Journal of Chemistry, Vol. 45 (2), P. 223 - 227, 2007

STUDY ON THE PATHWAYS OF THE REACTION OF KETENYL RADICALS AND NITROGEN DIOXIDE (HCCO + NO_2)

Received 23 May 2006

LAM NGOC THIEM [1], MAI THU HIEN[2], NGUYEN THANH LAM[3], SHAUN A. CARL[3], NGUYEN MINH THO[3]

[1]*Vietnam National University*

[2]*Institute of Industrial Chemistry*

[3]*Department of Chemistry, University of Leuven, Belgium*

SUMMARY

Using the G3B3 method, we constructed the portions of potential energy surface containing low-energy pathways of HCCO + NO_2 reaction. These show that only two separate reaction pathways are possible leading to HCNO + CO_2 and HCO + NO + CO.

I - INTRODUCTION

During hydrocarbon combustion under fuel-rich conditions, the chemical flux through the ketenyl radical is therefore expected to be one of the largest of all the small C-containing radicals [1]. The HCCO radical takes part significantly in the removal of NO in NO_x-reburning strategies [2 - 5] in which nitric oxide, formed in stationary combination 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.

In this context, we set out to determine the possible products of the reaction HCCO + 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.

II - 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 [7]. 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) basic 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 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:

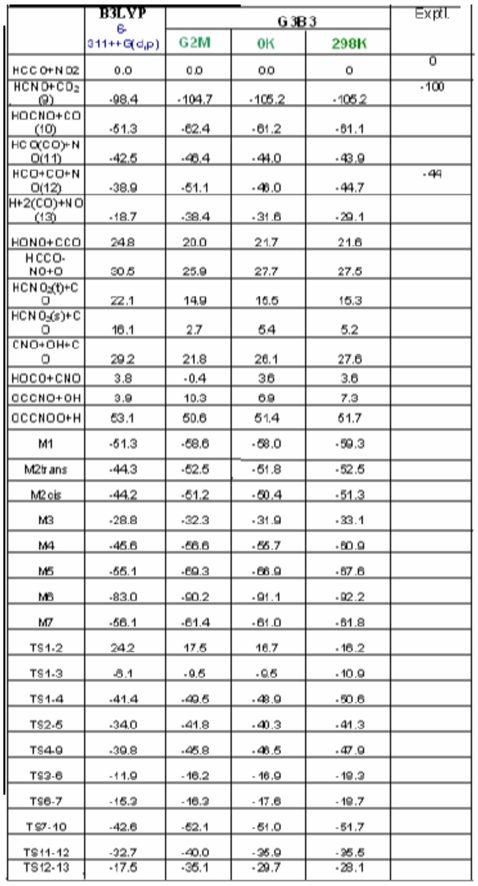
G2M = CCSD(T)/6-311++G(d,p) +[MP2/6-311++G(3df,2p) – MP2/6-311++G(d,p)] +

0.9806*ZPE(B3LYP) which was known as the G2M(CC,MP2) approach [8]. In addition, the G3B3 approach [9] 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 [10 - 13].

III - RESULTS AND DISCUSSION

1. Potential energy surface

As far as we are aware, there are no previous quantum chemical calculations on the (HCCO + NO_2) system, whose potential energy surface constructed using the G3B3 method is presented in Figure 1 and table 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 NO_2 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.



	B3LYP 6-311++G(d,p)	G3B3			Expt.
		G2M	0K	298K	
HCCO+NO2	0.0	0.0	0.0	0	0
HCNO+CO2 (9)	-98.4	-104.7	-105.2	-105.2	-100
HOCNO+CO (10)	-51.3	-62.4	-61.2	-61.1	
HC(O)(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	
HCNO2(t)+CO	22.1	14.9	15.5	15.3	
HCNO2(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	
M2trans	-44.3	-52.5	-51.8	-52.5	
M2cis	-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	-8.1	-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	-19.3	
TS6-7	-15.3	-16.3	-17.6	-19.7	
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	

Table 1: Calculated relative energy (kcal/mol) for various fragments in the HCCO + NO_2 reaction using different levels of theory

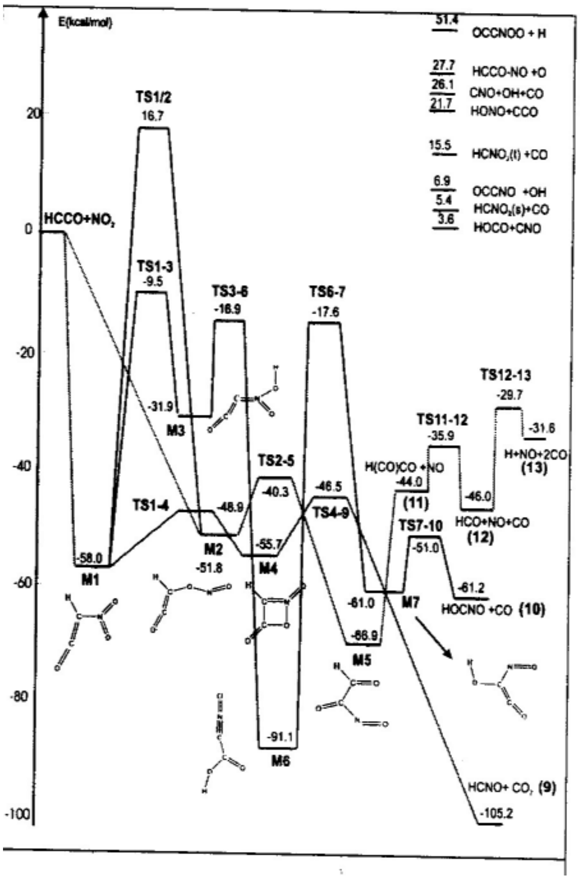


Figure 1: Portion of the potential energy surface for HCCO+NO_2 reaction constructed using the G3B3 method

