Kinetic and mechanistic study of the pressure and temperature dependence of the reaction $CH_3O + NO$

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New kinetic measurements for the $CH_3O + NO$ reaction have been performed using two different techniques. The discharge flow (DF) technique has been used to investigate the 0.5-5 Torr and 248-473 K pressure and temperature ranges and pulsed laser photolysis (PLP) has been used for the 30-500 Torr and 284-364 K ranges. These new results represent an extension of the pressure and temperature ranges investigated previously. This reaction is known to present two reaction pathways, the association pathway yielding CH_3ONO and the disproportionation pathway yielding $CH_2O + HNO$. Based on literature and present experimental data, using the results of ab initio calculations, a multichannel RRKM analysis was developed to interpret the experimental results. This analysis has shown that the disproportionation reaction occurs simultaneously by both a direct hydrogen abstraction reaction, and via the formation of energized CH₃ONO* complex in competition with the association reaction. The RRKM analysis, fitted to present and previous data, has yielded a second-order limiting low-pressure value of 2.5×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K, with a complex temperature dependence. The limiting high-pressure rate constant derived in the same way is k_{∞} = $(3.4 \pm 0.4) \times 10^{-11} (T/298)^{-0.75}$. The model allows the prediction of CH₃O loss rate constants and of the branching ratios in the 1-760 Torr and 220-600 K ranges. For a convenient presentation of the overall rate constant, an analytical expression using the conventional Troe expression with a temperature-dependent addition constant, has been fitted to the results of the RRKM analysis.

Bimolecular reactions involving two reaction channels (association and disproportionation channels) are important in both atmospheric and combustion chemistry. These two reaction channels may proceed either as parallel independent channels or *via* a common initially energized complex. As a result, the total reaction rate for the loss of reactants can exhibit complex pressure and temperature dependences. The theoretical analysis of such processes is an interesting question which has been nicely illustrated by Hippler *et al.*^{1,2} in their recent studies of OH + CO (common intermediate) and OH + OH (independent channels) reactions over very broad ranges of pressures and temperatures. A few important multichannel reactions in combustion have also been reviewed by Just.³.

The reactions of alkoxyl radicals, such as CH_3O or C_2H_5O , with NO or NO₂ are typical examples of radical-radical reactions proceeding *via* such competing channels, and the reaction of CH_3O with NO has been shown to proceed *via* the two following reaction channels:

$$CH_{3}O + NO \xrightarrow{(M)} CH_{3}ONO;$$

association channel (1a)
 $\rightarrow CH_{2}O + HNO;$

disproportionation channel (1b)

Various kinetic studies have already focused either on the total loss rate $k_{\rm loss}^{4-6}$ or on product yields^{7–9} over a rather extensive range of temperatures, pressures and bath gases.

Most experimental studies have been performed at room temperature and show a pressure fall-off dependence of $k_{\rm loss}$ typical of an association reaction. The main experimental conditions and results of these various literature studies are collected in Table 1 for comparison, including four sets of experimental data obtained at room temperature^{5,6,8,9} and two sets concerning the temperature dependence of the total CH₃O loss rate constant.^{5,8}

McCaulley et al.,8 have carried out experiments in a lowpressure range (0.75-5 Torr of He) and between 220 and 473 K. From their measurements of the CH₃ONO yield, they conclude that disproportionation is the major channel at low pressure and in their kinetic analysis they assume that disproportionation and recombination channels proceed independently. Therefore, the measured rate constants are fitted to a Troe expression of an association/dissociation reaction with an added disproportionation rate constant of ca. 3×10^{-12} cm^3 molecule⁻¹ s⁻¹ at room temperature, which exhibits a negative temperature dependence. Frost and Smith⁵ have determined the rate constant in a higher pressure range (3-100 Torr of Ar) at four temperatures between 296 and 573 K. They assume that disproportionation proceeds via rearrangement of an energized CH₃ONO* complex, in direct competition with the association reaction. Experimental data are fitted by an extended Lindemann-Hinshelwood expression, with the value of 5×10^{-12} cm³ molecule⁻¹ s⁻¹ for the limiting low-pressure disproportionation rate constant, almost independent of temperature. Ohmori et al.⁶ have determined values of the rate constant at room temperature with different

Table 1 Comparison of literature data for the measurement of k_{loss}

Temperature/K	Pressure/Torr	Bath gas	Technique	Results ^a	Ref.		
220-473	0.75–5	He, Ar	DF/LIF	$k_{\text{disp}} = 3 \times 10^{-12}$ $k_{\text{r}} = 1.8 \times 10^{-29}$	8		
298	0.72-8.5	He	DF/LIF	$k_{\text{disp}} = (3.2 \pm 1.0) \times 10^{-12}$ $k_{\text{o}} = 1.69 \times 10^{-29}$	9		
295	10-50	SF	PLP/LIF	$k_{\rm m} = 2 \times 10^{-11}$	7		
296-573	3–100	Ar	PLP/LIF	$k_{\infty}^{\omega} = 3.6 \times 10^{-11}$	5		
	30-125	CF_4	,	$k_{\rm disp} = 5.5 \times 10^{-12}$			
295	4-400	He	PLP/LIF	$k_{\infty} = 1.4 \times 10^{-11}$	4		
296	7–100	He		~			
	10–70	N ₂	PLP/LIF	$k_{\infty} = (4.5 + 1.5) \times 10^{-11}$	6		
	15–50	CF ₄					
	15-50	SF ₆					
Rate constants are in cm ³ molecule ⁻¹ s ⁻¹ except k_0 which is in cm ⁶ molecule ⁻² s ⁻¹ .							

bath gases and present a discussion regarding the value of the high-pressure limiting rate constant. Dobé et al.,⁹ in the most recent study of this reaction, have determined the overall rate constant and the branching ratio for HCHO product formation at room temperature over the pressure range 0.72-8.5 Torr; considering various possibilities for the reaction mechanism, they conclude that the available data are not sufficient for an exact analysis. This is not surprising, since these simple approaches do not take into account either the weak collision effects or the energy dependence of the microcanonical rate constants. In summary, there is a large body of experimental results concerning this reaction and the experimental pressure dependence of the CH₃O loss rate constant is rather well established at room temperature in the 1-100 Torr pressure range. However, only few sparse data are available concerning the temperature dependence of the rate constant at different pressures. As the mechanism of the reaction is not well established, there is no kinetic model which would account for the experimental results and allow reliable extrapolation outside the experimental range of pressure and temperature.

In the closely related $CH_3O + NO_2$ system, Biggs *et al.*¹⁰ developed a more realistic procedure based on a semiquantitative QRRK (quantum RRK) approach. A much more satisfying approach, based on the RRKM multichannel procedure proposed by Berman and Lin¹¹ has been recently applied by a few of us¹² to the reactive system CF₃O + NO₂ \rightarrow CF₃ONO₂ or CF₂O + FNO₂.

In this work we present a combined experimental and theoretical approach to tackle the problem of the two channel reaction $CH_3O + NO + M$. As the two channels may proceed either *via* a common intermediate or by parallel independent reactions, the kinetics of reaction will be discussed in terms of the following reaction scheme



From the experimental viewpoint, we focus our new measurements mainly on pressure ranges outside those of previous investigations; measurements at low pressures are especially useful in the case of the so-called "S" shaped fall-off curves^{1,2} and measurements up to 500 Torr allow a more precise determination of the high-pressure limiting rate constant.

Based on a careful examination of the experimental temperature and pressure dependences of the rate constant, together with the results of *ab initio* calculations (well depths, barrier heights and transition-state structures on the potential-energy surfaces), we establish a kinetic scheme of the reaction mechanism, based on the combination of a chemically activated pathway *via* a common energized intermediate (studied by an RRKM multichannel formalism) with an independent disproportionation channel.

