important applications of CK. In other cases with TDRC(s) such as energy transfer, mistakes from not applying CK may be even more striking[26] and the CK calculations simpler. Many important features of energy transfer, such as the influence of dimensionality, mutual orientation of partners and its dynamics, are far from being disclosed at present. As long as CK is not applied, misinterpretations will persist and spurious or trivial influences will not be recognized, especially if plain multiparametric curve fitting is practiced.

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(26) According to the RE treatment, no energy transfer takes place in the steady state.[1,2] In the three-dimensional homogeneous system without cooperative diffusion, the energy transfer appears only in $t^{1/2}$ terms of RE similar to ref 23.

CK is restricted to first- and zero-order processes, being a generalization of linear response theory. This limitation is unimportant in excited-state kinetics, except certain laser applications and triplet–triplet second-order processes. TDRCs may be operative in second-order elementary reactions too, of course. But the development of a procedure with performance comparable to that of CK is very difficult for such systems: in the simplest case, the shape of the δ-response depends on its amount, which could be allowed, if the temporally generated local reaction centers would develop in time without interaction. Proper linearization for application of CK is recommended rather than approximating with a description by RE, which are inapplicable anyway.

We are hopeful that our contribution will help progress in excited-state kinetics.

Products and Mechanisms of the Gas-Phase Reactions between NO₃ and a Series of Alkenes

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Products and mechanisms for the gas-phase reactions of NO₃ radicals with a series of alkenes in air have been studied. The experiments with propene, isobutene, *trans-* and *cis*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene were carried out at 295 ± 2 K and 740 ± 5 Torr in a 480-L Teflon-coated reaction chamber where NO₃ was generated by the thermal dissociation of N₂O₅. Reactants and products were observed to produce nitroxy–nitroperoxy intermediates that decayed with formation of carbonyl, nitroxycarbonyl, nitroxy alcohol, and dinitrate species. The product distribution was found to be dependent on the alkyl substitution pattern around the double bond. Evidence was also found of a reaction between NO₃ and organic peroxy radicals with a rate constant measured in the case of the 2,3-dimethyl-2-nitroxy-3-peroxybutane radical to be of the order of 5 × 10⁻¹² cm³ molecule⁻¹ s⁻¹.

Introduction

The nitrate radical, NO₃, is formed in the atmosphere by the reaction between O₃ and NO₂:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{1}$$
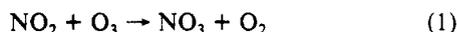
During the day NO₃ is rapidly photolyzed but at night it builds up and establishes the fast equilibrium

$$NO_2 + NO_3 \overset{M}{\rightleftharpoons} N_2O_5 \tag{2}$$
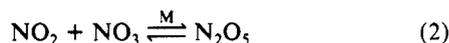
In recent years, the chemistry of NO₃ and N₂O₅ in air has been studied extensively and found to play an important role in the troposphere.[1] Kinetic studies have shown that the reactions between the nitrate radical and alkenes are relatively fast with reaction rate constants increasing with increasing alkyl substitution at the double bond.[2] However, investigations of mechanisms and products are still limited to the case of propene.[3-9] The first attempts to identify reaction products in air were reported in refs 3 and 4 where an absorption band at 1670 cm⁻¹ was tentatively attributed to a nitrite. This work was followed by a series of investigations[5-9] of the NO₃–propene–air reaction performed in smog chambers and specifically aiming at the understanding of the reaction mechanism.

Hoshino et al.[5] found 1,2-dinitroxypropane to be a major product together with acetaldehyde, propene oxide, NO₂, and HNO₃ as minor products. FT-IR and GC-MS were used as analytical techniques.

Bandow et al.[8] tentatively identified, using FT-IR, 2-nitroperoxy-1-nitroxypropane (and/or 1-nitroperoxy-2-nitroxypropane) as intermediates that subsequently reacted to form 1,2-dinitroxypropane, which was identified by comparison with the spectrum of the synthesized compound. Formaldehyde and acetaldehyde were found as minor products; evidence was also found for the formation of 2-nitroxypropanal.

Shepson et al.[9] employed a NO₂ to O₂ ratio about a 100 times lower than that used in the experiments of Bandow et al.[8] Applying GC-MS and HPLC as analytical techniques they found 1-nitroxy-2-propanone and nitroxypropanols as the dominant products, concluding that under tropospheric conditions the formation of the 1,2-dinitroxypropane was unimportant. Acetaldehyde and formaldehyde were observed together with minor amounts of 1,2-dinitroxypropane.

