**1. Introduction**

N-methylformamide (MF) and N,N-dimethylformamide (DMF) are High Production Volume (HPV) chemicals on the US HPV Challenge Program Chemical List along with around 2800 other compounds. MF and DMF have also been reported as important products in the atmospheric degradation of dimethylamine and trimethylamine, respectively. The toxicology of dimethyl and monomethyl derivatives of acetamide and formamide was recently reviewed; DMF is handled under the OECD HPV Screening Information Data Set (SIDS) Program while the test plan for MF has not yet been implemented.

The reactions of OH radicals with CH$_3$NHCHO (N-methylformamide, MF) and (CH$_3$)$_2$NCHO (N,N-dimethylformamide, DMF) have been studied by experimental and computational methods. Rate coefficients were determined as a function of temperature ($T = 260–295$ K) and pressure ($P = 30–600$ mbar) by the flash photolysis/laser-induced fluorescence technique. OH radicals were produced by laser flash photolysis of 2,4-pentanediione or tert-butyl hydroperoxide under pseudo-first order conditions in an excess of the corresponding amide. The rate coefficients obtained show negative temperature dependences that can be parameterized as follows: $k_{\text{OH}+\text{MF}} = (1.3 \pm 0.4) \times 10^{-12} \exp(3.7 \text{ kJ mol}^{-1}/RT) \text{ cm}^3\text{ s}^{-1}$ and $k_{\text{OH}+\text{DMF}} = (5.5 \pm 1.7) \times 10^{-15} \exp(6.6 \text{ kJ mol}^{-1}/RT) \text{ cm}^3\text{ s}^{-1}$. The rate coefficient $k_{\text{OH}+\text{MF}}$ shows very weak positive pressure dependence whereas $k_{\text{OH}+\text{DMF}}$ was found to be independent of pressure. The Arrhenius equations given, within their uncertainty, are valid for the entire pressure range of our experiments.

Furthermore, MF and DMF smog-chamber photo-oxidation experiments were monitored by proton-transfer-reaction time-of-flight mass spectrometry. Atmospheric MF photo-oxidation results in 65% CH$_3$NCO (methylisocyanate), 16% (CHO)$_2$NH, and NO$_x$-dependent amounts of CH$_2$=NH and CH$_3$NHNO$_2$ as primary products, while DMF photo-oxidation results in around 35% CH$_3$N(CHO)$_2$ as primary product and 65% meta-stable (CH$_3$)$_2$N(CHO)OONO$_2$ degrading to NO$_x$-dependent amounts of CH$_2$N=CH$_2$ (N-methylmethanimine), (CH$_3$)$_2$NNO (N-nitroso dimethylamine) and (CH$_3$)$_2$NNO$_2$ (N-nitro dimethylamine). The potential for nitramine formation in MF photo-oxidation is comparable to that of methylamine whereas the potential to form nitrosamine and nitramine in DMF photo-oxidation is larger than for dimethylamine. Quantum chemistry supported atmospheric degradation mechanisms for MF and DMF are presented. Rate coefficients and initial branching ratios calculated with statistical rate theory based on molecular data from quantum chemical calculations at the CCSD(T)-F12a/aug-cc-pVTZ/MP2/aug-cc-pVTZ level of theory show satisfactory agreement with the experimental results. It turned out that adjustment of calculated threshold energies by 0.2 to 8.8 kJ mol$^{-1}$ lead to agreement between experimental and predicted results.
reactions are relatively fast (rate coefficients in the order of $10^{-11}$ and $10^{-14}$ cm$^3$ s$^{-1}$, respectively), and the average global lifetimes of amides with respect to reactions with OH and NO$_3$ radicals will be less than a few days; reactions with Cl atoms and O$_3$ do not constitute important sinks for amides. The gas phase UV spectra of amides are structureless and show low absorption cross-sections ($<10^{-20}$ cm$^2$) above 270 nm. Consequently, tropospheric photolysis of amides is not an important loss process. Due to their solubility in water, uptake into droplets and subsequent deposition may be an important sink.

The present communication reports on experimental kinetic studies of MF and DMF reactions with OH radicals at atmospherically relevant temperatures and from product studies in photo-oxidation experiments of MF and DMF. The results are corroborated by high-level quantum chemical calculations and statistical rate theory.

2. Experimental methods

2.1. Laser photolysis experiments

The kinetic experiments were performed by using the flash photolysis/laser-induced fluorescence technique in a coolable slow-flow reactor with helium as bath gas. The experimental setup was described in detail elsewhere, so only a brief description will be given here.

The reaction cell has an inner volume of ca. 640 cm$^3$ and is enclosed in a steel housing that can be evacuated to prevent ice formation on the windows and to improve thermal insulation. The gas flows were controlled by calibrated mass flow controllers, and accumulation of reaction products is avoided by choosing appropriate flow rates. OH radicals were produced by pulsed photolysis of 2,4-pentanedione for (OH + DMF) or tert-butyl hydroperoxide (t-BuOOH, for OH + MF) with a KrF excimer laser at 248 nm. The OH concentration-time profiles were monitored by recording the laser-induced fluorescence (LIF) in a wavelength range of (308 ± 7.5) nm after excitation at 281.9 nm. For excitation a frequency-doubled dye laser was used that was operated with rhodamine 6G and pumped with a Nd:YAG laser. The fluorescence signal was detected with a photomultiplier oriented perpendicularly to the antiparallel excimer and dye laser beams. A variation of the pulse energy of the photolysis laser between 60 and 300 mJ corresponding to fluences of 20–100 mJ cm$^{-2}$ had no significant effect on the rate coefficient, which indicates that unwanted radical–radical reactions are unimportant under our experimental conditions.

A bath gas flow with a well-known concentration of the corresponding amide was produced by flowing helium through a saturator that consisted of a conventional gas washing bottle with a fritted disc. The washing bottle containing the pure amide was kept in a water bath at 294 K, and the possibility of evaporative cooling was checked by monitoring the temperature at the highest flow rates for 90 minutes. No change in temperature was observed. In general, one bottle (height of the liquid column: ca. 10 cm, helium flow: 5–50 sccm) was found to be sufficient for saturation under our experimental conditions. Test measurements with a second bottle in a two-stage arrangement gave identical results. The amide concentrations were calculated with the ideal gas law from the measured vapor pressures by assuming complete saturation.

To assess the measured values, the vapor pressure of DMF was calculated from Antoine equation, \[ \log(P/\text{bar}) = A - \frac{B}{(T/\text{K} + C)} \]

with the constants from ref. 12: \( A = 3.93068, B = 1337.716, C = -82.648 \) (determined in the temperature range 303–363 K). For \( T = 294 \text{ K} \), one obtains a vapor pressure of \( P = 3.99 \text{ mbar} \).

For the MF constants in ref. 12, \( A = 4.99796, B = 2134.031, \) and \( C = -45.071 \), were obtained in the temperature range 370–472 K. Because this is much higher than the temperature in our saturator, we determined the vapor pressure of MF at 294 K in separate experiments. We used a 200 cm$^3$ stainless steel vacuum line connected to a turbo pump and a capacitance manometer. The leak rate of this vacuum line was determined to be 0.002 mbar min$^{-1}$. The MF was purified by first purging it with helium in a gas washing bottle for 3 hours and then thoroughly degassing it in repeated freeze–pump–thaw cycles. The gas washing bottle was connected to the vacuum line, and the pressure rise was measured until the change in pressure reached the leak rate determined before. In this way, we obtained a vapor pressure of \( P = 0.33 \text{ mbar} \) at \( T = 294 \text{ K} \). This value is somewhat higher than the value of 0.266 mbar obtained with the above Antoine parameters. However, we note that extrapolations with the Antoine equation outside the temperature range, where the parameters were determined, have to be considered with great caution.

The mixtures of 2,4-pentanedione and t-BuOOH in helium were manometrically prepared in gas cylinders and allowed to homogenize for at least 16 hours before use.

