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Kinetic Studies of Nitrate Radicals: Flash Photolysis at 193 nm.

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ABSTRACT

Nitrate radicals, NO_3, were produced for the first time by 193 nm laser flash photolysis of N_2O_5 and HNO_3. Detection was achieved due to NO_3's strong absorption at 622.7 nm confirmed by measurements of the absorption spectrum in the range of 617 to 625 nm using both NO_3 precursors. Time-resolved kinetic studies allowed the determination of room temperature rate coefficients for the reactions of NO_3 with 2-methylbut-2-ene and NO_2 of $(1.28 \pm 0.11) \times 10^{-11}$ and $(8.4 \pm 1.2) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. The rate coefficients compare well to previous measurements with alternative techniques suggesting that the reported method is valid and may be applied in follow-up studies. The rate coefficient for 2-methylbut-2-ene is compared to previous measurements and predictions for the alkene as well as the related alkenol. The new data confirm a previously suggested deactivation of the reactive site of the double bond if adjacent to an OH group. A calculated atmospheric lifetime for 2-methylbut-2-ene with respect to NO_3-initated oxidation of less than 3 min suggests predominant removal by NO_3 in the atmosphere.

Keywords: nitrate radicals; kinetics; atmospheric oxidation; flash photolysis; N_2O_5; HNO_3.

INTRODUCTION

Nitrate radicals, NO_3, are important initiators of atmospheric oxidation during night-time [1]. Kinetic parameters of gas-phase reactions have been determined for many years experimentally while estimation methods are being developed to complement the set of experimentally accessible reactants [2–5]. For the development of new experimental approaches we required a reliable source of NO_3. Flash photolysis is a well established method for generation and investigation of short lived radical species. We found that flash photolysis at 193 nm has not been attempted before for the generation of NO_3, despite what is

stated in Table II.19 in [1]: the experiments referred to were only performed at 248 nm rather than 193 nm [6]. We thus conducted the experiments presented here to establish if this method is a suitable source for NO_3 and can be applied for future experimental studies at the air–water interface (compare [7] for an example of such experiments at the air–water interface).

EXPERIMENTAL

Laser Flash Photolysis

NO_3 was produced by flash photolysis of N_2O_5 and HNO_3 using a Coherent Compex 100 excimer laser operating at 193 nm (ArF fill). Photolysis laser pulses (energies ca. 50–70 mJ) were fired into a quartz reaction vessel of 4 cm diameter with demountable windows, at right angles to its main axis. The photolysis beam was rectangular in shape *ca.* 4 cm wide and 1 cm high. NO_3 concentrations were monitored in real time by means of a Coherent 699-21 single-mode dye laser pumped by an Innova 90-5 argon ion laser and operating with Rhodamine 6G. The monitoring laser beam was multipassed 28 to 32 times along the vessel axis (using White's optics), through the reaction zone, to give an effective absorption path of length of *ca.* 1.2 m and width of *ca.* 2 cm. A portion of the monitoring beam was split off before entering the vessel for reference purposes. The monitoring laser was tuned to 16060 cm^{-1} (622.67 nm), corresponding to the known vibronic transition $\tilde{B}^2E'(v_1=1) \leftarrow \tilde{X}\,^2A'_2$ in the NO_3 absorption band [1]. Light signals were measured by a dual photodiode/differential amplifier combination, and signal decays were stored in a transient recorder (Datalab DL 910) interfaced to a computer. This was used to average the decays of typically 3 to 10 photolysis laser shots (at a repetition rate of 0.5 or 1 Hz). Figure 1 shows an example of such a decay trace. The averaged decay traces were processed by fitting the data to an exponential form using a non-linear least-squares package. This analysis provided the initial absorbance values for the transient as well as values of the first-order rate coefficients, k_{obs}, for removal of NO_3 in the presence of known partial pressures of substrate gas. Static gas mixtures were used and the optics were cleaned regularly.

Gas mixtures for photolysis were made up containing fixed concentrations of the transient precursor, N_2O_5 (*ca.* 9.72×10^{15} molecule cm^{-3}), or HNO_3 (*ca.* 3.24×10^{16} molecule cm^{-3}), variable concentrations of reactive substrates and total concentrations made up with inert diluent, SF_6, mostly to 1.62×10^{17} molecule cm^{-3}. Pressures were measured to better than ± 1% with capacitance manometers (Chell Barocel) and converted to concentrations using the ideal

gas equation. Measurements were performed at room temperature of 295 ± 2 K. All gases used in this work were deoxygenated thoroughly prior to use.

