REMPI-MS and FTIR Study of NO₂ and Oxirane Formation in the Reactions of Unsaturated Hydrocarbons with NO₃ Radicals

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The yields of NO₂ and oxirane have been studied as a function of pressure in the reactions of NO₃ with selected unsaturated hydrocarbons. NO₂ yields were determined using a flow system with double resonance REMPI-MS technique in the range 1-30 mbar, argon being the buffer gas. The yields of oxiranes were studied using in situ FTIR technique in a static system in the pressure range 30-1000 mbar. With styrene, oxirane formation was also determined by REMPI-MS. The experiments revealed that the NO₂ yields decreased strongly with pressure in the case of aliphatic dienes and styrene, whereas only a negligible pressure dependence of NO₂ formation was observed with alkenes or cyclic dienes. These results were confirmed for 2,3-dimethyl-2-butene and for isoprene in the FTIR experiments in which the corresponding oxirane yields were measured at up to 1000 mbar of argon. Air as buffer gas reduced oxirane formation. In the reaction of *cis*-2-butene and *trans*-2-butene with NO₃ similar yields of *trans*-2,3-dimethyloxirane were obtained. This finding is taken as the most direct evidence for the NO₃ radical addition to the carbon double bond in alkenes in the primary reaction step in agreement with previous assumptions.

Introduction

In recent years NO₃ has been found to be one of the most important radical species in the night-time atmosphere initiating the degradation of unsaturated volatile organic compounds (VOC). Due to its strong absorption coefficient in the visible,¹ NO₃ is effectively photolyzed at sunrise and thus product formation from NO₃ reactions are not significant at day light.^{2,3} Although numerous product studies were conducted using FTIR and GC-MS techniques to elucidate the mechanism of gasphase⁴⁻¹⁰ and liquid phase¹¹⁻¹³ olefin-NO₃ reactions, only little analytical evidence is available on the primary species formed in the interaction of VOCs with this nitrogen oxide. Dlugokencky and Howard had shown¹⁴ in a low-pressure fastflow LIF study in the pressure range 0.6 mbar thatNO₂ is formed as a primary product in the reaction of NO₃ with trans-2-butene, isoprene, and α -pinene. Their NO₂ yield was >0.9 in the reaction of NO₃ radicals with *trans*-2-butene at total pressures $p \le 5.3$ mbar. For the isoprene-NO₃ reaction a yield of 0.4 was reported at 5.3 mbar. No other products were determined in this study. From the NO₂ data a reaction mechanism was inferred that included oxiranes as possible products in the interaction of NO3 with unsaturated VOCs. Oxiranes had previously been identified as product by Hoshino et al.⁴ Bandow et al.⁶ included oxirane formation in their proposed reaction scheme although these authors did not identify this product in their analysis. In more recent FTIR and GC-MS studies of the reaction between NO3 and unsaturated VOCs oxirane identification among the reaction products is missing.⁸⁻¹⁰ The general accepted pathway in air appears to be:

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$$R_1R_2C = CR_3R_4 + NO_3 \rightarrow R_1R_2C(NO_3) - CR_3R_4^*$$
(1a)

$$R_1R_2C(NO_3) - \dot{C}R_3R_4^* \xrightarrow{M} R_1R_2C(NO_3) - \dot{C}R_3R_4$$
 (2a)

$$R_1R_2C(NO_3) - \dot{C}R_3R_4 + O_2 \xrightarrow{M} R_1R_2C(NO_3) - C(O_2)R_3R_4$$
(3a)

