# FTIR studies of the $NO_3$ initiated degradation of but-2-yne: Mechanism and rate constant determination

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The products and mechanism of the gas-phase reaction of $NO_3$ radicals with but-2-yne in purified air have been investigated by FTIR spectroscopy. The experiments were carried out at $298 \pm 3$ K and $760 \pm 5$ Torr in a 250 l stainless-steel reactor in which $NO_3$ was generated by the thermal dissociation of $N_2O_5$. Experiments with $^{15}NO_3$ were also performed. Products include butadione, peroxyacetyl nitrate, ketene and acetic acid. Ketene was observed to react further with $NO_3$ and this reaction was also investigated. The rate constants for the $NO_3$ reaction with but-2-yne and ketene were determined by the relative-rate method as $7.0 \pm 0.8$ and $10.6 \pm 1.3 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively, using (*E*)-but-2-ene as a reference. Reaction mechanisms for the but-2-yne and the ketene degradations are proposed.

Over the last two decades the nitrate radical has been fully recognized as an important atmospheric oxidant in night-time chemistry. A substantial amount of work has been carried out to gain insight into the degradation mechanism for various groups of organic compounds and to determine the rate constants for these reactions.[1] Many reactions are now fairly well understood. However, there is little kinetic[2-4] information and no mechanistic information on reactions between $NO_3$ and alkynes.

Alkynes are emitted into the atmosphere by different combustion processes including biomass burning, which to a large extent is due to antropogenic activities. In the natural atmosphere, ethyne and propyne are the most abundant alkynes. Near the rain forest in Brazil their concentrations reach ppb level, which is of the same order as the most usual non-methane hydrocarbons (NMHCs).[5] The occurrence of larger alkynes, such as butynes and pentynes, are low, and they have little importance as pollutants. However, they can conveniently be employed as model compounds for reactions between $NO_3$ and alkynes, since they react much faster than ethyne and propyne. But-2-yne was therefore used in this study because of its symmetry and its relatively fast reaction with $NO_3$.

The rate constants for the reactions between $NO_3$ and alkynes ($<C_6$) lie in the region $10^{-17}$ to $10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[1] The reactions between these compounds and $O_3$ are too slow to be of importance, and their lifetimes in the natural atmosphere are determined by reactions with OH and $NO_3$.[1] The reactions with OH are *ca.* four orders of magnitude faster than the analogous $NO_3$ reactions. However, with a high night-time concentration of $NO_3$, the degradation of alkynes could be determined by $NO_3$.

In a study of the reaction between OH and ethyne, Schmidt *et al.*[6] found glyoxal, CHOCHO, as the major stable product. Hatakeyama *et al.*[7] investigated the reactions between OH and the simple alkynes ethyne, propyne and but-2-yne, and concluded that the initial attack is addition to the $\pi$-bond system, and that the following degradation is similar to that of the OH- or $NO_3$-initiated degradation of the alkenes. The identified products included dicarbonyl compounds and carboxylic acids.[7]

No systematic product study of the reaction between alkynes and $NO_3$ has so far been reported. Wayne *et al.*[1] speculated on the expected products assuming that $NO_3$ adds to the $\pi$-bond system and that the radical formed subsequently degrades by a mechanism similar to that of the alkenes. It was thus suggested that dicarbonyls are the final product in the alkyne reactions at atmospheric pressure. In a flow-tube study carried out at low pressure it was suggested that a short-lived epoxide might be formed or that alkyl migration might lead to a dialkyl ketene.[8]

In the present work it was found that butadione is the major product of the $NO_3$-initiated degradation of but-2-yne but that peroxyacetyl nitrate (PAN), acetic acid and ketene also are formed. It was observed that ketene reacts with $NO_3$, resulting in secondary products that complicate the analysis. Consequently, we also investigated the $NO_3$-initiated degradation of ketene and determined the rate constant for the initial step.

## Experimental

Both the mechanistic and kinetic experiments were performed in a 250 l stainless-steel reactor with an optical base length of 2 m. The reactor is equipped with a multiple-reflection White-type mirror system and adjusted to give a total optical path of 120 m. The optical system is connected to a Bruker IFS 88 FTIR spectrometer allowing *in situ* analysis of intermediates and end products. Spectra were recorded at 0.5 cm$^{-1}$ instrumental resolution co-adding 50 scans. The reactions were studied from the time of mixing and were followed for a maximum of 3 h.

The $NO_3$ radicals were generated in the reactor by the thermal dissociation of $N_2O_5$ which was either synthesized *in situ* by mixing $O_3$ with excess $NO_2$ in purified air or added to purified air in the reactor by evaporation of solid $N_2O_5$.[9] Ozone was generated in two ways: either by silent discharge in a flow of pure oxygen or by discharge in pure oxygen on a vacuum line where the formed ozone was condensed in a liquid-nitrogen-cooled trap. The latter synthesis, which is well suited for work with costly isotopes, resulted in $CF_2O$ as a byproduct, because the atomic oxygen formed also reacted with the Teflon stopcocks of the vacuum line. But-2-yne was of commercially available quality (Fluka) with a purity of 99%. Ketene was synthesized by pyrolysis of acetic anhydride at 500 °C.[10] Experiments were also performed with $^{15}NO_3$ produced from $^{15}NO$ (Cambridge Isotope Laboratories) and $O_3$ *via* formation of $^{15}N_2O_5$.