Identity and yields of the transient species

The transient absorption spectrum was obtained by monitoring the zero time absorbance (obtained by fitting of exponential decay curves) at sixteen different wavelengths of the single mode dye laser. In these experiments 1.62×10^{16} molecule cm^{-3} of N_2O_5 or 3.24×10^{16} molecule cm^{-3} of HNO_3 precursor were photolysed in the presence of SF_6 at a total concentration of 1.62×10^{17} molecule cm^{-3} and a photolysis laser energy of 60 ± 5 mJ/pulse. Strong signals were obtained over the wavelength range 617 to 625 nm with a maximum at 622–623 nm and no evident band structure. Figure 2 shows the resulting spectrum. Despite some scatter, this spectrum corresponds well to the published absorption spectrum [8,9] and shows that the 193 nm photolysis of both N_2O_5 and HNO_3 are possible sources for NO_3. We thus tuned the dye laser to the absorption maximum of 622.7 nm to carry out kinetic studies (the overall strongest absorption band for NO_3 at ~ 662 nm is not accessible with the dye laser set up employed here; based on literature the 662 nm peak should offer *ca.* double the absorption cross-section obtained at 622.7 nm and could thus further improve the signal-to-noise ratio for the kinetic studies). Because these findings are new, we attempted to estimate the quantum yields from the two precursors. From the NO_3 absorption coefficient (1.578×10^{-17} cm^2 $molecule^{-1}$ [9]) we obtained the following NO_3 yields: 1.04×10^{15} molecule cm^{-3} from N_2O_5 (1.00×10^{16} molecule cm^{-3}) and 1.53 x 10^{14} molecule cm^{-3} from HNO_3 (3.22×10^{16} molecule cm^{-3}). From absorption coefficients at 193 nm [9,11], these correspond to quantum yields of 49 ± 9% and 1.4 ± 0.6%, respectively. When compared with quantum yields at other wavelengths (*e.g.* 64% at 248 nm [12]) that found here for N_2O_5 is substantially less. This is consistent with similar wavelength trends for NO_3 formation in the photochemistry of $ClONO_2$ and $BrONO_2$ [9]. It should be pointed out that light absorption at 193 nm by HNO_3 is very strong and the intensity drops by *ca.* 53% across the detection zone. While this introduces an added uncertainty, we doubt it alters the order of magnitude of the result. There is some debate in the literature [13–18] about the existence of a pathway from HNO_3 leading to formation of H + NO_3. While its contribution is small, we are in no doubt of its existence.

Kinetic analysis

Rate coefficients were determined by least-squares linear regression of a plot of the pseudo first order rate coefficients as a function of the concentration of the co-reactant. The error bars shown for individual point measurements in the plots [Figures 3–6] represent the standard deviations of repeat measurements. In some cases there are clearly additional (but unknown) systematic errors. Quoted errors for the rate coefficients correspond to statistical errors at one standard deviation with 5% added for systematic uncertainties.

RESULTS AND DISCUSSION

General considerations

N_2O_5 was found to be the more convenient source of NO_3 for kinetic measurements. The low yield of NO_3 from HNO_3 effectively ruled out its use. In order to demonstrate suitability of N_2O_5 for rate coefficient measurements, it was important to check the sensitivity of the NO_3 signal to certain molecular species likely to be present either as contaminants or co-products of photolysis. For this reason we included amongst the experiments to find out the optimal conditions of study, some measurements to investigate the dependence of the NO_3 decay constant on the concentrations of both NO_2 and NO. In these experiments, SF_6 was used as a diluent, because it was conveniently to hand, but also because it is a strong collision partner and therefore likely to mitigate any effects of energy release by the photolysis laser.