Recent mass spectrometric results obtained in discharge flow experiments at pressures in the mbar range^{15,16} gave rise to an extension of the above reaction system. The question was raised whether the initial NO₃-olefin interaction may form oxirane and NO₂ directly via a stereochemically fixed π -complex (1b)

$$\mathbf{R}_{1}\mathbf{R}_{2}\mathbf{C}=\mathbf{C}\mathbf{R}_{3}\mathbf{R}_{4}+\mathbf{N}\mathbf{O}_{3}\rightarrow\mathbf{R}_{1}\mathbf{R}_{2}\mathbf{C}(\mathbf{O})\mathbf{C}\mathbf{R}_{3}\mathbf{R}_{4}+\mathbf{N}\mathbf{O}_{2}$$
 (1b)

or whether the radical adduct formed in reactions 1a and 2a undergoes a fast unimolecular decomposition into oxirane and NO_2 via (2b) and (3b).

$$\mathbf{R}_1 \mathbf{R}_2 \mathbf{C}(\mathbf{NO}_3) - \dot{\mathbf{C}} \mathbf{R}_3 \mathbf{R}_4^* \rightarrow \mathbf{R}_1 \mathbf{R}_2 \mathbf{C}(\mathbf{O}) \mathbf{C} \mathbf{R}_3 \mathbf{R}_4 + \mathbf{NO}_2 \quad (2b)$$

$$\mathbf{R}_{1}\mathbf{R}_{2}\mathbf{C}(\mathbf{NO}_{3}) - \mathbf{C}\mathbf{R}_{3}\mathbf{R}_{4} \rightarrow \mathbf{R}_{1}\mathbf{R}_{2}\mathbf{C}(\mathbf{O})\mathbf{C}\mathbf{R}_{3}\mathbf{R}_{4} + \mathbf{NO}_{2} \quad (3b)$$

If reaction 1b were to occur, the stereochemical configuration of the target molecule should be preserved in the oxirane formed. If reactions 2b or 3b are the predominant pathways, isomerization of the intermediate adduct should lead to formation of the two possible isomers independent of the sterical configuration of the target molecule. On the other hand, previous smog chamber experiments carried out in air at atmospheric pressure have shown to lead to the formation of high yields of organic nitrates.^{2,3} Because of a fairly low time resolution in these

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experiments, it cannot be decided to which extent formation of these organic nitrates might be attributed to primary processes such as 1b-3b followed by secondary reactions between oxiranes with HNO₃. In the present experiment a link has been established between high- and low-pressure experiments to validate the relevance of low-pressure studies to questions of atmospheric chemistry.

Experimental Section

All experiments were carried out in a fast-flow system with molecular beam sampling for REMPI-MS detection using a Bruker TOF1 time-of-flight mass spectrometer equipped with electron impact (EI) and photoionization facilities. The photo-ionization light source consisted of a Lambda Physik EMG 150 excimer laser operating in the two-color mode at $\lambda_1 = 308$ nm and $\lambda_2 = 248$ nm in combination with a Lambda Physik FL 3001 dye laser optically pumped by 308 nm XeCl* radiation. The 248 nm KrF* radiation obtained from the amplifier tube was strongly attenuated. Both laser beams were directed through the ion source perpendicularly to the sampled reaction mixture beam and counterpropagating each other.

Nitrate radicals were generated in a sidearm of a conventional quartz flow tube of ~ 1 in. diameter by reacting F atoms with HNO₃. Fluorine atoms were obtained by passing F₂/He mixtures (5%) through a microwave discharge. An alumina tubing was inserted into the flow tube at the site of the discharge to diminish the attack of F atoms on the tube walls. The flow tube was equipped with a sliding injector for the addition of the alkenes. The device was also employed in the titration experiments. The mixing point of the injector was >15 cm downstream of the site of HNO₃ addition.

To prevent FO formation in the system from F atoms reacting with NO₃ the flow conditions were adjusted such that [HNO₃] was in at least 20-fold excess over [F]₀. Under these conditions also interferences were eliminated from F reacting with the alkenes added. For [HNO₃] \leq [F] formation of FO had been observed. A rate constant of $k = 3 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ had been reported for this process.^{17,18} With HNO₃ being present in excess typical [NO₃] plateaus in the range (5–15) \times 10¹² radicals cm⁻³ were reached.