The experiments were performed at $298 \pm 3$ K and $760 \pm 5$ Torr. Typical but-2-yne and ketene initial mixing ratios were in the range 15–25 ppmv and 5–10 ppmv, respectively, while the initial $N_2O_5$ mixing ratio was 10–12 ppmv. NO was sometimes added at the end of the reaction to break down any peroxynitrate formed. In the kinetic measurements the concentrations of but-2-yne and ketene were kept somewhat lower.

Reference spectra were generated of the following compounds: but-2-yne, dinitrogen pentoxide, nitrogen dioxide, ketene, butadione, carbon monoxide, formaldehyde, acetaldehyde, PAN, (*E*)-but-2-ene, acetic acid, methyl nitrate and nitric acid. But-2-yne, carbon monoxide, butadione, acetic acid, acetaldehyde, (*E*)-but-2-ene and nitrogen dioxide were available commercially, while ketene, dinitrogen pentoxide, PAN[11] and methyl nitrate[12] were synthesized *in situ* following known procedures. Anhydrous $HNO_3$ was prepared from a 2 : 1 mixture of concentrated $H_2SO_4$ and $HNO_3$, while formaldehyde was prepared by careful heating of paraformaldehyde. The lifetime of each compound in the reaction chamber was investigated separately.

The concentration of reactants, intermediates and end products in the reaction mixture was determined by subtraction of calibrated spectra of the reference compounds. Calibration of all of the above-mentioned compounds was made by introducing various known amounts of each compound into the reaction chamber and integrating the absorption bands of the recorded spectra. Plots of concentrations *vs.* band areas gave straight lines with near-zero intercepts.

## Results

### But-2-yne

Survey spectra from the reaction between but-2-yne and the nitrate radical immediately after mixing and 2 h later are shown in Fig. 1. One can easily observe that several new absorption bands have built up. In fact, some of them can already be seen in the first spectrum. All products are identified from these infrared absorption bands alone. Thus, formaldehyde is identified from its band structure at 1745.6 $cm^{-1}$ and its characteristic absorption band between 2950 and 2700 $cm^{-1}$ (the latter area is not shown in Fig. 1), while carbon monoxide is identified by its rotational fine structure of the band at 2225–2055 $cm^{-1}$. Butadione was identified from its characteristic absorption bands at 1361 and 1116 $cm^{-1}$. Its carbonyl stretching band at 1730 $cm^{-1}$ is hidden by the intense absorption bands of $HNO_3$ and $N_2O_5$ in this region. The CO fine-structure band is partly covering a band structure centred at 2151.6 $cm^{-1}$. This absorption band is due to the asymetric C=C=O stretch in ketene. Other bands originating from ketene are too weak to be observed.

Weak bands due to acetic acid can be recognized in the spectra, as well as a carbonyl band at 1950 $cm^{-1}$. This latter band originates from carbonyl fluoride ($CF_2O$), which is a contamination from the synthesis of ozone. $CF_2O$ is not observed to react with any of the compounds in the reaction mixture.

In the experiments with $^{15}NO_3$ only two bands, excluding those of $N_2O_5$, $NO_2$ and $HNO_3$, show a wavenumber shift: the 1305 and 792 $cm^{-1}$ bands are shifted to 1289 and 782 $cm^{-1}$, respectively, and are typical of peroxynitrate compounds, $R{-}O_2NO_2$. The third typical peroxynitrate band around 1730 $cm^{-1}$ is hidden by the $HNO_3$ and $N_2O_5$ bands, as mentioned above. The absorption bands at 1305 and 792 $cm^{-1}$, combined with a fairly strong carbonyl band at 1841 $cm^{-1}$, lead us to the identification of PAN being a product in the but-2-yne reaction. There are no indications of organic nitrates ($R{-}ONO_2$) being formed. The characteristic, strong nitrate absorption bands around 1670, 1290 and 835 $cm^{-1}$ are not observed and neither are the expected wavenumber shifts in any of the bands observed in the experiments with $^{15}NO_3$.

Addition of excess NO to the reaction mixture forces a breakdown of the peroxy radicals present and thereby accelerates the formation of the subsequent oxidation products. The intensity of the absorption bands due to PAN are observed to decrease after the addition of NO, while new bands are building up at 853, 1019, 1201 and 1675 $cm^{-1}$, see Fig. 1, spectrum C. These bands all originate from methyl nitrate, $CH_3ONO_2$. In addition, new bands due to impurities of the NO employed appear at 1800 and 2225 $cm^{-1}$. The intensity of the formaldehyde bands is found to increase when NO is added, but no

