Volume 14 | Number 30 | 14 August 2012 | Pages 10357–10816

PCCP

Physical Chemistry Chemical Physics

www.rsc.org/pccp



Includes a collection of articles on new insights into organic chemistry from forefront physical measurements

ISSN 1463-9076

COVER ARTICLE Taatjes *et al.* Direct measurement of Criegee intermediate (CH₂OO) reactions with acetone, acetaldehyde, and hexafluoroacetone



1463-9076(2012)14:30;1-T

Cite this: Phys. Chem. Chem. Phys., 2012, 14, 10391-10400

www.rsc.org/pccp

PAPER

Direct measurement of Criegee intermediate (CH₂OO) reactions with acetone, acetaldehyde, and hexafluoroacetone

Craig A. Taatjes,^{*a} Oliver Welz,^a Arkke J. Eskola,^a John D. Savee,^a David L. Osborn,^a Edmond P. F. Lee,^{bc} John M. Dyke,^b Daniel W. K. Mok,^c Dudley E. Shallcross^d and Carl J. Percival^{*e}

Received 31st January 2012, Accepted 9th March 2012 DOI: 10.1039/c2cp40294g

Criegee biradicals, *i.e.*, carbonyl oxides, are critical intermediates in ozonolysis and have been implicated in autoignition chemistry and other hydrocarbon oxidation systems, but until recently the direct measurement of their gas-phase kinetics has not been feasible. Indirect determinations of Criegee intermediate kinetics often rely on the introduction of a scavenger molecule into an ozonolysis system and analysis of the effects of the scavenger on yields of products associated with Criegee intermediate reactions. Carbonyl species, in particular hexafluoroacetone (CF_3COCF_3) , have often been used as scavengers. In this work, the reactions of the simplest Criegee intermediate, CH₂OO (formaldehyde oxide), with three carbonyl species have been measured by laser photolysis/tunable synchrotron photoionization mass spectrometry. Diiodomethane photolysis produces CH_2I radicals, which react with O_2 to yield $CH_2OO + I$. The formaldehyde oxide is reacted with a large excess of a carbonyl reactant and both the disappearance of CH₂OO and the formation of reaction products are monitored. The rate coefficient for CH₂OO + hexafluoroacetone is $k_1 = (3.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, supporting the use of hexafluoroacetone as a Criegee-intermediate scavenger. The reactions with acetaldehyde, $k_2 = (9.5 \pm 0.7) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and with acetone, $k_3 = (2.3 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, are substantially slower. Secondary ozonides and products of ozonide isomerization are observed from the reactions of CH₂OO with acetone and hexafluoroacetone. Their photoionization spectra are interpreted with the aid of quantumchemical and Franck-Condon-factor calculations. No secondary ozonide was observable in the reaction of CH₂OO with acetaldehyde, but acetic acid was identified as a product under the conditions used (4 Torr and 293 K).

Introduction

Carbonyl oxides, known as "Criegee intermediates" after Rudolf Criegee, who proposed their participation in ozonolysis,¹ are important species in tropospheric chemistry. Most carbonyl oxides in the troposphere are produced by ozonolysis, but other tropospheric reactions can also produce Criegee intermediates.^{2,3} However, until recently^{2,4} no Criegee intermediate had been observed in the gas phase, and information about the

reactivity of Criegee intermediates in gas-phase ozonolysis or in the troposphere have relied on indirect determinations.^{5,6} One particularly useful approach has been to introduce "Criegee scavenger" molecules into ozone/hydrocarbon reactions and investigate the effect on products thought to originate from Criegee intermediates. One type of scavenger is a carbonyl compound; as in the liquid-phase Criegee ozonolysis mechanism,⁷ carbonyl oxide intermediates undergo cycloaddition with carbonyl compounds to form secondary ozonides. These secondary ozonide products can be detected, for example by infrared spectroscopy^{8,9} or gas chromatography¹⁰ and have been confirmed as products from ozonolysis in gas-phase¹¹ as well as in solution.⁷ Hexafluoroacetone (HFA) is a prominent representative of the carbonyl class of Criegee scavengers; Horie et al.⁸ deduced that HFA reacts rapidly with Criegee intermediates based on Fourier-transform infrared (FTIR) measurements of product formation from ozonolysis of small alkenes in the presence of added HFA. Horie et al. measured a product from adding HFA to the ethene ozonolysis system

^a Combustion Research Facility, Sandia National Laboratories, 7011 East Ave., MS 9055, Livermore, California 94551, USA. E-mail: cataati@sandia.gov

^b School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

^c Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong

^d School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

^e School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Williamson Building, Oxford Road, Manchester M13 9PL, UK. E-mail: carl.percival@manchester.ac.uk

and assigned it to the secondary ozonide, 3,3-di(trifluoromethyl)-1,2,4-trioxolane, resulting from CH₂OO addition to HFA, as shown in Scheme 1.



Scheme 1

The assignment was made by analogy to determinations by Neeb *et al.*⁹ of secondary ozonide formation in other gas-phase ozonolysis systems. Horie *et al.*⁸ described this assignment as tentative, but the analogy with other systems is compelling. Also, they carried out a relative-rate measurement to deduce that HFA reacts ~13 times faster than acetaldehyde with CH₂OO.

Recently it has become feasible to directly detect at least the simplest carbonyl oxide, CH₂OO, by tunable synchrotron photoionization mass spectrometry,⁴ and it has been shown that the reaction of CH₂I with O₂ is a convenient means for preparing CH₂OO in the laboratory and measuring its kinetics.² Additionally, photoionization mass spectrometry with a synchrotron light source is a powerful tool for analyzing isomeric products of chemical reactions.¹² As a result we can explicitly confirm the reactivity of carbonyl compounds with CH₂OO in the gas phase and investigate reaction products. Here we present absolute measurements of the rate coefficients for CH₂OO reacting with HFA, acetaldehyde, and acetone:

 $CH_2OO + CF_3COCF_3 \rightarrow products$ (1)

 $CH_2OO + CH_3CHO \rightarrow products$ (2)

$$CH_2OO + CH_3COCH_3 \rightarrow products$$
 (3)

Secondary ozonides (trioxolanes) are observed as products in the reactions with acetone and HFA, and are identified by comparison of measured photoionization spectra with results of quantum chemical calculations of the adiabatic ionization energies (AIE) and Franck–Condon factors (FCF) for ionization. Evidence for isomerization of the secondary ozonide is also observed. In contrast with the 730 Torr measurements of Horie *et al.*,⁸ no secondary ozonide is detected in the reaction of CH₂OO with acetaldehyde under the low-pressure conditions of the present experiments, but formation of acetic acid is identified as a product channel.