The results above could be accounted for with a reaction scheme that proceeds after the initial addition of NO₃ to the double bond, e.g., at the 1-position,

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(1) Finlayson-Pitts, B. J.; Pitts, Jr., J. N. *Atmospheric Chemistry*; Wiley: New York, 1986.
(2) Atkinson, R.; Aschmann, S. M.; Pitts, Jr., J. N. *J. Phys. Chem.* **1988**, *92*, 3454.
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(6) Akimoto, H.; Hoshino, M.; Inoue, G.; Sakamaki, F.; Bandow, H.; Okuda, M. *J. Environ. Sci. Health.* **1978**, *A13*(9), 677.
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(8) Bandow, H.; Okuda, M.; Akimoto, H. *J. Phys. Chem.* **1980**, *84*, 3604.
(9) Shepson, P. B.; Edney, E. O.; Kleindienst, T. E.; Pittman, J. H.; Namie, G. R.; Cupitt, L. T. *Environ. Sci. Technol.* **1985**, *19*(9), 1985.

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$$CH_3-CH=CH_2 + NO_3 \rightarrow CH_3-\dot{C}H-CH_2-ONO_2 \quad (3)$$
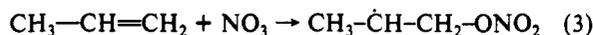
to the subsequent addition of O_2

$$CH_3-\dot{C}H-CH_2-ONO_2 + O_2 \rightarrow CH_3-\overset{OO\bullet}{\underset{|}{C}H}-CH_2-ONO_2 \quad (4)$$
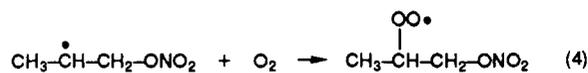
and in the presence of NO_2 to the equilibrium

$$CH_3-\overset{OO\bullet}{\underset{|}{C}H}-CH_2-ONO_2 + NO_2 \rightleftharpoons CH_3-\overset{OONO_2}{\underset{|}{C}H}-CH_2-ONO_2 \quad (5)$$
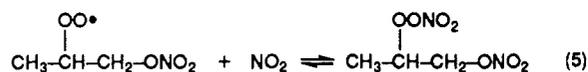
The alkylperoxy radical should be reduced by its self-reaction (or in the atmosphere by its reaction with NO) to the alkoxy radical

$$2CH_3-\overset{OO\bullet}{\underset{|}{C}H}-CH_2-ONO_2 \rightarrow 2CH_3-\overset{O\bullet}{\underset{|}{C}H}-CH_2-ONO_2 + O_2 \quad (6)$$
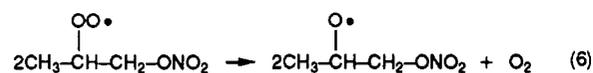
The fate of the alkoxy radical was then supposed to follow different reaction pathways according to the reaction

$$CH_3-\overset{O\bullet}{\underset{|}{C}H}-CH_2-ONO_2 + NO_2 \rightarrow CH_3-\overset{ONO_2}{\underset{|}{C}H}-CH_2-ONO_2 \quad (7)$$
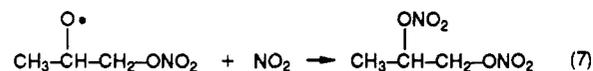
to form the dinitrate; to the reaction

$$CH_3-\overset{O\bullet}{\underset{|}{C}H}-CH_2-ONO_2 + O_2 \rightarrow CH_3-\overset{O}{\underset{\parallel}{C}}-CH_2-ONO_2 + HO_2 \quad (8)$$
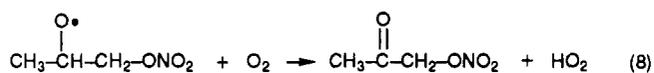
to form a carbonyl nitroxy species; and to the reaction

$$CH_3-\overset{O\bullet}{\underset{|}{C}H}-CH_2-ONO_2 \rightarrow CH_3-CHO + CH_2O + NO_2 \quad (9)$$
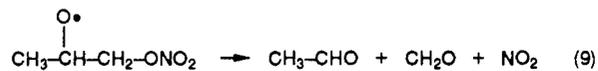
to form unsubstituted carbonyl compounds.

In addition to reaction 6 an alternative route for the peroxynitroxypropane radical consisting of the disproportionation reaction 10 was suggested by Shepson et al.[9]

$$2CH_3-\overset{OO\bullet}{\underset{|}{C}H}-CH_2-ONO_2 \rightarrow$$
$$CH_3-\overset{O}{\underset{\parallel}{C}}-CH_2-ONO_2 + CH_3-\overset{OH}{\underset{|}{C}H}-CH_2-ONO_2 + O_2 \quad (10)$$
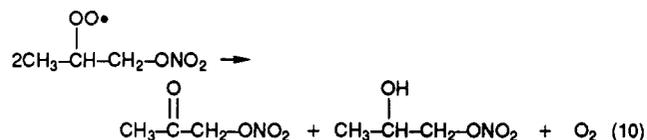
This reaction scheme, together with the analogous reactions that would take place after addition of the NO₃ radical at the 2-position, accounts for the products observed in the smog chamber studies of refs 8 and 9. The different yields were ascribed by Shepson et al.[9] to the different experimental conditions used.

