



The ozone–acetylene reaction: concerted or non-concerted reaction mechanism? A quantum chemical investigation

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Abstract

The ozone–acetylene reaction is found to proceed via an intermediate van der Waals complex (rather than a biradical), which is the precursor for a concerted symmetry-allowed [4 + 2] cycloaddition reaction leading to 1,2,3-trioxolene. CCSD(T)/6-311G+(2d, 2p) and CCSD(T)/CBS (complete basis set) calculations predict the ozone–acetylene van der Waals complex to be stable by 2.2 kcal mol⁻¹, the calculated activation enthalpy for the cycloaddition reaction is 9.6 kcal mol⁻¹ and the reaction enthalpy -55.5 kcal mol⁻¹. Calculated kinetic data for the overall reaction ($k = 0.8 \text{ l mol}^{-1} \text{ s}^{-1}$, $A = 1.71 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$, $E_a = 8.6 \text{ kcal mol}^{-1}$) suggest that there is a need for refined kinetic measurements. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The reaction of ozone with unsaturated hydrocarbons (ozonolysis) is one of the best investigated chemical reactions as is documented in more than a dozen review articles and hundreds of research papers published in the last 30 years [1–4]. Nevertheless, there is still a question about how the reaction actually proceeds, namely as a typical concerted symmetry allowed [4 + 2] cycloaddition reaction or as a two-step reaction involving a biradical intermediate. It is generally considered that the concerted reaction dominates the reaction mechanism of the ozonolysis in solution while

non-concerted paths may be present in the gas phase mechanism [1–7].

Experimental evidence for a biradical-involving two-step mechanism was put forward already in 1969 by DeMore [8] on the basis of kinetic measurements. He found an A factor of $3.16 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for the ozone–acetylene reaction which is much larger than that for the ozone–ethene reaction ($A = 2 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$). The Arrhenius activation energy E_a was measured to be $10.8 \pm 0.4 \text{ kcal mol}^{-1}$ in contrast to $4.7 \pm 0.2 \text{ kcal mol}^{-1}$ determined for the ozone–ethene reaction [8]. DeMore could explain the difference in the A factors by assuming for the ethene reaction a tight transition state (TS) as it would result from a five-membered ring-type approach typical of a symmetry-allowed concerted reaction; for the acetylene reaction he assumed a loose TS typical of

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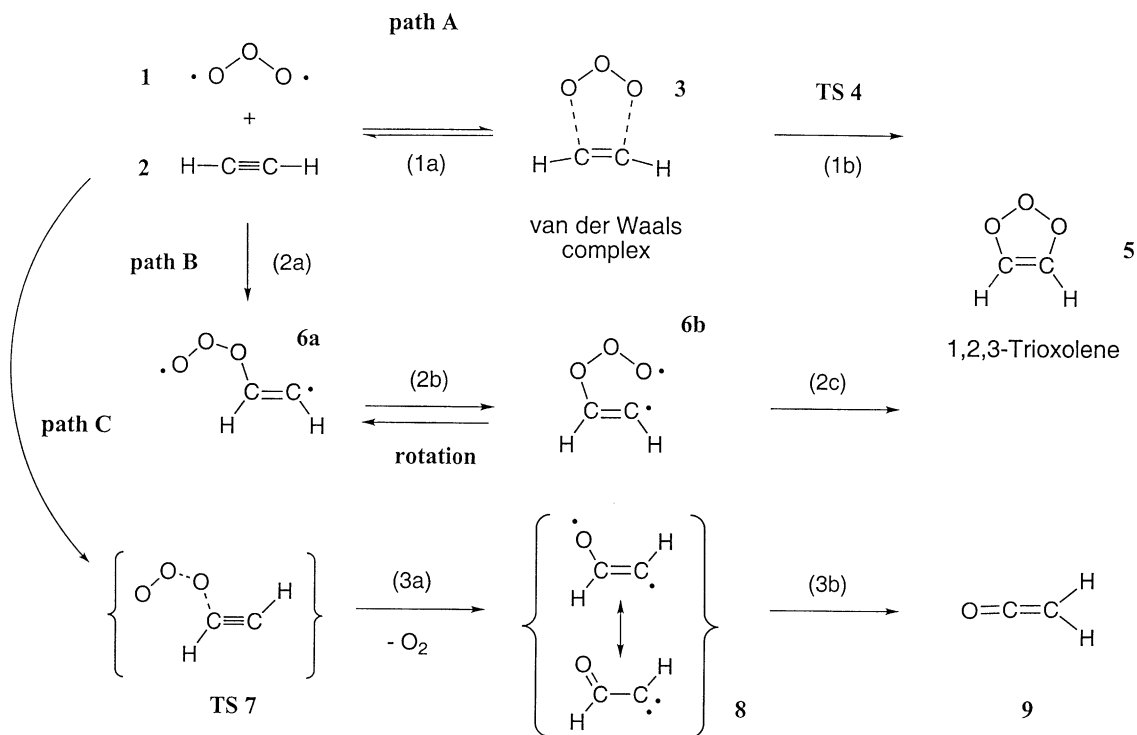
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an acyclic biradicaloid configuration. Model calculations of the activation entropy and the A factor confirmed this assumption. DeMore concluded that *the inertness of C_2H_2 to O_3 is not due to difficulty in disrupting the π bonds of C_2H_2 , but rather to the fact that this step is not rate-determining, i.e., the formation of a biradical is responsible for the increase of both the A factor and the Arrhenius energy.*