Methods

Synchrotron photoionization mass spectrometry

The kinetic measurements were carried out in the Sandia Multiplexed Chemical Kinetics Reactor,¹³ operating at the Chemical Dynamics Beamline (9.0.2) of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Reactants flow slowly through a quartz photolysis reactor coated with halocarbon wax. The contents of the reactor are continuously sampled through a small orifice in the sidewall. The emerging molecules are ionized by tunable synchrotron

radiation and are mass-analyzed in an orthogonal-acceleration time-of-flight mass spectrometer. Pulsed extraction of the continuous ion beam occurs at a 50 kHz repetition rate, so a full mass spectrum is obtained every 20 microseconds. Some experiments requiring analysis of larger-mass species were carried out with a 40 kHz repetition rate and a corresponding 25 us kinetic time step. Because the ionization photon energy can be readily tuned, the kinetic data is generally acquired as a threedimensional dataset of ion signal as a function of mass, kinetic time, and photon energy.¹² The measured signals are background-corrected by subtracting the signal levels before the firing of the photolysis laser, and are normalized to the ionizing photon flux (measured with a photodiode). The data taken at a fixed photon energy or integrated over photon energy gives a timeresolved mass spectrum of the reaction, as shown in Fig. 1. Integration over a range of kinetic time yields photoionization spectra of observed mass channels. Isomeric species can be identified based on their photoionization spectra.4,12,14 The mass axis was calibrated using mass peaks from a flow of a gas mixture containg H₂, ethene, propene, 1-butene, Kr, and Xe in an Ar buffer, and the photon energy was calibrated using autoionizing resonances in Xe. Additional kinetics measurements were carried out at the Combustion Research Facility, using a hydrogen discharge lamp (generating principally Lyman-a radiation at 10.20 eV) as a photoionization source.

Formaldehyde oxide, CH₂OO, is produced from the reaction of CH₂I with O₂.² Diiodomethane (99%) was introduced into the cell ([CH₂I₂] = 5.7×10^{12} molecule cm⁻³) by a He flow through a thermostatted bubbler and photolyzed at 248 nm or 351 nm in the presence of a large excess (~ 10^{16} molecule cm⁻³) of O₂. In some experiments ¹³CH₂I₂ (99 atom% ¹³C) was employed to produce ¹³CH₂OO. The absorption cross-sections of acetaldehyde and acetone are significantly higher than that



Fig. 1 Section of time-resolved mass spectra for the reaction of ¹³CH₂OO with HFA, integrated over photon energies from 10.5 eV–11.3 eV. Note the break in the *x*-axis scale between m/z = 51 and m/z = 125. The ¹³CH₂OO is observed at m/z = 47, and the prominent peak at m/z = 127 is the I atom produced in the CH₂I₂ photolysis. The secondary ozonide appears at m/z = 213 and dissociative ionization of (trifluoromethoxy)methyl trifluoroacetate appears at m/z = 162 and 164, IBr at m/z = 206 and 208) arise from side reactions of the I atom, including possibly with the halocarbon wax coating.

of HFA at 248 nm, so 351 nm photolysis of CH₂I₂ was employed for the CH₂OO + CH₃CHO and CH₂OO + CH₃COCH₃ reaction measurements in order to avoid photolysis of CH₃CHO and CH₃COCH₃ reactants. Known dilutions of the carbonyl reagent in He were prepared in 4-liter vessels and the mixture was flowed through the reactor at 293 K. Flows of the reagents and He diluent are controlled with calibrated mass flow controllers. The total pressure is maintained at 4 Torr by active control of the pumping speed, and the total flow is sufficient to replenish the reactor between laser pulses (repetition rates of either 4 Hz or 10 Hz were used). The reaction of CH₂I with O₂ is rapid¹⁵ and CH₂OO formation is observed almost immediately following the photolysis laser pulse $(k(CH_2I + O_2) \cdot [O_2] \approx 14000 \text{ s}^{-1})$. The CH₂OO can be distinguished from other isomers such as formic acid because of its different ionization energy.⁴ The decay of CH₂OO in the absence of added reagent is attributed to heterogeneous reaction in the present experiments, as the decay constant is dependent on the coating and history of the reactor tube. The "zero-reagent" decay was monitored at several points during every set of kinetic measurements to control for possible changes in the heterogeneous removal rate during the course of an experiment. The slowest first-order decay rate coefficient observed is \sim 75 s⁻¹, considerably slower than previous observations,² placing an experimental lower limit of ~ 13 ms on the lifetime of CH₂OO at room temperature (293 K). However, the removal of CH₂OO in the present experiments may still be dominated by heterogeneous or bimolecular reactions even at the lowest observed decay rates, so this lower limit may be far below the true unimolecular lifetime. Quantum chemical and Rice-Ramsperger-Kassel-Marcus (RRKM) calculations by Olzmann et al.¹⁶ predict a high-pressure limit of the CH₂OO lifetime that is more than a factor of 100 larger than the present lower limit.