2,4-Pentanedione (99%, Sigma Aldrich), t-BuOOH (80% in H$_2$O, Sigma Aldrich), MF (99% Sigma Aldrich), and DMF (99% Alfa Aesar) were purified by repeated freeze–pump–thaw cycles, and the gas washing bottles containing the amides were purged before each experiment by a helium flow for at least 30 minutes. The purity of the helium was >99.9999% (Air Liquide).

In our kinetic experiments pseudo-first order conditions were ensured by keeping the amide concentrations in large excess of the initial OH concentration. Typical amide concentrations were in the range $10^{14}$–$10^{16}$ cm$^{-3}$ whereas OH concentrations can be estimated from absorption cross-sections of our precursors as being typically in the order of $10^{11}$ cm$^{-3}$. The decay of the OH concentration, of which an example is shown in Fig. 1, is then given by a first-order rate law, \( \frac{d[OH]}{dt} = -k_{\text{pseudo}}[OH] \), where \( k_{\text{pseudo}} = k_{\text{bim}}[amide] + k_d \) with \( k_{\text{bim}} \) being the bimolecular rate coefficient of the OH + amide reaction and \( k_d \) characterizing other first-order loss processes of the OH radicals (diffusional loss, reaction with precursor etc.). If \( k_d \) is assumed to be constant for a given temperature and pressure, the bimolecular rate coefficient \( k_{\text{bim}} \) is given as the slope of \( k_{\text{pseudo}} \) plotted vs. amide concentration. An example plot is given in Fig. 2. We note that in some experiments we observed biexponential decays. However, because the scattering of the low LIF intensities at longer times was considerable, we refrained from performing biexponential analyses in these.
cases and determined the rate coefficients $k_{\text{pseudo}}$ always from the initial, linear part of the semi-logarithmic plots.

The experimental conditions for the OH + MF and OH + DMF experiments are summarized in Tables S1 and S2 of the ESL. Due to the multitude of parameters that influence the uncertainty of the experiments, and which are difficult to quantify exactly, a maximum error of 30% for the rate coefficients was estimated. We note, however, that the statistical error is smaller (see below).

### 2.2. Photo-oxidation studies

OH + amide reaction product studies were conducted in a 480 l Teflon coated reaction chamber made of glass and surrounded by 18 UV/Vis lamps ($\lambda \geq 300$ nm) to simulate sunlight. Experiments were performed in dry synthetic air at an absolute pressure of 970 mbar and temperatures in the range between 302 K and 306 K. OH radicals were produced by photolysis of isopropyl nitrate. The initial reaction conditions were 250 ppbV of the reagent amide, 100 ppb of NO and 250 ppbV of isopropyl nitrite. The reagent mixture was irradiated for 15 minutes. During photo-oxidation, NO was continuously added to the chamber at a rate of 6.8 ppb min$^{-1}$. Synthetic air was continuously added to the chamber at a flow rate of 3.26 slpm to replenish instrumental sampling flows. A large amount of NO was injected into the chamber 10 minutes after the lamps had been turned off for identification of rapidly decaying thermally unstable acylperoxynitrate compounds. Duplicate experiments were carried out for each reagent.

The chemicals and gases used in the experiments and their stated purities were as follows: N-methylformamide (99%, Sigma-Aldrich), N,N-dimethylformamide (99.8%, Sigma-Aldrich), synthetic air (5.0, Messer Austria), nitrogen oxide in nitrogen (401 mg m$^{-3}$ NO; Linde). Isopropyl nitrite was synthesized from sodium nitrite in water, isopropanol and sulfuric acid.

Analytical instrumentation coupled to the chamber included a high-resolution proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF 8000, Ionicon Analytik GmbH) for amide and amide photo-oxidation product measurements, a chemiluminescence NO-detection instrument (CLD770 AL ppt, ECO PHYSICS) combined with a photolytic converter (PLC 760 MH, ECO PHYSICS) for NO$_2$ detection, a UV photometric ozone analyzer (49i, Thermo Scientific) and a temperature/relative humidity sensor (UFT75-AT, MELTEC). The PTR-ToF-MS was interfaced to the chamber via a PEEK capillary tube (temperature: 50°C; flow: 0.15 slpm). The PTR-ToF-MS was operated at a reduced electric field of 52 Td and 85 Td, respectively, during the duplicate experiments.

For PTR-ToF-MS data analysis, we used the “PTR-TOF Data Analyzer” software.Instrumental response factors for amides and amide photo-oxidation products were derived from ion-molecule collision theory using calculated molecular properties.

### 3. Computational methods

#### 3.1. Electronic structure calculations

Stationary points on the potential energy surfaces for reactions of the amides with OH were characterized using second-order Møller–Plesset perturbation theory (MP2) as well as BHandHLYP density functional theory. Pre- and post-reaction adducts were located by following the reaction path (IRC) from the saddle points. In addition, reaction enthalpies were calculated using G3 model chemistry, while dipole moments and isotropic polarizabilities (employed in calculations of ion-molecule reaction rate coefficients, see above) were obtained in B3LYP/aug-cc-pVTZ calculations. The G3 results are summarized in Table S3 (ESI$^\dagger$).

DFT and MP2 calculations are often capable of giving very good geometries for minima on reactive potential energy surfaces, but may be less suitable for transition states as these may have significant multi-reference character. We have therefore re-optimized the geometries of the transition states using...
CASPT2 with an active space consisting of the bonding and antibonding orbital of the bond being broken in the amide and the unpaired electron in the OH radical, i.e. 3 electrons in 3 orbitals.

Energies of the stationary points were improved using coupled cluster singles and doubles with explicitly correlated wave functions using the F12a approximation with perturbative triples scaled as recommended in the MOLPRO manual, denoted CCSD(T*)-F12a.20,21 Dunning’s correlation consistent basis sets were used in all calculations.7

Unrestricted wave functions were used for the open-shell calculations. The G3, BHandHLYP, B3LYP and MP2 calculations were performed using Gaussian09,24 while the explicitly correlated coupled cluster calculations and CASPT2 calculations were performed using Molpro 2012.1.25

3.2. Statistical rate theory calculations

The reactions of amides with OH radicals proceed via pre-reaction complexes and the overall kinetics and may therefore be governed by forward reactions and back dissociation of the complex. Specific rate coefficients for the unimolecular forward reactions were calculated using RRKM theory based on energies and molecular data from CCSD(T*)-F12a/aug-cc-pVTZ//MP2/aug-cc-pVTZ calculations. Rate coefficients for back dissociation of the complex were obtained via detailed balancing from capture rate coefficients of complex formation. The capture rate coefficients were calculated with long-range transition state theory (LRTST).26 Spin–orbit coupling in the transition state was accounted for in the model by lowering the energy of the OH radical by half of the splitting and including the 2P3/2 and 2P1/2 spin–orbit states in the electronic partition function. It was assumed that spin–orbit coupling could be neglected in the pre-reaction adduct and in the transition states.

Lennard-Jones parameters of MF and DMF were approximated by the corresponding values for methyl acetal (ε/kB = 469.8 K, σ = 4.94 Å)22 and for collisional energy transfer an exponential-down model was assumed. The energy transfer parameter for collisions with He was set to (ΔE_down) = 200 cm⁻¹. Variation of this value between 100 and 300 cm⁻¹ lead only to minor changes (< 2%) in the calculated rate coefficients.

The temperature and pressure dependence of the phenomenological rate coefficients for the bimolecular overall reactions was obtained from the eigenvalues of a corresponding master equation by employing the Bartis–Widom method29,30 as implemented in the MESMER code.31

4. Results

There are three possible product channels in the MF + OH reaction:

(CH₃)₂NCHO + OH → (CH₃)₂NCHO + H₂O
ΔH˚ = −100 kJ mol⁻¹
(1a)

→ (CH₃)₂NCHO + H₂O
ΔH˚ = −40 kJ mol⁻¹
(1b)

→ (CH₃)₂NCHO + H₂O
ΔH˚ = −104 kJ mol⁻¹
(1c)

and also three possible product channels in the DMF + OH reaction:

(CH₃)₂NCHO + OH → (CH₃)₂NCHO + H₂O
ΔH˚ = −98 kJ mol⁻¹
(2a)

→ trans-CH₂N(CH₃)CHO + H₂O
ΔH˚ = −100 kJ mol⁻¹
(2b)

→ cis-CH₂N(CH₃)CHO + H₂O
ΔH˚ = −100 kJ mol⁻¹
(2c)

The reaction enthalpies listed refer to 298 K and to the lowest energy conformations of the species involved; they stem from G3 calculations.19 We note that the barrier for cis-trans isomerization of CH₂N(CH₃)CHO is 80 kJ mol⁻¹.