In the present study, the reaction of NO₃ radical with alkenes in air at 295 ± 2 K and 740 ± 5 Torr was investigated by using in addition to propene a series of other alkenes having various methyl substitutions around the double bond. In particular isobutene, *trans*- and *cis*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene were studied with the scope of obtaining more insight into the reaction mechanism and in particular achieving an understanding of the dependence of the product distribution upon the pattern of methyl substitution at the double bond.

The intermediates and products identified for the whole series of alkenes were similar to those reported in the previously quoted studies on the propene reaction with NO₃ in air.[8,9] However, the yields of unsubstituted carbonyl compounds and organic nitrate species were found to depend significantly on the alkyl substitution at the carbon–carbon double bond. Propene gave the lowest yield of unsubstituted carbonyl compounds and 2,3-dimethyl-2-butene gave the highest. The branched compounds (isobutene and 2-methyl-2-butene) gave less organic nitrate and more unsubstituted carbonyl compounds than the unbranched alkenes (*cis*- and *trans*-2-butene). These results can be explained by considering the most favorable pathway for the initial NO₃ addition to the double bond and the relative stability of the intermediate alkoxy radicals formed.

During these studies, evidence was found of a reaction between the intermediate peroxy radicals and NO₃ of the type

$$RO_2^\bullet + NO_3 \rightarrow RO^\bullet + NO_2 + O_2 \quad (11)$$
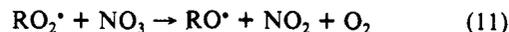
From the enhanced decay rate in the presence of NO₃ of the intermediate peroxynitrate species formed by the reaction between NO₃ and 2,3-dimethyl-2-butene, a rate constant for reaction 11 of about 5×10^{-12} molecule^{-1} cm^3 s^{-1} at 295 ± 2 K was estimated. 2,3-Dimethyl-2-butene was selected because it represents the most simple case, being a symmetrical species with no H atoms at the double bond. In this way there was no ambiguity in the NO₃ addition and reaction 10 could be excluded.

Experimental Section

The experiments were performed in a 480-L, 60 cm diameter cylindrical glass reaction chamber whose internal surface had been coated with Teflon. A multiple reflection White type mirror system connected to a Bruker IFS 113 V FT-IR spectrometer allowed in situ analysis of intermediates and end products. Spectra were generally recorded at time intervals from 30 s to 1 h at 1 cm^{-1} instrumental resolution co-adding 10–50 scans.

The NO₃ radicals were generated in the reaction chamber 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 chamber by evaporation of solid N_2O_5. The alkenes used were of commercially available quality with a minimum purity of 99% and were introduced into the reaction chamber with a stream of purified air.

The experiments were performed at 295 ± 2 K and 740 ± 5 Torr. Alkene and N_2O_5 initial mixing ratios were in the range 5–50 ppm with an NO_2 mixing ratio in the range 1–100 ppm.

Analysis of the recorded infrared spectra was used to follow the concentrations of reactants and to identify, and whenever possible to measure, the concentration of intermediates and end products. To this end, reference spectra were generated of the following compounds synthesized according to known procedures: 1,2-dinitroxypropane and 2,3-dinitroxybutane,[10] 1-nitroxy-2-propanol, 2-nitroxy-1-propanol, 3-nitroxy-2-butanol, and 3-nitroxy-2-butanone, 2-methyl-1-nitroxy-2-propanol, and 2-nitroxy-2-methyl-1-propanol,[11] and 2,3-dimethyl-2,3-dinitroxybutane.[12] The synthesized nitrates were all purified by distillation under reduced pressure on a ball tube distillation apparatus with the exception of 2,3-dimethyl-2,3-dinitroxybutane which was purified by recrystallization in cyclohexane. Mononitric acid esters of asymmetric diols were always obtained as a mixture of the two structural isomers.

The wall loss rates of the organic nitrate end products were measured by adding pure synthesized compounds to purified air in the reaction chamber to obtain concentrations of a few ppm. The disappearance of these compounds was found to proceed at a rate of less than 3% per hour, even in the case of 2,3-dimethyl-2,3-dinitroxybutane which is a solid at 295 K.

To convert spectral absorptions into molecular concentrations, band strengths were measured under the same experimental conditions as those used in the study by introducing a known amount of the compound (either known volumes of gases or evaporated liquids) into the reaction chamber.

Integrated band intensities were used for HNO_3 (1270–1350 cm^{-1}, ref 13), N_2O_5 (1225–1270 cm^{-1}, ref 13), CH_2O (1720–1800 cm^{-1}, ref 14), and CH_3CHO (2630–2890 cm^{-1}, ref 15).

Table I summarizes the band positions and strengths used for the other compounds measured. Reactants and product concentrations were measured by subtraction of calibrated spectra.

In the study of reaction 11, initial concentrations in the range of 5–15 ppm for 2,3-dimethyl-2-butene and N_2O_5 and in the range

(10) Mckay, A. F.; Meen, R. H.; Wright, G. F. *J. Am. Chem. Soc.* **1948**, *70*, 438.