Adding carbonyl compounds to the reaction mixture accelerated the decay of CH₂OO, as shown in Fig. 2 for the reaction of CH₂OO with HFA. The decay of CH₂OO was fit to an exponential, corrected for the instrument response function where appropriate (*i.e.* for the fastest decays).² The inverse time constant of the decay (\equiv the pseudo-first order rate coefficient), plotted as a function of added reagent concentration, yields a straight line, as shown in Fig. 3 for the reaction of CH₂OO with HFA. The slope of this line gives the second-order rate coefficient for the reaction. In addition, photoionization spectra were acquired for all three reactions at a high concentration of the carbonyl reactant. Products are identified by comparison of the obtained photoionization spectra with measured spectra of authentic samples or by comparison with calculated photoionization spectra (see below).

Geometry optimization and harmonic vibrational frequency calculations were performed at the B3LYP/6-311G** level using Gaussian09.¹⁷ Higher-level single-energy calculations were carried out for more reliable relative electronic energies at computed B3LYP/6-311G** geometries. They include CBS-QB3¹⁸ calculations using Gaussian09¹⁷ for all species considered, and RCCSD(T) and explicitly correlated UCCSD(T)-F12x



Fig. 2 Measured decay of ${}^{13}CH_2OO$ in the presence of varying concentrations of HFA. The signals are fit to exponential decays, convolved with the instrument response function.



Fig. 3 Plot of the pseudo-first order rate coefficient (decay constant) of CH_2OO removal as a function of HFA concentration. Two independent datasets are shown; error bars are 95% precision of the fit to the pseudo-first order decay. The intercept reflects other loss processes for CH_2OO , for example, heterogenous reaction on the walls.

calculations employing MOLPRO¹⁹ with various basis sets^{20–22} for 3,3-dimethyl-1,2,4-trioxolane and its cation. The purpose of carrying out RCCSD(T) and UCCSD(T)-F12x calculations is to obtain theoretical benchmarks for the adiabatic ionization energy (AIE) of 3,3-dimethyl-1,2,4-trioxolane. With the RCCSD(T) results, extrapolation to the complete basis set (CBS) limit was carried out using the 1/X³ formula.^{23,24} The RCCSD(T)/CBS approach using correlation-consistent basis sets has been considered as the "gold standard" of quantum chemistry.^{25–27} With the recently reported, explicitly correlated, UCCSD(T)-F12x (x = a or b) methods, which correct

the lack of derivative discontinuity (cusp) in standard wave functions,^{28,29} the scaled perturbative triples obtained by a simple scaling factor, $\Delta E(\text{Tsc}) = \Delta E(\text{T}) \times \text{E}_{\text{corr}}^{\text{MP2-F12}}/\text{E}_{\text{corr}}^{\text{MP2}}$ (*i.e.* the ratio between the computed correlation energies obtained at the MP2 and MP2-F12 levels) have been employed.³⁰ It has been shown that explicitly correlated methods, such as UCCSD(T)-F12, achieve a dramatic improvement of basis set convergence of correlation energies when compared with conventional correlation methods, such as RCCSD(T).³¹

In order to assist assignments of the observed photoionization mass spectra. Franck-Condon factor (FCF) calculations were carried out for the secondary ozonide products using the ezSpectrum code.32 All vibrational modes were considered in the FCF calculations, which include Duschinsky rotation³³ but are within the harmonic oscillator model. Because of the size of the molecular systems considered and the large number of combination bands excited upon ionization (see below), anharmonicity, which is expected to be significant particularly for vibrational modes involving CH stretches, has to be ignored. This approximation may result in an overestimate of the intensity of the simulated vibrational structure in the higher ionization energy (IE) region. In addition, the maximum number of vibrational excitations in the cationic state (the maximum value of $\sum v_i$, where v_i is the quantum number of vibrational mode i; i.e. the maximum total number of excitations in all normal modes combined for a certain vibrational component in the cationic state) has to be restricted to 7 (*i.e.*, 7 layers), and "hot" bands have been ignored, because of limitations on the total number of FCFs that ezSpectrum can manage. Nevertheless, comparison between the overall vibrational structures obtained using 6 and 7 layers in the FCF calculations suggests that using 7 layers should be adequate. As an example to show the size of the FCF calculations, for 3,3-di(trifluoromethyl)-1,2,4-trioxolane, with 7 layers, 53 524 680 vibrational states in the cationic state were considered, and the FCFs of 2140987200 combination bands were computed.

Results and discussion

The rate coefficients for reaction of CH_2OO with the three carbonyl compounds considered here are derived from the data in Fig. 3–5:

$$k_1 (CH_2OO + CF_3COCF_3)$$

= (3.0 ± 0.3) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹,
$$k_2 (CH_2OO + CH_3CHO)$$

= (9.4 ± 0.7) × 10⁻¹³ cm³ molecule⁻¹ s⁻¹,
$$k_3 (CH_2OO + CH_3COCH_3)$$

$$= (2.3 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The uncertainty limits are 95% precision of the fit. The reaction with hexafluoroacetone is markedly faster than the reaction with acetone or with acetaldehyde, corroborating earlier observations⁸ and tending to confirm the utility of HFA as a scavenger of Criegee intermediates.^{6,34} Horie *et al.*⁸ measured the rate constant of the reaction of CH₂OO with HFA relative to that with acetaldehyde by comparing the consumption of

HFA to the appearance of propene ozonide (methyl-1.2,4trioxolane, a product of the CH₂OO + CH₃CHO reaction) when HFA and acetaldehyde were added to an ethene ozonolysis reaction. In their experiments the ethene ozonolysis produced CH2OO biradical, which then reacted with both HFA and acetaldehyde. Horie *et al.*⁸ deduced $k_1/k_2 = 13$, approximately half the ratio of the rate constants in the present experiment. It is possible that this difference (which is well outside the stated uncertainties for the relative rate measurement) simply reflects different falloff behavior of the two reactions; the measurements of Horie et al.⁸ were carried out at 730 Torr of synthetic air, and the present measurements at 4 Torr in helium. We do not observe formation of methyl-1,2,4-trioxolane in the reaction of CH₂OO with acetaldehyde (see below), further suggesting that the stabilization channel observed by Horie et al.8 may be pressure dependent.