The reaction of $CH_3O + NO$ is not strictly relevant to atmospheric chemistry or to combustion; in the atmosphere the main sink of CH_3O is its reaction with O_2 , whereas at combustion temperatures CH_3O can also decompose unimolecularly ($CH_3O \rightarrow CH_2O + H$) or react with the H, O and OH species. However, in laboratory studies (smog chambers or shock tubes) the reverse reaction (decomposition of methyl nitrite CH_3ONO) is a very common source of CH_3O and relative rate constant measurements involving CH_3O often use the direct reaction (1) as a reference. Moreover, this reaction occurs in the chemical system used in the peroxyl radical amplifier (PERCA) instrument.¹³

Experimental

Two conventional experimental techniques have been used: (i) the DF/laser-induced fluorescence technique (DF/LIF) and (ii) the PLP/LIF technique. For both techniques, the same detection scheme has been adopted: the excitation wavelength ($\lambda \approx 293$ nm) pumps the v' = 4 vibrational level of the CH₃O excited state (A, v'' = 4)¹⁴ and the subsequent broad band fluorescence is selected by a cut-off filter ($\lambda > 320$ or 305 nm). The excitation wavelength is provided by a dye laser pumped by a Yag (both Quantel). The decay signals of CH₃O fluorescence are displayed on fast scopes and sampled by boxcar averagers.

DF/LIF technique

In the DF experiments, CH_3O radicals are usually formed by the reaction of F atoms (from a microwave discharge in F₂-He or CF_4 -He mixtures) with a slight excess of methanol:

$$F + CH_3OH \rightarrow CH_3O + HF$$
 (2a)

$$\rightarrow CH_2OH + HF$$
 (2b)

It is well known that both the CH₃O and CH₂OH radicals are formed in roughly equal yields (*ca.* 0.5 ± 0.1) over a large range of temperatures;^{15,16} to make sure that CH₂OH radicals are not interfering with the kinetics, a few control experiments have been conducted with another source of CH₃O (free of CH₂OH):

$$F + CH_4 \rightarrow CH_3 + HF \tag{3}$$

$$CH_3 + NO_2 \rightarrow CH_3O + NO$$
 (4)

Another interest of this alternative source is to provide an estimate of the CH_3O concentration based on the NO_2 flowrate when methyl radicals in excess are titrated by NO_2 via reaction (4). A few experiments have also been performed with the CD₃O radical (from the F + CD₃OD source reaction) and values of k_1 have been found similar to those of CH₃O + NO under the same experimental conditions.

Most experiments have been performed with the following configuration of the DF technique ("mobile discharge"): the microwave discharge, (generating F–He mixtures) is switched on in a side arm connected to the movable injector; the main He flow is added upstream and the CH₃OH–He mixture downstream to the discharge; the reactant mixture (NO–He) is flowed into the main flow tube and its flow rate deduced from the measurement of the rate of pressure increase in a calibrated volume. Both the injector and the flow tube are covered internally by a thin Teflon sleeve, to reduce the CH₃O wall decay rate and to allow experiments up to 473 K.

All measurements have been performed in the 0.5–5 Torr pressure range and the 248–473 K temperature range. For variable-temperature measurements, the flow tube is either cooled by circulation of cooled ethanol in a jacket or electrically heated by an oven. The temperature inside the flow tube is controlled by a thermocouple located at the tip of the movable injector. As in our previous work,¹² two corrections have been applied to the pseudo-first-order decay rate k_{obs} in order to obtain k_c :

The pressure gradient along the flow tube, resulting from the Poiseuille law, was taken into account by adopting as the average pressure (the "corrected" pressure P_c) the pressure prevailing in the middle of the reaction zone, the pressure gradient having been measured directly in a separate experiment using flow conditions similar to those of the kinetic experiments.

The observed pseudo-first-order decay rates k_{obs} (s⁻¹) were corrected for diffusion using the following relationship:

$$k_{\rm c} = k_{\rm obs} \left(1 + \frac{k_{\rm obs}D}{v^2} + \frac{k_{\rm obs}R^2}{48D} \right) \tag{I}$$

with $v \text{ (cm s}^{-1})$ and R (cm) being, respectively, the flow velocity and tube radius and $D \text{ (cm}^2 \text{ s}^{-1})$ the diffusion coefficient; we have adopted the value $D = 457/P_c (T/298)^{3/2}$, (with P_c being the corrected pressure in Torr) relevant to methanol.¹⁷

As usual, we have plotted the pseudo-first-order rate $k_c vs$. [NO] and derived (i) the bimolecular constant of the CH₃O disappearance k_{loss} as the slope and (ii) the wall decay k_w as the intercept; if the latter is very different from the wall decay, k_w^0 , measured in the absence of NO, the corresponding experiment is rejected (usually $k_w > k_w^0$). Taking into account various uncertainties, we have assumed a global uncertainty of $\pm 15\%$ (unless the statistical one is larger) of the rate constants.

A few examples of typical decay curves log [CH₃O] vs. reaction distance relevant to the DF/LIF technique are displayed in Fig. 1 and the corresponding pseudo-first-order plots are displayed in Fig. 2. However, at long reaction times, the initial linear decay of log [CH₃O] exhibited systematic upward curvature, pointing to a possible regeneration of CH₃O (X, v'' = 0); we will discuss this unusual feature in the following paragraph. The corresponding curves obtained by the PLP/LIF technique are displayed in Fig. 3 and 4.

PLP/LIF technique

The reaction cell for the laser photolysis experiment is made of stainless steel and can be heated to 600 K. The temperature is measured by a thermocouple, which can be moved into the reaction zone. The CH₃O radicals are generated by 248 nm laser photolysis (Lambda Physic LPX 202i) of methyl nitrite (CH₃ONO) which was synthesized according to a well known procedure.⁷ CH₃ONO, highly diluted in He, could be stored in a darkened glass bulb for weeks. Its purity was checked by gas chromatography–mass spectrometry (GC–MS). From the absorption coefficient of CH₃ONO at 248 nm,



Fig. 1 Decay curves of log [CH₃O] vs. reaction distance; experimental parameters: $P_c = 1.09$ Torr, v = 4540 cm s⁻¹, T = 298 K; [NO] (in 10¹³ molecule cm⁻³) and the corresponding decay rates k_c (in parentheses, in s⁻¹) are: 0 (30 ± 3), 2.44 (134 ± 6), 4.55 (211 ± 10), 8.73 (383 ± 16), 17.2 (653 ± 56), 21.5 (816 ± 52).



Fig. 2 Pseudo-first-order constant k_c vs. [NO]; lower curve: the experimental parameters are those of Fig. 1; $k_w^* = 30 \text{ s}^{-1}$, $k_{\text{loss}} = (3.55 \pm 0.24) 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_w = (58 \pm 30) \text{ s}^{-1}$. Upper curve: P = 5.03 Torr, T = 248 K, $v = 2172 \text{ cm} \text{ s}^{-1}$; $k_w^* = 18 \text{ s}^{-1}$, $k_{\text{loss}} = (7.29 \pm 1.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_w = (58 \pm 15) \text{ s}^{-1}$.



Fig. 3 Decay curves of log $[CH_3O]$ vs. reaction time for three NO concentrations (PLP/LIF experiments); pressure of He = 200 Torr.



Fig. 4 Pseudo-first-order rate constants k_{obs} vs. [NO] at three different temperatures (PLP/LIF experiments); pressure of He = 200 Torr; the derived rate constants (in 10^{-11} cm³ molecule⁻¹ s⁻¹) are: 293 K: $k_{loss} = 2.45$; 325 K: $k_{loss} = 2.0$; 359 K: $k_{loss} = 1.86$.