4.1. Structures and energies of stationary points

Stationary points on the amide + OH potential energy surfaces (PES) were located in MP2 and BHandHLYP calculations employing different basis sets. The results of the calculations are summarized in Tables S4 and S5 (ESI†) while Fig. 3 and 4 show the energies of the stationary points calculated using CCSD(T*)-F12a/aug-cc-pVTZ//MP2/aug-cc-pVTZ. Cartesian coordinates of the stationary points calculated using MP2/aug-cc-pVTZ are collected in Tables S6 and S7 (ESI†). The values from G3X-K32 model chemistry reported by Borduas et al.6 for MF are similar to the present results. The reactions of both amides with OH radicals are characterized by post- and pre-reaction van der Waals adducts and submerged barriers. To locate the pre- and post-reaction complexes, IRCs were followed in both BHandHLYP and MP2 calculations using the aug-cc-pVdz basis set.

The transition states of H abstraction from the methyl (TSCH₃) and the carbonyl (TSCHO) groups in MF are very similar in energy, and it is therefore difficult to calculate the branching ratio accurately as even small changes in the barrier heights have a large impact on the calculated branching ratio. It is intuitively clear that abstraction from the NH group (TSNH) will constitute only a minor route.

Fig. 3 Potential energy diagram (including zero-point energies) for the OH + MF reaction from CCSD(T*)-F12a/aug-cc-pVTZ//MP2/aug-cc-pVTZ calculations; energies are relative to reactant energies.
4.2. Rate coefficients of the OH + MF and OH + DMF reactions

Fig. 5 shows experimental and calculated rate coefficients of the OH + MF reaction as a function of temperature. The experimental values exhibit a weak negative temperature dependence that can be parameterized as follows: $k_{\text{calc}}(\text{OH} + \text{MF}) = (1.3 \pm 0.4) \times 10^{-12} \exp(3.7 \text{ kJ mol}^{-1}/(R\theta)) \text{ cm}^3 \text{ s}^{-1}$. The detailed experimental conditions for the individual data points along with the measured rate coefficients are collected in Table S1 (ESI†). We also note that our experiments in the pressure range 30–600 mbar seem to indicate a very weak positive pressure dependence (increase of ~20% in going from 30 to 600 mbar), which is illustrated in Fig. S2 (ESI†).

The rate coefficients calculated using the CCSD(T*)-F12a/aug-cc-pVTZ/MP2/aug-cc-pVTZ results are about a factor of 5 higher than the experimental values. The calculated capture rate coefficient is rather large, $k_{\text{cap}} = 7.59 \times 10^{-10} (T/298 \text{ K})^{-1/6} \text{ cm}^3 \text{ s}^{-1}$ (ESI† Table S8), but reducing it by a factor of 2 lowers the phenomenological rate coefficient only by less than 8% in the 250–300 K range. The relative branching fractions for H abstraction at the CHO and CH$_3$ group hardly varies with a change in the capture rate coefficient and are calculated to be 91.5% and 8.5%, respectively, at $T = 300$ K and 89.8% and 10.2%, respectively, at $T = 250$ K. The contribution of H abstraction from the NH group is negligible.

Lowering the threshold energy for abstraction from the NH group by 4 kJ mol$^{-1}$ and simultaneously increasing the threshold energies for abstraction from the CHO and the CH$_3$ group by 4 kJ mol$^{-1}$ changes the relative branching fractions merely to 89.7%, 10.2% and 0.1% for H abstraction from CHO, CH$_3$, and NH, respectively, but results in a 75% reduction of the overall rate coefficient (at $T = 300$ K). Therefore, we conclude that the overall reaction is governed by the inner transition states and that abstraction from the NH group is not important at atmospheric conditions.

Fig. 5, in connection with Table 1, illustrates that a very good agreement between calculated and experimentally determined rate coefficients can be achieved with only moderate adjustment of the barriers. We note that with the adjusted values also the branching fractions observed in our photo-oxidation experiments are very well reproduced (see below).
Table 1  Calculated and adjusted transition state energies for OH + MF, relative to the energy of the reactants (unit: kJ mol⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>(T_{CH_3})</th>
<th>(T_{CHO})</th>
<th>(T_{NH})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>-9.6</td>
<td>-7.7</td>
<td>12.6</td>
</tr>
<tr>
<td>Adjusted</td>
<td>-4.0</td>
<td>-4.1</td>
<td>12.6</td>
</tr>
</tbody>
</table>

⁷ CCSD(T*)-F12a/aug-cc-pVTZ//MP2/aug-cc-pVTZ results. ⁸ Adjusted barrier heights to reproduce experimental rate coefficients and relative product branching fractions from our photo-oxidation study (see below) with our master equation calculations. ⁹ Excluded from analysis.

Fig. 6 shows experimental and calculated rate coefficients of the OH + DMF reaction as a function of temperature. Also for this reaction system the experimental values exhibit a weak negative temperature dependence that can be parameterized as follows: \(k_{\text{exp}}(\text{OH} + \text{DMF}) = (5.5 \pm 1.7) \times 10^{-13} \exp(6.6 \text{ kJ mol}^{-1}/(RT)) \text{ cm}^3 \text{ s}^{-1}\). The detailed experimental conditions for the individual data points along with the measured rate coefficients are collected in Table S2 (ESI†). We note that no discernible pressure dependence of the rate coefficient could be observed within our experimental uncertainty (see ESI,† Fig. S3). The agreement between the calculated and experimental rate coefficients is not as good as for the MF + OH reaction. This can be seen from a comparison of the dashed and solid lines in Fig. 5 and 6. Whereas for OH + MF this difference is about a factor of 5, the difference for OH + DMF is a factor of \(\sim 10\). Accordingly, rather large adjustments of the barriers are necessary to reproduce the experimental rates as can be seen from Table 2.

The calculated capture rate coefficient for the DMF + OH reaction, \(k_{\text{cap}} = 7.55 \times 10^{-10} (T/298 \text{ K})^{-1/6} \text{ cm}^3 \text{ s}^{-1}\), is very similar to that for the MF + OH reaction (Table S8, ESI†). But since the energy barrier for the lowest H abstraction step relative to the bimolecular reactants is considerably lower than in the case of MF + OH, a reduction of the capture rate coefficient by a factor of two also leads to a stronger decrease of the phenomenological rate coefficient by up to 27% (compared to up to 8% for MF + OH) in the temperature range 250–300 K.

The differences in the temperature dependence between the two reaction systems can be rationalized in terms of the potential energy surface. The pre-reaction complexes are nearly equally stable with respect to the bimolecular reactants, but the lowest energy barrier for hydrogen abstraction is somewhat larger for the OH + MF reaction than for the OH + DMF reaction (cf. Tables 1 and 2). This may lead to a somewhat stronger (negative) temperature dependence in the latter case. The differences in the pressure dependence are too small compared to our experimental uncertainty for a reasonable further analysis (cf. Fig. S2 and S3, ESI†).

