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# EPOXIDE FORMATION IN THE REACTIONS OF THE NITRATE RADICAL WITH 2,3-DIMETHYL-2-BUTENE, *CIS-* AND *TRANS-2-BUTENE* AND ISOPRENE

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Abstract—Epoxide formation in the nighttime reaction of NO<sub>3</sub> with 2,3-dimethyl-2-butene, *cis*- or *trans*-2-butene or isoprene was studied in a 480  $\ell$  reaction chamber with *in situ* FTIR spectroscopy as analytical technique. Most experiments were carried out at either 20 Torr in argon or at 740 Torr in synthetic air. In the case of 2,3-dimethyl-2-butene the epoxide formation was studied in the range 20-740 Torr using either argon or air as diluent gas and its O<sub>2</sub> dependence was studied in N<sub>2</sub>/O<sub>2</sub> mixtures with O<sub>2</sub> concentrations in the range  $1.7 \times 10^{15}$ - $4.9 \times 10^{18}$  molec cm<sup>-3</sup>, at a total pressure of 740 Torr. In the experiments performed at 20 Torr in argon, epoxides were found in all reactions as main products.

In the experiments performed at 20 Torr in argon, epoxides were found in all reactions as main products. The measured molar yields were 95.3% for 2,3-dimethyl-2-butene, 50% for *cis*- and *trans*-2-butene and 20% for isoprene.

In the experiments performed at 740 Torr air, epoxides were below the detection limit in the case of *cis*and *trans*-2-butene and isoprene, whereas a yield of 17.4% of the epoxide was measured in the 2,3dimethyl-2-butene experiments.

Possible reaction mechanisms explaining the experimental results are discussed.

Key word index: Nitrate radical, alkenes, isoprene, epoxide formation.

#### INTRODUCTION

The reactions of alkenes and dienes (isoprene) with NO<sub>3</sub> radicals, the most important oxidizing species in the troposphere during the night, have been subject of a series of studies reviewed by Wayne *et al.* (1991). In this review a reaction mechanism in air valid for atmospheric pressure and 295 K is proposed, based on experimental evidence and discussion hereof in the literature.

Under laboratory conditions, using synthetic air with  $N_2O_5$  as  $NO_3$  source, and thus having high  $NO_2$ levels in the system, the first reaction steps (Reactions la, 2a, 3) lead to the formation of nitrate peroxynitrate compounds as intermediates:









 $(R_x = H \text{ or } CH_3).$ 

The nitroxy peroxy radical reacts via different pathways to form alcohol nitrates, carbonyl nitrates and simple unsubstituted carbonyl compounds as main products (Shepson *et al.*, 1985; Hjorth *et al.*, 1990; Barnes *et al.*, 1990; Skov *et al.*, 1992).

Dlugokencky and Howard (1989) studied the conversion efficiency of NO<sub>3</sub> to NO<sub>2</sub> in the reactions of *trans*-2-butene and isoprene at low pressures (0.44–4.5 Torr) and room temperature in He, N<sub>2</sub> and O<sub>2</sub> carrier gases. NO<sub>3</sub> was obtained by the thermal decomposition of N<sub>2</sub>O<sub>5</sub> with initial NO<sub>2</sub> concentration of  $6.2 \times 10^{10}$  molec cm<sup>-3</sup>. The yields of NO<sub>2</sub> decreased by increasing the pressure and the deactivation efficiency of the carrier gas. Among the possible reaction pathways of the adduct formed after the addition of NO<sub>3</sub>, the decomposition to form an epoxide and NO<sub>2</sub> was considered.

Recent studies have shown, that at low pressures the dominant products are indeed epoxides and  $NO_2$ , formed by decay of the initially formed radical (Benter *et al.*, 1991; Wille *et al.*, 1992).



Epoxides were not considered to be important products at atmospheric pressure due to the lack of experimental evidence for this type of compounds (Wayne *et al.*, 1991).