(11) Nichols, Jr., P. L.; Magnusson, A. B.; Ingham, J. D. *J. Am. Chem. Soc.* **1953**, *70*, 4255.

(12) Bertsch, R. B.; Ouellette, R. J. *J. Org. Chem.* **1974**, *39*(18), 2755.

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(14) Cantrell, C. A.; Stockwell, W. R.; Anderson, L. G.; Busarow, K. L.; Perner, D.; Schmeltekopf, A.; Calvert, J. G.; Johnston, H. S. *J. Phys. Chem.* **1985**, *89*, 139.

(15) Cantrell, C. A.; Davidson, J. A.; Busarov, K. L.; Calvert, J. G. *J. Geophys. Res.* **1986**, *91*, 5347.

TABLE I: Spectral Features Used Together with Their Absolute Integrated Band Intensities (IBI) Used for Analysis of the Spectra[a]

compound	wavelength region, cm^{-1}	IBI, $molecule^{-1}$ cm
2,3-dinitroxybutane	800–875	4.3×10^{-17}
3-nitroxy-2-butanol	775–960	3.0×10^{-17}
3-nitroxy-2-butanone	800–882	1.6×10^{-17}
2,3-dinitroxy-2,3-dimethylbutane	795–920	6.3×10^{-17}
acetone	1075–1140	6.5×10^{-19}
propane	2800–3200	1.7×10^{-17}
trans-2-butene	2800–3200	3.1×10^{-17}
cis-2-butene	2800–3200	3.1×10^{-17}
isobutene	2800–3200	3.3×10^{-17}
2-methyl-2-butene	2800–3200	3.0×10^{-17}
2,3-dimethyl-2-butene	2800–3200	3.3×10^{-17}

[a] $IBI = (1/cL) \int \ln (I_0/I) \, d\nu$.
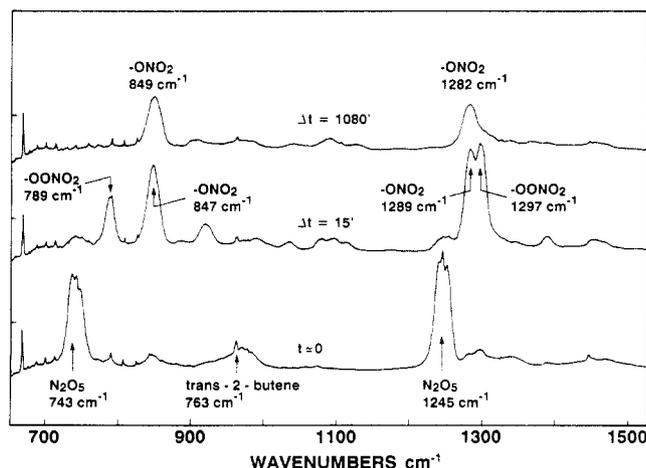
Figure 1. Typical sequence of IR spectra recorded during the reaction of *trans*-2-butene with NO_3 showing the buildup and decay of the nitroxy–nitroperoxy intermediate and the formation of stable organic nitrates.

of 5–12 ppm for NO_2 were used. The relative concentrations were set in order to be able to follow the decay of the peroxynitrate compound in conditions where NO_3 was present or absent during the decay. The concentration of NO_3 was evaluated from the measured concentrations of NO_2 and N_2O_5 by applying the equilibrium constant of ref 16.

The concentration of the peroxynitrate was evaluated from its absorption band at 790 cm^{-1}. The strength of this band (764–814 cm^{-1}) was estimated as 6.3×10^{-18} $molecule^{-1}$ cm under the assumption that the peroxynitrate concentration immediately after the fast reaction between 2,3-dimethyl-2-butene and NO_3 ($k_{11} = 6.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, ref 1) corresponded exactly to the amount of alkene consumed.

Results

The reactions between NO_3 and all of the alkenes studied followed a similar pattern, as evidenced by the analysis of the infrared spectra. Buildup of organic nitrate (845, 1280, and 1667 cm^{-1}) and peroxynitrate bands (790, 1300, and 1725 cm^{-1}) were observed. The peroxynitrate bands' subsequent decay was accompanied by a buildup of spectral features attributed to stable products (Figure 1) that were identified as simple aldehydes, alcohol nitrates, carbonyl nitrates, and dinitrates.

No significant amounts of HNO_3 were seen other than that known to be formed in the chamber from the heterogeneous (wall) reaction between N_2O_5 and H_2O.

The procedure of spectral subtraction is shown in Figure 2 for the study of the reaction between NO_3 and *trans*-2-butene.