The Criegee intermediates have a polar biradical electronic configuration and a singlet ground state.^{35–38} The reactions of carbonyl oxides with aldehydes and ketones are typically described as 1,3-dipolar cycloadditions,^{7,39} and the ordering of the rate coefficients, $k_1 > k_2 > k_3$, is in accordance with the expected relative susceptibility of the carbonyl species to dipolar attack. For example, in liquid phase ozonolysis the formation of ozonides from carbonyl oxide addition to ketones is less efficient than for addition to aldehydes,^{7,39,40} but the ketone reactivity can be increased by electron-withdrawing substituents.⁴¹ The substitution of the methyl groups in acetone by more electron withdrawing groups (H, CF₃) will tend to stabilize the transition state for attack of the electron-rich O end of the CH₂OO molecule to the carbonyl carbon.

The present experiments consider only the reaction of CH₂OO. For singly alkyl-subsituted Criegee biradicals, (at least) two conformers exist: *syn*- (O–O pointing towards the alkyl group)



Fig. 4 Plot of the pseudo-first order rate coefficient (decay constant) of CH_2OO removal as a function of acetaldehyde concentration. Error bars are 95% precision of the fit to the pseudo-first order decay. The intercept reflects other loss processes for CH_2OO , for example, heterogenous reaction on the walls.





Fig. 5 Plot of the pseudo-first order rate coefficient (decay constant) of CH_2OO removal as a function of acetone concentration. Error bars are 95% precision of the fit to the pseudo-first order decay. The intercept reflects other loss processes for CH_2OO , for example, heterogenous reaction on the walls.

and anti- (O-O pointing away from the alkyl group. Steric or electronic considerations in substituted Criegee intermediates may affect the reactivity of the radicals and produce different reactivity for the two conformers.^{6,38} Murray et al.⁴⁰ noted that aldehydic carbonyl oxides such as CH₃CHOO reacted more readily with acetone than did their ketonic counterparts such as (CH₃)₂COO. One might imagine that measurements of CH₂OO kinetics may be representative of *anti*-conformers because there is no methyl group for the O-O group to point towards. By comparison, Fenske et al.⁴² deduced an absolute rate coefficient of 1×10^{-12} cm³ molecule⁻¹ s⁻¹ (with a factor of 6 uncertainty) for the reaction of CH₃CHOO with acetaldehyde, a similar value to the present measurement of k_2 . The unimolecular decomposition of the *syn*-CH₃CHOO, through vinyl hydroperoxide, should be more rapid than decomposition of the anti-conformer.^{5,6} If as a result the observed secondary ozonide in the experiments of Fenske et al.⁴² principally arose from reaction of the anti-CH₃CHOO, the rough congruence of the present measurement with that of Fenske et al.⁴² might indeed suggest that the CH₂OO rate coefficients with carbonyl compounds are similar to those of the anti- conformer of larger Criegee intermediates. Explicit measurement of reactions of syn- and anti-carbonyl oxides is clearly desirable.

The present experiments detect the appearance of product species as well as the disappearance of reactants, as shown in Fig. 1. The major product of both liquid- and gas-phase reactions of Criegee biradicals with carbonyl compounds is generally thought to be the secondary ozonides.^{7,11} The dominant product signals in the reaction of ¹³CH₂OO with HFA are at the mass of the ozonide (m/z = 213) and that of the ozonide minus CF₃ (m/z = 144). The time traces of the rising product signals and the decaying Criegee intermediate are shown in

Fig. 6 for the reaction of ¹³CH₂OO with HFA. The use of ¹³CH₂OO moves the peak for the ozonide minus CF₃ away from the IO signal at m/z = 143. (Signal at m/z = 144 from HOI formation is negligible compared to the observed product signal.) The time behavior at the ozonide mass is identical to that of m/z = 144. Similar behavior is observed for the reaction of CH₂OO with acetone, where the main product signals are at the mass of the ozonide and the ozonide minus CH₃. Although these observations at first sight suggest that the signals corresponding to CH₃/CF₃ loss arise from dissociative ionization of the ozonides, certain aspects of the photoionization spectra, discussed later, argue against such an assignment.

No previous measurements of the photoionization spectra of secondary ozonides exist. Martinez *et al.*⁴³ observed signals at the mass of the secondary ozonides in photoionization mass spectrometry measurements of the ozonolysis of alkenes, but did not have the capability to measure photoionization spectra and could not definitively determine the isomeric nature of the observed molecules. In order to identify the signals at the ozonide masses we compare the measured photoionization spectra to calculated spectra based on quantum chemistry and Franck–Condon simulations. Such calculated spectra assume that the ionization is dominated by direct continuum ionization to the parent cation.

Table 1 reports the computed electronic energy difference, ΔE_{ion} , for the ionization of 3,3-dimethyl-1,2,4-trioxolane, the secondary ozonide expected from reaction of CH₂OO with acetone, obtained at different levels of calculation. When corrected for zero-point energies, this energy difference gives the AIE, which is defined as the energy from the ground



Fig. 6 Time behavior of the ${}^{13}CH_2OO$ and the product signals for the reaction with HFA. The slight long-time increase in products, and the slow secondary decay of ${}^{13}CH_2OO$ on the same timescale, is the result of small contributions of secondary reactions with CH_2I_2 that regenerate CH_2I and hence CH_2OO .