 $(\sigma = 1.6 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}),^{18}$ and a typical laser fluence of 10 mJ cm⁻², we estimate an average concentration of [CH₃O] $\approx 2 \times 10^{11}$ molecule cm⁻³ in the reaction cell. As usual, the decay curve of [CH₃O] vs. reaction time is simply obtained by plotting the LIF CH₃O signal vs. the delay time between the photolysis laser pulse and the probe laser pulse. A typical decay consists of 20–50 points at different delays between the two lasers, each averaged over, typically, 30 laser shots. Different delays are realized by a digital delay generator (EG&G 9650), which is controlled by a PC. All experiments have been performed at a repetition rate of 2 Hz.

With this technique, temperature-dependent measurements were performed at three pressures 50, 100 and 200 Torr He in the temperature range 284-364 K. At room temperature, the rate constant was measured in the pressure range 30-510 Torr of He and 14-500 Torr of Ar. The obtained decay curves were always exponential.

Results

Regeneration of CH₃O at long reaction times

Before considering the results in more detail, it is necessary to discuss briefly the origin of the apparent regeneration of CH₃O that we observed at long reaction times. Although we are aware that this peculiar feature has not been reported in the two previous investigations using the DF technique,^{8,9} we have routinely observed these small deviations in our lowpressure experiments at long reaction times under various experimental conditions. An example of such a curve exhibiting a significant deviation is displayed in Fig. 5. It should be added that McCaulley et al.⁸ mentioned two anomalies in their DF experiments: (i) the occurrence of curved semilog plots (log [CH₃O] versus injector position) in several experiments and (ii) the existence of a small CH₃O background LIF signal with the microwave discharge off but in presence of F2, NO, and NO2. In our experimental conditions, in agreement with McCaulley et al.,⁸ it is worth stressing that the initial part of the log [CH₃O] was always linear for a reaction distance large enough to derive a reliable slope.

A simple interpretation could be a slow population of the CH₃O (X, v'' = 0) ground level (the level which is probed by LIF) by cascading from upper vibrational levels within the same ground electronic state (X, $v'' \neq 0$) via collisions with NO or He:

$$CH_3O(X, v'' \neq 0) + NO \rightarrow CH_3O(X, v'' = 0) + NO^*$$
 (5)

This possibility is allowed by the energetic of the reaction (2a) of formation of CH₃O. Furthermore, the presence of v'' = 0, 1 and 2 vibrational states (v_3'' vibration) of the electronic ground state, with relative nascent populations of 1, 0.24 and 0.04 in



Fig. 5 Non-linear plot of log [CH₃O] vs. reaction distance; experimental parameters: $P_c = 1.09$ Torr, v = 3528 cm s⁻¹, T = 298 K, [NO] = 2×10^{14} molecule cm⁻³; the non-linear decay starts at *ca*. 6 ms.

Ar carrier have been observed by Agrawalla and Setser.¹⁹ To our knowledge, there are no data concerning the rate of reaction (5); only the electronic quenching rate of the CH₃O (A) state by a few colliders has been measured;²⁰ in contrast, a few data exist for the relaxation rates of the radical OH(X, $v'' \neq 0$).^{21,22}

Nevertheless, we rule out the possibility of reaction (5) for two main reasons: (i) The previous interpretation would require that reaction (5), a vibrational energy transfer, is rather slow, in particular, slower than the reaction (1) of chemical consumption of CH₃O in the pressure range studied (*ca.* 4×10^{-12} cm³ molecule⁻¹ s⁻¹). This is not in line with the few measurements^{21,22} concerning the relaxation rates of radicals with polar molecules, nor with the occurrence of frequent wall collisions at this reduced pressure. (ii) It has been recently shown,²³ on the basis of an extensive analysis of literature data, that the rates of vibrational relaxation are nearly as fast as the high-pressure recombination reaction chemical rates; for reaction (5), this would suggest a relaxation rate of *ca.* 4×10^{-11} cm³ molecule⁻¹ s⁻¹, well above the (chemical) reaction rate in the pressure range studied.

To conclude the above discussion, we tentatively suggest that the slow reaction of regeneration of CH_3O could arise from an unidentified chemical reaction.

Measurements at room temperature

Our room temperature results (from DF/LIF and PLP/LIF techniques) are collected in Table 2; the complete set of available data (from low or high pressure experiments) is displayed in Fig. 6 (when measurements have been performed in Ar bath gas, to account for the difference between the collision efficiencies β_c of Ar and He, the Ar gas concentrations were scaled by the ratio $Z_{LJ}(Ar)\beta_{c}(Ar)/Z_{LJ}(He)\beta_{c}(He) = 1.3$, assuming that $\beta_{\rm c}({\rm Ar})/\beta_{\rm c}({\rm He}) = 1.75$ where $Z_{\rm LJ}$ is the Lennard-Jones collisional frequency). As evidenced by this figure, our DF data are in overall good agreement with those of previous investigations. As an example, we can compare the different values of the CH₃O loss rate constant k_{loss} (in 10^{-12} cm³ molecule⁻¹ s⁻¹) measured at roughly 0.9 Torr: 3.97 ± 0.57 (0.85 Torr, ref. 8), 3.16 (0.88 Torr, ref. 9), 4.8 \pm 0.4 (1 Torr, ref. 24) and 3.51 + 0.5 (0.88 Torr, this work). However, Fig. 6 also shows that our set of values at the lowest pressures (below 0.75 Torr) are obviously below any reasonable extrapolation. We have not noticed any particular anomaly in this range of pressures (the decay curves are well behaved); interestingly, in

Table 2 Room-temperature measurements of $k_{\text{loss}} vs$. bath gas pressure^{*a*}

<i>P</i> /Torr		1 (10-12
He	Ar	$\kappa_{\rm loss}/10^{-12} {\rm cm}^{3}$ molecule ⁻¹ s ⁻¹
0.47		1.82 ± 0.3
0.57		2.45 ± 0.6
0.66		2.39 ± 0.36
0.7		3.27 ± 0.5
0.8		2.9 ± 0.45
0.88		3.51 ± 0.5
1.05		2.9 ± 0.43
1.1		3.3 ± 0.55
1.13		3.65 ± 0.55
1.3		4.01 ± 0.6
2.04		4.11 ± 0.6
	18.2	12 ± 2
	40	14.7 ± 2
50		15.3 ± 2.3
	65	17.6 ± 2.6
75		19.2 ± 3
100		20 ± 3
150		22 ± 3.3
200		23.4 ± 3.5
250		24.6 ± 3.7
300		24.7 <u>+</u> 4
410		26 ± 4
510		26.5 ± 4
	520	27.2 ± 4

^{*a*} The data of the upper part of the table are from the DF/LIF technique whereas those from the lower part are from the PLP/LIF technique. A systematic uncertainty of $\pm 15\%$ has been applied.

the literature, there are hardly any measurements performed at reduced pressure, *i.e.* below 0.5 Torr, probably because of the increasing importance of the corrections (larger diffusion, reduced flow velocity). Nevertheless, it is worth mentioning that Grother *et al.*²⁵ have shown the applicability of flow reactors down to pressures as low as 0.25 Torr, provided two corrections (similar to those used here) are applied: Poiseuille law and diffusions [eqn. (I)]. These points are not included in the fit.

As predicted¹ for reaction proceeding *via* two pathways [reactions (1a) and (1b)], the pressure dependence of the rate constant k_{loss} is S-shaped, similar to the fall-off curve of a dissociation/recombination reaction, however, with a finite second-order limiting low-pressure rate constant. The analysis of such a curve is developed in the subsequent discussion.