DeMore's kinetic data were later revised several times (for a summary of the relevant literature, see [9]). For example, Atkinson and Aschmann [10] measured a rate constant k of $4.7 \text{ l mol}^{-1} \text{ s}^{-1}$ at room temperature, which is 10 times smaller than the original value of DeMore ($k = 48.3 \text{ l mol}^{-1} \text{ s}^{-1}$). The NASA panel for data evaluation in connection with stratospheric modeling [9] stated that the kinetic data for the ozone–acetylene reaction are not well established. Deviations in the various measurements are probably caused by secondary chemistry involving the destruction of ozone by radical products so that too high rate

constants result. The NASA panel recommended a k value of $6.0 \text{ l mol}^{-1} \text{ s}^{-1}$, and an activation energy E_a of $8.1 \pm 1.0 \text{ kcal mol}^{-1}$, and an assumed A factor of $6.0 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$, which was based on the measured value of the ozone–ethene reaction.

In view of the fact that the kinetic data of the ozone–acetylene reaction are not exactly known, it is understandable that DeMore's assumption of a biradical mechanism has never been questioned and is nowadays even discussed in connection with the mechanism of the ozone–alkene reaction [1–7]. There is a need to base the discussion of the ozone–acetylene reaction on reliable data as they can be provided by the computational tools nowadays available. Therefore, we report in this Letter a high level coupled cluster (CC) investigation of the the first step of the $O_3-C_2H_2$ reaction with the goal of (a) providing reliable kinetic data for the reaction, (b) checking DeMore's analysis of the reaction mechanism and (b) combining it with a more recent microwave investigation carried out



Scheme 1.

by Gillies and co-workers [11] who reported on the existence of an ozone–acetylene van der Waals complex in the gas phase. We will show that contrary to DeMore's claims the ozone–acetylene addition reaction in the gas phase is a true concerted reaction and does not involve any biradicals. There is however, beside the ozone–acetylene addition reaction, at higher energy the possibility of an O transfer from ozone to acetylene, which leads to ketene and molecular oxygen via a carbene intermediate with potential biradical character.

2. Computational methods

The molecules investigated in this Letter (Scheme 1) cover both closed shell systems, biradicals with multireference character, and van der Waals complexes. Therefore, it was necessary to apply different methods for a reasonable description of the reaction paths shown in Scheme 1. First, we carried out exploratory calculations using the complete active space SCF (CASSCF) approach [12] in connection with the 6-31G(d,p) basis [13] to obtain reasonable starting geometries for geometry optimizations with the larger 6-311+G(2d,2p) basis set [14]. Although the CASSCF calculations lead to a correct wave function, geometries obtained with this method are often not reliable: bond lengths are mostly too long, typical of a method that contains just a limited amount of electron correlation effects. The more accurate CASPT2 method [15] requires large ANO basis sets to lead to reasonable geometries, which in addition would have to be calculated numerically because of the lack of routinely working optimization methods based on analytical CASPT2 energy gradients.

Therefore, we used parallel to the CASSCF calculations also density functional theory [16] employing the B3LYP hybrid functional [17], which is known to lead to reasonable results in connection with the ozonolysis [5–7,18]. However, DFT is also known to become unreliable for van der Waals complexes (underestimating their stability) [19]. Furthermore, it is a single determinant approach, which for the functionals presently in

use covers predominantly dynamic electron correlation. Cremer and co-workers [20] showed that unrestricted DFT (UDFT) with the semiempirical B3LYP functional is also able to compensate for some static electron correlation, which helps to provide reasonable results in the case of typical organic biradicals where however the usefulness of this approach has to be tested from case to case. For a typical singlet biradical with multireference character it is better to use the ROSS method by Gräfenstein et al. [21], which is equivalent to a two-determinantal approach where dynamic electron correlation is added by the DFT exchange–correlation functional. Hence, ROSS/6-311+G(2d,2p) calculations were used besides CASSCF to search for possible biradicals **6**.