Benter et al. (1993) have recently investigated the yields of  $NO_2$  and epoxide as function of total pressure and of partial oxygen pressure in the reaction of  $NO_3$  with a series of alkenes and dienes, including *cis*and *trans*-2-butene, 2,3-dimethyl-2-butene and isoprene. In the reactions of  $NO_3$  with alkenes they could not detect any decrease in the yield of epoxide or  $NO_2$  by increasing the total pressure from a few Torr up to 30 Torr. Extrapolation of the results to atmospheric pressure suggest that epoxide formation from the reaction of alkenes with  $NO_3$  should be important. The results of Dlugokencky and Howard, on the other hand, indicate that reaction (2b) should be negligible under atmospheric conditions.

In the reactions of NO<sub>3</sub> with dienes. Benter *et al.* (1993) observed a pronounced pressure effect, so that only a very minor oxirane yield would be predicted for these systems at atmospheric pressure.

For these reasons we have carried out a co-operative study to get a deeper insight into the reaction mechanisms and epoxide yields of these reactions.

Experiments were performed reacting NO<sub>3</sub> radicals with *cis*- and *trans*-2-butene, 2,3-dimethyl-2-butene and isoprene, in argon at 20 Torr (O<sub>2</sub> concentration below  $4.7 \times 10^{13}$  molec cm<sup>-3</sup> in the chamber) or at 740 Torr in air. Furthermore, for the reaction of 2,3dimethyl-2-butene, the dependence of the epoxide yield upon the O<sub>2</sub> concentration in a mixture of O<sub>2</sub> and N<sub>2</sub> at 740 Torr total pressure, with the O<sub>2</sub> concentration varying from  $1.5 \times 10^{15}$  molec cm<sup>-3</sup> to  $4.9 \times 10^{18}$  molec cm<sup>-3</sup> in the reaction chamber, was studied. Also, the epoxide yields in air and in argon at various pressures in the range 20–740 Torr were studied in the case of 2.3-dimethyl-2-butene.

For the reaction of NO<sub>3</sub> with all the alkenes investigated in argon at 20 Torr pressure, epoxides were found to be among the main products. In air at 740 Torr, epoxides were still important reaction products in the case of 2,3-dimethyl-2-butene, but were below the detection limit for *cis*- and *trans*-2-butene and isoprene.

#### **EXPERIMENTAL**

The experiments were performed in a 480  $\ell$  evacuable cylindrical Teflon-coated reaction chamber, equipped with a White type mirror system connected to a Bruker 113V FTIR spectrometer. The mirror system was adjusted to an optical path length of 81 m and the IR spectra were recorded at 1 cm<sup>-1</sup> instrumental resolution in the spectral range 700-4000 cm<sup>-1</sup>, co-adding 10-50 interferograms per spectrum.

The experiments on the reaction of NO<sub>3</sub> with isoprene and *cis*- and *trans*-2-butene were performed either at 20 Torr in argon or at 740 Torr in air. The product formation in the reaction of NO<sub>3</sub> with 2.3-dimethyl-2-butene was studied in the range 20-740 Torr using either argon or synthetic air as diluent gas as well as at 740 Torr in N<sub>2</sub>.O<sub>2</sub> mixtures with O<sub>2</sub> concentrations varied in the range  $1.7 \times 10^{15}-4.9 \times 10^{18}$  molect cm<sup>-3</sup>. The pressure in the chamber was measured using an MKS Baratron manometer.

 $NO_3$  was obtained in situ from the thermal decomposition of  $N_2O_5$ :

...

$$N_2O_5 \rightleftharpoons NO_3 + NO_2.$$
 (±5)

 $N_2O_5$  was synthesized by the procedure of Scott and Davidson (1958). The solid  $N_2O_5$  was purified from  $O_2$  by repeating several cycles of flushing with argon followed by oil pump vacuum before it was introduced into the reaction chamber with a flow of diluent gas. After equilibrium  $(\pm 5)$  was established (which happens within a few seconds) the experiments were started, introducing the respective alkene or isoprene into the chamber with a flow of diluent gas. This operation caused a pressure increase in the chamber of about 5 Torr.

The duration of the experiments was at maximum 15 min and typical initial concentrations were:  $N_2O_5 \cong 2.5 \times 10^{14}$  molec cm<sup>-3</sup>,  $NO_2 \cong 2.5 \times 10^{13}$  molec cm<sup>-3</sup> and alkene (isoprene) =  $2.5 \times 10^{14} - 5.0 \times 10^{14}$  molec cm<sup>-3</sup>. These experimental conditions ensured that the interfering reactions between  $NO_2$  and alkenes could be neglected (Skov *et al.*, 1992). The consumption of reactants and the yield of oxiranes were measured by spectral subtraction of calibrated reference spectra of the respective compounds.