The positions of the characteristic absorption bands attributable to the nitroxy group were found to be relatively insensitive to

(16) Graham, R. A.; Johnston, H. S. *J. Phys. Chem.* **1978**, *82*, 254.
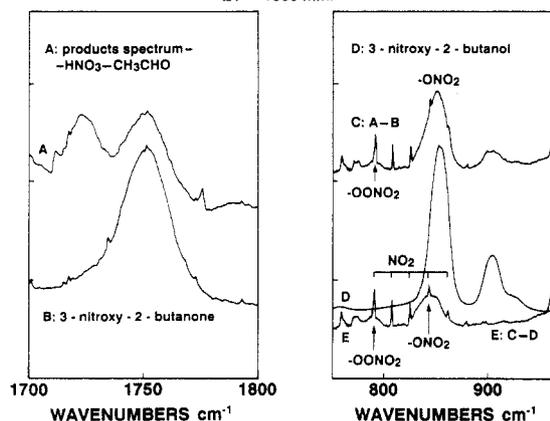
Figure 2. Comparison of authentic spectra of 3-nitroxy-2-butanone and 3-nitroxy-2-butanol with the spectrum of the reaction products of *trans*-2-butene with NO_3 after subtraction of HNO_3 and acetaldehyde. The procedure of spectral subtraction is demonstrated.

TABLE II: Yield of Unsubstituted Carbonyl Compounds Formed Expressed as Percentage of the Reacted Hydrocarbon and the Ratio between the Integrated Band Absorption of a Nitrate Band (at 845 cm^{-1}) and the Concentration of the Unsubstituted Carbonyl Compounds[a]

alkene	% yield of $1/2$ carbonyl species	R
propene	10 ± 5	13.3 ± 1.2
cis,trans-2-butene	17 ± 6	7.5 ± 0.4
isobutene	24 ± 8	4.2 ± 1.2
2-methyl-2-butene	22 ± 6	1.2 ± 0.7
2,3-dimethyl-2-butene	52 ± 13	0.3 ± 0.2

[a] R = average of the ratio of the integrated absorption of the $-ONO_2$ band at ~845 cm^{-1} divided by one-half the concentration of carbonyl species, measured for the different runs. Uncertainties are given as one standard deviation.

TABLE III: Yield of Main Products Expressed as Percentage of the Reacted Hydrocarbon Observed in Different Runs for the Reaction of *cis*- and *trans*-2-Butene with NO_3

initial concn, ppmv			% yield of			
N_2O_5	NO_2	2-butene	3-nitroxy-2-butanone	3-nitroxy-2-butanol	acetaldehyde[a]	run
9.2	1.1	9.5	25	8	24	1
6.3	1.4	30.2	50	15	23	2
		7.8	31	–	11	3
2.7	8.1	7.8	32	13	9	4
6.4	12.3	10.7	40	20	17	5
9.5	36.0	15.4	57	23	13	6
14.4	7.7	23.2	55	13	22	7
			av 41 ± 13	av 15 ± 5	av 17 ± 6	

[a] Yield of acetaldehyde divided by one-half (see text). Uncertainties given as 1 standard deviation.

changes in the molecular structure of the different alkenes studied. For this reason the detection and quantification of the dinitrate products were particularly difficult as they had no other functional groups with characteristic sharp absorption bands.

Table II shows the results obtained for the yield of unsubstituted (non nitrate) carbonyl compounds and for the ratio between the integrated absorption of a typical nitrate band (845 cm^{-1}) and one-half the concentration of carbonyl compounds. This ratio is indicative of the distribution of the products between nitrate and unsubstituted carbonyl species; the factor 1/2 applied to the carbonyl species accounts for the fact that, in the decay of the alkoxy radical, one molecule of the nitroxy compound is formed according to reaction 7, 8, or 10, but two molecules of the carbonyl species are generated by reaction 9.

Tables III and IV show the product distribution obtained in a series of experimental runs performed for the reactions of *cis*-

TABLE IV: Yield of Main Products Expressed as Percentage of the Reacted Hydrocarbon Observed in Different Runs for the Reaction of 2,3-Dimethyl-2-butene with NO$_3$

initial concn, ppmv			% yield of		
			2,3-dimethyl-2,3-dinitroxy-		
N$_2$O$_5$	NO$_2$	2,3-dimethyl-2-butene	butane	acetone[a]	run
10.4	5.4	10.1	2	40	1
6.6	6.8	7.0	7	41	2
7.4	0.6	7.0	6	50	3
11.7	77.0	9.7	6	72	4
4.1	2.3	10.1	4	55	5
			av 5 ± 2	av 52 ± 13	

[a] Yield of acetone divided by one-half (see text). Uncertainties given as 1 standard deviation.
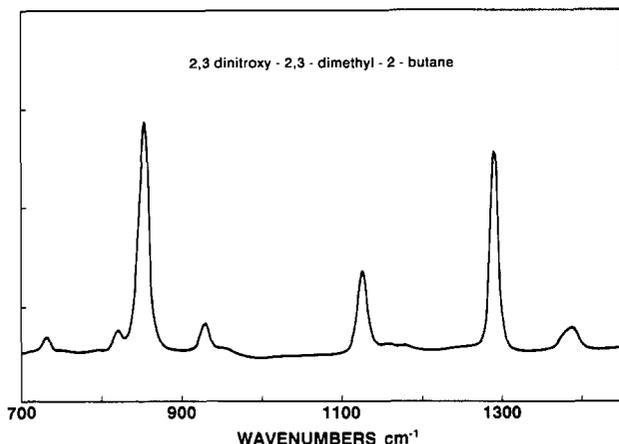
Figure 3. Gas-phase IR spectrum of 2,3-dimethyl-2,3-dinitroxybutane, 1 cm^{-1} instrumental resolution.

and *trans*-2-butene and of 2,3-dimethyl-2-butene with NO$_3$ where all the main products were measured. Also in this case a factor 1/2 was applied to the yield of unsubstituted carbonyl compounds for the same reason as previously discussed.