The hydrocarbons were added to the gas flow always in excess over $[NO_3]_0$ to deplete the radical as far as possible within the time domain of the flow experiment of 40 ms $\leq t \leq 200$ ms. Concentrations for all organics were $(5-50) \times 10^{13}$ molecules cm⁻³.^{19,20} However for 2,3-dimethyl-2-butene even with $\leq 5 \times 10^{13}$ molecules cm⁻³ hydrocarbon added complete NO₃ consumption was obtained due to the high rate constant for this reaction of $k = 4 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

The NO₃ concentration was measured in each experiment by adding excess [NO] to the flow system without hydrocarbon present and following the NO₃ signal by EI at m/e = 62 and/or the NO₂ REMPI signal at m/e 46:

$$NO_3 + NO \rightarrow 2NO_2$$
 (4)

The flow reactor was operated in the pressure range 1 mbar mbar.

FTIR experiments were performed in a 480 L volume cylindrical reactor consisting of a 1.5 m long and 0.6 m i.d. Pyrex glass tube coated with a Teflon film. The flanges were equipped with a White type mirror system adjusted to an optical path length of 81 m and with a Bruker IFS 113 V FT spectrometer on-line. Spectra were recorded in situ at 1 cm⁻¹ instrumental resolution by co adding 5–50 scans with time intervals between the spectra of a few seconds up to 10 min.



Figure 1. Low-resolution two-color mass-selected REMPI signal of NO₂ at m/e = 46 in the wavelength range 465 nm $< \lambda_1 < 505$ nm and $\lambda_2 = 248$ nm (for details see ref 16). Squares indicate changes in dye laser power. Spectrum obtained under flow conditions at $p_{\text{total}} = 5$ mbar and T = 298 K.

Spectral parameters of the reactants presented earlier^{9,10,21} were used to follow the reactions. For product analysis calibrated IR spectra of tetramethyloxirane, *cis*-2,3-dimethyloxirane and *trans*-2,3-dimethyloxirane were recorded. NO₃ radicals were obtained from the thermal decomposition of N₂O₅:

$$N_2O_5 \rightleftharpoons NO_3 + NO_2 \tag{5}$$

The results from these experiments are presented in detail elsewhere.²²

Results and Discussion

REMPI Experiments. In Figure 1 is presented the TOF MS signal at m/e = 46 as function of dye laser wavelength obtained from authentic NO₂ samples added to the main gas flow in the reactor at a total pressure of p = 3 mbar. Included is the dye laser pulse energy at eight different wavelengths λ_1 . The KrF* radiation at $\lambda_2 = 248$ nm was attenuated to a pulse energy of 1 mJ. Both laser beams overlapped spatially and temporally. The strong (1 + 1' + 1) feature at $\lambda_1 = 483.7$ nm was chosen for the quantitative determination of the product NO₂ formed in the reactions studied.

To suppress photofragmentation of HNO_3 which was present in excess in all these experiments according to

$$HNO_3 + h\nu (\lambda = 248 \text{ nm}) \rightarrow NO_2 + OH$$
 (6)

the KrF* radiation was slightly defocused. This way the REMPI signal at m/e = 46 from HNO₃ was always <2% of the net NO₂ signal detected after addition of excess [NO] (see below).

The radical NO₃ itself also gave a contribution at m/e = 46. This REMPI signal was quantified by passing metered HNO₃/ F_2 mixtures through the system with the discharge switched on or off. With the discharge being off the signal from HNO₃ photofragmentation was obtained (see above). With the discharge turned on, for $[NO_3]_0 = 1 \times 10^{13}$ molecules cm⁻³ as determined by gas titration using reaction 4 and applying EI ionization, a REMPI signal was registrated the intensity of which was 20% of the signal observed at m/e = 46 after complete conversion of NO₃ to NO₂ through reaction 4. To avoid this interference from NO₃ contributing measurably to the signal at m/e = 46, all determinations of NO₂ as reaction product were taken under conditions where >95% of $[NO_3]_0$ had been consumed in reaction with the alkenes investigated. Under these conditions a detection limit of $[NO_2]$ = 5 \times 10^{11} molecules cm⁻³ was obtained in the presence of $[HNO_3] \geq 2 \times 10^{14}$ molecules cm⁻³.¹⁶

For all reactions studied, the two-color double-resonance spectrum of the reactor effluent was recorded at m/e = 46 in the wavelength region 465 nm $< \lambda_1 < 505$ nm. Within experimental error all spectra were identical with the spectrum shown in Figure 1.