The stability with respect to the reaction with NO<sub>3</sub> of tetramethyl oxirane, formed in the reaction between 2.3dimethyl-2-butene and NO<sub>3</sub>, was measured by introducing into the chamber tetramethyl oxirane, N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub> with air at concentrations of  $3.92 \times 10^{14}$ ,  $3.03 \times 10^{14}$  and  $2.66 \times 10^{13}$  molec cm<sup>-3</sup>, respectively. After nearly 3 h reaction time only about 6% of the oxirane had disappeared.

In some experiments with *cis*- and *trans*-2-butene, *cis*-2,3-dimethyl oxirane was introduced into the reaction chamber before the experiments were started. At 740 Torr in air, no increase was observed in the epoxide concentration during the experiments, but the added *cis*-2,3-dimethyl oxirane was always recovered. Based on these experiments, it was concluded that no significant sink of epoxides was present in the reaction chamber under the experimental conditions applied.

The concentrations of reactants and reaction products were found by spectral subtraction of calibrated reference spectra. Cis- and trans-2-butene were supplied by SIO with a stated purity of 99%; 2,3-dimethyl-2-butene and isoprene were supplied by Aldrich, both with a purity of 99%. Trans-2,3-dimethyl oxirane, supplied by Bayer with a purity of 93%, was column-distilled to a purity better than 99%. The gaseous 2-butenes were used as received, while 2,3-dimethyl-2-butene, isoprene and the oxiranes were degassed by several freeze-pump-thaw cycles before introduction into the chamber. Finally, cis-2,3-dimethyl oxirane, 2-methyl-2-vinyl oxirane and tetramethyl oxirane were synthesized with a purity of 99, 99 and 97%, respectively, as determined by GC-MS analysis. In the case of tetramethyloxirane, methylenechloride and chloroform were found as the main impurities. Spectral subtraction using reference spectra of chloroform and methylenechloride was then applied to generate a pure spectrum of tetramethyloxirane. Due to the low concentrations of the impurities, this subtraction was not significantly contributing to the overall uncertainty in the calibration of tetramethyl oxirane.

Carrier gases were supplied by SIO with the following purities: argon <99.999%; nitrogen <99.9999% and synthetic air <99.999%. The oxygen content in pure argon and nitrogen was always below  $1.69 \times 10^{15}$  molec cm<sup>-3</sup> as measured in the chamber with an OXYMAC oxygen analyser (Osaka Sanso Kogyo Ltd).

#### RESULTS

### Reference spectra

The integrated band intensities  $(IBI = (1/cI) \int \ln(I_0/I) dv)$  obtained in the calibration of reference spectra are listed in Table 1 together with the IBI values taken from the literature for the other spectral features used in this study.

Due to the characteristics of the IR absorption bands with no resolved fine structure, the IBI values were, within experimental error and for the pressure range applied here, independent of pressure.

## cis-2-butene or trans-2-butene + $NO_3$

Spectral subtraction of *cis*- and trans-2,3-dimethyl oxirane from a product spectrum of the reaction between *cis*-2-butene and NO<sub>3</sub> at 20 Torr argon is shown in Fig. 1. The yields of *cis*- and *trans*-2,3dimethyloxirane in the reaction of NO<sub>3</sub> with *cis*- and *trans*-2-butene in argon at 20 Torr are given in Table 2, together with the partitioning between the two steric isomers. Yields are expressed as the percentage of mole of the respective 2-butene consumed in the reaction. At 740 Torr, the two epoxides were below the detection limit of *ca*.  $2.4 \times 10^{12}$  molec cm<sup>-3</sup>.

# 2,3-dimethyl-2-butene + NO<sub>3</sub>

Spectral subtraction of tetramethyl oxirane from a typical product spectrum for an experiment carried out at 740 Torr in synthetic air is shown in Fig. 2. Spectrum (a) shows the product spectrum after subtraction of the spectral contributions of water,  $HNO_3$ .