Although DFT covers a relatively high, but unspecified amount of dynamic electron correlation, its well-known failure in the case of van der Waals complexes and loose TSs caused us to use projected CC theory at the CCSD(T) level [22], which includes all single (S) and double (D) excitations and adds triple (T) excitations in a perturbative manner. CCSD(T) covers all infinite order electron correlation effects in the SD space and also about 70% of the T correlation effects in the SDT space [23], which leads to rather accurate results provided a VTZ+P basis set such as 6-311+G(2d,2p) is used. Hence, our most accurate geometries are those obtained with CCSD(T)/6-311+G(2d,2p), which are explicitly documented in this Letter.

Since f-type and even g-type polarization functions can lead to substantial changes in the description of peroxides and polyoxides [24], energies based on CCSD(T)/6-311+G(2d,2p) geometries were improved by extrapolating them to the complete basis set limit (CBS) at the CCSD(T) level of theory. For this purpose, Dunning's [25] aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets were used in slightly altered versions not containing the diffuse equivalent of the polarization functions with the highest angular momentum quantum number: (10s 5p 1d/5s 1p) [4s 3p 1d/3s 1p], (11s 6p 3d 1f/6s 3p 1d) [5s 4p 3d 1f/4s 3p 1d], and (13s 7p 4d 3f 1g/7s 4p 3d 1f) [6s 5p 4d 3f 1g/5s 4p 3d 1f]. The inclusion of two sets of f-type, one set of g-type, and sets of diffuse spdf functions leads

to rather reliable CBS-CCSD(T) energies, but implies costly calculations with up to 433 basis functions. The CBS energies were determined using extrapolation procedures described elsewhere [26].

DFT-B3LYP was used to obtain vibrational frequencies and zero-point energies ZPE (at B3LYP/6-311+G(2d,2p) geometries), which made it possible to estimate vibrational and temperature corrections for CCSD(T) energy differences ΔE . In this way, enthalpy differences $\Delta H(298)$, entropies S , and relative free energies $\Delta G(298)$ were obtained. This approach, although just approximate, is useful because it makes a direct comparison with measured energy and entropy parameters possible. In the case of the ozone–acetylene complex, the DFT-B3LYP/6-311+G(2d,2p) frequencies were checked by numerical CCSD(T)/6-311+G(2d,2p) frequency calculations because of the known deficiencies of DFT when describing van der Waals

complexes. These led to an improvement of calculated entropies needed for the evaluation of the kinetic data.

The calculation of the stability of van der Waals complexes using truncated basis sets and ab initio methods is flawed by basis set superposition errors (BSSEs). We handled this problem by applying the counterpoise method by Boys and Bernardi [27] calculating the monomers forming the van der Waals complex in the dimer centered basis set. For the calculations the program systems ACES II [28], COLOGNE 2000 [29], GAMESS [30], and GAUSSIAN 98 [31] were used.

3. Results and discussion

Calculated energies and geometries obtained in this Letter are summarized in Table 1 and Fig. 1.

Table 1

Energies E , relative energies ΔE , zero-point energies ZPE, enthalpies H , relative enthalpies $\Delta H(298)$, free energies G , relative free energies $\Delta G(298)$, entropies S , and dipole moments μ for molecules 1–5 calculated at the B3LYP/6-311+G(2d,2p), CCSD(T)/6-311+G(2d,2p), and CCSD(T)/CBS levels of theory^a