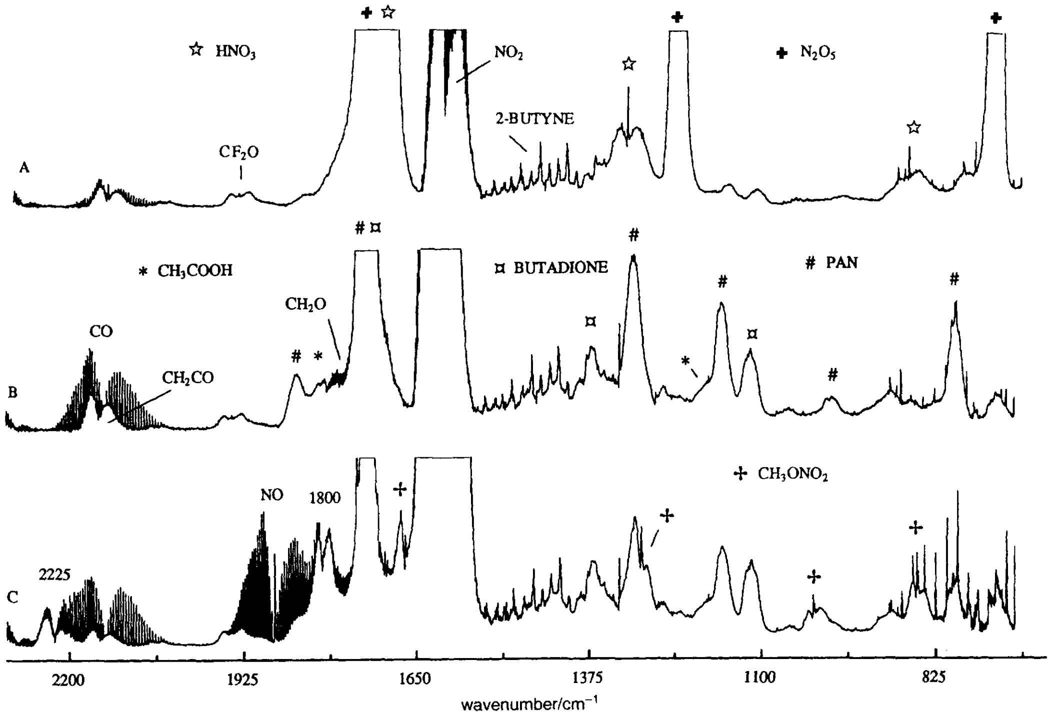

**Fig. 1** IR spectra of the reaction between but-2-yne and nitrate radical: A, immediately after mixing; B, 2 h later; C, after adding excess NO. For A, B and C, *y* scale corresponds to 0.6 absorption units from the baseline to the top of the peaks. The absorption bands at 1800 and 2225 $cm^{-1}$ in spectrum C are due to impurities in the NO employed.

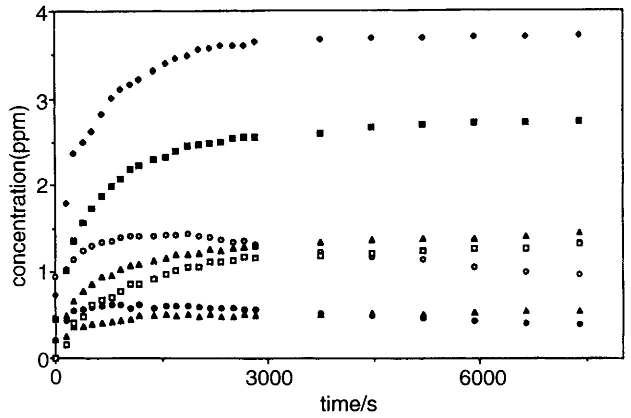

**Fig. 2** Measured concentration–time profiles for a typical reaction of but-2-yne with $NO_3$: (◇) butadione; (■) carbon monoxide; (○) nitric acid; (▲) PAN; (□) formaldehyde; (●) ketene; (△) acetic acid

other changes can be observed. Separate experiments with a PAN reaction mixture show exactly the same changes in the PAN and formaldehyde absorption bands and formation of methyl nitrate when excess NO is added.

The concentration–time profiles of the products in the but-2-yne reaction are plotted in Fig. 2. It can clearly be seen that butadione is the major product, and that the concentration of ketene and nitric acid goes through a maximum. The carbon mass balance of the but-2-yne reaction *ca.* 2 h after the reaction start is given in Table 1. Only 68% of the reacted but-2-yne can be accounted for in terms of the identified products.

### Ketene

Ketene is unstable at room temperature and is observed to decompose slowly in 1 atm† of synthetic air in the reactor. The decomposition follows a first-order decay, but the decay rate actually depends on the conditions in the reactor: the average decay rate is estimated to be $2 \times 10^{-5}$ $s^{-1}$ corresponding to a lifetime of ketene of *ca.* 13 h in the reactor.

During the natural decay of ketene we observe new absorption bands at 1818, 1726, 1159, 798 and 727 $cm^{-1}$ and some very weak bands at 1311, 995, 893 and 852 $cm^{-1}$, but it has not been possible to identify their origin. Only the 1726, 995, 798 and 727 $cm^{-1}$ bands appear reproducible. Acetic acid and acetic anhydride were sometimes observed during the natural decay, but this formation varied from experiment to experiment, and the absorption bands above do not originate from either acetic acid or acetic anhydride. In the liquid phase, ketene polymerizes but the unidentified bands are not explained by diketene or other polymers.

The concentration of ketene is seen to go through a maximum during the time of the but-2-yne experiment, see Fig. 2. The natural decay of ketene cannot alone explain this decrease, and in order to investigate this, separate experiments with ketene and the nitrate radical were performed. Survey spectra of this reaction are shown in Fig. 3. As seen, most of the ketene has reacted within 30 min. The dominant products are carbon monoxide and formaldehyde, which are formed in equal amounts, accounting for more than 80% of the reacted ketene, see Table 2. In addition, one can observe absorption bands due to the natural decay of ketene, see above. Again, the concentration of nitric acid decreases during the reaction. In experiments with $^{15}NO_3$, wavenumber shifts are only observed for $N_2O_5$, $NO_2$ and $HNO_3$. Thus, no nitrate or peroxynitrate are being formed in the ketene degradation.

**Table 1** Observed products and their yields in $NO_3$-initiated degradation of but-2-yne in 1 atm of synthetic air at 298 K, *ca.* 2 h after reaction start

| compound | average product yield wrt carbon mass[a] (%) |
|---|---|
| butadione | 42 |
| PAN | 9 |
| ketene | 2 |
| formaldehyde | 4 |
| carbon monoxide | 8 |
| acetic acid | 3 |
| total yield | 68 |

[a] Relative uncertainty ≤10%.