Table 1 Computed difference in electronic energy (eV) between the ground neutral and cationic states (ΔE_{ion}) of 3,3-dimethyl-1,2,4-trioxolane at different levels of calculations

RMP2/cc-pVDZ	9.0274	138
RCCSD/cc-pVDZ	8.8960	138
RCCSD(T)/cc-pVDZ	8.8232	138
RMP2/cc-pVTZ	9.3455	322
RCCSD/cc-pVTZ	9.1611	322
RCCSD(T)/cc-pVTZ	9.1169	322
RMP2/aug-cc-pVDZ	9.2981	233
RCCSD/aug-cc-pVDZ	9.1112	233
RCCSD(T)/aug-cc-pVDZ	9.0747	233
RMP2/aug-cc-pVTZ	9.4530	506
RCCSD/aug-cc-pVTZ	9.2465	506
RMP2/cc-pVDZ-F12	9.3017	$282, 638, 688^a$
RMP2-F12/cc-pVDZ-F12	9.5251	
UCCSD-F12a/cc-pVDZ-F12	9.2708	
UCCSD-F12b/cc-pVDZ-F12	9.2450	
UCCSD(T)-F12a/cc-pVDZ-F12	9.2337	
UCCSD(T)-F12b/cc-pVDZ-F12	9.2078	
$RCCSD/CBS(1/X^3:VTZ;VDZ)$	9.2727	
$RCCSD/CBS(1/X^3:VTZ,VDZ) + \Delta(T)/VTZ^b$	9.2285	
RCCSD/CBS(1/X ³ :AVTZ;AVDZ)	9.3035	
$RCCSD/CBS(1/X^3:AVTZ;AVDZ) + \Delta(T)/AVDZ^b$	9.2670	
$RCCSD(T)/CBS(1/X^3:VTZ;VDZ)$	9.2406	
Best estimated ΔE_{ion}^{c}	9.245 ± 0.022	
Best estimated AIE^d	9.21 ± 0.03	

^{*a*} AO, RI and DF basis sets: VDZ-F12, cc-pVDZ-F12/OPTRI and aug-cc-pVDZ/MPFIT. ^{*b*} Δ (T) is the correction due to contributions of triple excitations obtained at the basis set given. ^{*c*} The best estimate is obtained as the average of the RCCSD/CBS(1/X³:VTZ,VDZ) + Δ (T)/VTZ, RCCSD/CBS(1/X³:AVTZ;AVDZ) + Δ (T)/AVDZ and RCCSD(T)/CBS(1/X³:VTZ;VDZ) values. The estimated uncertainty is the difference between the best estimate and the RCCSD/CBS(1/X³:AVTZ;AVDZ) + Δ (T)/AVDZ + Δ (T)/AVDZ value. ^{*d*} Zero-point energy corrections from computed B3LYP/6-311G** vibrational frequencies.

vibrational and electronic state of the neutral to the ground vibrational and electronic state of the cation. From the results culminating in RCCSD(T) calculations-RMP2, RCCSD and RCCSD(T)-with different basis sets shown in Table 1, it is clear that basis-size effects increase the computed ΔE_{ion} values, while electron-correlation effects decrease the computed ΔE_{ion} values. Similar conclusions can be drawn from the results obtained from calculations leading to UCCSD(T)-F12x/ cc-pVDZ-F12: RMP2, RMP2-F12, UCCSD-F12x and UCCSD(T)-F12x with the cc-pVDZ-F12 basis set as shown in Table 1. The best theoretical estimate of the ΔE_{ion} value obtained based on various RCCSD(T)/CBS values is 9.245 \pm 0.022 eV (see footnotes b and c of Table 1). It is pleasing that this best estimate agrees very well with the explicitly correlated UCCSD(T)-F12a value of 9.234 eV and the UCCSD(T)-F12b value of 9.208 eV. The consistency of these high-level results confirms their reliability. Including corrections for zero-point energies (see footnote d of Table 1), the best theoretical AIE value is 9.21 ± 0.03 eV, whereas CBS-QB3 predicts a value of 9.29 eV. Two conformers exist for the ground state cation of 3,3-dimethyl-1,2,4-trioxolane. They are mirror images of each other and as such have the same energy. However the computed FCFs to these two cationic conformers are very different, because the geometry changes to one conformer are considerably larger than those to the other, giving considerably smaller computed overlap integrals. In this connection, only the conformer with the more favorable FCF has been included in spectral simulations (a similar situation applies to the 3,3-di(trifluoromethyl)-1,2,4-trioxolane).

Fig. 7 and 8 show the photoionization spectra of the observed products of the reactions of CH2OO with acetone and with HFA, compared with the calculated photoionization spectra of the secondary ozonides. The calculated spectrum for the 3,3-dimethyl-1,2,4-trioxolane product arising from the reaction of CH₂OO with acetone (Fig. 7) uses the best-estimate AIE and is scaled vertically to match the amplitude of the experimental signal. The calculated 3,3-di(trifluoromethyl)-1,2,4-trioxolane spectrum in Fig. 8 employs a lower-accuracy CBS-OB3 estimate of the adiabatic ionization energy and is additionally shifted to higher energy by 55 meV (5.3 kJ mol^{-1}). Such a discrepancy is not unreasonable for the calculation of a relatively heavy fluorinated molecule by CBS-QB3. The good agreement of the calculated and experimental spectra identifies the carriers as the expected secondary ozonide products. Calculated AIEs (Table 2) for other possible isomers (Scheme 2) are in poor agreement with the observed photoionization spectra.





Fig. 7 also shows the calculated (CBS-QB3) asymptotic product energy for formation of CH_3 and $C_3H_5O_3^+$ by simple



Fig. 7 Photoionization spectra of the m/z = 104 product from the reaction of CH₂OO with acetone, compared with the calculated spectrum of the secondary ozonide. The simulated spectrum uses the best high-level theoretical estimate of the AIE and Franck–Condon calculations, as described in the text. The AIE for the methoxymethyl acetate isomer and the calculated energetic threshold for dissociative ionization of the secondary ozonide isomer ("DI threshold for ozonide") are also shown for reference. The m/z = 89 signal is attributed to dissociative ionization of methoxymethyl acetate.