	Wavelength	(IBI) $(10^{-17} \text{ molec cm}^{-1})$	Reference	
	(cm )	(10 110)20 011 )	Kelefenee	
N <sub>2</sub> O <sub>5</sub>	1225-1270	3.81	1	
NO <sub>2</sub>	1580-1650	1.8	2	
2,3-dimethyl-1,3-butadiene	2800-3200	3.3	3	
Cis-2-butene	2800-3200	3.1	3	
Trans-2-butene	2800-3200	3.1	3	
Isoprene	796-952	2.1	3	
Acetone	1075-1140	$6.5 \times 10^{-2}$	3	
Acetaldehyde	2630-2890	1.72	4	
Tetramethyl oxirane	2792-3070	$3.0 \pm 0.3$	This work	
Cis-2,3-dimethyl oxirane	2780-3110	$3.1 \pm 0.3$	This work	
Trans-2,3-dimethyl oxirane	2675-3229	$2.3 \pm 0.3$	This work	
2-methyl-2-vinyl oxirane	2765-3165	$0.62 \pm 0.06$	This work	

Table 1. Absolute integrated band intensities (IBI) applied in this study

1: Hjorth et al., 1987. 2: Cantrell et al., 1985. 3: Hjorth et al., 1990. 4: Cantrell et al., 1986.



Fig. 1. Upper spectrum is the product spectrum of the reaction between NO<sub>3</sub> and *cis*-2-butene at 20 Torr of argon. Initial concentrations are: *cis*-2-butene:  $47.90 \times 10^{13}$  molec cm<sup>-3</sup>; N<sub>2</sub>O<sub>5</sub>:  $23.18 \times 10^{13}$  molec cm<sup>-3</sup> and NO<sub>2</sub>:  $1.68 \times 10^{13}$  molec cm<sup>-3</sup>. Spectra of *cis*-2-butene, HNO<sub>3</sub>, NO<sub>2</sub> and small quantities of acetaldehyde have been subtracted from the original spectrum. Spectra (a) and (b) are recorded with concentrations of  $23.71 \times 10^{13}$  and  $31.94 \times 10^{13}$  molec cm<sup>-3</sup> of *cis*- and *trans*-2,3-dimethyl oxirane, respectively. The lower spectrum is the result of subtracting spectra (a) and (b) from the original spectrum.

	Yield of 2,3-di	methyl oxirane trans-	Total yield of epoxide	
2-butene	(as percentage of reacted 2-butene)			
Cis	7.5 (15)	41.4 (85)	48.9	
	7.3 (13)	49.0 (87)	56.3	
Trans	5.0 (9)	48.6 (91)	53.6	
	9.2 (15)	53.5 (85)	62.7	

Table 2. Yield of *cis*- and *trans*-2,3-dimethyl oxirane in the reaction between  $NO_3$  and *cis*- or *trans*-2-butene expressed as percentage of reacted alkene. Numbers in parentheses indicate the percentage of the two epoxides formed.

2,3,-dimethyl-2-butene, acetone and NO<sub>2</sub>; spectrum (b) shows the spectrum of pure tetramethyl oxirane; and finally; spectrum (c) shows the result of the sub-traction of (b) from (a).

The percentage yield of tetramethyl oxirane relative to the reacted 2,3-dimethyl-2-butene (in moles) is shown in Table 3 at various pressures with either argon or synthetic air as diluent gases. Table 4 similarly shows the yield of tetramethyl oxirane in experiments performed in N<sub>2</sub> with O<sub>2</sub> concentration varied from  $1.7 \times 10^{15}$  to  $4.92 \times 10^{18}$  molec cm<sup>-3</sup> in the reaction chamber at a total pressure of 740 Torr. The uncertainties in Tables 3 and 4 are the combination of two standard deviations and estimated systematic errors. The results in Tables 3 and 4 are visualized in Fig. 3.