Fig. 6 Pressure dependence of the bimolecular rate constant k_{loss} of the reaction of CH₃O with NO at room temperature; (*): this work; (\Box): ref. 6; (\odot): ref. 5; (Δ): ref. 9; (X): ref. 8. The continuous line is the result of a two-channel RRKM calculation (see text).

Measurements at variable temperature

Measurements have been performed between 248 and 473 K for the low-pressure range 0.8-5 Torr and between 286 and 364 K for the pressure range 50-200 Torr. They are presented in Table 3. Low-pressure data do not exhibit a clear pressure dependence; some of them, along with the results of ref. 5, 8 and 9, are presented in Fig. 7 and 8, which display the temperature dependence of k_{loss} at total gas concentration $[M] = 3.25 \times 10^{16}$ molecule cm³ and $[M] = 1.62 \times 10^{17}$ molecule cm³ (P = 1 Torr and P = 5 Torr at T = 298 K, respectively). These two pressures have been chosen since this is where the three sets of experimental data, this work and ref. 5 and 8, overlap. Despite the scatter of data, it can be observed that these Arrhenius plots are non-linear. This will be analyzed subsequently. High-pressure data show a classical pressure fall-off behaviour and a negative temperature dependence, which is shown in Fig. 9 for $[M] = 1.62 \times 10^{18}$ molecule cm³ (P = 50 Torr at T = 298 K) pressure, where the results of this work and those of Frost and Smith⁵ overlap.

Table 3 Results for the temperature dependence of k_{loss}

[He]/ 10^{16} molecule cm ⁻³	T/K	$k_{\text{loss}}^{a}/10^{12} \text{ cm}^3$ molecule ⁻¹ s ⁻¹
3.47	248	6.1 ± 0.9
4.17	248	5.74 ± 1.1
7.98	248	6.7 ± 1
19.6	248	7.3 ± 1.1
7.47	273	5.6 ± 1.1
2.12	373	3.2 ± 0.8
2.60	423	1.6 ± 0.4
7	423	2.0 ± 0.15
11.5	423	1.7 ± 0.25
2.04	473	1.6 ± 0.5
675	286	26 ± 4
338	286	24.1 ± 4
169	286	19.3 ± 3
659	293	23 ± 4
638	303	23 ± 4
598	323	21 ± 3
300	323	17 ± 3
150	323	13 ± 2
580	333	20 ± 3
273	354	14 ± 2
137	354	12 ± 2
530	364	16 ± 2.5

^{*a*} Due to a large scatter, the values of k_{loss} above room temperature derived from the DF/LIF technique exhibit larger uncertainties.



Fig. 7 Arrhenius representation of the bimolecular rate constant k_{loss} of the reaction of CH₃O with NO. [M] = 3.25×10^{16} cm³ molecule⁻¹ s⁻¹ (P = 1 Torr at T = 298 K). (\bigcirc): this work; (\square): ref. 9; (\bullet): ref. 8. Lines are the results of calculations (see text); (.....): disproportionation by direct H-abstraction; (---): disproportionation simultaneously via both pathways.



Fig. 8 Arrhenius representation of the bimolecular rate constant k_{loss} of the reaction of CH₃O with NO. $[M] = 1.62 \times 10^{17} \text{ cm}^3$ molecule⁻¹ s⁻¹ (P = 5 Torr at T = 298 K). (O): this work; ([]): ref. 9; (\oplus): ref. 8; (Δ): ref. 5. Lines are the results of calculations (see text); (.....): disproportionation by direct H-abstraction; (---) disproportionation via an energized adduct: (.....): disproportionation simultaneously via both pathways.

Altogether these data correspond to a variation of k_{loss} in $T^{\approx 2.1}$.

A kinetic analysis, based on the reaction scheme presented in the Introduction and supported by these experimental results together with all the previous data,^{5,6,8,9} will be developed in the following section. We first perform quantum chemical calculations of the enthalpies of formation and of molecular parameters of all species involved in these reactions. These results are then used as input data in a multichannel RRKM calculation.

Calculation

Ab initio quantum chemical calculations

Two different theoretical methods have been used to explore the potential energy surface (PES), the BAC-MP4 method and density functional theory (DFT). Calculations were performed to determine equilibrium structures and saddle points on the singlet PES of the $CH_3O + NO$ reaction using the GAUSSIAN94 and Melius BAC programs.

The BAC-MP4 method has been described in detail previously.^{26–28} In a first step, equilibrium and saddle-point geometries as well as harmonic frequencies are computed at the HF/6-31G(d) level of theory using the GAUSSIAN94 package of programs.²⁹ Vibrational frequencies calculated at this level are systematically scaled down by a factor of 0.89 since they are known to be systematically larger than experimental values.³⁰ Electronic correlation is taken into account by performing MP4(SDTQ) single-point calculations using the 6-31G(d,p) basis set. In a second step, the Melius BAC



Fig. 9 Temperature dependence of the bimolecular rate constant of the reaction of CH₃O with NO. $[M] = 1.62 \times 10^{18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (P = 50 \text{ Torr at } T = 298 \text{ K}). (\bigcirc)$: this work; (\triangle): ref. 5. Line is the result of calculation (see text).

program improves the results obtained by empirical corrections using bond-additivity approximations for the systematic errors in the *ab initio* calculations, resulting mainly from basis set truncation. Additional corrections for electron spins are made, either to remove spin contamination for open-shell systems or to account for the UHF instability of closed-shell systems.

Regarding the DFT theory, Becke's three-parameter function and the non-local correlation provided by the LYP expression, $(B3LYP)^{31}$ have been used, together with Dunning's correlation consistent cc-PVDZ basis set³² which includes polarization functions.

Results of calculations. Both theoretical methods yielded nearly the same results for energies and structures and, therefore, lead to the same interpretation.

A minimum in the singlet PES has been found, corresponding to the formation of CH₃ONO, 176.6 kJ mol⁻¹ (BAC-MP4) and 160.7 kJ mol⁻¹ (DFT) below the reactants level (at temperature 0 K). No barrier between this structure and the reactants was found. A saddle point, (TS1), has been located on the reaction path (d) connecting CH₃ONO to the products CH_2O and HNO. This saddle point lies 8.8 kJ mol⁻¹ below the reactant energy at the BAC-MP4 level. Using the DFT method, this saddle point is at the same energy level as the reactants. A pathway (r), corresponding to the direct abstraction of H by NO to give HNO has also been considered. Unlike the similar disproportionation reaction in the $CF_3O + NO_2$ system,¹² no barrier was found using either the BAC-MP4 or the DFT method. The computed enthalpies of formation, corrected for the zero-point energy, vibrational frequencies and rotational constants of reactants, intermediate structures, and transition state are summarized in Table 4. Also given in the Table 4 are the estimated errors for the enthalpies of formation, corresponding to the size of the BAC spin correction and the consistency of the BAC-MP4 method²⁸ with other levels of theory. The large estimated error calculated for the transition state is mainly due to the UHF instability found in the system. In the value proposed in Table 4 a correction has been included to account for this shortcoming. The results of the BAC-MP4 calculation are presented graphi-

Table 4Molecular and transition-state parameters computed using
the BAC-MP4 method for the $CH_3O + NO$ reaction

CH ₃ O	NO	CH ₃ ONO	TS1			
Vibrational frequencies ^{<i>a</i>} /cm ^{-1}						
2918 (2992)	2221 (1992)	3004 (3172)	2879 (2952)			
2901 (2952)		2979 (3115)	2814 (2880)			
2842 (2888)		2905 (3037)	2007 (1919)			
1487 (1493)		1748 (1707)	1530 (1536)			
1423 (1339)		1469 (1461)	1434 (1478)			
1414 (1339)		1462 (1442)	1291 (1370)			
1082 (1117)		1440 (1414)	1264 (1255)			
990 (951)		1194 (1172)	1236 (1209)			
726 (723)		1149 (1137)	1188 (1197)			
		1094 (1003)	721 (735)			
		903 (867)	516 (532)			
		788 (671)	481 (440)			
		355 (372)	291 (282)			
		330 (352)	223 (223)			
		222 (184)	i1502 (i1082)			
Rotational constants/cm ^{-1}						
5.346	1.778	0.718	0.806			
0.920		0.257	0.172			
0.918		0.196	0.159			
$\Lambda_{*}H^{0}(\Lambda_{*}H^{0} 298)/kI \text{ mol}^{-1}$ BAC-MP4 values						
35.6 + 4.6	90.4 + 8.4	-50.6 ± 5	117.2 + 67			
(27.6)	(90.4)	(-64)	(104.2)			

^a Values of frequencies in parentheses are from DFT calculations.