The uncertainty for the measurement of the concentrations of nitroxy carbonyl compounds is estimated to be about ±25%; the same uncertainty can be attributed to the measurement of 3-nitroxy-2-butanol while for the dinitrate this value must be increased to ±50%. An exception is the evaluation of the 2,3-dimethyl-2,3-dinitroxybutane, since in this compound the C–O stretch at 1127 cm^{-1} is sufficiently strong to permit a more precise determination (±25%); see Figure 3.

Carbon mass balances were calculated for the reaction of *cis*- and *trans*-2-butene and 2,3-dimethyl-2-butene: the measured total product yields were found to account for 54–93% and 42–78%, respectively, of the reacted alkenes. These ranges reflect analytical errors as well as loss of material from the gas phase. Organic nitrate end products and unsubstituted carbonyl compounds were found to disappear rather slowly from the gas phase in the chamber. Therefore, the main source of the mass deficit was attributed to wall deposition of the reaction intermediates.

Discussion

The reactions of NO$_3$ with all of the alkenes tested led to intemediates and products similar to those previously reported for the reaction of NO$_3$ with propene in air,[8,9] thus confirming the basic reaction sequence proposed by Bandow et al.,[8] extended by Shepson et al.,[9] and shown in the Introduction.

The mechanism expressed in a more general form useful for discussing all of the alkenes examined, can be indicated by the following sequence of reactions (R$_n$ = CH$_3$ or H).

The scheme includes two more reactions, as a result of this study, namely the reaction of the peroxy radical with NO$_3$ and the 1,4-H shift of the alkoxy radical which appears to be a minor but not negligible pathway (eqs 12–17).

$$C=C + NO_2 \rightarrow {}^{\bullet}C-C-ONO_2 \xrightarrow{O_2}$$

$${}^{\bullet}O_2-C-C-ONO_2 \quad (12)$$

$${}^{\bullet}O_2-C-C-ONO_2 + NO_2 \overset{M}{\rightleftharpoons} O_2NO_2-C-C-ONO_2 \quad (13)$$

$$2\,{}^{\bullet}O_2-C-C-ONO_2 \rightarrow 2\,{}^{\bullet}O-C-C-ONO_2 + O_2 \quad (14)$$

$${}^{\bullet}O_2-C-C-ONO_2 + NO_3 \rightarrow$$

$${}^{\bullet}O-C-C-ONO_2 + NO_2 + O_2 \quad (15)$$

$${}^{\bullet}O-C-C-ONO_2 \rightarrow R_1CR_2 + R_3CR_4 + NO_2 \quad (16)$$

$${}^{\bullet}O-C-C-ONO_2 + NO_2 \rightarrow O_2NO-C-C-ONO_2 \quad (17)$$
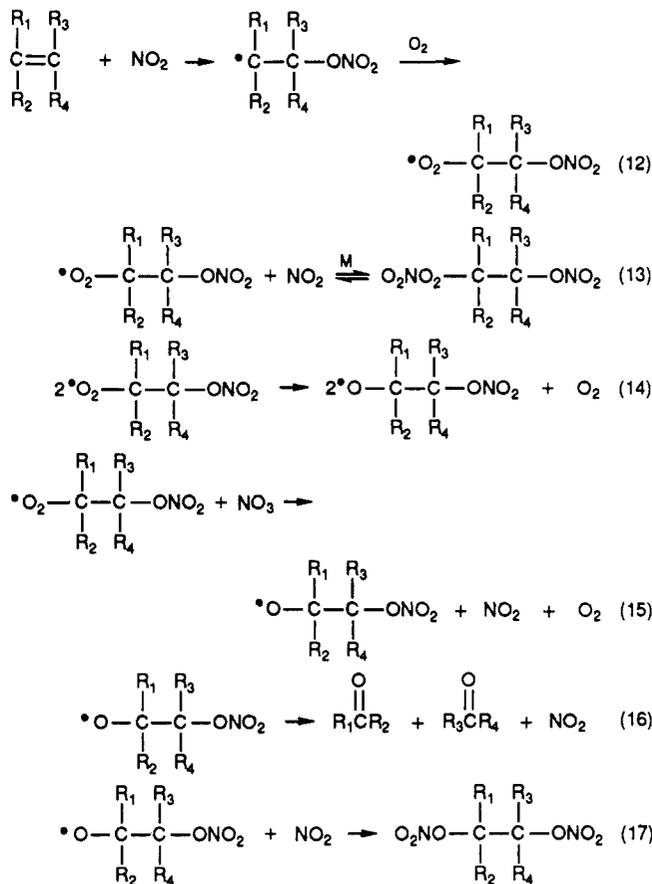
If an atom is available adjacent to the alkylperoxy group also, the following reactions are possible: the disproportionation of the peroxy radical (18) and H abstraction by O$_2$ from the alkoxy