Table 3 summarizes the currently available kinetic data for reactions of OH radicals with different amides. The rate coefficients reported by Solignac et al.⁴⁴ are somewhat higher than those from both Koch et al.⁴⁴ and the present work but agree within the combined error bars. An interesting feature of the data is that the values from relative measurements are consistently higher than those from absolute measurements. This is probably related to the nature of the experiments: in the relative rate measurements,⁵,⁶,¹³,¹⁵,³⁵,³⁶ the rate of amide removal is measured relatively to the removal rate of a reference compound, and any additional process that removes the amide will increase the observed rate. In the absolute measurements (this work and Koch et al.⁴⁴), the measured quantity is the removal rate of OH radicals in an excess of amide, and any process removing the amide will give a smaller observed rate. Despite all our efforts to detect and prevent any wall loss, we cannot completely rule out that some of the amide has been lost by other processes before passing the detection volume in our photolysis cell. The negative activation energies from this work nicely agree with the other available values for N-methylacetamide, N,N-dimethylacetamide, N-methylpropanamide, and N,N-dimethylpropanamide.

4.3. \(\text{CH}_3\text{NHCHO}\) photo-oxidation studies

Barnes et al.⁵ carried out OH and Cl atom initiated photo-oxidation experiments with MF employing long-path FTIR detection and reported (CHO)₂NH and CH₂NCO as the main products with
Table 3 Rate coefficients and Arrhenius activation energies for the reactions of OH with different amides

<table>
<thead>
<tr>
<th>Amide</th>
<th>$k/10^{-12}$ cm$^3$ s$^{-1}$</th>
<th>$E_a$/kJ mol$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formamide</td>
<td>$4.44 \pm 0.46^b$</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>N-Methylformamide</td>
<td>$10.1 \pm 0.6^b$</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$8.6 \pm 2.4^b$</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$5.7 \pm 1.7^c$</td>
<td>-3.7 This work</td>
<td></td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>$14 \pm 3^a$</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$8.5 \pm 2.6^d$</td>
<td>-6.6 This work</td>
<td></td>
</tr>
<tr>
<td>Acetamide</td>
<td>$3.5 \pm 1^a$</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0.77 \pm 0.35^a$</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>N-Methylacetamide</td>
<td>$11 \pm 3^a$</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$5.2^c$</td>
<td>-4.1 34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$5.42 \pm 0.19^a$</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>N,N-Dimethylacetamide</td>
<td>$19 \pm 3^a$</td>
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</tr>
<tr>
<td></td>
<td>$13.6^d$</td>
<td>-5.2 34</td>
<td></td>
</tr>
<tr>
<td>Propanamide</td>
<td>$1.78 \pm 0.43^a$</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>N-Methylpropanamide</td>
<td>$7.6^f$</td>
<td>-3.3 34</td>
<td></td>
</tr>
<tr>
<td>N,N-Dimethylpropanamide</td>
<td>$20.7^f$</td>
<td>-4.4 34</td>
<td></td>
</tr>
<tr>
<td>1-Methyl-2-pyridinedione</td>
<td>$21.5 \pm 3.6^f$</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$22 \pm 4^f$</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>1-Methyl-2,2-pyridinediene</td>
<td>$14 \pm 3^a$</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>2-Oxo-1-pyridinediene-carboxaldehyde</td>
<td>$6 \pm 1^a$</td>
<td>36</td>
<td></td>
</tr>
</tbody>
</table>

* $T = 298$ K, $P = 1$ bar (air), the errors given represent the standard deviation of multiple experiments, the authors estimate a total uncertainty closer to 20%. $^b$ $T = 298$ K, $P = 1$ bar (air). $^c$ Measurements at $T = 294$ K, $P = 600$ mbar (helium). $^d$ Measurements at $T = 294$ K, $P = 30-600$ mbar (helium). $^e$ $T = 298$ K, $P = 1$ bar (air). $^f$ $T = 300$ K, $P = 130$ mbar (helium). $^g$ $T = 296$ K, $P = 1$ bar (air). $^h$ $T = 300$ K and $P = 1$ bar (air).

yields of roughly 50% and 30%, and with variable amounts of the peroxynitrate-type compound, CH$_3$NHC(O)OONO$_2$, depending on the NO$_2$-level in the experiment. Unfortunately, the lack of calibrated reference spectra prevented the authors from making a proper quantification of the product yields. Borduas et al. recently carried out NO$_2$-free OH-initiated photo-oxidation experiments with MF employing PTR-MS detection and reported a CH$_3$NCO yield around 40%; they further reported formamide (≈15% yield) and HNCO as oxidation products. Diformamide, (CHO)$_2$NH, was only detected as a trace product and was not quantified.

Fig. 7 shows the time evolution of the main ion signals observed by PTR-ToF-MS during a photo-oxidation experiment. Fig. S4 and S5 (ESI†), respectively, illustrate the difference in PTR-ToF-MS mass spectra taken after and just before the photo-oxidation experiment, and the NO and NO$_2$ mixing ratios during the experiment. The NO level is nearly constant around 25 ppbV during the photo-oxidation, whereas the NO$_2$ level increases from a single-digit value to nearly 400 ppbV in the same period. Reacting compounds are MF (detected in its protonated form at m/z 60.042 and its $^{13}$C isotopologues at m/z 61.043) and isopropyl nitrite, which is detected at m/z 29.996 [NO$_2$], m/z 43.055 [C$_3$H$_5$N], m/z 61.066 [C$_3$H$_5$O] and m/z 79.074 [C$_3$H$_7$O$_2$]. Signals that increased during the photo-oxidation experiment are m/z 58.029 [C$_3$H$_5$NO$_2$] (protonated methylisocyanate), m/z 74.024 [C$_3$H$_5$NO$_2$] (protonated N-formylformamide), m/z 76.041 [C$_3$H$_5$NO$_2$] (protonated methylisocyanate water cluster) and m/z 77.032 [CH$_3$N$_2$O$_2$] (protonated methylisocyanate). We also observed an increase in the ion signals at m/z 43.018 (C$_3$H$_5$O$_2$), m/z 45.034 (C$_3$H$_5$O$_2$), m/z 45.992 [NO$_2$], m/z 59.049 [C$_3$H$_5$O] and m/z 77.056 (C$_3$H$_5$O$_3$). These signals stem from compounds (acetaldehyde, acetone and nitric acid) typically formed in any smog chamber photo-oxidation experiment in the presence of isopropyl nitrite and NO$_2$, i.e. even in the absence of MF. In our product analysis, we only included signals with a larger than 1% increase relative to decrease in the protonated MF signal. In spite of every effort made no trace of CH$_3$NHC(O)OONO$_2$ was ever detected in any of the present experiments.

Wall loss of MF was significant in the experiments. Additional loss was inflicted by synthetic air that was constantly added to compensate for instrumental sampling flows ($k_{\text{duration}} = 1.13 \times 10^{-4}$ s$^{-1}$); analysis of the MF loss curve before and after the 15 min photo-oxidation period suggested an MF wall loss rate coefficient $k_{\text{wall loss}} \approx 2.6 \times 10^{-4}$ s$^{-1}$.

There is apparently a mismatch in Fig. 7 between the amount of N-methylformamide reacted and the amounts of products formed in the experiment. However, the apparent discrepancy is deceptive: N-nitro methyamine, CH$_3$NHNO$_2$, formed with a ≈5% yield in the experiment shown, can only be formed in the reaction between CH$_3$NH radicals and NO$_2$, and even under conditions with high NO$_2$ levels, as in the present case, the major loss of CH$_3$N radicals is due to reaction with O$_2$ resulting in methanimine, CH$_3$=NH, which is extremely difficult to detect and to quantify due to polymerization and surface-induced reactions.

It is highly significant that there is no discernable change in the N-nitro methyamine volume mixing ratio upon addition of excess NO to titrate peroxy radicals present in the chamber. This indicates that either very little CH$_3$NHC(O)OONO$_2$ was ever formed during the experiment or that the lifetime of the compound is very short, or a combination of both of the above. FTIR-spectroscopic evidence for formation of CH$_3$NHC(O)OONO$_2$ in N-methylformamide photo-oxidation experiments is rather limited, and the weak bands reported as characteristic of...
The CH3NHC(O)OOO2 actually have their counterparts in the IR spectrum of CH3NHNHO2.27

Given the scarcity of well-documented mechanistic information on amide photo-oxidation chemistry, a first principles mapping of the reaction thermochemistry was undertaken and additional mechanism elucidating calculations carried out. The present quantum chemistry results have many similarities with those reported by Borduas et al.;6 there are, however, significant differences in approach, results and, consequently, in the mechanistic conclusions.