Experiments with the precursor N_2O_5

With the probe beam set at 622.74 nm (16058 cm^{-1}) a series of experiments was carried out. N_2O_5 concentrations were varied between 3.24×10^{15} molecule cm^{-3} and 2.59×10^{16} molecule cm^{-3} in SF_6 with a constant total concentration of 1.62×10^{17} molecule cm^{-3}. Figure 3 shows that the NO_3 signal decays at increasing rates with increasing precursor concentration. In order to optimise the signal without it decaying too rapidly we chose 9.72×10^{15} molecule cm^{-3} of N_2O_5 and a total concentration of 1.62×10^{17} molecule cm^{-3}. The decay constants showed a weak dependence on SF_6 ($12–18 \times 10^3$ s^{-1} between 4.2×10^{16} molecule cm^{-3} and 1.00×10^{18} molecule cm^{-3}). This was not investigated further. However a brief investigation was carried out on the dependence of the NO_3 decays on the intensity (pulse energy) of the excimer laser. The results are shown in Figure 4. This test clearly shows that NO_3 decays faster at higher intensities. Although there may be several possible reasons for this (*e.g.* formation of other products such as $O(^3P)$) we suspect that increased

concentrations of the co-product NO_2, are probably responsible (see below). This warrants further investigation.

Experiments with added NO

Because NO is a possible photolysis product of N_2O_5 at 193 nm, several experiments were carried out with added NO. After several runs with different quantities of NO (0.32–3.24 × 10^{16} molecule cm^{-3}) it became clear from the fairly rapid loss of signal that NO apparently reacts with N_2O_5 *in situ*. Increased background absorption suggests that NO_2 is formed. In the absence of added NO there is no significant loss of precursor in the cell during photolysis (for up to 10 laser shots) suggesting that little if any NO is actually formed in the photolysis. It should be added that NO is known [19] to react rapidly with NO_3 (to form 2 NO_2) [9] and that small amounts of NO_3 are present in equilibrium with N_2O_5 and NO_2 [1,9,20]. Thus the most likely explanation for our observations is that NO is reacting with NO_3, disturbing the equilibrium with N_2O_5 and NO_2 causing further decomposition of N_2O_5. From kinetic data [20], it can be calculated that N_2O_5 will decompose on a time scale of minutes to try to restore the equilibrium.

Experiments with added NO_2

Because NO_2 is a co-product of the photolysis of N_2O_5 to produce NO_3, several experiments were carried out to test the effect of added NO_2. NO_2 alone absorbs at the probe beam wavelength of 622.7 nm, but does not produce any transient signal upon exposure to 193 nm photolysis laser pulses. With N_2O_5 present (9.72 × 10^{15} molecule cm^{-3}) and a total concentration of 1.62 × 10^{17} molecule cm^{-3} of SF_6 a series of experiments was carried out with added NO_2 (3.24 × 10^{15} – 2.92 × 10^{16} molecule cm^{-3}). From values of initial absorbances, values of $[NO_3]_o$ were calculated to lie in the range 1.2 – 7.1 x 10^{14} molecule cm^{-3}, a factor of at least 4.5 less than $[NO_2]$, thus justifying the use of pseudo-first order kinetics, confirmed by the exponential character of the decay traces. The results are plotted in Figure 5. A linear fit to the data points in Fig. 5 produces a reasonably linear second order plot, despite some scatter at higher pressures of NO_2 giving a rate coefficient of k = (8.4 ± 1.2) × 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. This is higher than the value of 1.7 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} estimated for the rate coefficient in 1.62 × 10^{17} molecule cm^{-3} N_2 from a pressure dependence plot [21] but is well below the limiting high pressure value of 1.9 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} based on an extensive evaluated literature review [22]. Given that SF_6 is a stronger collider than N_2, this is reasonable agreement. We note that the intercept for Figure 5

is fairly high, but this is consistent with the data of Figure 3. We have no specific explanation for this.