C-C bond fission after photoexcitation of the neutral 3,3dimethyl-1,2,4-trioxolane. The apparent experimental threshold of the methyl loss channel, ~9.9 eV, is ~20 kJ mol⁻¹ below the CBS-QB3 asymptotic energy. Such a discrepancy is unusually large for CBS-QB3 calculations; for comparison, the CBS-QB3 value of 9.29 eV for the adiabatic ionization energy of 3,3-dimethyl-1,2,4-trioxolane (Table 2) is only 80 meV (7.7 kJ mol⁻¹) higher than the best estimate of (9.21 ± 0.03) eV. It is possible that a lower-energy pathway to a more stable $C_3H_5O_3^+$ cation in the dissociative ionization explains the energetic discrepancy. However, the unexpectedly large intensity of the methyl-loss peak compared with the parent $C_4H_8O_3^+$ ion suggests that the methyl loss channel is not from dissociation of the 3,3-dimethyl-1,2,4-trioxolane cation. Nevertheless, the kinetic time traces of the daughter peaks (Fig. 6) are those of a stable product, not of a reactive radical, so the methyl- or CF₃- loss must occur after ionization. Some alternatives may be ionization to a dissociative excited state of the cation, or autoionization arising from excitation to an excited electronic state of neutral 3,3-dimethyl-1,2,4-trioxolane that then autoionizes to the daughter ion and CH₃. In this case the unusually large intensity may reflect a near-resonance excitation to the excited state of interest.

A more likely alternative is ionization from a different neutral $C_4H_8O_3$ isomer, for which dissociative ionization dominates. The methoxymethyl acetate isomer (calculated AIE 9.79 eV) can be formed by a 1,4-methyl shift following O–O bond scission of the secondary ozonide.^{10,44} A low-lying dissociative



Fig. 8 Photoionization spectra of the m/z = 213 product from the reaction of 13 CH₂OO with HFA, compared with a calculated spectrum of the secondary ozonide. The simulated spectrum uses a calculated Franck–Condon envelope and is shifted up by 55 meV from the CBS-QB3 estimate of the AIE. The signal at m/z = 144 is tentatively assigned to dissociative ionization of the (trifluoromethyl)methoxy trifluoroacetate isomer.

Table 2 Adiabatic ionization energies (AIE) for the secondary ozonides formed from the reaction of CH₂OO with acetaldehyde, acetone, and HFA. AIEs and relative reaction enthalpies $\Delta H_{0,rel}$ at 0 K for potential products from isomerization of 3,3-dimethyl-1,2,4-trioxolane and 3,3-di(trifluoromethyl)-1,2,4-trioxolane are also shown. All energies are obtained from CBS-QB3 calculations

Species	AIE (eV)	$\Delta H_{0,\text{rel}}$ (kJ mol ⁻¹)
3-Methyl-1,2,4-trioxolane	9.44	_
3,3-Dimethyl-1,2,4-trioxolane Methoxymethyl acetate (Dimethyl)hydroxymethyl formate	9.29 ^{<i>a</i>} 9.79 10.20	0 -235 -307
3,3-Di(trifluoromethyl)-1,2,4-trioxolane (Trifluoromethoxy)methyl trifluoroacetate Di(trifluoromethyl)hydroxymethyl formate	10.59 	0 -297 -304
^{<i>a</i>} Best-estimate value from higher-level calcu (Table 1). ^{<i>b</i>} The cation ground state is calcu	lations is 9.2 lated to be u	$21 \pm 0.03 \text{ eV}$

ionization pathway exists (Scheme 3) where energies (in kJ mol⁻¹) are at 0 K relative to the methoxymethyl acetate cation (from CBS-QB3 and G3MP2B3⁴⁵ calculations). The energies given below the reaction arrows in Scheme 3 are for the transition states. Both CBS-QB3 and G3MP2B3 predict that the transition state of the C–C bond fission is the highest-energy configuration in the pathway shown in Scheme 3 leading to methyl loss. The energy of this transition state relative to the cation



of methoxymethyl acetate differs between the two methods (CBS-QB3: 20 kJ mol⁻¹; G3MP2B3: 2 kJ mol⁻¹). The calculations on this transition state show substantial spin contamination $(\langle S^2 \rangle \sim 0.90-0.96$ in the different single-point calculations), which will result in an increased uncertainty in the calculated energies. Nevertheless, based on the AIE of methoxymethyl acetate obtained from CBS-QB3, the appearance energy for the methyl loss channel is 9.81 eV (G3MP2B3) and 10.00 eV (CBS-QB3). Both values are in reasonable agreement with the observed threshold for m/z = 89 in Fig. 7. Because the dissociation channel has only a small barrier, significant ion signal at the parent mass of methoxymethyl acetate is not expected, in accordance with the experiment. Based on these observations we attribute the m/z = 89 signal to dissociative ionization of the methoxymethyl acetate species. The ionization energy of the other isomerization product of the secondary ozonide, hydroxyisopropyl formate,¹⁰ is calculated as 10.20 eV. No significant onset in the photoionization spectrum at m/z = 104 around this energy is observed, and if methyl loss were a significant dissociative ionization channel in its cation, the appearance energy of $C_3H_5O_3^+$ would be at least 10.20 eV, too high to explain the experimental onset.

Similar arguments apply to the origin of the m/z = 144product signal from the reaction of ¹³CH₂OO with HFA. The energy of the products from simple C-C bond fission in the cation of the secondary ozonide, CF₃ and C₃H₂F₃O₃⁺, relative to the neutral secondary ozonide is 11.47 eV, which is ~ 0.5 eV higher than the experimental onset in the m/z = 144 product spectrum (see Fig. 8). Di(trifluoromethyl)hydroxymethyl formate has an AIE of 11.28 eV. Although one of the C-C bonds in the cationic structure is already substantially elongated, CF₃ loss would still have an appearance energy of at least the value of the AIE. No secondary threshold that could correspond to this isomerization product is observed in the m/z = 144 and 213 photoionization spectra. The cationic state of methoxymethyl acetate analogue in the HFA reaction, (trifluoromethoxy)methyl trifluoroacetate, is calculated to be unbound and undergoes dissociative ionization. It seems likely that CF₃ loss occurs in this cation, and we assign the m/z = 144 product signal from the reaction of ¹³CH₂OO with HFA to the dissociative ionization of (trifluoromethoxy)methyl trifluoroacetate.