Fig. 2. (a) FT-IR product spectrum of the reaction between NO<sub>3</sub> and 2,3-dimethyl-2-butene at 740 Torr of air. Initial concentrations:  $N_2O_5$ : 24.63 × 10<sup>13</sup> molec cm<sup>-3</sup>; 2,3-dimethyl-2-butene: 30.68 × 10<sup>13</sup> molec cm<sup>-3</sup>; NO<sub>2</sub>: 0.76 × 10<sup>13</sup> molec cm<sup>-3</sup>; HNO<sub>3</sub>: 14.00 × 10<sup>13</sup> molec cm<sup>-3</sup>. Spectra of water, 2,3-dimethyl-2-butene, NO<sub>2</sub>. HNO<sub>3</sub> and acetone have been subtracted from the original spectrum. (b) Spectrum of 15.00 × 10<sup>13</sup> molec cm<sup>-3</sup> tetramethyl oxirane. (c) Spectrum obtained after subtraction of spectrum (b) from (a).

Table 3. Tetramethyl oxirane yield as percentage of reacted alkene in the reaction between  $NO_3$ and 2,3-dimethyl-2-butene in experiments carried out in argon or synthetic air at various pressures. The  $O_2$  partial pressure in Torr is shown as well.

Carrier gas	O <sub>2</sub> partial pressure	Total pressure	Tetramethyl oxirane yield as % of reacted 2,3-dimethyl-2-butene
Argon		20.0	95.1
		24.0	95.5
		50.5	85.9
		50.2	91.2
		98.6	73.5
		99.1	89.5
		299.2	76.3
		300.0	67.5
		740.5	80.1
		734.5	84.2
		739.5	87.2
		740.0	90.6
Air	4.6	23.0	83.0
	20.6	103.1	39.3
	20.7	103.5	55.9
	59.3	298.7	29.5
	60.3	301.7	24.4
	148.5	742.6	17.4

 $Isoprene + NO_3$ 

Product spectrum (a), the reference spectrum of 2-methyl-2-vinyl oxirane (b) and the resulting spectrum (c) after subtraction of (b) from (a) are shown in

Fig. 4. In experiments performed at 20 Torr in argon the yield of 2-methyl-2-vinyl oxirane was measured as  $16.2\pm3\%$  (in moles) of the reacted isoprene. At 740 Torr in air 2-methyl-2-vinyl oxirane was below the detection limit of *ca*.  $2.4 \times 10^{12}$  molec cm<sup>-3</sup>.

Table 4. Tetramethyl oxirane yield as percentage of reacted alkene in the reaction between NO<sub>3</sub> and 2,3-dimethyl-2-butene in experiments carried out at 740 Torr total pressure with N<sub>2</sub> as diluent gas and with various concentrations of O<sub>2</sub> shown as molec cm<sup>-3</sup> or as Torr partial pressure

Oxygen content (10 <sup>17</sup> molec cm <sup>-3</sup> )	O <sub>2</sub> partial pressure	Tetramethyl oxirane yield as % of reacted 2.3-dimethyl-2-butene
0.0017		64.2
0.0017		62.6
0.10	0.3	42.5
0.08	0.2	55.5
0.65	2.0	31.5
0.65	2.0	30.7
1.3	3.9	29.6
1.3	3.9	29.0
1.3	3.9	25.8
2.5	7.5	24.8
2.2	6.6	21.4
12.0	36.1	17.0
12.0	36.1	27.6
19.5	58.7	17.6
19.5	58.7	24.0
26.1	78.5	31.2
25.9	77.9	31.5
32.4	97.5	29.4
32.4	97.5	28.0
38.9	117.0	29.3
38.9	117.0	22.8



Fig. 3. Plot of tetramethyl oxirane yield from Tables 3 and 4 vs pressure or  $O_2$  concentration. \*Experiments performed in argon (points refer to lower horizontal axis only).  $\blacktriangle$  Experiments performed in air (points refer to lower as well as upper horizontal axis).  $\bigcirc$  Experiments performed in  $N_2/O_2$  mixture at a total pressure of 740 Torr and with varying  $O_2$  concentration (points refer to upper horizontal axis only).



Fig. 4. (a) Product spectrum of the reaction between NO<sub>3</sub> and isoprene at 20.6 Torr argon. Initial concentrations: isoprene,  $29.54 \times 10^{13}$  molec cm<sup>-3</sup>; N<sub>2</sub>O<sub>5</sub>,  $27.33 \times 10^{13}$  molec cm<sup>-3</sup>; NO<sub>2</sub>,  $3.3 \times 10^{13}$  molec cm<sup>-3</sup> and HNO<sub>3</sub>,  $4.87 \times 10^{13}$ molec cm<sup>-3</sup>. (b) Spectrum of  $23.38 \times 10^{13}$  molec cm<sup>-3</sup> [2-propylen] oxirane. (c) Spectrum obtained after subtraction of spectrum (b) from (a).