Fig. 10 Energy diagram and transition-state geometrical structures of the CH₃O–NO system. Enthalpies of formation of molecular and transition state at 0 K were computed by the BAC-MP4 method. Units: kJ mol⁻¹; the origin of the energy is set at the energy level of the reactants CH₃O + NO. Geometrical distances of TS1 and CH₃ONO in units of Å.

cally in Fig. 10. The most recent experimental determination of the enthalpy of formation of CH₃O from a study of the dissociation dynamics of this radical³³ gives $\Delta_{\rm f} H_{298}^0 = 20.5$ kJ mol⁻¹, a value which agrees with *ab initio* calculations by Curtiss *et al.*³⁴ and with the value, 21 kJ mol⁻¹, resulting from a unimolecular dissociation study of CH₃O.³⁵ Our calculated value is 6.6 kJ mol⁻¹ higher than these values. Previous values of the enthalpy of formation of CH₃ONO, -67^{36} and -64^{37} kJ mol⁻¹, are in good agreement with our calculated value.

These results, therefore, indicate that the production of $CH_2O + NO$ can occur not only by rearrangement of the CH_3ONO adduct *via* the transition state (TS1), but also by direct hydrogen atom abstraction from the methyl group by the nitrogen atom of the radical NO. The structural and thermochemical data are employed in the RRKM calculations for different reaction channels described below. To be consistent, all the energetic input data used in the statistical RRKM calculation. This yields $\Delta H_0^0 = (-176.6 \pm 13)$ kJ mol⁻¹ for the enthalpy difference between the reactants $CH_3O + NO$ and the intermediate CH_3ONO and a barrier height E_d of (168 ± 63) kJ mol⁻¹ for the exit channel (d) through the transition state (TS1).

RRKM calculations

A statistical RRKM procedure has been used for calculations in the two-channel chemically activated process. The disproportionation involving the CH₃ONO* adduct formation, the collision stabilization by buffer gas [M] (st) and the formation of the products $CH_2O + HNO$ (d) proceed via this same intermediate (see reaction scheme in the Introduction). As a result, calculations must take into account the competition between the collision stabilization of this species (st), and its dissociation back to the reactant (-a) or into the product (d). RRKM theory is used to describe these two unimolecular dissociation pathways of CH₃ONO. The steady-state formulation proposed by Berman and Lin¹¹ for such a process has been improved to take into account the conservation of the total angular momentum. All species are treated as symmetric tops and the conservation of total angular momentum J is taken into account. The external K-rotor, associated with the smallest moment of inertia is treated as an active degree of freedom completely coupled with vibrations. The total rate

$$k_{\text{loss}} = \frac{Q_{\text{CH}_3\text{ONO}}^{\text{e,t}}}{Q_{\text{CH}_3\text{O}}Q_{\text{NO}}} \sum_{J=0}^{\infty} (2J+1) \int_0^\infty \frac{\omega + k_{\text{d}}(E, J)}{\omega + k_{\text{d}}(E, J) + k_{-\text{a}}(E, J)}$$
$$\times k_{-\text{a}}(E, J)N(E, J) e^{-E/RT} dE$$

where *E* is the total energy; $Q_{CH_{3}ONO}^{e,t}$ is the product of the translational and electronic partition function of the intermediate CH₃ONO; $Q_{CH_{3}O}$ and Q_{NO} are the total partition functions of the reactants; $\omega = \beta_e Z_{LJ}[M] = k_{st}[M]$ is the effective collision frequency where β_e , is the collision efficiency and Z_{LJ} is the Lennard–Jones collision frequency; N(E, J) is the vibrational density of states of CH₃ONO; $k_d(E, J)$ and $k_{-a}(E, J)$ are the microcanonical rate constants at total energy *E* and total angular momentum *J* for the unimolecular dissociations of CH₃ONO* given by RRKM theory as

$$k(E, J) = \frac{G(E, J)}{hN(E, J)}$$

where G(E, J) is the sum of states at the corresponding transition state for either channel (d) or (-a). G(E, J) is evaluated in two different ways, depending on the nature of the transition state (tight or loose). For the tight exit transition state TS1, vibration frequencies and rotational constants are taken from the *ab initio* calculations (Table 4) and, G(E, J) is derived by taking the inverse Laplace transform of the calculated partition function of this species. Calculation of the corresponding microcanonical rate constant k_d (E, J) is carried out using the program FALLOFF.³⁸ For the case of the loose entrance transition state TSe where there is no barrier involved, the MVIPF theory (microcanonical variational theory by inversion of the interpolated partition function)^{39,40} is implemented to determine the transition state variationally along the reaction coordinate r. Only a brief outline of this method is presented. The partition function of the transition state as a function of the distance r, $Q^*(r)$, is obtained by interpolation of the logarithms of the appropriate reactant and products partition functions using a Gaussian switching function characterized by an adjustable parameter c. $Q^*(r)$ is inverted to obtain the state count G(E, J, r) for the transition state, which is then minimized with respect to r at a given energy E and angular momentum J, and used in the k (E, J) expression of the loose transition state. The reaction is assumed to take place under an effective potential $V_{eff}(r)$ which is approximated by treating the dissociation as the fragmentation of a quasidiatom:

$$V_{\rm eff}(r) = V(r) + B_{\rm e}(r_{\rm e}/r)^2 J(J+1)$$

where V(r) is taken as a simple Morse function, r_e is the equilibrium bond length and B_e is the nearly doubly degenerate rotational constant of CH₃ONO. This calculation of k_{-a} (*E*, *J*) is performed with the program INTERVAR.⁴¹

It seems useful to split k_{loss} into that component which corresponds to CH₃ONO formation and that which corresponds to the formation of the products CH₂O + HNO:

$$\begin{split} k_{\rm st(loss)} &= \frac{Q_{\rm CH_3ONO}^{\rm e,t}}{Q_{\rm CH_3O}Q_{\rm NO}} \sum_{J=0}^{\infty} (2J+1) \int_0^\infty \frac{\omega}{\omega + k_{\rm d}(E,J) + k_{\rm -a}(E,J)} \\ &\times k_{\rm -a}(E,J)N(E,J){\rm e}^{-E/RT}{\rm d}E \\ k_{\rm d(loss)} &= \frac{Q_{\rm CH_3ONO}^{\rm e,t}}{Q_{\rm CH_3O}Q_{\rm NO}} \sum_{J=0}^\infty (2J+1) \int_0^\infty \frac{k_{\rm d}(E,J)}{\omega + k_{\rm d}(E,J) + k_{\rm -a}(E,J)} \\ &\times k_{\rm -a}(E,J)N(E,J){\rm e}^{-E/RT}{\rm d}E \end{split}$$

It is worth noting that if $k_{st(loss)}$ exhibits the classical behaviour of a fall-off curve (*i.e.* $k_{st(loss)}$ increases with pressure), $k_{d(loss)}$ has a quite different behaviour, since it increases when [M] (*i.e.* ω) decreases, reaching a plateau at [M] = 0. Thus, over a large range of pressure, the expected theoretical pressure dependence of k_{loss} is similar to the fall-off curve of a dissociation/ recombination reaction, but with a finite second-order limiting low-pressure rate constant, $k_{d(\text{loss})0}$. Therefore, this curve is Sshaped, flattening out at both high and low-pressure.