#	Molecule	Sym	ΔE , ΔE^{\ddagger}	ZPE	$\Delta H(298)$, $\Delta H^{\ddagger}(298)$	$\Delta G(298)$, $\Delta G^{\ddagger}(298)$	S	μ
B3LYP/6-311+G(2d,2p)								
(1)	O ₃	C _{2v}	-225.49017	4.58	-225.47897	-225.50598	56.86	0.68
(2)	C ₂ H ₂	D _{∞h}	-77.35933	16.88	-77.32867	-77.35137	47.79	0
(1+2)	O ₃ + C ₂ H ₂		0.91	21.46	0	-5.42	104.65	
	BSSE corrected		0.72		0.19	-5.61		
(3)	O ₃ -C ₂ H ₂ , vdW	C _s	0	22.04	0	0	86.45	0.58
(4)	O ₃ -C ₂ H ₂ , TS	C _s	4.52	22.88	3.93	8.64	70.66	2.04
(5)	1,2,3-trioxolene	C _s	-64.18	25.90	-66.18	-56.60	67.74	2.93
CCSD(T)/6-311+G(2d,2p) and CCSD(T)/CBS								
(1)	O ₃	C _s	-225.11945	4.58	-225.10825	-225.13526	56.86	0.56
(2)	C ₂ H ₂	D _{∞h}	-77.20073	16.88	-77.17007	-77.19277	47.79	0
(1+2)	O ₃ + C ₂ H ₂		2.13	21.46	2.10	-2.59	104.65	
	BSSE corrected		1.13		1.10	-3.59		
	CBS-limit		2.19		2.15	-2.53		
(3)	O ₃ -C ₂ H ₂ , vdW	C _s	0	20.98*	0	0	88.94*	0.51*
(4)	O ₃ -C ₂ H ₂ , TS	C _s	10.24	22.88	10.51	15.95	70.66	1.85
	CBS-limit		9.28		9.56	15.01		
(5)	1,2,3-trioxolene	C _s	-58.42	25.90	-55.55	-49.23	67.74	2.90

^a Energies, enthalpies, and free energies in hartree. Relative energies, relative enthalpies, relative free energies, and zero-point energies in kcal mol⁻¹, entropies in cal mol⁻¹ K⁻¹, and dipole moments in Debye. All energy values are given relative to the energy of the van der Waals complex 3. In the case of CCSD(T), zero-point energies and thermal corrections were taken from the B3LYP/6-311+G(2d,2p) results with the exception of complex 3, for which ZPE, entropy, and thermal corrections (starred values) were calculated at the CCSD(T)/6-311+G(2d,2p) level of theory. CCSD(T)/CBS limit energies are -225.36450 (1), -77.29694 (2), -302.66492 (3), and -302.650131 hartree (4).

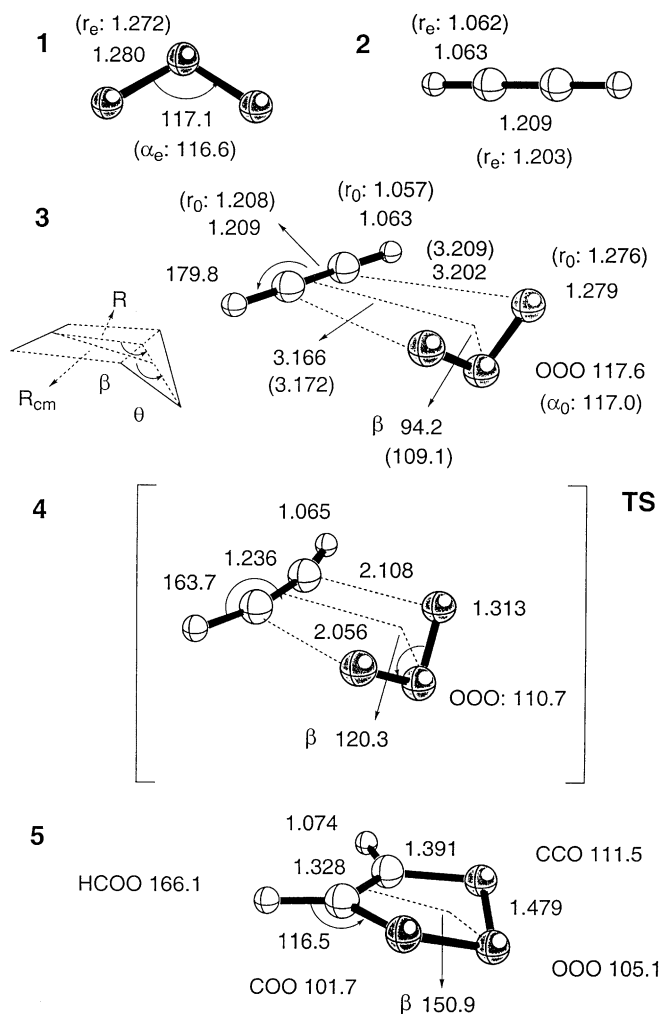


Fig. 1. CCSD(T)/6-311+G(2d,2p) geometries of molecules **1**–**5**. Numbers in parentheses are experimental values. In the case of **3**, r_0 values are taken from the monomer geometries. The insert compares geometrical parameters used in the microwave investigation [11] (R_{cm} : distance between the centers of mass of **1** and **2**; θ : folding angle related to R_{cm}) with the geometrical parameters used in this Letter (R : distance between the center of the CC bond and the midpoint between the terminal O atoms; β : folding angle related to R). Distances in Å, angles in degrees.