The CH3NHCHO reaction with OH radicals may, as already mentioned, proceed via hydrogen abstraction from either the CHO group, the NH group or the CH3 group. The N–H abstraction route is calculated to have a medium-sized barrier of around 12 kJ mol⁻¹, while the C–H abstraction routes have barriers well below the entrance energy of the reactants. The quantum chemistry calculations therefore unambiguously show that the N–H abstraction route is of no importance in the CH3NHCHO + OH reaction at atmospheric conditions, and it will not be addressed any further here.

Route (1a), hydrogen abstraction from the CHO group, is expected to be followed by either radical dissociation leading to isocyanates or to the CH3NH radical, or by addition of O2:

\[
\text{CH}_3\text{NHCHO} + \text{OH} \rightarrow \text{CH}_3\text{NHC} + \text{H}_2\text{O} \quad \Delta H^\ddagger = -100 \text{ kJ mol}^{-1}
\]

(1a)

\[
\text{CH}_3\text{NHC} + \text{H} \rightarrow \text{HNCO} + \text{CH}_3 \quad \Delta H^\ddagger = +116 \text{ kJ mol}^{-1}
\]

(3a)

\[
\text{HNCO} + \text{CH}_3 \rightarrow \text{HN} + \text{CO} \quad \Delta H^\ddagger = +29 \text{ kJ mol}^{-1}
\]

(3b)

\[
\text{CH}_3\text{NH} + \text{CO} \rightarrow \text{CH}_3\text{NCO} + \text{H} \quad \Delta H^\ddagger = +75 \text{ kJ mol}^{-1}
\]

(3c)

\[
\text{CH}_3\text{NHCO} + \text{O}_2 \rightarrow \text{CH}_3\text{NHC} + \text{O}_2 \quad \Delta H^\ddagger = -157 \text{ kJ mol}^{-1}
\]

(4)

The barriers to the N–H and N–C bond scission reactions (3a) and (3b) are around 168 and 117 kJ mol⁻¹, respectively, which place both substantially above the entrance energy of the reactants in (1a); the barrier to reaction (3c) leading to CH3NH + CO is barely 1 kJ mol⁻¹ above the entrance energy of the reactants. Considering the amount of internal energy available in the CH3NHCO radical upon its formation and the energy partitioning between CH3NHCO and H2O, it can be concluded that these routes will not be important at atmospheric conditions. CCSD(T*)-F12a/aug-cc-pVTZ/MP2/aug-cc-pVQZ results for reactions (3a)–(3c) are illustrated in Fig. S6 and documented in Tables S9 and S10 (ESI†).

The initially hot, chemically activated CH3NHCO(O)O* radicals (° denotes rovibrational activation) may initiate two H transfer reactions followed by radical dissociations; the corresponding net reactions are:

\[
\text{CH}_3\text{NHCO} + \text{O}_2 \rightarrow \text{CH}_3\text{NCO} + \text{HO}_2 \quad \Delta H^\ddagger = -93 \text{ kJ mol}^{-1}
\]

(5)

\[
\text{CH}_3\text{NHCO} \rightarrow \text{CH}_3\text{NCO} + \text{H} \quad \Delta H^\ddagger = +116 \text{ kJ mol}^{-1}
\]

(6)

The barrier to H transfer from the NH group is found to be far below the entrance energy of the reactants, and an IRC calculation links a post-reaction adduct between CH3NCO and HO2 on the exit side. The barrier to H transfer from the CH3 group is also below the initial entrance energy of the reactants; subsequent dissociation of the resulting CH3NH(C(O)O)OH radical to CH3=NH + CO2 + OH proceeds via another barrier below the entrance energy of the reactants. Fig. 8 illustrates the energetics of the CH3NHC(O) + O2 reaction (quantum chemistry results collected in Tables S11 and S12, ESI†).

The branching between reactions (4)–(6) at atmospheric pressure was examined using a master equation model based on the potential energy surface shown in Fig. 8 and including the CH3NHCO(O)O NO reaction as a bimolecular sink with a rate coefficient of 2 × 10⁻¹¹ cm³ s⁻¹, which is a typical value for RC(O)O + NO reactions.38 With a rate coefficient for the CH3NHC(O) + O2 reaction of around 5 × 10⁻¹² cm³ s⁻¹ (typical value for RC(O) + O2 reactions),38 the CH3NHCO radicals will be thermalized before reaction with O2 at atmospheric conditions. The calculations show that reaction (6) is of no importance and that ca. 90% of the CH3NHC(O) + O2 reaction results in CH3NCO. Increasing the energy of the saddle point TS3 by 4 kJ mol⁻¹, decreases the CH3NCO yield to around 80%.

The CH3NHCO(O)OO° radicals formed in reaction (4) and subsequently thermalized by collisions are expected to react with NO2 resulting in the formation of a meta-stable peroxytrate, and with NO leading to CH3NH radicals:

\[
\text{CH}_3\text{NHCO(O)O} + \text{NO}_2 \rightarrow \text{CH}_3\text{NHCO(O)O} + \text{NO} \quad \Delta H^\ddagger = -118 \text{ kJ mol}^{-1}
\]

(7)

\[
\text{CH}_3\text{NHCO(O)O} + \text{NO} \rightarrow \text{CH}_3\text{NHCO} + \text{O}_2 \quad \Delta H^\ddagger = -35 \text{ kJ mol}^{-1}
\]

(8)

\[
\text{CH}_3\text{NHCO(O)O} \rightarrow \text{CH}_3\text{NH} + \text{CO}_2 \quad \Delta H^\ddagger = -81 \text{ kJ mol}^{-1}
\]

(9)

The enthalpy of reaction (7) is calculated to be -118 kJ mol⁻¹, which compares to -130 kJ mol⁻¹ for the corresponding
(CH$_3$)$_2$NC(O)OONO$_2$ reaction (see later). The lifetime of (CH$_3$)$_2$NC(O)OONO$_2$ is around 14 minutes at 298 K and 1 bar. Even allowing for a considerable uncertainty in the G3 results, the 12 kJ mol$^{-1}$ difference in reaction enthalpies for the two peroxyinitrates in question suggests a much shorter lifetime for CH$_3$NH(C(O)OONO$_2$ than for (CH$_3$)$_2$NC(O)OONO$_2$. The G3 results imply a lifetime of CH$_3$NH(C(O)OONO$_2$ of around only 1 s at 298 K and 1 bar. In conclusion, the theoretical results suggest that not only will a minor amount of CH$_3$NH(C(O)O radicals be formed during N-methylformamide photo-oxidation, but also that the lifetime of the corresponding peroxyinitrate, CH$_3$NH(C(O)ONO$_2$, will be very short.

The atmospheric fate of the CH$_3$NH radical is well established from experimental and theoretical studies of the CH$_3$NH + OH reaction:

$$\text{CH}_3\text{NH} + \text{O}_2 \rightarrow \text{CH}_2\text{NH} + \text{HO}_2 \ \Delta H^\circ = -81 \text{ kJ mol}^{-1} \quad (10)$$

$$\text{CH}_3\text{NH} + \text{NO}_2 \rightarrow \text{CH}_2\text{NH} + \text{HONO} \ \Delta H^\circ = -199 \text{ kJ mol}^{-1} \quad (11a)$$

$$\rightarrow \text{CH}_2\text{NHNO}_2 \ \Delta H^\circ = -213 \text{ kJ mol}^{-1} \quad (11b)$$