Analysis of the experimental results at room temperature. The calculations are first developed at room temperature, where the largest body of experimental data have been reported and where the highest pressure measurements have been performed. Two mechanisms will be successively assumed: (i) the disproportionation reaction proceeds *via* an energized adduct and a RRKM calculation will be performed for chemical activation. (ii) The disproportionation reaction occurs by a parallel independent reaction and the calculated k_{loss} is obtained by adding a constant value to a classical dissociation/recombination RRKM calculation.

In the first case, the rate constant $k_{-a}(E, J)$ of the dissociation of CH₃ONO* back into the reactants involving the loose transition state TSe is calculated variationally by the INTERVAR⁴¹ procedure, as explained above. The Morse parameter β of the effective potential is estimated from the frequency of the reaction coordinate, the r_{e} and B_{e} values are from *ab initio* calculations (Table 4). The parameter c of the switching function is adjusted to obtain the best agreement between the calculated and experimental values measured in the present work at the highest pressure (ca. 500 Torr He). The rate constant, k_d (E, J) of the CH₃ONO^{*} dissociation into the products, involving the tight transition state TS1, is calculated by the program FALLOFF³⁸ using the structural parameters deduced from ab initio calculations (Table 4). The calculated value of $k_{d(loss)}$ depends to a major extent on the height of the exit barrier E_d or more precisely on the difference $E_0 - E_d$ where E_0 is the CH₃ONO potential-well depth equal to the absolute value of ΔH_0^0 , since the entrance channel is barrierless (Fig. 10). For the *ab initio* calculated value E_0 $-E_{\rm d} = 8.8 \text{ kJ mol}^{-1}$, the calculated second-order limiting low-pressure is $k_{d(loss)0} = 0.3 \times 10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value turns out to be too low to account for the low-pressure experimental data. Taking into account that the ab initio values are calculated with a fairly large uncertainty, we reduce the exit barrier height until the experimental data are well reproduced. The best fit is obtained with $E_0 - E_d = 19.2$ kJ mol⁻¹ giving $k_{d(loss)0} = 2.5 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. The value of the high-pressure limiting rate constant k_{∞} , obtained by adjusting the parameter c, is equal to 3.4×10^{-11} cm^3 molecule⁻¹ s⁻¹. The resulting curve, shown in Fig. 6, is obtained with $\beta_c = 0.28$, a slightly high value for He used as the buffer gas. It can be seen that, except for the three lowest pressure data, all the available experimental rate constants are well reproduced. The pressure dependence of the branching ratios for the $CH_2O + NO$ products and for the CH_3ONO formation, defined by $\Gamma_{\rm CH_2O+HNO} = k_{\rm d(loss)}/k_{\rm loss}$ and $\Gamma_{\rm CH_3ONO} =$ $k_{\rm st(loss)}/k_{\rm loss}$, respectively, can be easily calculated and compared to the experimental results. It is seen in Fig. 11 (solid line) that the experimental values of the branching ratio are well predicted by the model. From this analysis it can be concluded that this chemically activated two-channel mechanism accounts well for most of the experimental data at room temperature.

However, as suggested by the results of quantum chemical calculations, the occurrence of disproportionation by a direct hydrogen abstraction cannot be discarded. In this event, the CH₃O loss being assumed to proceed *via* two independent channels, the pressure dependence for the overall rate constant should be calculated by adding a pressure-independent rate coefficient to a conventional RRKM association/dissociation fall-off. By this procedure, a curve $k_{\text{loss}} = f([M])$ quasi-identical to that calculated by the chemically activated mechanism is obtained with the additive constant $k_r \approx 2.2$

 $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, and with $k_{\infty} = 3.3 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and $\beta_{\rm c} = 0.25$. The comparison between the calculated and experimental pressure dependences of the branching ratio is slightly less satisfactory but still correct (Fig. 11). Therefore, the room-temperature data alone do not provide evidence as to whether a direct route or a route *via* an energized adduct is prominent in the mechanism. More information may be inferred from analysis of the temperature dependence of the rate constant.

Analysis of the temperature dependence of the rate constant k_{loss} . Firstly, it is assumed that the disproportionation reaction only occurs by a direct hydrogen abstraction. Calculations are then performed at several temperatures with the value of the variational constant c adjusted to room temperature and assuming a temperature dependence of $\beta_c \approx 0.25$ $(T/298 \text{ K})^{-0.5}$. It was observed that the best representation of the experimental data was obtained with the additive constant k_r independent of the temperature and equal to the roomtemperature value. In the low-pressure range, for P < 30 Torr, the calculated temperature dependences of k_{loss} are displayed in Fig. 7 and 8 for $[M] = 3.25 \times 10^{16}$ molecule cm⁻³ and $[M] = 1.62 \times 10^{17}$ molecule cm⁻³ and compared to the experimental ones. The comparison is not convincing, especially at 1 Torr where calculated values are too low at temperatures below 298 K and too high at those above. In spite of the dispersion of the experimental results, it appears that a minimum of the rate constant should be observed at $T \approx 400$ K, followed by a slight increase beyond this value. This is particularly apparent from the data of Frost and Smith⁵ reproduced in Fig. 8.

The two-channel RRKM calculation involving CH₃ONO* adduct formation is then carried out at several temperatures using the values of $E_0 - E_d$ and of the parameter *c* determined at room temperature. Calculation produces, without any fitting, the following temperature dependence of the rate coefficients: $k_{\infty} = 3.4 \times 10^{-11} (T/298 \text{ K})^{-0.75} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{d(loss)0} = 2.5 \times 10^{-12} (T/298 \text{ K})^{-1.85} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; a temperature dependence of $\beta_c \approx 0.28 (T/298 \text{ K})^{-0.5}$ is again assumed. The calculated curves are displayed in Fig. 7 and 8. A good representation of the experimental results is obtained for $T \leq 350 \text{ K}$. For higher temperatures, calculated values are below the experimental data and the experimental minimum is not predicted by this two-channel model.



Fig. 11 pressure dependence of the branching ratio Γ_{CH_2O+HNO} : (\bullet) ref. 9; (X) ref. 8; (\Box): ref. 45. Lines are the results of calculations. (-): T = 298 K, disproportionation via an energized adduct; ($\cdots\cdots$): T = 298 K, disproportionation by direct H-abstraction; (- - -) T = 573 K, disproportionation simultaneously via both pathways.