All attempts to find a potential biradical **6** with the help of either CASSCF or ROSS-DFT failed. Since both methods are capable of describing biradicals correctly, we conclude that path B in Scheme 1 is not a feasible reaction path. However, a structure similar to **6a** was found to be the TS (TS **7** in path C, Scheme 1) of an O transfer reaction from **1** to **2**. For a particular collision mode between the two molecules, C,O binding interactions develop, **2** is distorted into a trans form, and

the OO bond of **1** involving the interacting O atom is weakened. Transfer of the O atom requires an activation enthalpy $\Delta H^\ddagger(298)$ of 15.6 kcal mol⁻¹ (CASPT2/6-311+G(2d,2p)) and yields beside triplet molecular oxygen biradical **8**, which can stabilize in the form of triplet formyl carbene (Scheme 1).

Scott and co-workers [32] showed that carbene **8** in its singlet state easily rearranges via H migration to ketene **9** (barrier: 5.7 kcal mol⁻¹). We

calculate for the triplet carbene an activation enthalpy of 39 kcal mol⁻¹, which in view of an excess energy of 53 kcal mol⁻¹ set free in reaction (3a) can be surmounted in the gas phase by **8**. Ketene **9** is stable enough to be observed as final product of the O transfer reaction (3). The question is only whether the O transfer reaction can compete with the concerted cycloaddition reaction (1) of Scheme 1.

At all levels of theory applied (even DFT), van der Waals complex **3** was calculated to be more stable than the separated reactants **1** and **2**. After correcting for BSSEs, the CCSD(T) energy of complex **3** is 1.13 (CCSD(T)/CBS: 2.19) kcal mol⁻¹ below that of **1** + **2** where ZPE differences and temperature corrections hardly change the complex stability. We note that the CCSD(T)/VTZ+P geometry (Fig. 1) agrees nicely with the *r*₀ geometry of Gillies and co-workers [11]. These authors detected the ozone–acetylene complex in the gas phase and were able to exactly determine the distance *R*_{cm} between the center-of-mass of **1** and that of **2** (*R*_{cm} = 3.251 Å [11]). This corresponds to a distance *R* (measured between the midpoint of the CC bond and the midpoint of the non-bonded OO distance, Fig. 1) of 3.172 Å, which has to be compared with a CCSD(T) value of 3.166 Å (Fig. 1). Accordingly, the CO interaction distances agree also very well (CCSD(T): 3.202; exp. 3.209 Å, Fig. 1), which are smaller than the sum of the van der Waals radii of C and O (1.85 + 1.40 = 3.25 Å [33]).

The approach distance *R* in **3** is still too large to lead to any substantial changes in the geometries in the monomers (Fig. 1) so that the use of fixed monomer geometries for the complex as made in the experimental investigation [11] is confirmed by the complete geometry optimization of complex **3**. In the microwave investigation, the distance *R*_{cm} between the centers of mass for **1** and **2** (see Fig. 1) and the folding angle θ , which defines the orientation of **1** relative to **2**, were determined by least squares fitting the measured moments of inertia. This led to an ambiguity in θ being either 67.3° (central O atom of **1** oriented toward **2**) or 112.7° (central O atom of **1** oriented away from **2**). MP4(SDQ)/6-31G(d, p) calculations [11] suggested an angle θ of 105.6° supporting an outward ori-

entation of the central O atom, but with smaller folding.

From an electronic point of view, the configuration of complex **3** should be determined by dispersion and exchange repulsion interactions while induction forces should play a minor role. Molecule **1** has four π electrons perpendicular to the molecular plane and five σ -type electron lone pairs in the molecular plane. Since π electrons are easier to polarize than σ electrons and since there are less electrons in the π than the σ space (hence exchange repulsion is lower in the π direction), the favorable approach direction should lead to a folding angle β close to 90° (Fig. 1). The CCSD(T) value is 94.2° while the microwave investigation suggest an angle of 109.1° (corresponding to $\theta = 112.7^\circ$, Fig. 1). Considering the difficulties in measuring this angle, there is need to reconsider experimental results on the basis of the very reliable CCSD(T) geometry obtained in this Letter.