### Rate-constant determination

The rate constants were determined by the relative-rate technique in which the organic compound of interest competes with a reference compound for the available nitrate radicals.[13] The degradation of both compounds is measured simultaneously, and the rate constant is estimated from the following expression

$$\ln \frac{[\text{organic}]_0}{[\text{organic}]_t} = \frac{k_{\text{org}}}{k_{\text{ref}}} \times \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} \qquad \text{(I)}$$

where the subscripts refer to the start time 0 and time *t*. (*E*)-But-2-ene with a rate constant of $(3.78 \pm 0.41) \times 10^{-13}$, (ref. 14) was chosen as the reference compound for both but-2-yne and ketene. Fig. 4(*a*) and (*b*) show plots of the but-2-yne–(*E*)-but-2-ene and ketene–(*E*)-but-2-ene data sets, respectively.

## Discussion

The observed products from the but-2-yne reaction are listed in Table 1, and Fig. 5 shows our proposed reaction mechanism. In many respects the mechanism resembles that of the alkene degradation, except that the formation of nitrates and nitrooxy peroxynitrates are not observed. Each step and its relative importance in the reaction mechanism is discussed below. As ketene also reacts with the $NO_3$ radical we discuss our findings for this molecule first.

### Ketene

The rate constant for the reaction between ketene and the nitrate radical has previously been studied at low pressure and low oxygen concentration.[15] Several reaction channels were proposed as thermodynamically feasible for the initial step, each initiated by addition of $NO_3$ to the C=C bond, as was also suggested for the analogous reaction with OH at normal pressure.[16] In the present experiments we observe that the concentration of nitric acid is decreasing during the reaction, which indicates that hydrogen abstraction is of minor importance, if occurring at all. We therefore propose that the initial step is addition of the nitrate radical to the C=C bond.

**Table 2** Observed products and their yields in $NO_3$-initiated degradation of ketene in 1 atm synthetic air at 298 K *ca.* 1 h after reaction start

| compound | average product yield wrt carbon mass[a] (%) |
|---|---|
| formaldehyde | 40 |
| carbon monoxide | 41 |
| natural decay of ketene[b] | 9 |
| total yield | 90 |

[a] Relative uncertainty ≤10%. [b] $k_{\text{ketene}} = 2 \times 10^{-5}$ $s^{-1}$.

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† 1 atm = 101 325 Pa.

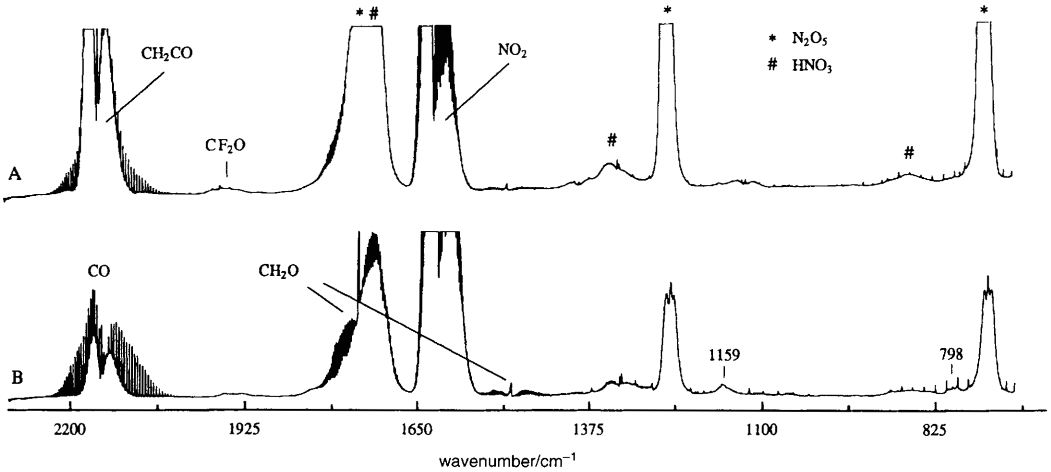


**Fig. 3** IR spectra of the reaction between ketene and nitrate radical: A, immediately after mixing; B, 30 min later. For A and B, *y* scale corresponds to 1.1 absorption units from the baseline to the top of the peaks. The absorption bands at 798 and 1159 $cm^{-1}$ are due to the natural decay of ketene.

In principle, the nitrate radical may add to either the carbonyl or the alkenic carbon; the electron density is higher around the latter carbon.[16] Addition to the carbonyl carbon will subsequently lead to a 1 : 1 formation of formaldehyde and carbon dioxide. In contrast, it is formaldehyde and carbon monoxide that are formed in the ketene reaction, Table 2, and within the uncertainty limits, these products account for approximately all the reacted ketene. Consequently, we propose that the nitrate radical adds to the alkenic carbon.

$$CH_2{=}CO + NO_3 \rightarrow CH_2(ONO_2){-}\dot{C}O \qquad (1)$$

The alkyl radical formed in reaction (1) can either dissociate or react with molecular oxygen. Additional experiments were performed with oxygen concentrations of 0.4 and 0.01%, but the product distribution appeared to be unaffected within the oxygen concentrations employed. We therefore conclude that the alkyl radical intermediate has a lifetime that is shorter than the time between collisions, even under atmospheric con-