This could provide a hint for the occurrence of the direct reaction channel (negligible at temperatures lower than ca. 350 K) with a rate coefficient exhibiting a positive temperature dependence and taking place simultaneously with the chemically activated process just described. To test this hypothesis, analysis of the experimental data is then carried out assuming that a pressure-independent rate coefficient $k_{\rm s}$, increasing with temperature, has to be added to the chemically activated calculated rate constant k_{loss} . The best representation of most experimental data is then obtained with $k_r = 4 \times 10^{-11}$ exp $(-1760 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where the preexponential factor and the temperature coefficient are adjusted parameters. The resulting curve is presented in Fig. 7 and 8 (solid line). It is noticeable that the experimental minimum of the rate constant is now correctly predicted by the model. However, due to the scatter of the experimental results, there is a large uncertainty regarding these two adjusted parameters and the relative contribution of the two processes. This last mechanism, including the direct reaction channel,

is also used for analyzing the experimental results obtained in the higher pressure range P > ca. 30 Torr. In this pressure range, the stabilization process is now dominant and experimental and calculated rate constants, which are in good agreement, exhibit negative temperature dependence. Calculated values are fitted to the expression $k = A (T/298 \text{ K})^{-n}$. A comparison is displayed in Fig. 9 at P = 50 Torr, where the results from this work and from ref. 5 overlap. At this pressure $n \approx 2$. Similar curves should be obtained at higher pressures; it is worth mentioning that, in this pressure range, most experimental results are well fitted by the model.

To conclude, a detailed kinetic modelling taking into account all the available experimental results covering different pressure and temperature ranges, points to the simultaneous occurrence of two pathways for the disproportionation channel $CH_2O + HNO$ of the reaction of CH_3O with NO. This could be anticipated by the *ab initio* calculations of the PESs of this system. However, the scatter of the available experimental results from different authors and the fairly large uncertainty in the *ab initio* calculations do not really allow a quantitative determination of their relative contributions.

Discussion

It is of interest to compare the present analysis with previous related works.

Value of k_{∞}

Most previous experimental results obtained at room temperature between 1 and 100 Torr are consistent. However, as the values of k_{∞} resulted from long extrapolation they are scattered (see Table 1). Present experiments, performed up to 500 Torr, allow us a better determination of k_{∞} and consequently of the value of the microcanonical rate constant $k_{-a}(E)$. Moreover, our data obtained at several temperatures in this pressure range, as well as the highest pressure data of Frost and Smith,⁵ are well accounted for by our kinetic model, thus confirming the calculated negative temperature coefficient of k_{∞} : the expression determined in this work, $k_{\infty} = 3.4 \times 10^{-11} (T/298 \text{ K})^{-0.75} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is not far from that of these authors $k_{\infty} = 3.6 \times 10^{-11} (T/298 \text{ K})^{-0.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Branching ratio

The pressure dependence of the branching ratio for the CH_2O + HNO channel calculated by our model fits correctly the experimental data, obtained by Dobé *et al.*⁹ at room temperature, in contrast to the extended Lindemann-Hinshelwood model proposed by these authors.

Detailed chemical mechanism

In the low-pressure range, there are two sets of results concerning the temperature dependence of the rate constant of CH₃O loss.^{5,8} Two different analyses of these results are proposed, each one being appropriate in its range of experimental conditions. From measurements performed between 5 and 100 Torr in the range 298-573 K, Frost and Smith⁵ found the disproportionation rate constant $k_{d(loss)0} = 5 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, almost independent of temperature. This value is clearly too high compared to the experimental values of k_{loss} at 1 Torr and 298 K which are *ca*. 3×10^{-12} cm³ molecule⁻¹ s^{-1.8,9, this work}. From measurements in the lower pressure and temperature ranges, 1-5 Torr and 223-470 K, MacCaulley et al.⁸ have derived a negative temperature dependence $[\exp (+400 \text{ K}/T)]$ with a value of ca. 3×10^{-12} cm^3 molecule⁻¹ s⁻¹ at 298 K, in better agreement with our own analysis, which gives a value of $ca. 2.5 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. However, at higher temperatures, the analysis of MacCaulley et al.8 predicts too low values for the CH₃O loss rate constants compared to the experimental results of Frost and Smith.⁵ Our "combined" modelling by two simultaneous pathways for the disproportionation reaction, which accounts for most of the experimental results in the pressure range lower than ca. 30 Torr, allows us to fit simultaneously: (i) the negative temperature dependence of the CH₃O loss rate constant in the temperature range 220-400 K and, (ii) at temperatures beyond 400 K, the increasingly small temperature coefficient of the rate constant.

Our analysis shows that neither of the two possible disproportionation pathways, rearrangement of an energized CH₃ ONO* complex and direct hydrogen abstraction, can, alone, account for the whole set of experimental data in the low-pressure range. However, though our suggested combination of these two processes allows us to account for most experimental results, the scatter of data prevents us from definitely discarding other combinations. A few experimental data cannot be included in this representation and there is a lack of consistent experimental results in the low-pressure and hightemperature range. Therefore, the presented adjusted values of the pre-exponential factor and of the temperature coefficient factor of the rate constant k_r must only be considered as fitting parameters having a large uncertainty and some other combinations of the two pathways for the disproportionation reaction could be proposed. For instance an expression for $k_{\rm c}$ independent of temperature, as suggested by ab initio calculations, is not totally inconsistent with the experimental data.

Furthermore, the analysis predicts the pressure and temperature dependence of the branching ratio. At room temperature, the disproportionation channel is negligible near atmospheric pressure ($\Gamma_{CH_2O} \approx 0.01$), represents *ca.* 50% of the total loss of CH₃O at *ca.* 3 Torr and becomes the major channel below *ca.* 1 Torr. The calculated pressure dependence of Γ_{CH_2O} at 573 K is reported in Fig. 11. At all pressures the branching ratio for CH₂O + HNO products increases with increasing temperature and, at T = 573 K, the calculated value of Γ_{CH_2O} is predicted to be *ca.* 0.2 at atmospheric pressure. Qualitatively, this increase in the branching ratio results essentially from the broadening of the fall-off for the association pathway, together with the simultaneous increase of the rate constant of the direct disproportionation.

It is interesting to compare the kinetic behaviour of the $CH_3O + NO$ reaction with that of the analogous $CF_3O + NO$ reaction studied earlier.⁴² For this reaction, the *ab initio* calculated PES⁴² is similar to that calculated here for the $CH_3O + NO$ reaction but with a much lower exit barrier for the disproportionation channel. In this case, $E_0 - E_d \approx 83.7 \text{ kJ mol}^{-1}$ (instead of *ca*. 16.7 kJ mol⁻¹ for $CH_3O + NO$) resulting in a much higher rate constant for the disproportionation pathway than for the stabilization pathway and

thus predicting a pressure-independent rate constant for the CF₃O loss (as observed experimentally). In the same way, the energetics of the $CH_3O + NO_2^{43}$ and $CF_3O + NO_2^{12}$ systems show barrier heights for the exit channel similar to that of the $CH_3O + NO$ reaction and, consequently, exhibit similar kinetic behaviour, *i.e.* a pressure-dependent rate con-

It is convenient to express the pressure and temperature dependence of $k_{\rm loss}$ using an analytical representation which will easily provide values of this rate constant in the ranges 1–760 Torr and 220–600 K. Such an expression may be obtained by adding a constant value to the conventional Troe expression,⁴⁴

$$k_{\text{loss}} = \text{Cst}(T) + \frac{k_0(T)[\text{M}]}{1 + k_0(T)[\text{M}]/k_{\infty}(T)} F\{F_c(T), [\text{M}]\}$$

where $k_0(T) = k_0^{298}(T/298 \text{ K})^{-n}$; $k_{\infty}(T) = k_{\infty}^{298}(T/298 \text{ K})^{-m}$; $F_c = \exp(-T/C)$; $\text{Cst} = A \exp(B/T) + D(T/298 \text{ K})^F$. The four parameters Cst(T), $k_0(T)$, $k_{\infty}(T)$, $F_c(T)$ are obtained at each temperature by non-linear least-square fitting of this k_{loss} expression to the calculated values obtained from our "combined mechanism." The calculated value of F_c , according to the Troe procedure, is *ca*. 0.55–0.6 at 298 K, corresponding to $C \approx 600$. However, as the best fit obtained at each temperature leads to $C \approx 900$, ($F_c \approx 0.7 \text{ at } 298 \text{ K}$), this latter value is retained. The following optimized expressions are then derived: $k_0(T) = 2.65 \times 10^{-29} (T/298 \text{ K})^{-2.8}$ $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$; $k_{\infty} = 3.26 \times 10^{-11} (T/298 \text{ K})^{-0.6}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $\text{Cst} = 1.25 \times 10^{-11} \text{ exp} (-1015 \text{ K}/T) + 1.92 \times 10^{-12} (T/298 \text{ K})^{-2.56} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $F_c = \exp(-T/900 \text{ K})$, for He as buffer gas.