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; and finally (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 CH_3 + NO_2 reaction, a similar barrier height of 69 kcal/mol computed at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ level was also found [14]. 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 ≤ 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 + CO_2 via **TS4-9**. The barrier heights are 6.8 and 9.2 kcal/mol for the former and latter channel, respectively. Therefore, the 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 ps to ~3 ps.

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 migration. 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 NO_2 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, 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 ≤ 1 atm and T ≤ 1500 K. The structure **M5** is 66.9 kcal/mol lower in energy than the initial reactants. It can dissociate to HC(=O)CO + 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 **M5** → HC(=O)CO + NO step is kinetically and thermodynamically more favoured than the **M5** → **TS2-5** → **M2** step. The intermediate product HC(=O)CO containing a high internal energy of 44 kcal/mol will decompose rapidly into HCO + CO via a **TS11-12** with a barrier of 8.1 kcal/mol, followed by a direct dissociation of HCO to final products H + 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) HCCO + NO_2 → **M1** → **M4** → HCNO + CO_2 and (ii) HCCO + NO_2 → **M2** → **M5** → HCO + NO + CO (or H + NO + 2CO).

2. 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 work. The observed negative temperature dependence for the HCCO + NO_2 reaction is consistent with the attractive entrance channels given in this work 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 also observed for the HCCO + NO reaction and described theoretically by Tokmakov et al [6]. 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 figure 1 that only two pathways to products can be significant: that leading to HCNO + CO_2 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 site one would expect the formation of **M2** (ONO—C) to be more favoured than **M1** (O_2N—C) given that the distance of the NO_2 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 O_2N—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 NO_2 rotation, NO_2 and HCCO come together very quickly so the NO_2 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 + CO_2 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 + CO_2, it is conceivable that a fraction of HCNO undergoes isomerisation to HNCO via HONC and cyclic C(H)NO($^1A_1$), requiring about 80 kcal/mol [14]. 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 CO_2. 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], [CO_2] 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 NO_2). Nevertheless our PES supports the general conclusions of Meyer and Hersberger of only two pathways being operative, leading to HCNO + CO_2 and HCO + NO + CO, with a fraction of HCO possibly dissociating to H + CO.

IV - CONCLUSION

At combustion temperatures below about 1300 K where it is expected that a significant fraction of NO_x is in the form of NO_2 the title reaction had the potential to contribute to NO_x-reburning if the products NH_2, N, NCO, and NH were formed. This is because there remains only one final step of reaction with NO to yield N_2. 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 N_2. The title reaction could however be a significant competitive removal pathway for HCCO and should therefore been included in NO_x combustion models, especially at temperatures below about 1300 K.

REFERENCES

1. J. Warnatz. Symp. Int. Combust., 24, 553 (1992).
2. P. Kilpinen, P. Glarborg, M. Hupa. Ind. Eng. Chem. Res., 31, 1477 (1992).
3. P. Dagant, F. Lecomte, S. Chevailler, M. Cathonnet. Combus Flame, 119, 494 (1999).
4. C. T. Bowman. Symp. Int. Combust. Boc., 24, 859 (1992).
5. P. Glarborg, M. U. Alzueta, K. Dam-Johansen. J. A. Miller. Combust. Flame 115, 1 (1998).
6. I. V. Tokmakov, L. V. Moskeleva, D. V. Paschenko, M. C. Lin. J. Phys. Chem. A, 107, 1066 (2003).
7. M. J. Frisch et al, Gausian 03, Revision B.03.
8. A. M. Mebel, K. Morokuma, M. C. Lin. J. Chem. Phys., 103, 7414 (1995).
9. A. G. Baboul, L. A. Curtiss, P. C. Redfern. J. Chem. Phys., 110, 7650 (1999).
10. D. H. Mordaunt. J. Chem. Phys., 105, 6078 (1996).
11. D. L. Osborn, D. H. Mordannt, H. Choi, R. T. Bise, D. M. Neumark, C. Mc. Rohlfing. J. Chem. Phys., 106, 10087 (1997).
12. J. M. Oaker, M. E. Jones, V. M. Bierbaum, G. B. Ellison. J. Phys. Chem., 87, 4810 (1983).
13. B. Schäfer-Bung, B. Engels, T. R. Taylor, D. Neumark, P. Botschwina, M. Peric. J. Chem. Phys, 115, 1777 (2001).
14. M. T. Nguyen, H. T. Le, B. Hajgato, T. Veszpremi, M. C. Lin. J. Chem. Phys. A, 107, 4286 (2003).
15. W. A. Shapely, G. B. Bacskay. J. Phys. Chem. A 103, 6624 (1999).