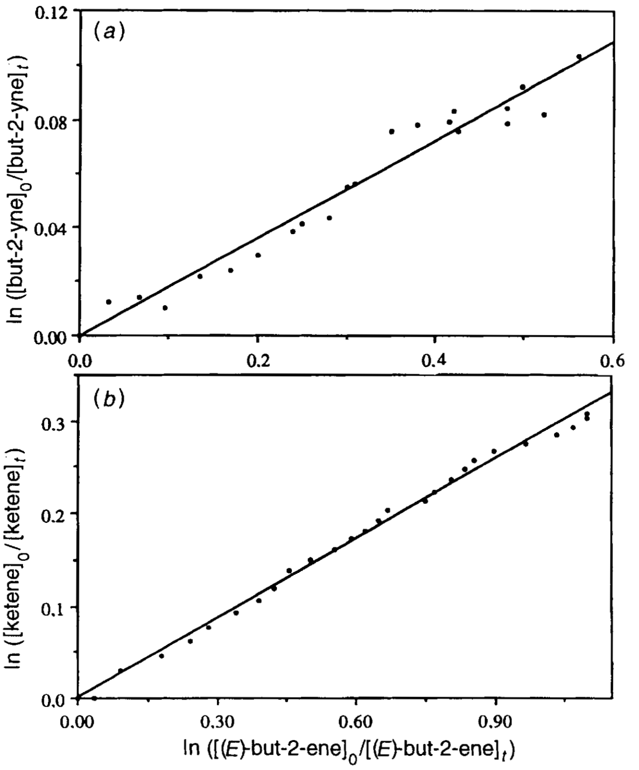


**Fig. 4** Plot of eqn. (I) for (*a*) but-2-yne with (*E*)-but-2-ene as reference organic ($k_{\text{but-2-yne}}/k_{(E)\text{-but-2-ene}} = 0.181 \pm 0.007$), (*b*) ketene with (*E*)-but-2-ene as reference organic ($k_{\text{ketene}}/k_{(E)\text{-but-2-ene}} = 0.269 \pm 0.015$)

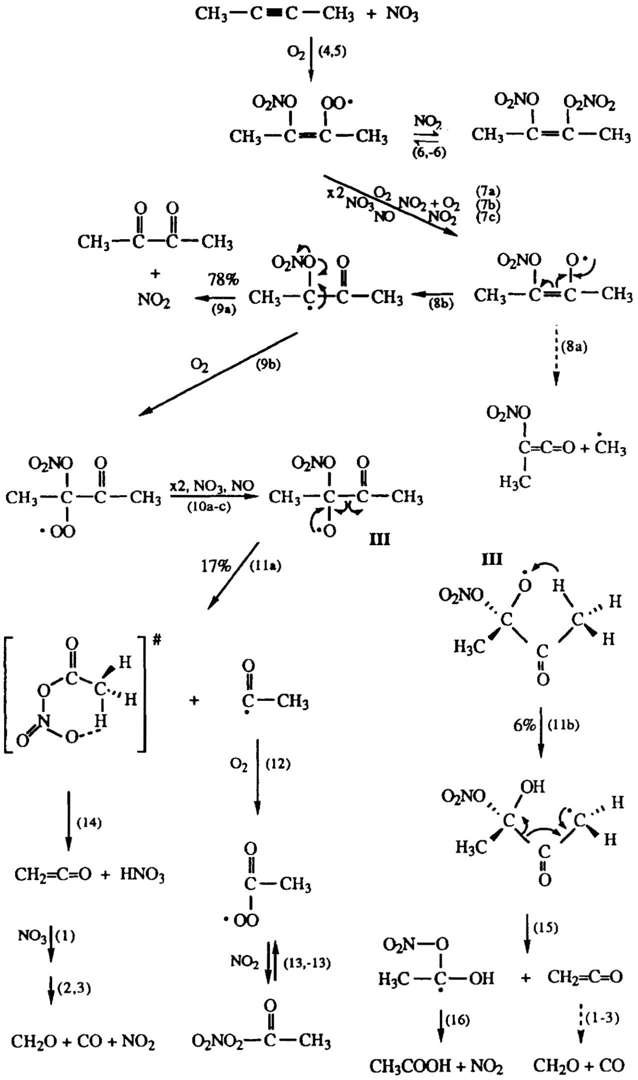


**Fig. 5** Proposed mechanism for the reaction between the nitrate radical and but-2-yne. The relative importance of reactions (9a), (11a) and (11b) are estimated from the products butadione, PAN and acetic acid.

ditions. The alkyl radical formed in reaction (1) will thus dissociate, as was also proposed for the analogous OH–ketene reaction.[16]

We tentatively suggest a two-step dissociation. First, the C—C bond is broken, leading to carbon monoxide and a nitrooxy methylene radical which subsequently dissociates to formaldehyde and nitrogen dioxide.

$$CH_2(ONO_2)\text{—}\dot{C}O \rightarrow \dot{C}H_2(ONO_2) + CO \qquad (2)$$

$$\dot{C}H_2(ONO_2) \rightarrow CH_2O + NO_2 \qquad (3)$$

## But-2-yne

This work is the first investigation of the mechanism for the $NO_3$-initiated degradation of alkynes. The reactivity of the nitrate radicals towards alkynes have been studied previously, and the rate constants are found to increase with increasing alkyl substitution at the $\pi$-bond system.[3] It was found that the $NO_3$–alkyne reactions have a substantial activation energy, which was interpreted in terms of a relatively stable adduct being formed.[4] There are several indications that the reaction between but-2-yne and the nitrate radical is an addition reaction. First, the rate constant for the but-2-yne reaction is much faster than normally observed for hydrogen abstractions. Thus, the rate constant for the but-2-yne reaction is *ca.* three orders of magnitude larger than the reaction between $NO_3$ and butane. Second, the observed products cannot be explained by a degradation following hydrogen abstraction. Third, we do not observe any substantial formation of nitric acid. (This latter argument does not weigh heavily, since the concentration of nitric acid almost always decreases in our reactor due to wall loss, Fig. 2.) Consequently, we support the suggestion by Canosa-Mas *et al.*[3] and propose that the initial step in the reaction between but-2-yne and the nitrate radical is addition to the $\pi$-bond system, as was also suggested for the analogous OH reaction[7]

$$H_3C\text{—}C{\equiv}C\text{—}CH_3 + NO_3 \rightarrow H_3C\text{—}C(ONO_2){=}\dot{C}\text{—}CH_3 \qquad (4)$$

followed by rapid addition of molecular oxygen forming a nitrooxy peroxy radical.