Experiments with added alkenes

The reactions between NO_3 and smaller alkenes (ethene, propene and butenes) were too slow for convenient measurement with this technique. Therefore, these experiments were limited to highly reactive alkenes. We thus picked a compound with a high and well established rate coefficient for reaction with NO_3: 2-methylbut-2-ene. The only drawback to the use of 2-methylbut-2-ene is that it is a strong absorber at 193 nm. The experimental data obtained at 295 K are displayed in Fig. 6. In these experiments the total concentration, made up with SF_6, was varied between 3.24×10^{16} and 7.13×10^{17} molecule cm^{-3}. The linear fit for these results confirms that the reaction is not pressure dependent and gives a second order rate coefficient of $(1.28 \pm 0.11) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. This falls within the reported uncertainty of the recommended value of $(9.38 \pm 3.32) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} [23] for NO_3 + 2-methylbut-2-ene, but is considerably higher than the most recent experimental determination by Noda *et al.* [24] of $(3.2 \pm 0.5) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. It is possible that our value contains a small contribution from reaction of free radicals produced by photodecomposition of 2-methylbut-2-ene. The likelihood of this is hard to assess since there has been no 193 nm study of the photolysis of 2-methylbut-2-ene. It is known that free radicals are produced by photolysis at 184.9 nm [25]. To have a serious effect (> 10%) would require a radical concentration of *ca.* 10% of that of 2-methylbut-2-ene itself and a rate constant of *ca.* 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, comparable with the highest values found for reactions of NO_3 with free radicals [1]. This we feel is unlikely. Our new value for this alkene compared to that for the associated OH-substituted 3-methylbut-2-en-1-ol of $(1.0 \pm 0.1) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} [24] supports the suggestion reported previously [26] that an OH group adjacent to the reactive site reduces the reactivity of the double bond towards NO_3-initiated attack. Unfortunately, we were unable to confirm the rate coefficient for the alkenol directly by flash photolysis experiments. Interestingly, the ratio of $k_{alkenol}/k_{alkene}$ for these two experimental determinations is virtually identical to that found by estimation methods based on correlations for alkenes [27] and for alkenols [28]: 0.078 in both cases suggesting a more than ten-fold deactivation of the double bond when adjacent to an OH group. However, the absolute values from the experiments are significantly higher than those predicted by these simple correlations: the estimated rate

coefficients for alkenol and parent alkene are 2.65×10^{-13} cm^3 molecule^{-1} s^{-1} and 3.40×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively.

The atmospheric lifetime of 2-methylbut-2-ene with respect to NO_3-initiated oxidation is somewhat shorter based on this latest determination compared to the best previous estimate [23] and only a quarter of that based on Noda *et al.*'s [24] rate coefficient (156 s *vs.* 213 s *vs.* 625 s); lifetimes were calculated as described in [27] with the 12-h night-time average concentration for NO_3 assumed to be 5×10^8 molecule cm^{-3}. However, we would not expect much impact on atmospheric chemistry caused by this shorter lifetime given the fairly low abundance of this particular alkene in the atmosphere and the fact that this type of alkene was already assumed to be predominantly removed by NO_3-initiated oxidation (compare Fig. 7 in [27]).

CONCLUSIONS

We successfully generated NO_3 by photolysis at 193 nm from the two precursors HNO_3 and N_2O_5, measured the absorption spectrum in the range 617 to 625 nm and used the absorption peak for determination of kinetic parameters for two co-reactants. These time-resolved kinetic studies yielded rate coefficients for the reactions of NO_3 with 2-methylbut-2-ene and NO_2 of $(1.28 \pm 0.11) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(8.4 \pm 1.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. Comparison with literature confirms that the values are consistent with several previous determinations using alternative methods. Comparison with the associated OH-substituted alkene of 2-methylbut-2-ene, 3-methyl but-2-ene-1-ol, suggests a more than tenfold deactivation of the double bond when adjacent to an OH group. The relative deactivation of alkenol *vs.* alkene is consistent with predictions relying on simple correlation methods while the absolute rate coefficients are considerably higher than the predicted ones. The calculated atmospheric lifetime for 2-methylbut-2-ene with respect to NO_3-initated oxidation of less than 3 min suggests rapid removal in the atmosphere predominantly by NO_3.

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10. From the recommended value [9] of K_{eq} for N_2O_5 <-> NO_2 + NO_3, we estimate *ca* 1.8 x 10^{13} molecule cm^{-3} of NO_3 (and NO_2) are present at equilibrium. This corresponds to only 0.2% decomposition of N_2O_5 which, while sufficient to react with NO, is not enough to affect pressure measurements of N_2O_5.

11. The JPL compilation [9] does not list absorption coefficients for N_2O_5 between 200 and 190 nm. At 193 nm we measured a value of 1.12×10^{-17} cm^2 $molecule^{-1}$.