The use of photoelectron spectroscopy to study small Criegee intermediates and the secondary ozonides produced in their reaction with aldehydes and ketones would be extremely valuable in resolving the vibrational structure in their first photoelectron bands to establish ionic state vibrational separations and to test the Franck–Condon simulations, as used, for example, in obtaining the simulated photoionization spectra shown in Fig. 7 and 8.



Fig. 9 Photoionization spectrum of the mass-60 product of the CH₂OO reaction with acetaldehyde, compared to a calibration spectrum of acetic acid.

The secondary ozonides and their isomerization products are not the only products observed. In the reaction of CH₂OO with HFA a contribution from formic acid was observed, although it was not quantified. (Studies did not go to high enough photon energy to investigate formic acid production in the reaction of CH₂OO with acetone.) Moreover, in the reaction of ¹²CH₂OO with acetaldehyde, no product signal is observed at either the ozonide mass (m/z = 90) or the ozonide minus CH₃ at m/z = 75. The product channels observed are formaldehyde at m/z = 30, and a second product at m/z = 60. Evidence of formic acid is visible in the photoionization spectrum of the reaction of ¹²CH₂OO with acetaldehyde, but the large background from doubly-¹³C substituted acetaldehyde nearly obscures it. The photoionization spectrum of the mass-60 product is in reasonable agreement with the photoionization spectrum of acetic acid (Fig. 9).

If the pathway for reaction of CH₂OO with carbonyl compounds is cycloaddition, as the body of ozonolysis experiments indicates, decomposition and isomerization of the secondary ozonide (Scheme 4) might contribute to the product spectrum. The *thermal* decomposition of the secondary ozonide product is very slow; using the reported Arrhenius parameters for unimolecular decomposition of methyl-1,2,4-trioxolane (propene ozonide)⁴⁶ yields a rate coefficient of only $\sim 4 \times 10^{-8} \text{ s}^{-1}$ at 295 K. However, if isomerization and dissociation channels exist with barriers near or below the CH₂OO + carbonyl entrance barrier, the chemically activated secondary ozonides may isomerize and/or dissociate before collisional stabilization can occur under the low-pressure conditions of the present experiments.



Isomerization and decomposition of excited secondary ozonide products has been implied in previous experiments. For example, the yield of secondary ozonides in gas-phase 1-alkene ozonolysis experiments was found to decrease substantially with increasing temperature,¹⁰ which was rationalized as a decomposition of excited initial secondary ozonide species from reactions of the CH₂OO and aldehyde products of the initial ozonolysis step. The CO₂-laser excitation of 3.5-dimethyl-1,2,4-trioxolane yielded the ester products 1-hydroxyethyl acetate and 1-methoxyethyl formate.44 These products would result from breaking the O-O bond in the secondary ozonide, followed by a 1,4-H or 1,4-methyl shift, and their presence in laser-sensitized decomposition suggests that such rearrangements may precede decomposition of the secondary ozonide to carboxylic acid and ketone or aldehyde products. The observation of similar products in the present direct reactions of CH₂OO with carbonyl species indicates that the transition states for such transformations likely lie near or below the energy of the reactants.

Conclusions

Absolute total rate coefficients have been directly measured for the removal of CH_2OO by reaction with hexafluoroacetone (HFA), acetone, and acetaldehyde. The reaction with HFA is rapid, tending to validate the use of HFA as a Criegee intermediate scavenger. Secondary ozonide products are observed for reactions of CH_2OO with acetone and HFA, but the presence of ozonide isomerization products and the observation of acetic acid as a product of the reaction of CH_2OO with acetaldehyde suggest that transition states for isomerization and decomposition pathways of the secondary ozonide are near or below the energy of the reactants.

Author contributions

The investigations were conceived by CJP, DES, and CAT. The experimental studies were designed, carried out and analyzed by CAT, OW, AJE, JDS, DLO, and CJP, with assistance from DES. EPFL, JMD, OW, JDS, and DWKM were responsible for quantum chemistry and Franck–Condon calculations.

Acknowledgements

This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the U. S. Department of Energy. DES, CJP, and JMD thank NERC for funding. EPFL, JMD and DKWM acknowledge support from Research Grant Council (RGC) of the Hong Kong Special Administrative Region (HKSAR, Grant No. PolyU 5018/09P), the National Service for Computational Chemistry Software (NSCCS), EPSRC (UK), and the IRIDIS High Performance Computing Facility at the University of Southampton. JMD thanks the Leverhulme Trust for an Emeritus Fellowship. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the U. S. Department of Energy under Contract DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.