The complex **3** is a precursor to TS **4**, which is reached by reducing the interaction distance *R* from 3.166 to 2.056 Å (CO distances from 3.202 to 2.108 Å, Fig. 1). It was not possible to get biradical **6b** (Scheme 1) starting from **3**, which suggests that once complex **3** is formed the two reaction partners are oriented in such a way that a [4 + 2] symmetry-allowed cycloaddition is the logical consequence. Since the changes in the geometry of the reactants **1** and **2** are still moderate in TS **4** (CC distance: 1.236; OO distance: 1.313 Å, Fig. 1) and since the approach distances are larger than those found for TSs leading to new CO bonds (normally 1.8–2 Å), it is justified to speak of an early TS with relatively small activation enthalpy typical of a strongly exothermic concerted cycloaddition reaction.

The CCSD(T)/6-311+G(2d, 2p) activation enthalpy $\Delta^\ddagger(298)$ is 10.5 kcal mol⁻¹, which is reduced to 9.6 kcal mol⁻¹ for the CCSD(T)/CBS limit (Table 1). Since the stability of the ozone–acetylene complex is not known, the activation enthalpy cannot directly be compared with the available experimental data (see below). The formation of trioxolene **5** is exothermic by 55.5 kcal mol⁻¹ (relative to **3**) in line with an early TS. It is noteworthy that the conformation of **3** verified by experiment (apart from the exact value of

the folding angle not directly measurable) is retained throughout the reaction thus leading to the envelope conformation of **5**. The folding angle β increases from 94 to 120 (**4**) and 151° (**5**). A planar geometry of **5** is not favorable because of (antiaromatic) 8π interactions while a stronger folding as found in 1,2,3-trioxolane (product of the ethene–ozone reaction) [5–7] is not required because of an improvement of bond staggering. Since **5** is formed with an excess energy of more than 70 kcal mol⁻¹, it should decompose immediately. The fate of **5**, e.g., in the ozonolysis of acetylene, will be investigated elsewhere [34].

For the clarification of the reaction mechanism it is necessary to reconsider DeMore's non-concerted reaction mechanism [8] (path B in Scheme 1) considering (a) that the activation energy associated with the second step of reaction (1) (1b in Scheme 1) is more than twice as large as that measured for the ethene–ozone reaction [8,9] and (b) that the A factor measured or assumed varies strongly [8,9]. The high activation enthalpy of reaction (1b) (Scheme 1) is caused by the strength of the triple bond of **2**, which is characterized by sp-hybridization and a higher electronegativity of the C atoms. Consequently, the π electrons in **2** are more tightly bound than in ethene, which is confirmed by the measured first ionization potentials of the two molecules: 10.5 eV for ethene vs. 11.4 eV for **2** [33]. According to the frontier orbital theory of Fukui [35], the activation energy is influenced by orbital interactions between HOMO and LUMO of the reactants, which decrease with a lowering of the HOMO energy of the unsaturated hydrocarbon. Hence, HOMO–LUMO interactions are smaller for **2** and a larger activation enthalpy results for reaction (1b) (as compared to the corresponding ozone–ethene reaction) in line with the Fukui theory.

As for the comparison of measured and calculated activation energies, one has to clarify how the measured kinetic data relate to the mechanism verified by the CCSD(T) calculations. The measured rate constant k has to be associated with the fast equilibrium (1a) between reactants **1** and **2** and complex **3** (rate constants k_{1a} and k_{-1a}) and the cycloaddition step (1b) with rate constant k_{1b} . According to calculated entropies and the free

energy difference $\Delta G(298) = -2.5$ kcal mol⁻¹ (Table 1), equilibrium (1a) is shifted by more than 98% to the side of the reactants. Steady state theory suggests that the rate constant of the overall reaction (1) is given by

$$k_1 = \frac{k_{1a}k_{1b}}{k_{-1a}} = K_{\text{eq}}k_{1b} = \frac{A_{1a}A_{1b}}{A_{-1a}} \exp[-E_a(1)], \quad (1)$$

where $E_a(1) = E_a(1b) - \Delta E_a(-1a)$ is the activation energy measured with regard to the reactants. Applying TS theory the equilibrium constant K_{eq} and the rate constant k_{1b} of the second step are given by Eqs. (2) and (3), respectively,

$$K_{\text{eq}} = \frac{Q_3}{Q_1Q_2} \exp[-\Delta H(-1a)], \quad (2)$$

$$k_{1b} = \frac{k_B T}{h} \frac{Q_{\text{TS4}}}{Q_3} \exp[-\Delta H(1b)], \quad (3)$$

where the various Q denote the partition function of reactants **1** + **2**, van der Waals complex **3**, and TS **4**. Hence, the measured rate constant for the overall reaction (1) can be calculated from Eq. (4),

$$k_1 = \frac{k_B T}{h} \frac{Q_{\text{TS4}}}{Q_1Q_2} \exp[-\Delta H(1)]. \quad (4)$$