$$H_3C\text{—}C(ONO_2){=}\dot{C}\text{—}CH_3 + O_2 \xrightarrow{M} H_3C\text{—}C(ONO_2){=}C(\dot{O}_2)\text{—}CH_3 \qquad (5)$$

In reactions with alkenes this nitrooxy peroxy radical enters an equilibrium with $NO_2$, forming a nitrooxy peroxy nitrate compound which acts as a reservoir for the nitrooxy peroxy radical.[1] This equilibrium may also occur in the alkyne reaction.

$$H_3C\text{—}C(ONO_2){=}C(\dot{O}_2)\text{—}CH_3 + NO_2 \overset{M}{\rightleftarrows} H_3C\text{—}C(ONO_2){=}C(O_2NO_2)\text{—}CH_3 \qquad (6, -6)$$

However, nitrooxy peroxy nitrate compounds normally have strong, characteristic absorption bands due to the peroxynitrate and nitrate groups, and such bands are not observed in the spectra, except those originating from PAN. Thus, it seems that the nitrooxy peroxy radical formed in reaction (5) is too short-lived to form substantial amounts of a nitrooxy peroxynitrate compound. This is also in accordance with Hatakeyama *et al.*[7] who reported that the OH-substituted peroxy radical has a short lifetime, quickly decomposing through the reaction channels leading to dicarbonyls and carboxylic acids.

The next step in the but-2-yne degradation is proposed to be reduction of the nitrooxy peroxy radical as in the alkene reactions, and an alkoxy radical is formed.

$$H_3C\text{—}C(ONO_2){=}C(\dot{O}_2)\text{—}CH_3 + \begin{cases} \times 2 \\ NO_3 \\ NO \end{cases}$$

$$\rightarrow H_3C\text{—}C(ONO_2){=}C(\dot{O})\text{—}CH_3 + \begin{cases} O_2 & (7a) \\ NO_2 + O_2 & (7b) \\ NO_2 & (7c) \end{cases}$$

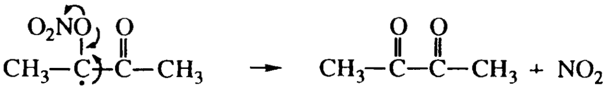
Reaction (7c) is not important under our experimental conditions owing to low concentrations of NO. Alkoxy radicals may decompose *via* several paths like hydrogen abstraction, isomerization, dissociation and addition reactions. Hydrogen abstraction from the alkoxy radical formed in reaction (7) cannot occur since there are no hydrogen atoms bonded to the $\alpha$-carbon. Dissociation can take place in principle, leading to a substituted ketene and a methyl radical.

$$H_3C\text{—}C(ONO_2){=}C(\dot{O})\text{—}CH_3 \rightarrow H_3C\text{—}C(ONO_2){=}C{=}O + \dot{C}H_3 \qquad (8a)$$

The methyl radical will eventually form formaldehyde, which is among the observed products. However, ketenes have a very strong and characteristic absorption band at *ca.* 2150 $cm^{-1}$ and the only such band we observe is due to ketene itself.[16] We therefore conclude that if occurring, reaction (8a) has no significance. The main fate of the alkoxy radical is likely to be $NO_2$ rupture from the carbonyl resonance structure. This leads to the main product butadione, which accounts for 42% of the reacted but-2-yne, Table 1:

$$CH_3\text{—}\overset{O_2NO}{\overset{|}{C}}{=}\overset{O\cdot}{\overset{|}{C}}\text{—}CH_3 \rightarrow CH_3\text{—}\overset{O_2NO}{\overset{|}{\dot{C}}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3$$

(8b)



$$CH_3\text{—}\overset{O_2NO}{\overset{|}{\dot{C}}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3 \rightarrow CH_3\text{—}\overset{O}{\overset{\|}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3 + NO_2$$

(9a)

Butadione is also the main product in the reaction between OH and but-2-yne.[7] It is stable and does not react appreciably with $N_2O_5$, $NO_3$ or $NO_2$. Thus, to explain the formation of the other products observed (PAN, ketene and acetic acid) the alkyl radical must degrade by an additional reaction channel. Provided the alkyl radical does not dissociate immediately, molecular oxygen may add to the alkyl radical formed in (8b)

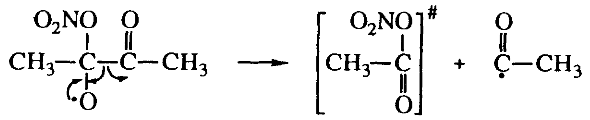
$$H_3C\text{—}\dot{C}(ONO_2)\text{—}CO\text{—}CH_3 + O_2 \xrightarrow{M} H_3C\text{—}C(\dot{O}_2)(ONO_2)\text{—}CO\text{—}CH_3 \qquad (9b)$$