References

- 1 R. Criegee and G. Wenner, Justus Liebigs Ann. Chem., 1949, 564, 9-15.
- 2 O. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu, C. J. Percival,
- D. E. Shallcross and C. A. Taatjes, *Science*, 2012, 335, 204–207.
 R. Asatryan and J. W. Bozzelli, *Phys. Chem. Chem. Phys.*, 2008, 10, 1769–1780.
- 4 C. A. Taatjes, G. Meloni, T. M. Selby, A. J. Trevitt, D. L. Osborn, C. J. Percival and D. E. Shallcross, J. Am. Chem. Soc., 2008, 130, 11883–11885.
- 5 D. Johnson and G. Marston, Chem. Soc. Rev., 2008, 37, 699-716.
- 6 N. M. Donahue, G. T. Drozd, S. A. Epstein, A. A. Presto and
- J. H. Kroll, *Phys. Chem. Chem. Phys.*, 2011, **13**, 10848–10857.
- 7 R. Criegee, Angew. Chem., Int. Ed. Engl., 1975, 14, 745–752. 8 O. Horie, C. Schäfer and G. K. Moortgat, Int. J. Chem. Kinet.,
- O. Holle, C. Schaler and G. K. Moortgat, Int. J. Chem. Kinet., 1999, 31, 261–269.
 O. B. Nick, O. Haria and C. K. Maartgat. Tetrahadran Lett. 1006
- 9 P. Neeb, O. Horie and G. K. Moortgat, *Tetrahedron Lett.*, 1996, 37, 9297–9300.
- 10 R. Fajgar, J. Vítek, Y. Haas and J. Pola, J. Chem. Soc., Perkin Trans. 2, 1999, 239–248.
- 11 O. Horie and G. K. Moortgat, Acc. Chem. Res., 1998, 31, 387-396.
- 12 C. A. Taatjes, N. Hansen, D. L. Osborn, K. Kohse-Höinghaus, T. A. Cool and P. R. Westmoreland, *Phys. Chem. Chem. Phys.*, 2008, **10**, 20–34.
- 13 D. L. Osborn, P. Zou, H. Johnsen, C. C. Hayden, C. A. Taatjes, V. D. Knyazev, S. W. North, D. S. Peterka, M. Ahmed and S. R. Leone, *Rev. Sci. Instrum.*, 2008, **79**, 104103.
- 14 C. A. Taatjes, N. Hansen, A. McIlroy, J. A. Miller, J. P. Senosiain, S. J. Klippenstein, F. Qi, L. S. Sheng, Y. W. Zhang, T. A. Cool, J. Wang, P. R. Westmoreland, M. E. Law, T. Kasper and K. Kohse-Höinghaus, *Science*, 2005, **308**, 1887–1889.
- 15 A. J. Eskola, D. Wojcik-Pastuszka, E. Ratajczak and R. S. Timonen, *Phys. Chem. Chem. Phys.*, 2006, 8, 1416–1424.
- 16 M. Olzmann, E. Kraka, D. Cremer, R. Gutbrod and S. Andersson, J. Phys. Chem. A, 1997, 101, 9421–9429.
- 17 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A. J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A1.
- 18 J. A. Montgomery, M. J. Frisch, J. W. Ochterski and G. A. Petersson, J. Chem. Phys., 1999, 110, 2822–2827.
- 19 H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz, P. Celani, G. Knizia, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang and A. Wolf, MOLPRO, version 2010.1, a package of *ab initio* programs. http://www.molpro.net.
- 20 T. H. Dunning, J. Chem. Phys., 1989, 90, 1007-1023.
- 21 K. A. Peterson, Thomas B. Adler and H.-J. Werner, J. Chem. Phys., 2008, 128, 084102.

- 22 J. G. Hill, S. Mazumder and K. A. Peterson, J. Chem. Phys., 2010, 132, 054108.
- 23 T. Helgaker, W. Klopper, H. Koch and J. Noga, J. Chem. Phys., 1997, 106, 9639–9646.
- 24 A. Halkier, T. Helgaker, W. Klopper, P. Jørgensen and A. G. Császár, *Chem. Phys. Lett.*, 1999, **310**, 385–389.
- 25 M. E. Harding, J. Vázquez, B. Ruscic, A. K. Wilson, J. Gauss and J. F. Stanton, J. Chem. Phys., 2008, 128, 114111.
- 26 E. F. Valeev and T. D. Crawford, J. Chem. Phys., 2008, 128, 244113.
- 27 G. Czakó, B. Nagy, G. Tasi, Á. Somogyi, J. Šimunek, J. Noga, B. J. Braams, J. M. Bowman and A. G. Császár, *Int. J. Quantum Chem.*, 2009, **109**, 2393–2409.
- 28 X. Huang, E. F. Valeev and T. J. Lee, J. Chem. Phys., 2010, 133, 244108.
- 29 F. Neese and E. F. Valeev, J. Chem. Theory Comput., 2010, 7, 33-43.
- 30 G. Knizia, T. B. Adler and H.-J. Werner, J. Chem. Phys., 2009, 130, 054104.
- 31 T. Helgaker, W. Klopper and D. P. Tew, *Mol. Phys.*, 2008, 106, 2107–2143.
- 32 V. A. Mozhayskiy and A. I. Krylov, ezSpectrum. http://iopenshell. usc.edu/downloads This work was conducted using the resources of the iOpenShell Center for Computational Studies of Electronic Structure and Spectroscopy of Open-Shell and Electronically Excited Species (http://iopenshell.usc.edu) supported by the National Science Foundation through the CRIF:CRF program.

- 33 F. Duschinsky, Acta Physicochim. URSS, 1937, 7, 551.
- 34 G. T. Drozd and N. M. Donahue, J. Phys. Chem. A, 2011, 115, 4381–4387.
- 35 D. Cremer, T. Schmidt, W. Sander and P. Bischof, J. Org. Chem., 1989, 54, 2515–2522.
- 36 M. T. Nguyen, T. L. Nguyen, V. T. Ngan and H. M. T. Nguyen, *Chem. Phys. Lett.*, 2007, 448, 183–188.
- 37 W. Sander, Angew. Chem., Int. Ed. Engl., 1990, 29, 344-354.
- 38 L. B. Harding and W. A. Goddard, J. Am. Chem. Soc., 1978, 100, 7180–7188.
- 39 W. H. Bunnelle, Chem. Rev., 1991, 91, 335-362.
- 40 R. W. Murray, P. R. Story and L. D. Loan, J. Am. Chem. Soc., 1965, 87, 3025–3026.
- 41 R. Criegee, S. S. Bath and B. von Bornhaupt, *Chem. Ber.*, 1960, **93**, 2891–2897.
- 42 J. D. Fenske, A. S. Hasson, A. W. Ho and S. E. Paulson, *J. Phys. Chem. A*, 2000, **104**, 9921–9932.
- 43 R. I. Martinez, J. T. Herron and R. E. Huie, J. Am. Chem. Soc., 1981, 103, 3807–3820.
- 44 L. Khachatryan, R. Fajgar, Y. Haas and J. Pola, J. Chem. Soc., Perkin Trans. 2, 1996, 1981–1984.
- 45 A. G. Baboul, L. A. Curtiss, P. C. Redfern and K. Raghavachari, J. Chem. Phys., 1999, 110, 7650–7657.
- 46 L. A. Hull, I. C. Hisatsune and J. Heicklen, *J. Phys. Chem.*, 1972, **76**, 2659–2665.