Conclusion

stant for the CX₂O loss.

By a multichannel RRKM analysis of the pressure and temperature dependence of the rate constant for the reaction $CH_3O + NO$, it is established that the disproportionation reaction to $CH_2O + HNO$ products may occur simultaneously (i) by a direct hydrogen abstraction reaction and (ii) *via* the formation of energized CH_3ONO^* complex in competition with the association reaction. This analysis is confirmed by the result of *ab initio* calculation of the PES of this system. The proposed kinetic modelling, accounts for the major part of the available experimental results. It allows a reliable representation of the branching ratios, for the 1–760 Torr and 220–600 K pressure and temperature ranges.

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References

- 1 D. Fulle, H. F. Hamann, H. Hippler and J. Troe, J. Chem. Phys., 1996, 105, 983.
- 2 R. Forster, M. Frost, D. Fulle, H. F. Hamann, H. Hippler, A. Schlepegrell and J. Troe, J. Chem. Phys., 1995, 103, 2949.
- 3 Th. Just, *Twenty-Fifth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1994, p. 687.
- 4 R. Zellner, J. Chim. Phys., 1987, 84, 403.
- 5 M. J. Frost and I. W. M. Smith, J. Chem. Soc., Faraday Trans., 1990, 86, 1757.
- 6 K. Ohmori, K. Yamasaki and H. Matsui, Bull. Chem. Soc. Jpn., 1993, 66, 51.
- 7 N. Sanders, J. E. Butler, L. R. Pasternack and J. R. McDonald, *Chem. Phys.*, 1980, **49**, 17.

- 8 J. A. McCaulley, A. M. Moyle, M. F. Golde, S. M. Anderson and F. Kaufman, J. Chem. Soc., Faraday Trans., 1990, **86**, 4001.
- 9 S. Dobé, G. Lendway, I. Szilagyi and T. Bérces, Int. J. Chem. Kinet., 1994, 26, 887.
- 10 P. Biggs, C. E. Canosa-Mas, J. M. Fracheboud, A. D. Parr, D. E. Shallcross, R. P. Wayne and F. Caralp, J. Chem. Soc., Faraday Trans., 1993, 89, 4163.
- 11 M. R. Berman and M. C. Lin, J. Phys. Chem., 1983, 87, 3933.
- 12 F. Caralp, M. T. Rayez, W. Forst, C. Bourbon, M. Brioukov and P. Devolder, J. Chem. Soc., Faraday Trans., 1997, 93, 3751.
- 13 K. C. Clemitshaw, L. J. Carpenter, S. A. Penkett and M. E. Jenkin, J. Geophys. Res., 1997, 102, 25405.
- 14 S. R. Lin, Y. P. Lee and J. B. Nee, J. Chem. Phys., 1988, 88, 171.
- 15 J. L. Durant Jr., J. Phys. Chem., 1991, 95, 10701.
- 16 S. Dobé, T. Bercès, F. Temps, H. Gg. Wagner and H. Ziemer, ref. 3, p. 775.
- 17 L. Elmaimouni, Thèse Lille, 1994.
- 18 F. Lahmani, C. Lardeux and D. Soldagi, Chem. Phys. Lett., 1983, 102, 523.
- B. S. Agrawalla and D. W. Setser, J. Phys. Chem., 1986, 90, 2450.
 P. J. Wantuck, R. C. Oldenborg, S. L. Baughum and K. R. Winn, J. Phys. Chem., 1987, 91, 3253.
- J. Phys. Chem., 1987, 91, 3253.
 K. J. Rensberger, J. B. Jeffries and D. R. Crosley, J. Chem. Phys.,
- 1989, 90, 2174.
 22 E. Silvente, R. C. Richter and A. J. Hynes, J. Chem. Soc., Faraday
- Trans., 1997, 93, 2821.
- 23 I. W. M. Smith, J. Chem. Soc., Faraday Trans., 1997, 93, 3741.
- 24 V. Daele, G. Laverdet, G. Le Bras and G. Poulet, J. Phys. Chem., 1995, 99, 1470.
- H. Oser, D. Walter, N. D. Stothard, O. Grotheer and H. H. Grotheer, *Chem. Phys. Lett.*, 1991, **181**, 521.
 C. F. Melius and J. S. Binkley, *Twentieth Symposium*
- 26 C. F. Melius and J. S. Binkley, Twentieth Symposium (International) on Combustion. The Combustion Institute, Pittsburgh, 1984, p. 575; C. F. Melius, in Chemistry and Physics of Energetic Materials, NATO SAI 309, ed. S. N. Bulusu, Kluwer, Dordrecht, 1990, p. 21.
- 27 P. Ho and C. F. Melius, J. Phys. Chem., 1990, 94, 5120.
- 28 M. D. Allendorf and C. F. Melius, J. Phys. Chem., 1993, 97, 720.
- 29 GAUSSIAN 94, Revision C.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Peterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomberts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
- 30 J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. De Frees, J. S. Binkley, M. J. Frisch and R. A. Whiteside, *Int. J. Quantum Chem.*, 1981, **S15**, 269.
- 31 A. D. J. Becke, J. Chem. Phys., 1993, 98, 5648; C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785.
- 32 T. H. Dunning Jr., J. Chem. Phys., 1989, 98, 1007.
- 33 D. L. Osborn, D. J. Leahy, E. M. Ross and D. M. Neumark, *Chem. Phys. Lett.*, 1995, 235, 484.
- 34 L. A. Curtiss and L. D. Koch, J. Chem. Phys., 1991, 95, 4040.
- 35 S. Dertinger, A. Geers, J. Kappert, J. Wiebrecht and F. Temps, Faraday Discuss., 1995, 102, 31.
- 36 R. Silverwood and J. H. Thomas, *Trans. Faraday Soc.*, 1967, **63**, 2476.
- 37 D. R. Stull, E. F. Jr. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
- 38 W. Forst, Programm FALLOFF, QCMP, 121, QCPE, 1993, 13, 21.
- 39 W. Forst, J. Phys. Chem., 1991, 95, 3612.
- 40 W. Forst and F. Caralp, J. Chem. Soc., Faraday Trans., 1991, 87, 2307.
- 41 W. Forst, Programm INTERVAR, QCMP, 121, QCPE, 1993, 13, 21.
- 42 Chr. Fockenberg, H. Sommitz, G. Bednarek and R. Zellner, Ber. Bunsen-Ges Phys. Chem., 1997, 101, 1411.
- 43 P. Biggs, C. E. Canosa-Mas, J-M. Fracheboud, A. D. Parr, D. E. Shallcross, R. P. Wayne and F. Caralp, J. Chem. Soc., Faraday Trans., 1993, 89, 4163.
- 44 W. C. Gardiner and J. Troe, in *Combustion Chemistry*, ed. W. C. Gardiner, Springer Verlag, Berlin, 1984, p. 173.
- 45 H. Saathoff, H. Schmidt and R. Zellner, cited in ref. 46.
- 46 I. W. M. Smith, J. Chem. Soc., Faraday Trans., 1991, 87, 2271