Apparently, this nitrooxy peroxy radical does not enter an equilibrium with $NO_2$ for the same reasons as explained above and is quickly transformed into the corresponding alkoxy radical

$$H_3C\text{—}C(\dot{O}_2)(ONO_2)\text{—}CO\text{—}CH_3 + \begin{cases} \times 2 \\ NO_3 \\ NO \end{cases}$$

$$\rightarrow H_3C\text{—}C(\dot{O})(ONO_2)\text{—}CO\text{—}CH_3 + \begin{cases} O_2 & (10a) \\ NO_2 + O_2 & (10b) \\ NO_2 & (10c) \end{cases}$$

We propose that the alkoxy radical formed in reaction (10) will either decompose or go through a 1,4-hydrogen shift. The decomposition is most likely a cleavage of the $C_2$—$C_3$ bond resulting in an acetyl radical and an (excited) acetyl nitrate.



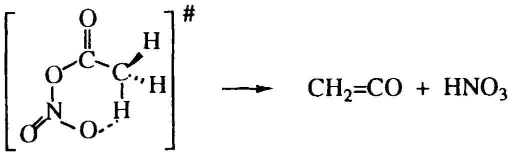
(11a)

A simple estimate of the excess energy based on bond energies results in reaction (11a) being exothermic by *ca.* 150 kJ $mol^{-1}$.[17] Hatakeyama *et al.*[7] observed that acetic acid and PAN were formed in equal amounts in the analogous OH reaction with but-2-yne and concluded that these products probably originate from the same intermediate. Our results support this conclusion since acetyl nitrate is the analogue to acetic acid and the acetyl radical reacts with molecular oxygen and $NO_2$ to give the observed PAN.

$$H_3C-\dot{C}O + O_2 \rightarrow H_3C-CO(\dot{O}_2) \qquad (12)$$

$$H_3C-\dot{C}O(O_2) + NO_2 \overset{M}{\rightleftarrows} H_3C-CO(O_2NO_2) \qquad (13, -13)$$

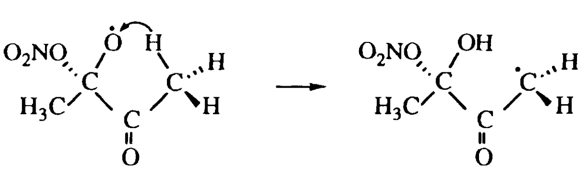
In reaction (11a) above, we indicated that acetyl nitrate might be formed in an excited state. Acetyl nitrate is a stable compound and it is likely that the excited state should be quenched. However, the spectra do not give any indication of this compound being formed in significant amounts. We have no *in situ* spectrum of acetyl nitrate, but previous studies[18] show that the strongest absorption bands are overlapping the bands of PAN. However, after adding an excess of NO to the reaction mixture, the only nitrate compound found in the vapour is methyl nitrate, see below. We suggest that the excited acetyl nitrate may undergo a 1,5-hydrogen shift and then dissociate to ketene and nitric acid.



(14)

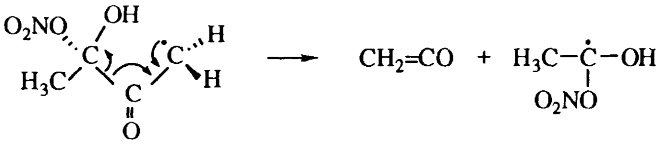
According to this mechanism, ketene and nitric acid should be formed in equal amounts. Unfortunately, the concentration of nitric acid cannot be measured accurately since it is slowly lost to the walls of the reactor, and reaction (14) cannot be confirmed. However, reaction (14) seems reasonable when looking at the primary yield of ketene and the other products observed. We want to point out that in the reaction between OH and the simple alkynes, Hatakeyama *et al.*[7] did not observe ketene. This is not surprising since the OH analogue in reaction (14) cannot proceed *via* either a 1,5- or a 1,4-hydrogen shift. However, substituted ketenes have been observed in reactions with ethyne and propyne at low pressure.[19]

Small amounts of acetic acid are observed to build up during the reaction. This can only be explained by an isomerization involving a hydrogen shift. A 1,4-hydrogen shift is suggested as a minor channel for alkoxy radicals in reactions with alkenes and $NO_3$,[20] and the alkoxy radical formed in reaction (10) is proposed to go through such a shift.

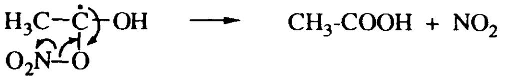


(11b)

The alkyl radical in reaction (11b) may then decompose, thereby forming ketene and a bifunctional alkyl radical which is expected to decompose into acetic acid and nitrogen dioxide.



(15)



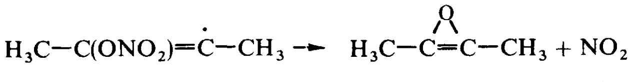
(16)

Consequently, there are two reaction channels leading to ketene, see Fig. 5. The product distribution in Table 1 shows that reaction (11a) leading to formation of ketene and PAN is *ca.* three times more important than reaction (11b) which leads to formation of ketene and acetic acid.