#### DISCUSSION

cis- and trans-2-butene + NO<sub>3</sub>

Cis- and trans-2,3-dimethyl oxirane were below the detection limit in the study of the reactions of cis- and trans-2-butene with NO<sub>3</sub> performed at 740 Torr in air; epoxide formation is then of negligible importance for the reactions of these two species with NO<sub>3</sub> in the atmosphere.

At 20 Torr argon a yield of epoxides of about 50% of the reacted alkene was found. For both *cis*- and *trans*-2-butene, *trans*-2,3-dimethyl oxirane was found as the dominant products (Table 2). The latter observation strongly suggests that  $NO_3$  adds to the double bond forming an alkyl radical adduct intermediate;





The radicals formed in Reactions (6a) and (6b) have free rotation around the central C-C bond

$$\begin{bmatrix} ONO_{2} \\ CH_{3} - CH - C - CH_{3} \\ H \end{bmatrix}^{*} \longleftrightarrow \begin{bmatrix} ONO_{2} \\ H \end{bmatrix}^{*} \\ CH_{3} - CH - C - H \\ CH_{3} - CH - C - H \\ CH_{3} \end{bmatrix}^{*}$$

and will rearrange towards the most stable configuration. In this case the *trans* configuration must be the favoured configuration (Table 2) because *trans*-2,3dimethyl oxirane is the dominant oxirane product, as already mentioned

$$\begin{bmatrix} ONO_{2} \\ H_{3}-CH-C-H \\ CH_{3} \end{bmatrix}^{*} \longrightarrow \\CH_{3}-C-C-H+NO_{2}. \qquad (7)$$

Strong spectral features remained in the spectra after subtraction of all known compounds (Fig. 1). In fact, absorption bands assigned to an organic nitrate (see e.g. Hjorth *et al.*, 1990) were observed at 850, 1280 and 1667 cm<sup>-1</sup>, together with spectral features at 770, 1576 and 1692 cm<sup>-1</sup>. This second set of absorptions were very similar to the spectral features (768, 1580 and  $\cdot 1692 \text{ cm}^{-1}$ ) observed by Bandow *et al.* (1980) studying the system N<sub>2</sub>O<sub>5</sub>, NO<sub>2</sub>, propene and N<sub>2</sub> (in

the absence of  $O_2$ ) and assigned by these authors to nitrite groups. Similarly, the spectral features observed here might be assigned to 3-nitrite-2-nitroxy butane; however, the absorption band at 1576 cm<sup>-1</sup> could very well be assigned to a nitro group (e.g. Niki *et al.*, 1986). Based on the absorption of the nitrate group at  $\approx 850 \text{ cm}^{-1}$  and using an (IBI) value of  $3.0 \times 10^{-17} \text{ molec}^{-1} \text{ cm}$  from 3-nitroxy-2-butanol (Hjorth *et al.*, 1990), 3-nitrite-2-nitroxy butane is estimated to be formed with a yield of 35% of reacted alkene, via Reaction (8)

Reaction (8) can explain the strong difference between the epoxide yield measured in this study, with respect to the results of studies using flow systems at about the same total pressure, but with an NO<sub>2</sub> concentration close to zero (Wayne *et al.*; 1991; Benter *et al.*, 1991, 1993; Wille *et al.*, 1992). In our experiments NO<sub>2</sub> was in fact present at an initial concentration of  $2.5 \times 10^{13}$  molec cm<sup>-3</sup> and Reaction (8) competes with Reaction (2b), thus reducing the formation of *cis*- and *trans*-2,3-dimethyl oxirane.

The same argument can be applied to explain the difference observed between the results obtained by Dlugokencky and Howard (1989), who had an initial concentration of NO<sub>2</sub> equal to  $6.2 \times 10^{10}$  molec cm<sup>-3</sup> in their reaction system, and the results obtained by Benter *et al.* (1993).