The following additional observations support the assignment that the two-color REMPI signal at m/e = 46 was due to ionization of free NO₂ molecules formed in reactions 1b, 2b, and/or 3b and not due to photofragmentation of either nitrate and nitro compounds or of an adduct in the ion source:

(i) Addition of up to 1×10^{15} molecules cm⁻³ of the alkyl nitrates isopropyl- and *tert*-butyl nitrate, respectively, did not lead to any two-color REMPI signal at m/e = 46.

(ii) In a second set of experiments, F atoms were added to a flow of isopropyl nitrate with $[(CH_3)_2CH-ONO_2] = 2 \times 10^{14}$ molecules cm⁻³ at a total pressure of 3 mbar of argon. H atom abstraction from the organic nitrate will lead to production of the isomeric isopropyl nitrate radicals. Even at $[F] = 3 \times 10^{13}$ atoms cm⁻³ no two-color REMPI signal at m/e = 46 could be detected.

(iii) Titration of REMPI signals at m/e = 46 were also carried out with H atoms:

$$NO_2 + H \rightarrow NO + OH$$
 (7)

whereby the disappearance of NO₂ and formation of the products OH and NO were observed by photoionization. For this purpose H atoms were generated in a second microwave discharge and added to the main flow in a moveable injector. The injector tip was positioned downstreams, where the NO₃ radicals had reacted away to >99.5% of completion. At contact times of ≈ 1 ms, production of OH radicals was observed using a (2 + 1) REMPI process at $\lambda = 244.16$ nm and recording the ion signal at $m/e = 17.^{23}$ NO was identified by following the TOF MS NO⁺ signal at m/e = 30 generated in a (2+2) REMPI transition in the wavelength range 448 nm < λ < 454 nm.^{16,24} Both signals vanished when the H₂ discharge was turned off. The [NO] produced in the flow tube with excess H atoms was within experimental error of $\leq 15\%$ the same as the [NO₂] without H atoms present.

Furthermore, these titration experiments were turned into a kinetic investigation by calibration with NO₂ the REMPI signals for H atoms at m/e = 1 obtained in an until now unreported (2+1) process at $\lambda = 243.06$ nm. The system (2,3-dimethyl-2-butene + NO₃) was evaluated. From the rate of NO build-up under conditions of complete NO₃ consumption a rate constant of $k = (1.2 \pm 0.3) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ was derived, which is within experimental error limits identical to the reported value²⁵ for reaction 7. This kinetic argument was taken as further evidence that free NO₂ molecules had been reacted with H atoms.

In the reaction of styrene with NO₃ radicals, also the second reaction product was identified with a (1+1) REMPI process in the wavelength range 250 nm < λ < 270 nm. In Figure 2a is shown the (1+1) REMPI spectrum of an authentic styrene epoxide sample recorded at the parent ion mass m/e = 120. Trace b in Figure 2 was obtained from the reactor effluent. Thus, styrene epoxide was unambiguously identified as major product in this reaction at low pressure.

The NO₂ yield, $\phi(NO_2)$, as function of total pressure in the MS experiments performed with the hydrocarbons 2,3-dimethyl-2-butene, *trans*-2-butene, *cis*-2-butene, cyclohexene, isoprene,



Figure 2. (a) Low-resolution (1+1) mass-selected REMPI signal of styrene epoxide recorded at parent ion mass m/e = 120 in the wavelength range 252 nm $< \lambda < 272$ nm. (b) Mass-selected REMPI spectrum of the reactor effluent of the styrene + NO₃ reaction at m/e = 120 ($p_{\text{total}} = 5$ mbar, T = 298 K). For clarity, the spectrum was enhanced by a factor of 10.