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FIGURES

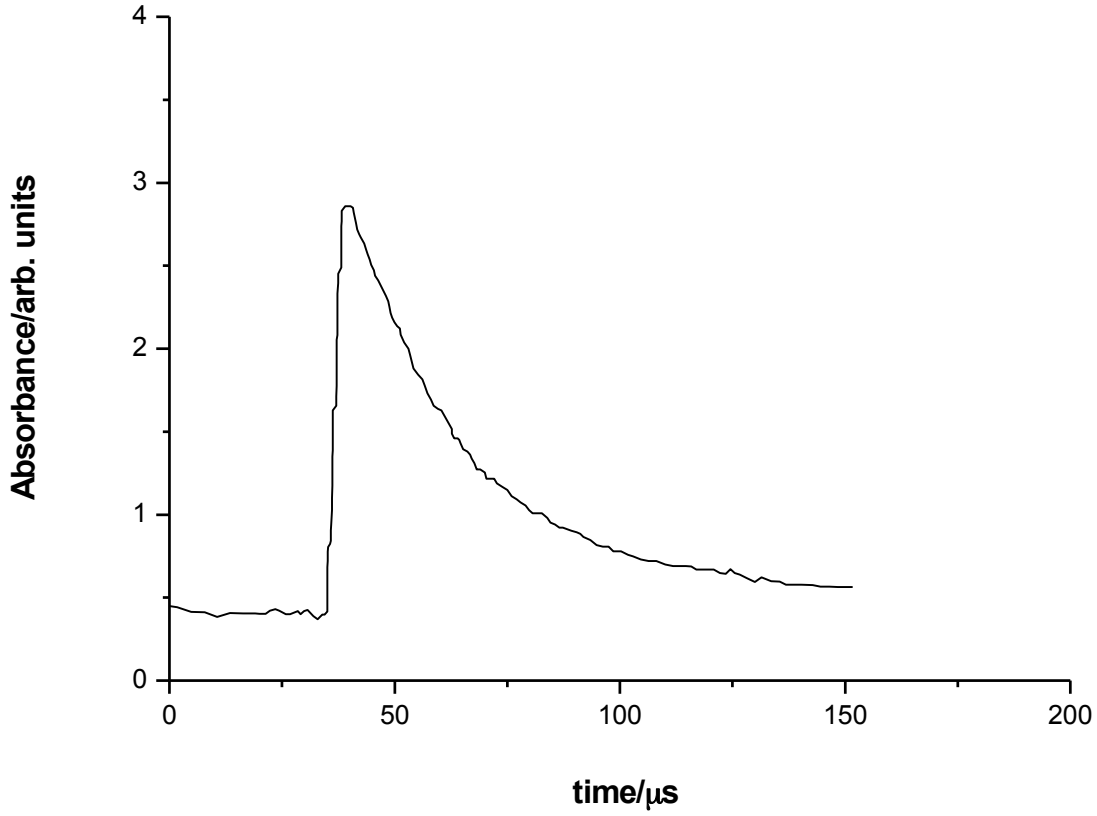

Figure 1. NO_3 decay trace obtained at 193 nm from N_2O_5 [2.35×10^{16} molecule cm^{-3}] in SF_6 [total concentration: 1.65×10^{17} molecule cm^{-3}]. $[NO_3]_o$ = 1.14 x 10^{15} molecule cm^{-3}, path length = 128 cm.

