to products can be significant: that leading to HCNO + CO₂ and that leading to HCO + NO + CO. These pathways are well separated from each other by relatively high barriers so that exchange between them once the initial complexes are formed should be negligible. Selection between one or other pathway must therefore occur in the entrance channel at relatively large internuclear distances. At first sight one would

expect the formation of **M2** (ONO–C) to be more favoured than **M1** (O₂N–C) given that the distance of the NO₂ centre of mass from the C is significantly larger for **M2** (ca 2.2 Å) than for **M1** (ca 1.4 Å). Since the complexes have about the same energy one would expect that attraction due to ONO–C orientation begins earlier than that for O₂N–C. That there appears to be no significant selectivity between these two channels might imply that once a critical relative distance is reached, at which point there is still little hindrance to NO₂ rotation, NO₂ and HCCO come together very quickly so the NO₂ orientation after this critical distance is effectively frozen. This would then give an approximate 50:50 branching ratio to **M1** and **M2**.

Following their formation, **M1** and **M2** are expected to quickly traverse TS1-4 → **M4** → TS4-9 → HCNO + CO₂ and TS2-5 → **M5** → H(CO)CO + NO → TS11-12 → HCO + NO + CO, respectively. The fate of both HCNO and HCO depends on their nascent vibrational energy content. Given the 104 kcal/mol excess energy available to HCNO + CO₂, it is conceivable that a fraction of HCNO

undergoes isomerisation to HNCO via HONC and cyclic C(H)NO(¹A₁), requiring about 80 kcal/mol [35]. The structure of **TS4-9** though suggests a sizable portion of the energy associated with final fission to products (60 kcal/mol), will be associated with relative translation of HCNO and CO₂. For this channel, a statistical portioning of internal energy of the products is unlikely given the relative low-lying TS's to products following formation of chemically-activated **M1**.

The HCO product on the other hand requires only about 16 kcal/mol from the excess energy of 46 kcal/mol to dissociate to H + CO. Thus the channel H + NO + 2CO might be significant, in which case the experimentally-determined branching fractions [1] would slightly be altered, as they were based on [CO], [CO₂] and [HCNO] measurements with the assumption of an average of 1.63 CO being produced for every HCO product (owing to further reactions involving excess NO₂). Nevertheless our PES supports the general conclusions of Meyer and Hersberger of only two pathways being operative, leading to HCNO + CO₂ and HCO + NO + CO, with a fraction of HCO possibly dissociating to H + CO.

4. Concluding remarks

At combustion temperatures below about 1300 K where it is expected that a significant fraction of NO_x is in the form of NO₂ the title reaction had the potential to contribute to NO_x-reburning if the products NH₂, N, NCO, and NH were formed. This is because there remains only one final step of reaction with NO to yield N₂. However we show clearly that this is not the case. A predicted major product, HCNO, can also take part in NO_x reburning, but its influence is diluted given: (1) the possibility of regenerating NO (via reaction with O or OH) and (2) that several more reaction steps are required to give N₂. The title reaction could however be a significant competitive removal pathway for HCCO and should therefore be included in NO_x combustion models, especially at temperatures below about 1300 K.

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