Figure 3. Pressure dependence of NO₂ yield obtained in REMPI experiments at T = 298 K using argon as buffer gas. The error bar indicates the estimated overall uncertainty in these measurements.

TABLE 1: FTIR Results for Oxirane Formation in the Reaction of 2,3-Dimethyl-2-butene with NO₃ Radicals at T = 298 K Using Argon or Air as Buffer Gas

p [mbar] ϕ tetramethyloxirane [%]	
30	90 ± 10
1000	75 ± 10
30	90 ± 10
1000	20 ± 10
	<i>p</i> [mbar] 30 1000 30 1000

2,3-dimethyl-1,3-butadiene, styrene, 1,3-cyclohexadiene and α -terpinene is presented in Figure 3. Also, the oxirane yield in the reaction of styrene with NO₃ is included. Within experimental error the styrene epoxide yield was identical with the NO₂ yield. Thus, formation of acetophenone or phenyl-ethanal which are also possible stable products formed after NO₂ elimination from the intermediate nitrate radical adduct with subsequent hydrogen or phenyl migration can be excluded.¹⁶

FTIR Experiments. In Table 1 are summarized the experimental conditions and results for the 2,3-dimethyl-2-butene + NO₃ reaction. Only results for total pressures of 30 and 1000 mbar in the reaction chamber are shown. The oxirane concentration after completion of the reaction was calculated by spectral

TABLE 2: FTIR Results for Oxirane Formation in the Reaction of *cis*- and *trans*-2-Butene in Argon at $p_{\text{total}} = 50$ mbar and T = 298 K

	φ oxirane total [%]	branching ratio	
species		$\overline{\phi(trans-\text{oxirane})}/{\phi(\text{total})}$	$\phi(cis-oxirane)/\phi(total)$
cis-2-butene trans-2-butene	50 50	0.8 0.8	0.2 0.2

subtraction of calibrated reference spectra of tetramethyloxirane. It was found that even at a total pressure of 1000 mbar of synthetic air 20% of the reacted hydrocarbon was converted into the oxirane. No reaction between tetramethyloxirane and NO₃ was observed within the time scale of the 2,3-dimethyl-2-butene + NO₃ experiments.

In the reaction of *cis*- and *trans*-2-butene 50% of hydrocarbon was converted into oxirane at a total pressure of 50 mbar of argon. In Table 2 is shown that independent from the stereochemical structure of hydrocarbon added, both stereo-isomeres *cis*-2,3-dimethyloxirane and *trans*-2,3-dimethyloxirane were formed with the same distribution from the two alkenes. We conclude from these results that the reaction of alkenes with nitrate radicals proceeds via an electrophilic addition of NO₃ to the hydrocarbon double bond with simultaneous π -bond rupture to form a nitrate radical adduct. Free rotation about the C-C bond makes cis-trans isomerization possible. Since both stereoisomeres are formed, reaction 1b can be excluded to be an important pathway.

The formation of high yields of tetramethyloxirane in the reaction of 2,3-dimethyl-2-butene with NO₃ in argon at atmospheric pressure confirms the results obtained in the low-pressure discharge flow MS experiments.^{15,16} Air as pressure gas in addition to being an effective deactivator may also act as through process 3a. More information on oxirane formation from 2,3-dimethyl-2-butene and *cis*- and *trans*-2-butene as well as from isoprene in air at atmospheric pressure is given elsewhere.²²