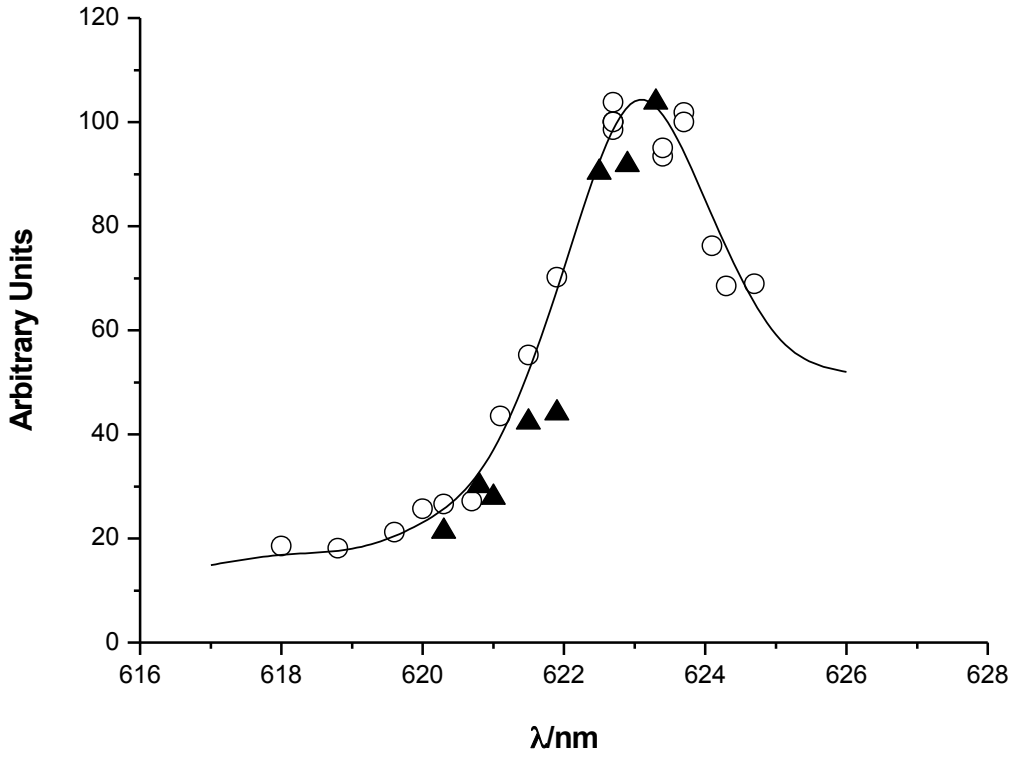

Figure 2. Absorption spectrum of NO_3 obtained experimentally from two precursors at 193 nm photolysis: N_2O_5 (○) and HNO_3 (▲). Line corresponds to scaled data from reference [9].

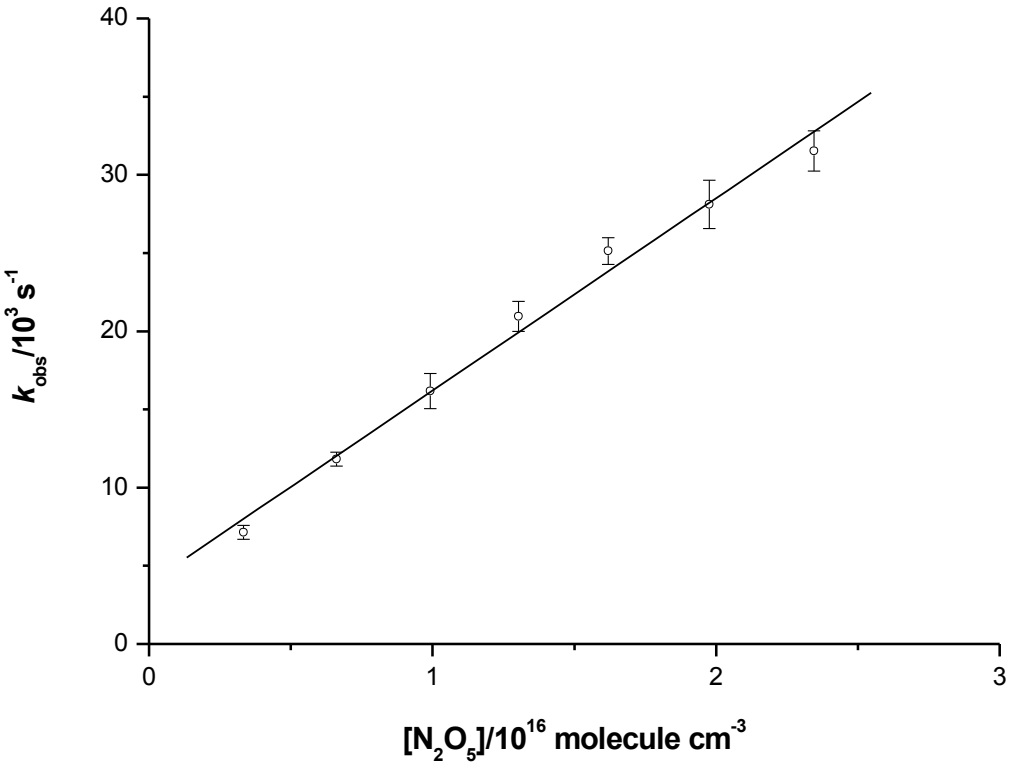

Figure 3. Study of the variation of the NO_3 decay constant with $[N_2O_5]$ at 16058 cm^{-1}.