$$2\,{}^{\bullet}O_2-C-C-ONO_2 \rightarrow$$

$$R_1-C-C-ONO_2 + HO-C-C-ONO_2 + O_2 \quad (18)$$
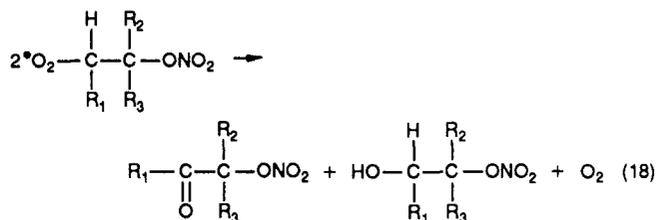
radical (19). A minor reaction pathway for the alkoxy radical

$${}^{\bullet}O-C-C-ONO_2 + O_2 \rightarrow R_1-C-C-ONO_2 + HOO^{\bullet} \quad (19)$$
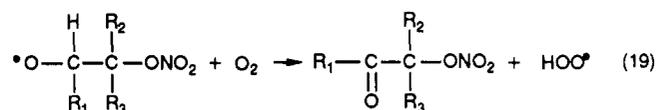
is apparently the isomerization with 1,4-H shift (20)

$${}^{\bullet}O-C-C-ONO_2 \rightarrow HO-C-C-ONO_2 \quad (20)$$
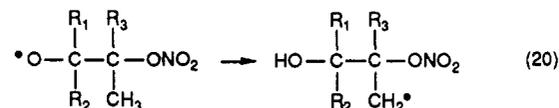
Reaction 20 leads to the generation of a radical which in air forms a peroxy radical likely to react according to the above-indicated reaction scheme.

An attempt has been made to rationalize the distribution of products observed for the different alkenes examined. It appears that the distribution of products between organic nitrates and unsubstituted aldehydes and ketones is largely dependent upon three factors:

(a) the predominant mode of the initial NO$_3$ addition;

(b) the availability of an H atom adjacent to the alkylperoxy carbon atom;

(c) the relative stability of the alkoxy radical intermediate with respect to decomposition.
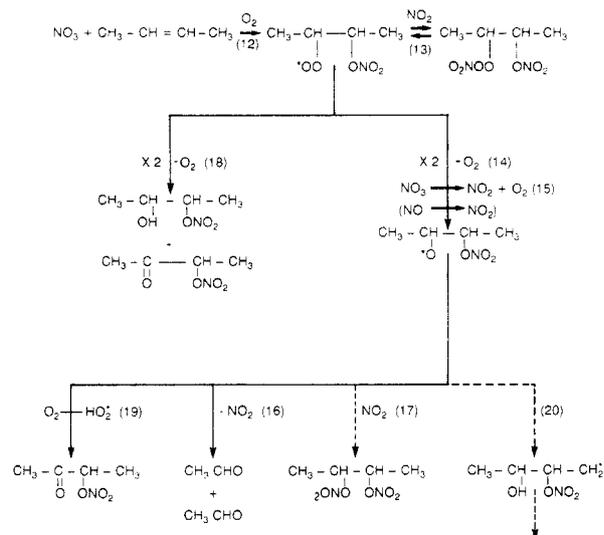
Figure 4. Proposed pathways for the reactions of the *cis-* and *trans-*2-butene–NO_3–air system. Minor reaction pathways are shown with dashed arrows. Numbers in parentheses refer to the reaction type as discussed in the text.

In fact:

(a) It is a characteristic of free-radical addition to a carbon–carbon double bond that it occurs preferentially to the less alkyl substituted carbon (see e.g., in refs 1 and 9).

(b) The presence of the H atom is necessary to permit the occurrence of reactions 18 and 19.

(c) The study of Baldwin et al.[17] has shown that primary alkoxy radicals decompose with rate constants about 2 orders of magnitude lower than those of tertiary and secondary radicals.

These principles are demonstrated by the following discussion of each one of the alkenes examined.

Propene. The yield of organic nitrate (Table II) appears to be the highest among all the alkenes investigated. This result can be justified by the analysis of the possible reaction mechanisms. The addition of NO_3 both in position 1, which is expected to be the main reaction route, and in position 2 lead to alkoxy radicals with extractable H atoms. Moreover, in the case of the position 2 addition, a primary alkoxy radical is formed which should be relatively stable with respect to decomposition. This situation which favors the formation of organic nitrates rather than simple carbonyl compounds occurs only in the case of propene among the alkenes investigated.