Having established that the reaction of NO₃ with alkenes proceeds via a radical adduct, the frequencies for the unimolecular decomposition of these intermediates were estimated.²⁶ Using a simple model based upon collision theory, the excited adduct A* as well as the *deactivated* adduct A may decompose with the unimolecular rate constants k_{2b} and k_{3b} , respectively, to form NO₂ and oxirane. The deactivated adduct may also be *stabilized* with the rate constant k_{3a} to a state from which no NO₂ elimination occurs. The following reaction scheme is used for the calculation of unimolecular decomposition rate constants from the experimental data:



Within this scheme the rate of the deactivation step 2a can be expressed through a pressure-dependent collision frequency ω (see below). D_1 and D_2 represent product formation in the two decomposition steps, 2b and 3b. It follows for complete conversion of A* into S, D₁, and D₂:

$$\frac{k_{2b}}{\omega} = \frac{[D_2]}{[D_1] + [S]}$$
 and $\frac{k_{3b}}{k_{3a}} = \frac{[D_1]}{[S]}$

which rearrange with $[D] = [D_1] + [D_2]$ to



□ / ■ NO2 yield (DF~REMPI) O TME-code yield (FTIR)

Figure 4. Pressure dependence of the branching ratio D/S in the reactions of 2,3-dimethyl-2-butene and isoprene with NO₃ obtained from the combined FTIR and REMPI data. In all experiments argon was used as buffer gas.

$$\frac{[D]}{[S]} = \frac{k_{3b}}{k_{3a}} + \left[k_{2b} + k_{2b}\frac{k_{3b}}{k_{3a}}\right]\frac{1}{\omega}$$

where $[S] = [NO_3]_0 - [D]$.

The collision frequency ω may be written in pressure units using

$$\omega = \frac{\sigma_{AB}^{2} N_{a}}{R} \left[\frac{8\pi R}{\mu_{AB} T} \right]^{1/2} p$$

where the diameters of the colliding molecules combine to $\sigma_{AB} = \frac{1}{2} (\sigma_A + \sigma_B)$ and the reduced mass μ is expressed as $\mu_{AB} = \frac{m_A m_B}{(m_A + m_B)}$. The collision diameters for the adducts were estimated using the group properties given in ref 27, the value for σ_{argon} was taken from ref 28:

$$\sigma(\text{TME-ONO}_2) \approx 6.7 \times 10^{-10} \text{ m}$$

$$\sigma(\text{isoprene-ONO}_2) \approx 6.3 \times 10^{-10} \text{ m}$$

$$\sigma(\text{Ar}) = 3.5 \times 10^{-10} \text{ m}$$

From the above it follows, that a plot of the ratio [D]/[S] vs1/pressure should result in a straight line with a slope of $\{k_{2b} + (k_{2b}k_{3b}/k_{3a})\}$ and an intercept of k_{3b}/k_{3a} . In Figure 4 the combined FTIR and REMPI data for the reaction of 2,3-dimethyl-2-butene and isoprene with NO₃ are plotted. The unimolecular decomposition rate constants for the chemical activated TME-ONO₂* adduct and isoprene-ONO₂* adduct derived from the experimental data are given as

$$k_{uni}$$
(TME-ONO₂*) = (2.0 ± 0.6) × 10⁹ s⁻¹
 k_{uni} (isoprene-ONO₂*) = (9.1 ± 0.1) × 10⁷ s⁻¹

The difference of a factor of at least 50 in the two slopes obtained for the reactants isoprene and 2,3-dimethyl-2-butene might be explained by different configurations of the transition state for NO_2 elimination when changing from systems containing isolated double bonds to systems with conjugated double bonds.

Support for this interpretation was obtained from calculations on the unimolecular decomposition rate constants with the RRKM treatment.²⁹

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Note Added in Proof. Since submission of this contribution a paper by T. Berndt and O. Böge (*Ber. Bunsen-Ges. Phys. Chem.* 1994, 98, 869) was published in which the kinetics of oxirane formation was studied in the NO₃/2,3-dimethyl-2-butene system under flow conditions at total pressures up to 1000 mbar. The results and proposed reaction pattern are in full agreement with the present findings.

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