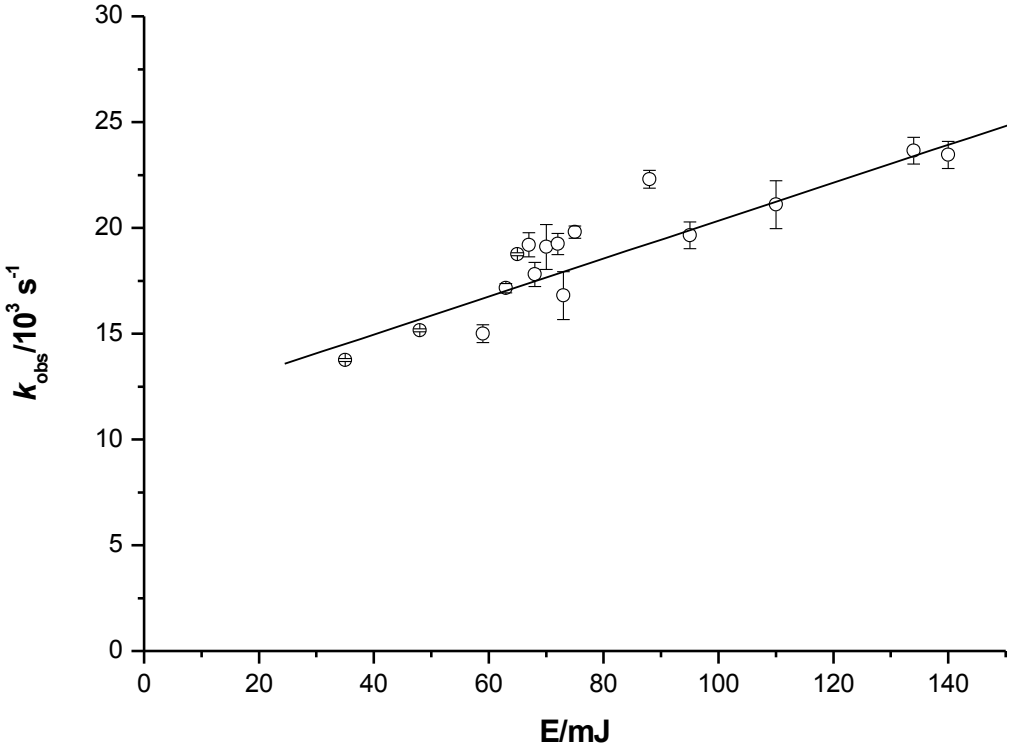

Figure 4. Study of the variation of the NO_3 decay constant with pulse energy at 16060 cm^{-1} using N_2O_5 as precursor.