The other important abstraction route (1c) leading to the CH$_3$NCHO radical is expected to be followed by O$_2$ addition forming a vibrationally excited peroxy radical that may initiate internal H abstraction reactions before reacting with NO (RO$_2$ + HO$_2$ reactions can be neglected with around 25 ppbV NO present in the chamber experiments):

$$\text{CH}_3\text{NCHO} + \text{OH} \rightarrow \text{CH}_2\text{NCHO} + \text{H}_2\text{O} \ \Delta H^\circ = -104 \text{ kJ mol}^{-1} \quad (1c)$$

$$\text{CH}_3\text{NCHO} + \text{O}_2 \rightarrow \text{OOCN}_2\text{NCHO}^* \ \Delta H^\circ = -126 \text{ kJ mol}^{-1} \quad (12)$$

$$\text{OOCN}_2\text{NCHO}^* \rightarrow \text{CH}_2\text{NCHO} + \text{HO}_2 \ \Delta H^\circ = +119 \text{ kJ mol}^{-1} \quad (13a)$$

$$\rightarrow \text{HOOCN}_2\text{NCHO}^* \ \Delta H^\circ = +32 \text{ kJ mol}^{-1} \quad (13b)$$

$$\text{OOCN}_2\text{NCHO} + \text{NO} \rightarrow \text{OOCN}_2\text{NCHO} + \text{NO}_2 \ \Delta H^\circ = -53 \text{ kJ mol}^{-1} \quad (14)$$

Reaction (13a) proceeds via a saddle point 0.6 kJ mol$^{-1}$ below the entrance energy of the reactants and a post-reaction complex on the exit side. The competing H transfer reaction from the CHO group has an around 18 kJ mol$^{-1}$ lower barrier towards formation of the intermediate HOOCN$_2$NCHO radical, which in turn has a barrier around 32 kJ mol$^{-1}$ above the entrance energy of the reactants towards dissociation to HNCO via another intermediate radical that can be described as a HNCO-CH$_3$OOH complex:

$$\text{HOOCN}_2\text{NCHO}^* \rightarrow \text{HNCO} + \text{OH} + \text{CH}_3\text{O} \ \Delta H^\circ = -96 \text{ kJ mol}^{-1} \quad (15)$$

The branching between reactions (13a) and (14) at atmospheric pressure was examined using master equation model based on the potential energy surface shown in Fig. 9 and including a bimolecular reaction between OOCN$_2$NCHO and NO with a rate coefficient of 9 $\times$ 10$^{-12}$ cm$^3$ s$^{-1}$ (typical value for ROOH + NO reactions). The results show that less than 1% CH$_3$=NCHO is formed in the reaction of O$_2$ with thermalized CH$_3$NCHO radicals at 298 K (NO level assumed >1 ppbV). The CH$_3$NCHO radicals may, however, not be thermalized at the time of reaction with O$_2$; reaction (1c) is exothermic by 104 kJ mol$^{-1}$ and part of the reaction enthalpy could be available to CH$_3$NCHO in subsequent reactions. The master equation calculations show that with an additional 10, 20 or 30 kJ mol$^{-1}$ available to reaction, the yield of CH$_3$=NCHO increases to respectively 6.6%, 26% and 56%. The actual amount of additional energy available to CH$_3$NCHO in reaction with O$_2$ will implicitly depend on the rate coefficient of the reaction and explicitly on the energy partitioning in the preceding CH$_3$NCHO + OH reaction. Assuming equipartitioning of the reaction enthalpy, the CH$_3$NCHO radical will be formed with an additional internal energy of around 60 kJ mol$^{-1}$ available for reaction. Assuming that the water molecule formed in reaction (1c) has one quantum of OH stretching vibration (∼3000 cm$^{-1}$) and that the remaining reaction enthalpy is divided according to the equipartitioning principle then the CH$_3$NCHO radical will be formed with an additional internal energy of around 43 kJ mol$^{-1}$. A typical rate coefficient for the reaction of a medium-sized alkyl radical with O$_2$ is around 10$^{-11}$ cm$^3$ s$^{-1}$, corresponding to a CH$_3$NCHO radical lifetime ∼20 ns at atmospheric conditions. Assuming an average energy transfer in collisions with N$_2$ of $\langle \Delta E_{\text{down}} \rangle = 250$ cm$^{-1}$, the initially 60 kJ mol$^{-1}$ hot CH$_3$NCHO radicals will be thermalized in less than 3 ns at atmospheric conditions. Decreasing the barrier height of reaction (13a) by 4 kJ mol$^{-1}$ increases the CH$_3$=NCHO yield to 2.6%. A conservative
estimate is therefore that less than 5% of the \( \text{CH}_2\text{NHCHO} + \text{O}_2 \) reaction leads to \( \text{CH}_2=\text{NCHO} \).

The \( \text{OCH}_2\text{NHCHO} \) radicals may, in principle, either dissociate or undergo H abstraction by \( \text{O}_2 \); the dissociation reaction is, however, highly endothermic ruling out this route at atmospheric conditions. Consequently, at atmospheric conditions the by far dominating primary product resulting from H abstraction from the \( \text{CH}_3 \) group will be \( N \)-formylformamide:

\[
\text{OCH}_2\text{NHCHO} \rightarrow \text{NHCHO} + \text{CH}_2\text{O} \quad \Delta H^\circ = +90 \text{ kJ mol}^{-1}
\]

\( \text{(16)} \)

\[
\text{OCH}_2\text{NHCHO} + \text{O}_2 \rightarrow \text{CHONHCHO} + \text{HO}_2 \quad \Delta H^\circ = -179 \text{ kJ mol}^{-1}
\]

\( \text{(17)} \)

In summary: the theoretical study shows that OH radicals initiate MF photo-oxidation by H abstraction from the CHO and \( \text{CH}_3 \) groups, and that H abstraction from the NH group is not important at atmospheric conditions. Abstraction from the \( \text{CH}_3 \) group leads, almost exclusively, to \( N \)-formylformamide although minor amounts of \( \text{CH}_2=\text{NCHO} \) cannot be ruled out. Abstraction from the CHO group is followed by a branching in the \( \text{O}_2 \) reaction with the \( \text{CH}_2\text{NCHO} \) radical leading to either \( \text{CH}_3\text{NCO} \) or via the \( \text{CH}_3\text{NHCl} \text{O} \text{OO} \) radical to \( \text{CH}_2=\text{NH} \) and \( \text{CH}_3\text{NNO} \). Each route results in different products, and the branching ratios can therefore be quantified from the product distribution shown in Fig. 7. The possible formation of \( \text{CH}_2=\text{NCHO} \), which is an isomer of the major photo-oxidation product, \( \text{CH}_3\text{NCO} \), could not be confirmed in the present experiments. It should be noted that the conservative upper estimate of its yield is 0.85% (0.05 × 0.17).

\( \text{CH}_2=\text{NH} \) was observed in traces. \( \text{CH}_3\text{O} \) and HCN were also observed in traces, but both compounds are difficult to quantify by PTR-ToF-MS. Our recent theoretical study on the atmospheric chemistry of \( \text{CH}_2=\text{NH} \) concludes unambiguously that HCN is the main product of methanimine photo-oxidation.\(^{43}\) However, no firm conclusion concerning \( \text{CH}_2=\text{NH} \) formation and subsequent reaction to HCN can be made from the available experimental data. Assuming branching in the \( \text{CH}_3\text{NH} \) radical reactions with \( \text{O}_2 \) and \( \text{NO}_2 \) to be the same as in the corresponding \( \text{CH}_3\text{N} \) radical reactions,\(^{10,44}\) the observed amounts of \( \text{CH}_3\text{NCO} \), \( \text{(CHO)}_2\text{NH} \), \( \text{CH}_3\text{NNO} \), and the modeled amount of \( \text{CH}_2=\text{NH} \) accounts for >90% of MF reacted.

### 4.4. \( \text{(CH}_3\text{)}_2\text{NCHO} \) photo-oxidation studies

Barnes et al.\(^5\) carried out both OH and Cl atom initiated photo-oxidation studies of DMF and reported \( \text{CH}_3\text{N} \text{[(CHO)}_2 \) as the major product in the degradation (~70% yield) and unquantified amounts of \( \text{CH}_3\text{N}\text{[(CHO)}_2\text{OONO}_2 \) depending on the \( \text{NO}_x \) level in the experiment. The lack of calibrated reference spectra prevented the authors from making a proper quantification of the product yields.