# 2,3-dimethyl-2-butene + NO3

For the experiments performed in argon, the yield of tetramethyl oxirane appears practically constant over the pressure range investigated (Fig. 3). Using synthetic air as diluent gas the oxirane yield was strongly affected by raising the pressure from 20 to 740 Torr (Fig. 3). In fact, at 740 Torr of air, tetramethyl oxirane accounted only for  $17.4 \pm 3.5\%$  of reacted alkene, against a yield of  $83 \pm 17\%$  in 23 Torr air.

It is now well established that as a first step, NO<sub>3</sub> adds to alkenes: the resulting radical is formed with an excess energy of  $\cong 20$  kcal mol<sup>-1</sup> and might decompose unimolecularly to form tetramethyl oxirane or it might be collisionally stabilized. The pressure independence of the epoxide yield in the argon experiments can be explained if it is assumed that the stabilized radical can still decompose unimolecularly to tetramethyl oxirane and NO<sub>2</sub>. However, this step will

be in competition with addition reactions of either  $NO_2$  or  $O_2$ , see Fig. 5.

Due to the high epoxide yield observed in the argon experiments, Reaction IIa (see Fig. 5) must be much faster than the alternative reactions under the experimental conditions applied here.

In the presence of oxygen, the stabilized radical may react further with O<sub>2</sub> (Reaction IIb) to form a peroxy radical which decomposes according to ambient conditions (Hjorth et al., 1990). In the experiments performed in air a strong decrease in the epoxide yield is observed with increased total pressure and thus increasing O<sub>2</sub> concentration, see Table 3 and Fig. 3. However, in experiments with N<sub>2</sub> as diluent gas at a total pressure of 740 Torr with various concentrations of O<sub>2</sub> an even larger dependence of the epoxide yield on the O<sub>2</sub> concentration was observed. For example, in the reaction in air 23 Torr total pressure an 83% epoxide yield was measured whereas at 740 Torr total pressure in  $N_2$  with approximately the same O<sub>2</sub> content a yield of about 25% was observed (see Tables 3 and 4 and Fig. 3). These observations can be explained by Fig. 5: the rate of Reaction IIb (which competes with the epoxide-forming Reaction IIa) depends on [O<sub>2</sub>]. Pressure increase stabilizes the initially formed reaction adduct (Reaction Ib) and also the peroxy radical formed in Reaction IIb; in this way the pressure adds to the effect of  $O_2$ , resulting in a stronger dependence of epoxide formation on the O<sub>2</sub> concentration at higher pressures. The small change in tetramethyl oxirane yield in the argon experiments is most probably due to the presence of various amounts of  $O_2$  impurities in the chamber and



Fig. 5. Scheme of the reaction between NO<sub>3</sub> and 2.3-dimethyl-2-butene in the presence of NO<sub>2</sub> and  $O_2$ .

not caused by pressure effects; in fact, the lowest yield was observed at 300 Torr and not at 740 Torr.

Using the yield of  $17.4 \pm 3\%$  for the oxirane together with the yields of previously identified products (Hjorth *et al.*, 1990)  $75 \pm 19\%$  of the carbon mass balance in this particular reaction has been accounted for.

## $Isoprene + NO_3$

As for the reaction of 2-butenes, the epoxide yield was below the detection limit in the experiments performed at 740 Torr of air while a  $16.2 \pm 4\%$  2-methyl-2-vinyl oxirane yield was measured when the reaction was performed at 20 Torr in argon.

Because isoprene is asymmetrical, two epoxides may be formed, one by Reaction (9a) followed by Reaction (10a) another by Reaction (9b) followed by Reaction (10b).

$$NO_{3} + CH_{2} = C + CH_{2} - CH_{2}$$

$$NO_{3} + CH_{2} = CH_{3} \xrightarrow{M} CH_{2} \xrightarrow{M} CH_{2} \xrightarrow{M} CH_{3} \xrightarrow{CH_{3}} CH_{2} = CH_{2} \xrightarrow{M} CH_{2} \xrightarrow{CH_{3}} (9b)$$