Formaldehyde and carbon monoxide are products in the secondary reaction between ketene and the nitrate radical, reaction (1) *via* reaction (3). In the ketene reaction these products are formed in approximately the same amount, but in the but-2-yne reaction about twice as much carbon monoxide as formaldehyde is formed, see Tables 1 and 2. Previous studies show that formaldehyde reacts with the nitrate radical and that carbon monoxide is a product.[21] However, when the reaction rates of but-2-yne and formaldehyde are compared under the experimental conditions employed, it is found that the rate of the but-2-yne reaction is at least 100 × faster than the formaldehyde reaction. To compare, the rate of the ketene reaction is approximately equal to the but-2-yne reaction. Furthermore, if a substantial amount of formaldehyde reacts with the nitrate radical, it should also do so in the ketene reaction. Consequently, the formaldehyde reaction cannot explain the large difference in the amount of formaldehyde and carbon monoxide formed. The other products formed in the but-2-yne degradation do not react to give significant amounts of carbon monoxide either. This means that carbon monoxide probably originates from the primary reaction between but-2-yne and the nitrate radical. Unfortunately, we have not succeeded finding a reasonable explanation for the higher yield of carbon monoxide.

The carbon mass balance for the but-2-yne reaction is given in Table 1. Only 68% of the reacted but-2-yne can be accounted for in terms of the identified products. This discrepancy may reflect the uncertainties in the mass determination, unidentified products or products that are difficult to observe by IR spectroscopy, particle formation or wall losses in the reactor. The relative uncertainty in the mass determination is estimated to be less than 10% and cannot alone explain the large mass deficiency. Furthermore, it is not likely that large amounts of an unidentified compound would be present, since all distinct absorption bands can be accounted for in terms of the identified products. $CO_2$ measurements are problematic in our system owing to the high background level, and $CO_2$ may actually be formed in the but-2-yne reaction. However, it is not likely that sufficient $CO_2$ is formed to explain the whole discrepancy. Thus, the most likely explanations are the formation of particles and unstable species that are lost to the walls or a product that is difficult to observe by IR spectroscopy.

It has been suggested that oxiranes even at atmospheric pressure may be a major product in reactions with $NO_3$ and unsaturated hydrocarbons.[22] However, oxirane formation was only observed for 2,3-dimethylbutene and not for any of the other but-2-enes investigated. In the but-2-yne reaction the analogous compound would be dimethyl oxirene.



$$H_3C-C(ONO_2)=\dot{C}-CH_3 \rightarrow H_3C-\overset{O}{C=C}-CH_3 + NO_2$$

(17)

**Table 3** Rate constants for the $NO_3$-initiated degradation of but-2-yne and ketene at 298 ± 3 K

| | rate constant/$10^{-14}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ | |
|---|---|---|
| | this work[a] | literature |
| but-2-yne | 7.0 ± 0.8 | 6.7 ± 1.5[b] |
| ketene | 10.6 ± 1.3 | 16[c] |

[a] One standard deviation. [b] Ref. 3. [c] Ref. 15.

Dimethyl oxirene is unstable at room temperature, which may explain why it is not observed.[23] In addition, the characteristic absorption bands of oxirene are expected to be rather weak as they are for the oxirane analogue.

Consequently, we cannot rule out that an unstable oxirene intermediate is formed.

Excess NO was sometimes added to the reaction mixture, causing a decrease in PAN, an increase in formaldehyde and the build-up of new absorption bands due to methyl nitrate. These observations are in accordance with the well known NO initiated degradation of PAN.[24] The concentration of PAN is not observed to decrease during the time of the experiment. Without addition of NO, PAN is quite stable in the cell and will only very slowly break down following a mechanism similar to the NO-initiated degradation.

### Rate constant determination

The results of the rate constant determination in this work are summarized in Table 3 and compared with literature values from fast-flow discharge studies.[3,15] The natural decay of ketene is significant and had to be accounted for when estimating the rate constant in this work. It should be mentioned that the literature value for the but-2-yne reaction is considered to be an upper limit since there was some uncertainty concerning the secondary reactions involved.[3] However, the real value is assumed to be not much lower. The literature value for the ketene reaction is possibly at least a factor of two greater than the real value because of uncertainties concerning the concentration of $NO_3$ and the secondary chemistry.[15] It seems therefore that the rate constants determined by the two different methods are in overall agreement.

## Atmospheric implications

The concentration of $NO_x$ in the reactor is quite different from that in the troposphere. However, if we examine the proposed reaction mechanism for the but-2-yne degradation, Fig. 5, it is only the formation of PAN, reaction (13), that is affected by the changed conditions. Thus, with a low $NO_2 : NO$ ratio PAN will be formed in smaller quantities. The relative importance of reaction (11a) which leads to the PAN precursor will, however, not be affected. Consequently, assuming the same temperature, the ratio of reactions (9a) : (9b) and (11a) : (11b) should be the same in the troposphere as in the reactor. Butadione will therefore be the major product in the but-2-yne reaction in the troposphere. Butadione absorbs in the actinic region and will be relatively quickly photolysed.[25] The other products in the reaction will eventually form carbon monoxide and carbon dioxide by photolysis or by oxidation with OH or $NO_3$, or be rained out.

Alkynes in general are assumed to follow the same $NO_3$-initiated degradation mechanism as but-2-yne. Consequently, dicarbonyls are expected to be dominating products in these reactions, as observed in reactions between the hydroxyl radical and alkynes passing from ethyne to but-2-yne.[7] Ketene-type compounds are also expected to be formed for propyne and the higher homologues, while PAN is less likely to build up for homologues lower than but-2-yne. Except for PAN, there are no nitrate-containing compounds being formed, and reactions with alkynes are not considered to be a sink for $NO_x$. An interesting point to note about alkyne reactions is that, following the same reaction mechanism as for but-2-yne, HCO radicals will be formed in the degradation of, for example, ethyne and propyne. The HCO radicals react with molecular oxygen forming $HO_2$, which then react to give $H_2O_2$ or OH radicals. Thus, alkynes can be a source of OH radicals in the night-time chemistry.

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