Fig. 10 shows the time evolution of the main compounds detected by PTR-ToF-MS during a DMF photo-oxidation experiment, while Fig. S7 and S8 (ESI\(^\dagger \)), respectively, show the difference in PTR-ToF-MS mass spectra taken after and before the photo-oxidation experiment, and the \( \text{NO} \) and \( \text{NO}_2 \) mixing ratios during the experiment. The \( \text{NO} \) level is nearly constant

![Scheme 1](image-url)

**Scheme 1** Reaction scheme for OH initiated photo-oxidation of \( N \)-methylformamide (MF). Compounds in boldface colored type have been detected in photo-oxidation experiments. The grey colored \( (\text{CH}_3\text{)}_2\text{N}\text{[(CHO)}_2\text{OONO}_2 \) is predicted to have a short lifetime and was not detected in the experiments. The branching ratios given have estimated uncertainties ±0.05.
around 25 ppbv during the photo-oxidation, whereas the NO₂ level increases from single-digit ppbv values to nearly 500 ppbv in the same period. Reacting compounds are DMF (detected in its protonated form at m/z 74.059 and its 13C isotope at m/z 75.068) and isopropyl nitrite which is detected at m/z 29.996 (NO⁻), m/z 43.054 (C₂H₅⁻), m/z 61.064 (C₃H₆O⁻) and m/z 79.074 (C₅H₁₂O⁻). Signals that increased during the photo-oxidation experiment are m/z 44.049 (C₂H₄N⁺, 8% of total signal from protonated N-methylmethanimine), m/z 75.055 (C₂H₄N₂O⁺, protonated N-nitroso dimethylamine), m/z 88.037 (C₂H₅NO₂⁺, protonated N-formyl N-methylformamide), m/z 91.050 (C₂H₅N⁺, protonated N-nitro dimethylamine) and m/z 151.035 (C₃H₇N⁺, protonated (CH₃)₂NC(O)OOONO₂). The signals at m/z 44.049 (C₂H₄N⁺, ~92% of total signal), m/z 72.044 (C₃H₅NO⁺), m/z 89.043 (C₃H₆NO⁺), and m/z 105.044 (C₃H₇NO₂⁺) are produced from (CH₃)₂NC(O)OOONO₂. Signals from N-formyl N-methylformamide oxidation are m/z 105.029 (C₂H₅O₂N⁺, protonated NCH₃CH₂O⁺), m/z 165.015 (C₃H₇NO₂⁺, protonated NCH₃CH(O)CH₂O⁺). We also observed an increase in the ion signals at m/z 31.017 (CH₃O⁻), m/z 43.017 (C₂H₅O⁻), m/z 45.033 (C₃H₆O⁻), m/z 45.991 (NO₂⁻), m/z 59.049 (C₃H₅O⁻), m/z 60.049 (13C1₂C₃H₆O⁻), m/z 77.022 (C₅H₇O⁺) and m/z 77.056 (C₅H₇O₂⁺). As mentioned above, these signals stem from compounds (formaldehyde, acetaldehyde, acetone, nitric acid and peroxyacetyl nitrate) typically formed in any smog chamber photoxidation experiment in the presence of isopropyl nitrite and NO₂, i.e. even in the absence of (CH₃)₂NCHO. In our product analysis, we only included signals with a >1% increase relative to decrease in the protonated N,N-dimethylformamide signal.

The wall loss of DMF was significant in the experiments. Additional loss was caused by instrumental sampling flows that were compensated for by constantly adding synthetic air (k_{dilution} = 1.13 \times 10^{-4} \text{ s}^{-1}); analysis of the MF loss curve before and after the photo-oxidation period gave a wall loss rate coefficient k_{wall loss} ≈ 2.8 \times 10^{-4} \text{ s}^{-1}. Also in the DMF experiments there is apparently a mismatch between the amount of DMF reacted and the amount of products formed, and, again, the apparent mismatch is deceptive. N-Nitro dimethylamine, (CH₃)₂NNO₂, formed with a ~5% yield in the experiment shown, can only be formed in the reaction between (CH₃)₂N radicals and NO₂, and even under conditions with high NO₂ levels, as in the present case, the major reaction of (CH₃)₂N radicals is with O₂ resulting in N-methyl methanimine, CH₃N—CH₂, which is difficult to quantify due to polymerization and surface induced reactions.

Fig. 10 shows a clear change in the (CH₃)₂NC(O)OOONO₂, CH₃N—CH₂, (CH₃)₂NNO₂ and (CH₃)₂NNO volume mixing ratios upon addition of excess NO titrating peroxy radicals present in the chamber. This will be addressed later.

Hydrogen abstraction from the CHO group in (CH₃)₂NCHO is expected to be followed by either O₂ addition or dissociation of the (CH₃)₂NCO radical:

\[
\text{(CH₃)₂NCHO + O₂ → (CH₃)₂NCO + HO₂} \quad \Delta H^\circ = -98 \text{ kJ mol}^{-1}
\]  

The barrier to C–C scission is high, around 23 kJ mol⁻¹ above the entrance energy of the reactants in (2a), and this route will therefore not be of importance at atmospheric conditions. Results from CCSD(T)⁺-F12a/aug-cc-pVTZ/MP2/aug-cc-pVTZ calculations of reaction (19) are collected in Table S15 and S16 (ESI†) and the energetics are illustrated in Fig. S9 (ESI†).

The hot (CH₃)₂NC(O)OO⁺ radical may initiate H transfer reactions from the CH₃ groups followed by dissociation and OH regeneration:

\[
\text{(CH₃)₂NC(O)OO + H₂O → CH₃CH₂NC(O)OOH} \quad \Delta H^\circ = -11 \text{ kJ mol}^{-1}
\]  

\[
\text{CH₃CH₂NC(O)OOH → CH₃NCH₃ + CO₂ + OH} \quad \Delta H^\circ = -125 \text{ kJ mol}^{-1}
\]  

The barrier to H-transfer (20) is found well below the entrance energy of the reactants. However, the path towards dissociation of the intermediate CH₃CH₂NC(O)OOH radical to CH₃NCH₃ + CO₂ + OH proceeds via a barrier well above the entrance energy of the reactants. The internal H transfer route is consequently of no importance at atmospheric conditions. Fig. 11 illustrates the energetics of the (CH₃)₂NCO + O₂ reaction (quantum chemistry results collected in Tables S17 and S18, ESI†).

The thermalized peroxy radical may react with NO₂ and NO resulting in the formation of a meta-stable peroxy nitrate and eventually in the (CH₃)₂N radical:

\[
\text{(CH₃)₂NC(O)OO + NO₂ → (CH₃)₂NC(O)ONO₂} \quad \Delta H^\circ = -130 \text{ kJ mol}^{-1}
\]
Kirchner et al.\textsuperscript{39} investigated the thermal stabilities of peroxynitrates and reported $k_{-21} = 1.2 \times 10^{-3}$ s$^{-1}$ at 298 K and 1 bar, and $E_a = (111.5 \pm 5.8)$ kJ mol$^{-1}$. An analysis of the (CH$_3$)$_2$NC(O)OONO$_2$ decay upon the addition of excess NO, see Fig. 10, gave a loss rate coefficient $k_{-21} = 2.86 \times 10^{-3}$ s$^{-1}$ at 304 K and 1 bar, which is in excellent agreement with the results of Kirchner et al.\textsuperscript{39} for the same temperature.