Measured and calculated data related to Eq. (4) are compared in Table 2. The frequency factor A for reaction (1) obtained from the CCSD(T)/CBS data of Table 1 is 1.7×10^6 , which is almost a factor 2000 smaller than the A factor given by DeMore [8], however comparable (smaller by a factor of 3.5) to the assumed value of 6.0×10^6 given in [9]. The calculated activation energy $E_a(1) = 8.6$ kcal mol⁻¹ is within the error limits given by NASA (8.1 ± 1.0 kcal mol⁻¹ [9]) while the calculated rate constant $k_1 = 0.8$ l mol⁻¹ s⁻¹ is significantly smaller than the values given in the literature [9,10]. We note that when using measured rate constants in connection with assumed or calculated A -factors, activation energies (Table 2) result that all fall within the error limits of the recommended activation energy.

Of course, both theory and experiment can be in error where in the former case, this will be less due to the quantum chemical energy calculations than the dynamic theory used in this Letter. The use of more advanced dynamic theory such as

Table 2
Comparison of experimental and measured kinetic data^a

k_1	A_1	$E_a(1)$	$\Delta H^\ddagger(1)$	Authors, year [Ref.]
48.3	3.16×10^9	10.8 ± 0.4	9.6 ± 0.4	DeMore, 1969 [8]
4.7				Atkinson and Aschmann, 1984 [10]
6.0	6.02×10^6	8.1 ± 1.0	6.9 ± 1.0	NASA, 2000 [9]
6.0	1.71×10^6	7.4 ± 1.0	6.2 ± 1.0	k from [9]; A from this work
4.7	6.02×10^6	8.3 ± 1.0	7.1 ± 1.0	k from [10], A from [9]
4.7	1.71×10^6	7.6 ± 1.0	6.4 ± 1.0	k from [9]; A from this work
0.8	1.71×10^6	8.6	7.4	This work

^a Rate constants k in $1 \text{ mol}^{-1} \text{ s}^{-1}$, A factors in $1 \text{ mol}^{-1} \text{ s}^{-1}$, activation energies E_a and activation enthalpies $\Delta H^\ddagger(1)$ at 298 K in kcal mol^{-1} .

variational TS theory would be desirable to confirm the results of TS theory, however this is outside our current calculational possibilities. If however TS theory is considered to be sufficient in the present case, our results indicate that measured rate constants are still flawed, probably due to impurities that lead to side reactions of ozone. For example, calculations show that **4** once formed rapidly decomposes to secondary products [34], which in turn can react with ozone. Further experiments are needed to clarify this question.

The calculated value of rate constant k_{1b} is 38.6 s^{-1} , and that of frequency factor A_{1b} is $3.9 \times 10^8 \text{ s}^{-1}$. Equilibrium (1a) reduces k_{1b} by a factor of 50 ($K_{\text{eq}} = 2.0 \times 10^{-2} \text{ l mol}^{-1}$) thus leading to the low value of rate constant k_1 .

The calculated entropy S of TS **4** (70.7 e.u., Table 1) is in line with the prediction made by DeMore (69 e.u.) [8]. However, the obvious errors in the measured rate constant of $48.3 \text{ l mol}^{-1} \text{ s}^{-1}$ (Table 2) flawed also his analysis of the reaction mechanism. Neither the entropy difference between reactants and TS **4** ($\Delta S = -34$ e.u.) nor that between complex **3** and TS **4** ($\Delta S = -18.3$ e.u., Table 1) can explain an A factor of 3.2×10^9 (Table 2), which probably was the reason for invoking an intermediate biradical such as **6** to explain the measured kinetic data [8].

We conclude that both experiment and theory support a concerted [4 + 2] cycloaddition for the ozone–acetylene reaction rather than a non-concerted reaction involving a biradical intermediate. The calculated kinetic data confirm that DeMore's measurements [8] were flawed by secondary consumption of ozone, however they also suggest that there is still a need for refined kinetic measure-

ments. [9] Beside the concerted symmetry-allowed cycloaddition reaction, an O-transfer from **1** to **2** (activation enthalpy: 16 kcal mol^{-1}) will play a significant role at elevated temperatures. We note in this connection that O-transfer reactions leading to ketene were found in low temperature studies when ozone is irradiated in the presence of alkynes. [36] This suggests that ketene formation can also be expected in a thermochemical reaction of an ozone–alkyne reaction system provided the temperature is high enough.