$$CH_{3}$$

$$CH_{2} - C - CH = CH_{2} - \cdots$$

$$\downarrow \bullet$$

$$ONO_{2}$$

CU

$$CH_2 - C - CH = CH_2 + NO_2 \quad (10a)$$

$$CH_{2} = CH_{3}$$

$$CH_{2} = C-CH-CH_{2} \longrightarrow ONO_{2}$$

$$CH_{3}$$

$$CH_{2} = C-CH-CH_{2} + NO_{2}. \quad (10b)$$

$$O$$

In fact, [2-propylen]oxirane formed in Reaction (10b) could not be identified due to the lack of a reference spectrum of this epoxide. It has been previously shown that Reaction (9a) has a fractional branching yield of 75% against 25% of Reaction (9b) (Skov et al., 1992); based on this branching ratio the epoxide of Reaction (10b) should not account for more than about 5.4% of the reaction products provided that the radical formed in Reaction (9a) and the radical formed in Reaction (9b) are forming the epoxide with the same efficiency. The total epoxide yield is thus expected to be about 20% in the experiments at 20 Torr argon. In air at 740 Torr, 2-methyl-2-vinyl oxirane was below the detection limit as already mentioned and the total formation of epoxide can not be higher than  $2.4 \times 10^{12}$  molec cm<sup>-3</sup> (1% of reacted alkene). Epoxide formation in the reaction of NO<sub>3</sub> with isoprene in ambient air is thus of negligible importance.

A third possible reaction pathway leads to the formation of 2,5-dihydro-3-methyl furane



The importance of Reaction (10c) both at 20 Torr in argon and at 740 Torr in air is unknown; however, in a low-pressure mass spectrometric study furane formation was excluded (Wille *et al.*, 1991).

In the experiments at 20 Torr in argon the spectral features remaining after the subtraction of 2-methyl-2-vinyl oxirane were attributed to nitrite-nitrate compounds, using the same arguments as discussed in the case of the 2-butene experiments. The absorption bands at 847, 1287 and 1669 cm<sup>-1</sup> were assigned to organic nitrate groups. The absorption bands at 781 and 1572 cm<sup>-1</sup> were assigned to an organic nitrite; in the spectrum, the third characteristic band of the nitrite group (in the 1650–1700 cm<sup>-1</sup> range) is presumably hidden under the strong nitrate absorption band at 1669 cm<sup>-1</sup>. Using the same procedure as applied in the case of 2-butene, the yield of nitroxynitrite compounds at 20 Torr in argon was estimated as 60%.

#### CONCLUSION

The reaction of NO<sub>3</sub> with alkenes leads to formation of oxirane products when occurring at low pressures in the absence of oxygen; however, the yield is dramatically reduced in air at atmospheric pressure. In fact, the oxirane yield was found to be negatively correlated with the oxygen concentration at atmospheric pressure; a negative correlation with total pressure was also found, but only in the presence of oxygen.

For the reactions of 2-butenes and of isoprene under atmospheric conditions epoxide formation has no relevance, while at 20 Torr in argon the reactions lead to a total epoxide yield of *ca*. 50 and 16%, respectively, of the reacted hydrocarbons. The reactions at low pressure in argon is *cis*- and *trans*-2-butene with NO<sub>3</sub> have been shown to give the same yields of *cis*- and *trans*-2,3-dimethyloxirane; this strongly suggests that NO<sub>3</sub> initially adds to the alkene, forming an alkyl radical immediately, prior to the formation of the oxirane.

In the case of 2,3-dimethyl-2-butene, in the reaction at low pressure, in argon or in synthetic air, nearly 100% of the alkene reacts to form tetramethyloxirane. Under simulated atmospheric conditions (air, 740 Torr), the epoxide is still an important product, accounting for ca. 17% of the reacted alkene.

Epoxide formation is also expected in the reaction between  $O({}^{3}P)$  and alkenes; however, this is the first time that it is demonstrated that an epoxide may be an important product of an atmospheric reaction.

The study of the reaction between NO<sub>3</sub> and 2.3dimethyl-2-butene establishes the link between the low-pressure experiments (Dlugokencky and Howard, 1989; Wille *et al.*, 1992; Benter *et al.*, 1993) and the high pressure experiments (Barnes *et al.*, 1990; Hjorth *et al.*, 1990; Skov *et al.*, 1992). In fact, the study shows that the yield of tetramethyloxirane appears to result from a competition between unimolecular decomposition of the radical intermediate formed after NO<sub>3</sub> addition and the addition of oxygen to the stabilized intermediate (Fig. 5).

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