The atmospheric reactions of the (CH$_3$)$_2$N radical are well established from previous studies of dimethylamine photodissociation:\textsuperscript{40-42}

\[
\text{(CH}_3\text{)}_2\text{N} + \text{O}_2 \rightarrow \text{CH}_3\text{NCH}_2\text{CHO} \quad \Delta H^\circ = -71 \text{ kJ mol}^{-1} \quad (25)
\]

\[
\text{(CH}_3\text{)}_2\text{N} + \text{NO} \rightarrow \text{CH}_3\text{NCH}_2\text{CHO} + \text{HOONO} \quad \Delta H^\circ = -190 \text{ kJ mol}^{-1} \quad (26a)
\]

\[
\rightarrow \text{(CH}_3\text{)}_2\text{NNO}_2 \quad \Delta H^\circ = -203 \text{ kJ mol}^{-1} \quad (26b)
\]

\[
\text{(CH}_3\text{)}_2\text{N} + \text{NO} \rightarrow \text{(CH}_3\text{)}_2\text{NNO} \quad \Delta H^\circ = -192 \text{ kJ mol}^{-1} \quad (27a)
\]

\[
\text{(CH}_3\text{)}_2\text{NNO} \rightarrow \text{(CH}_3\text{)}_2\text{N} + \text{NO} \quad \Delta H^\circ = +192 \text{ kJ mol}^{-1} \quad (27b)
\]

Hydrogen abstraction from one of the CH$_3$ groups in (CH$_3$)$_2$NCHO is expected to be followed by O$_2$ addition. The cis-trans rotational barrier in CH$_2$NCHO is quite high (around 100 kJ mol$^{-1}$ from BHandHLYP/aug-cc-pVDZ calculations), which may prevent thermal equilibrium to be established before further reaction takes place; the energy difference between the two rotamers is, however, small. We will not make a distinction between the radical cis- and trans-rotamers here as they eventually end up as the same product.

\[
\text{(CH}_3\text{)}_2\text{NCHO} + \text{OH} \rightarrow \text{trans-CH}_2\text{N}(\text{CH}_3\text{)}\text{CHO} + \text{H}_2\text{O} \quad \Delta H^\circ = -100 \text{ kJ mol}^{-1} \quad (2b)
\]

\[
\rightarrow \text{cis-CH}_2\text{N}(\text{CH}_3\text{)}\text{CHO} + \text{H}_2\text{O} \quad \Delta H^\circ = -100 \text{ kJ mol}^{-1} \quad (2c)
\]

\[
\text{CH}_2\text{N}(\text{CH}_3\text{)}\text{CHO} + \text{O}_2 \rightarrow \text{OOCH}_2\text{N}(\text{CH}_3\text{)}\text{CHO}^* \quad \Delta H^\circ = -129 \text{ kJ mol}^{-1} \quad (28)
\]

The hot peroxy radical, OOCH$_2$N(CH$_3$)CHO*, may initiate H transfer reactions; two routes are conceivable:

\[
\text{OOCH}_2\text{NCH}_2\text{CHO}^* \rightarrow \text{HOOCH}_2\text{NCH}_2\text{C}(\text{O})^* \quad \Delta H^\circ = +34 \text{ kJ mol}^{-1} \quad (29a)
\]

\[
\rightarrow \text{HOOCH}_2\text{N}(\text{CH}_3\text{)}\text{CHO}^* \quad \Delta H^\circ = +36 \text{ kJ mol}^{-1} \quad (29b)
\]

The barriers to the H transfer reactions (29) are found well below the entrance energy of the reactants in the O$_2$ addition reaction (28), but the paths towards dissociation of the intermediates proceeds via barriers well above, Fig. 12 (quantum chemistry results are documented in Tables S19 and S20, ESI\textsuperscript{\textsuperscript{\texttrademark}}). These H transfer initiated routes are therefore of no importance at atmospheric conditions.

With around 25 ppbV NO present in the chamber peroxy radical reactions with other peroxy radicals can be neglected: the oxynitrals may either undergo H abstraction by O$_2$ or dissociate:

\[
\text{OOCH}_2\text{NCH}_2\text{CHO} + \text{NO} \rightarrow \text{OCOH}_2\text{N}(\text{CH}_3\text{)}\text{CHO} + \text{NO}_2 \quad \Delta H^\circ = -48 \text{ kJ mol}^{-1} \quad (30)
\]

\[
\text{OCOH}_2\text{N}(\text{CH}_3\text{)}\text{CHO} + \text{O}_2 \rightarrow \text{CHON}(\text{CH}_3\text{)}\text{CHO} + \text{HO}_2 \quad \Delta H^\circ = -183 \text{ kJ mol}^{-1} \quad (31)
\]

\[
\text{OCOH}_2\text{N}(\text{CH}_3\text{)}\text{CHO} \rightarrow \text{CH}_2\text{NCHO} + \text{CH}_2\text{O} \quad \Delta H^\circ = +76 \text{ kJ mol}^{-1} \quad (32)
\]

The rate of OC$_2$N(CH$_3$)CHO dissociation was estimated to be $1 \times 10^{-3}$ s$^{-1}$ employing the Méreau et al.\textsuperscript{43} structure–activity relationship (SAR).

Fig. 12 Relative energies of stationary points on the potential energy surface of the CH$_2$(CH$_3$)NCHO + O$_2$ reaction. Results from CCSD(T\textsuperscript{*})-F12a/aug-cc-pVTZ//MP2/aug-cc-pVTZ calculations.
relationship for alkoxy radical decomposition reaction. Assuming a typical value for \( k_{30} = 1 \times 10^{-14} \text{ cm}^3 \text{s}^{-1} \), the \( \text{O}_2 \) abstraction reaction will therefore completely dominate the atmospheric fate of the \( \text{OCH}_2\text{N(CH}_3\text{)CHO} \) radical.

The major routes in the \( \text{OH} \) initiated photo-oxidation of \( \text{N}_2\text{N}-\text{dimethylformamide} \) is outlined in Scheme 2 together with relative branching fractions derived from analysis of the time profiles presented in Fig. 10. The observed amounts of \( \text{CH}_3\text{NCO} \), \( \text{(CHO)}_2\text{NCH}_3 \), \( \text{(CH}_3\text{)}_2\text{NO} \), \( \text{(CH}_3\text{)}_2\text{NNO}_2 \), and the modelled amount of \( \text{CH}_2\equiv\text{NCH}_3 \) accounts for >90% of DMF reacted.

5. Summary and conclusions

The rate coefficients of the reactions of \( \text{OH} \) radicals with \( \text{N}-\text{methylformamide} \) and \( \text{N}_2\text{N-dimethylformamide} \) have been experimentally determined at \( T = 294 \text{ K} \) to be \( (5.7 \pm 1.7) \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \) and \( (8.5 \pm 2.6) \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \), respectively. Taking \([\text{OH}]_{24h} = 10^6 \text{ cm}^{-3} \) into account, one obtains atmospheric lifetimes with respect \( \text{OH} \) reaction of 1.5 to 2 days. The major MF photo-oxidation product is methyl isocyanate, \( \text{CH}_3\text{NCO} \), which is not a benign compound in the environment. Methylnitramine, \( \text{CH}_3\text{NHNO}_2 \), is only a minor product. However, the potential to nitramine formation (18% yield of \( \text{CH}_3\text{NH} \) radicals in photo-oxidation of MF) is almost as high as for methylamine (25% yield of \( \text{CH}_3\text{NH} \) radicals).\(^{40,42}\) For DMF the situation is perhaps even more worrisome; we find the potential to formation of dimethylnitrosamine, \( \text{(CH}_3\text{)}_2\text{NNO} \), and dimethylnitramine, \( \text{(CH}_3\text{)}_2\text{NNO}_2 \), in DMF photo-oxidation actually being larger than for dimethylamine, 65% yield of \( \text{(CH}_3\text{)}_2\text{N} \) radicals in DMF photo-oxidation versus ~40% in dimethylamine.\(^{40,42,44}\)

Considering the recent recommendation by the Norwegian Institute of Public Health that the total amount of nitrosamines and nitramines should not exceed 0.3 ng m\(^{-3} \) in air and 4 ng L\(^{-1} \) in drinking water to ensure minimal or negligible risk of cancer for the public from exposure to these substances,\(^{46}\) immediately raises the question if emission regulations of MF and DMF should be implemented.

Acknowledgements

This work is part of the Atmospheric Degradation of Amines (ADA) project supported by Masdar, Statoil, Vattenfall, Shell and the CLIMIT program under contracts 193438, 201604 and 208122, and by the Research Council of Norway through a Centre of Excellence Grant (Grant No. 179568/V30). A. J. C. B. is grateful for an Erasmus Student Mobility Grant.

References