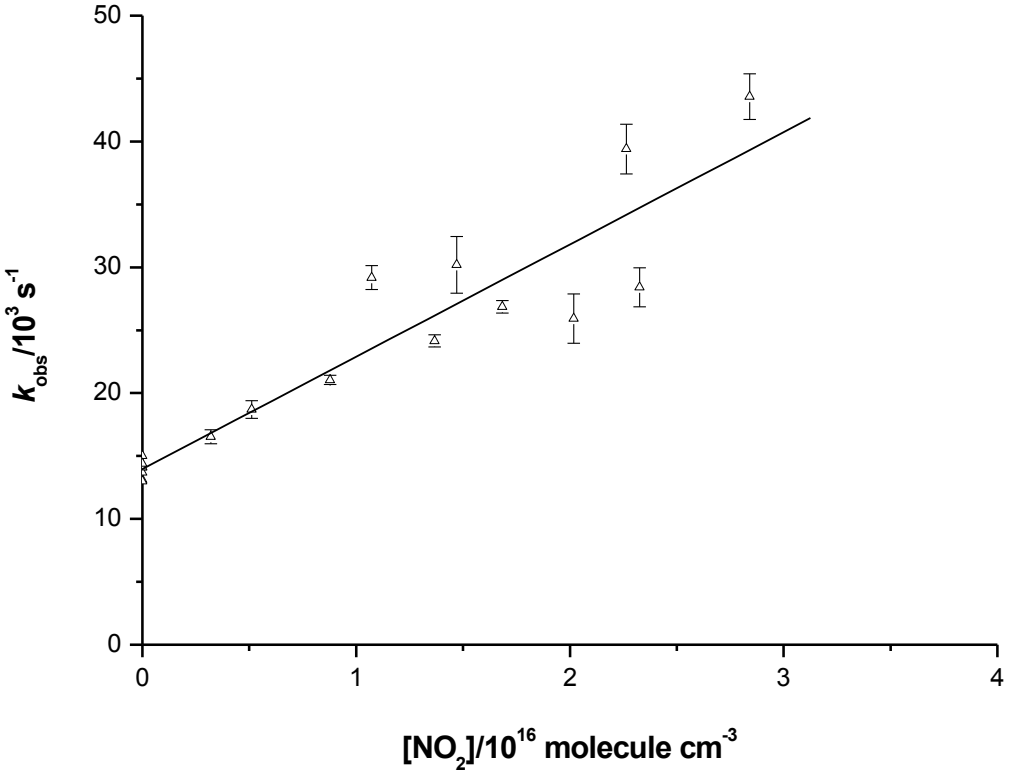

Figure 5. Second order plot for NO_3 reacting with NO_2 (T = 295 ± 2 K; total concentration: 1.62×10^{16} molecule cm^{-3}).

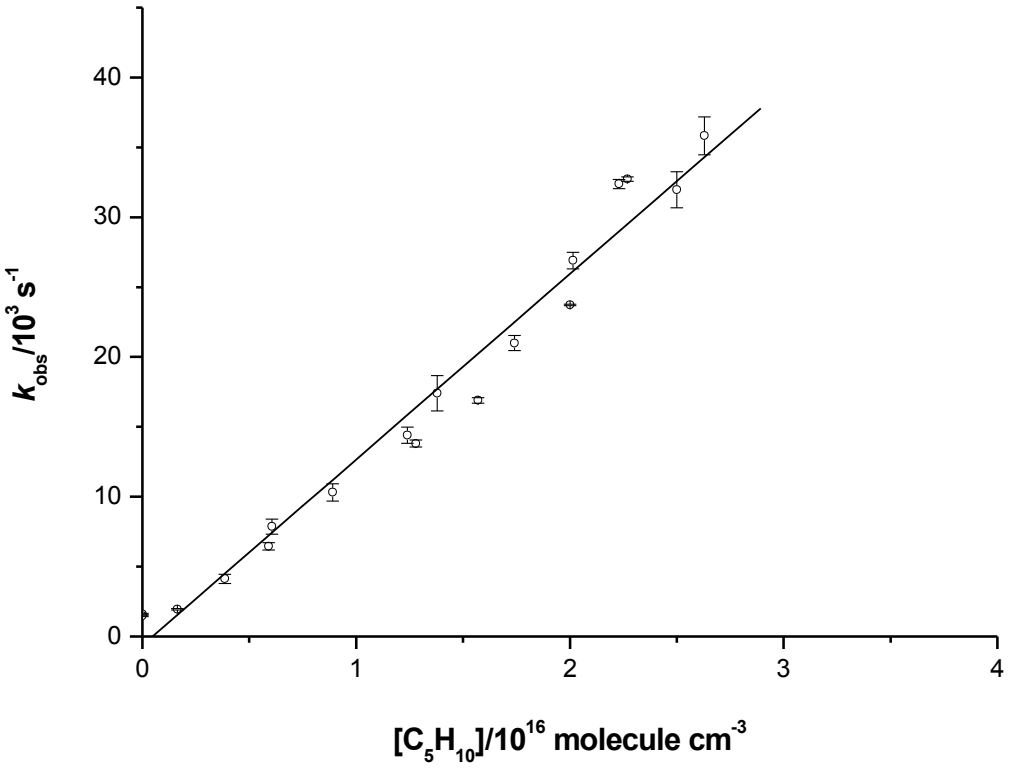

Figure 6. Second order plot for the reaction of NO_3 with 2-methylbut-2-ene, C_5H_{10} (T = 295 ± 2 K; variable total concentration).