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References

- [1] For a review, see P.S. Bailey, in: *Ozonation in Organic Chemistry*, vol. I and II, Academic Press, New York, 1968.
- [2] W. Sander, *Angew. Chem. Int. Ed. Engl.* 29 (1989) 344.

- [3] W.H. Bunnelle, Chem. Rev. 91 (1991) 335.
- [4] R.L. Kuczowski, Acc. Chem. Res. 16 (1983) 42.
- [5] D. Cremer, J. Am. Chem. Soc. 103 (1981) 3627.
- [6] M. Olzmann, E. Kraka, D. Cremer, R. Gutbrod, S.J. Andersson, Phys. Chem. 101 (1998) 9421.
- [7] J.M. Anglada, R. Crehuet, J.M. Bofill, Chem. Eur. J. 5 (1999) 1809.
- [8] W.B. DeMore, Int. J. Chem. Kinet. 1 (1969) 209.
- [9] Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling, Evaluation Number 13, NASA Panel for Data Evaluation, Jet Propulsion Laboratory, 2000.
- [10] R. Atkinson, S.M. Aschmann, Int. J. Chem. Kinet. 16 (1984) 259.
- [11] J.Z. Gillies, C.W. Gillies, F.J. Lovas, K. Matsumura, R.D. Suenram, E. Kraka, D. Cremer, J. Am. Chem. Soc. 113 (1991) 6408.
- [12] B.O. Roos, Adv. Chem. Phys. 69 (1987) 399.
- [13] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.
- [14] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650.
- [15] K. Anderson, P.A. Malmqvist, B.O. Roos, J. Chem. Phys. 96 (1992) 1218.
- [16] See, e.g., R.G. Parr, W. Yang, International Series of Monographs on Chemistry 16: Density-Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.
- [17] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [18] D. Cremer, E. Kraka, P.G. Szalay, Chem. Phys. Lett. 292 (1998) 97.
- [19] R. Wrobel, W. Sander, E. Kraka, D. Cremer, J. Phys. Chem. A 103 (1999) 3693.
- [20] J. Gräfenstein, A. Hjerpe, E. Kraka, D. Cremer, J. Phys. Chem. A 104 (2000) 1748.
- [21] J. Gräfenstein, E. Kraka, D. Cremer, Chem. Phys. Lett. 288 (1998) 593.
- [22] J.A. Pople, M. Head-Gordon, K. Raghavachari, J. Chem. Phys. 87 (1987) 5968.
- [23] Z. He, D. Cremer, Theor. Chim. Acta 85 (1993) 305.
- [24] S.-J. Kim, H.F. Schaefer, E. Kraka, D. Cremer, Mol. Phys. 88 (1996) 93.
- [25] R.A. Kendall, R.J. Harrison, T.H. Dunning Jr., J. Chem. Phys. 96 (1992) 6796.
- [26] Y. He, D. Cremer, Mol. Phys. 98 (2000) 1415.
- [27] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.
- [28] J.F. Stanton, J. Gauss, J.D. Watts, W.J. Lauderdale, R.J. Bartlett, ACES II, Quantum Theory Project, University of Florida, 1992.
- [29] E. Kraka, J. Gräfenstein, J. Gauss, Y. He, F. Reichel, L. Olsson, Z. Konkoli, Z. He, D. Cremer, COLOGNE 2000, Göteborg University, Göteborg, 2000.
- [30] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, J.H. Jensen, S. Koseki, M.S. Gordon, K.A. Nguyen, T.L. Windus, S.T. Elbert, QCPE Bull. 10 (1990) 52.
- [31] M.J. Frisch et al., GAUSSIAN 98, Revision A.3, Gaussian, Inc., Pittsburgh PA, 1998.
- [32] A.P. Scott, R.H. Nobes, H.F. Schaefer III, L. Radom, J. Am. Chem. Soc. 116 (1994) 10159.
- [33] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics on CD-ROM, 2000 Version, CRC Press LLC.
- [34] D. Cremer, R. Crehuet, J. Anglada, J. Am. Chem. Soc. 123 (2001) 6127.
- [35] K. Fukui, Angew. Chem. Int. Ed. Engl. 21 (1982) 801.
- [36] J.K. Parker, S.R. Davies, J. Phys. Chem. A 103 (1999) 7280, and references cited therein.