The predominant pathway via H-atom abstraction was confirmed by the observation of HO_2NO_2 formed via reaction 21:

$$HO_2{}^\bullet + NO_2 \overset{M}{\rightleftharpoons} HO_2NO_2 \qquad (21)$$

The 2-nitroxy propanal which would be formed after NO_3 addition in position 2 was not identified for a certainty because this product was not synthesized. However, a weak absorption at 2812 cm^{-1} in the spectrum might be attributed to this species.

cis- and *trans-2-Butene.* These two compounds were observed, as expected, to form the same products since the isomerism disappears after the addition of the NO_3 radical to the double bond. The proposed reaction mechanism is shown in Figure 4.

The measurements (Table III) show that the organic nitrates account for more than 50% of the identified products which are mainly 3-nitroxy-2-butanone and 3-nitroxy-2-butanol. The observation of the 804-cm^{-1} HO_2NO_2 Q-branch in the product spectrum clearly supports the importance of H-atom abstraction (reaction 19). A weak absorption feature at 2740 cm^{-1}, characteristic of aldehyde functional groups and not attributable to acetaldehyde, leads to the suggestion of a minor reaction route through 1,4-H shift (reaction 20).

(17) Baldwin, A. C.; Barker, J. R.; Golden, P. M.; Hendry, D. G. *J. Phys. Chem.* **1977**, *81*, 2483.
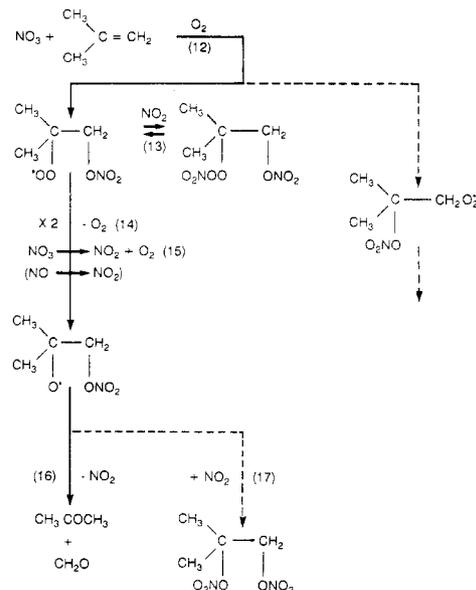
Figure 5. Proposed pathways for the reactions of the isobutene–NO_3–air system. Minor reaction pathways are shown with dashed arrows. Numbers in parentheses refer to the reaction type as discussed in the text.

From the data of the 2-butene runs, an analysis of some aspects of the kinetics of these reactions could be done. To simplify the reaction scheme, excess 2-butene was reacted with NO_3 (N_2O_5). In this way the decay of the largest fraction of the peroxynitrate took place after the disappearance of N_2O_5 and the reaction between NO_3 and the peroxy radical (reaction 15) could be ignored. In this case if R_a and R_b represent the rate of formation of 3-nitroxy-2-butanone and 3-nitroxy-2-butanol, respectively:

$$R_a = (1/2)k_{18}[RO_2{}^\bullet]^2 + k_{19}[RO^\bullet][O_2]$$

$$R_b = (1/2)k_{18}[RO_2{}^\bullet]^2$$

Assuming a steady-state condition for the very reactive alkoxy radical and ignoring reactions 15 and also 17 (little dinitrate was formed), the following equation is obtained:

$$k_{19}[RO^\bullet][O_2] + k_{16}[RO^\bullet] = k_{14}[RO_2{}^\bullet]^2$$

Deriving $RO^\bullet$ from the steady-state equation and substituting it into the ratio $a = R_a/R_b$ using the equations above, we find the ratio as

$$a = 1 + 2\frac{k_{14}}{k_{18}}\frac{k_{19}[O_2]}{k_{16} + k_{19}[O_2]}$$

From the experimental data, the average value of a equals 2.9 with a standard deviation of 0.8. It follows that k_{18} and $k_{14}(k_{19}[O_2]/(k_{19}[O_2] + k_{16}))$ must be of the same magnitude. This implies that reaction 18 and reaction 14 followed by reaction 19 contribute about equally to the formation of organic nitrates in the system. The rate of formation of 3-nitroxy-2-butanone by reaction 19 is then equal to $(2/3)R_a$ (see Figure 4). If the rate of formation of acetaldehyde by reaction 16 is indicated with R_c, the branching ratio β between reactions 19 and 16 is equal to

$$\beta = \frac{k_{19}[O_2]}{k_{16}} = \frac{4R_a}{3R_c}$$

From the measured concentrations of 3-nitroxy-2-butanone and acetaldehyde, β equals 1.9 with a standard deviation of 0.5.

Isobutene. The expected reaction mechanism is shown in Figure 5.

The yield of unsubstituted carbonyl compounds is comparable to but larger than that measured for *cis-* and *trans-*2-butene. The less favored reaction pathway with NO_3 addition at the 2-position is also shown because the presence of weak absorptions in the
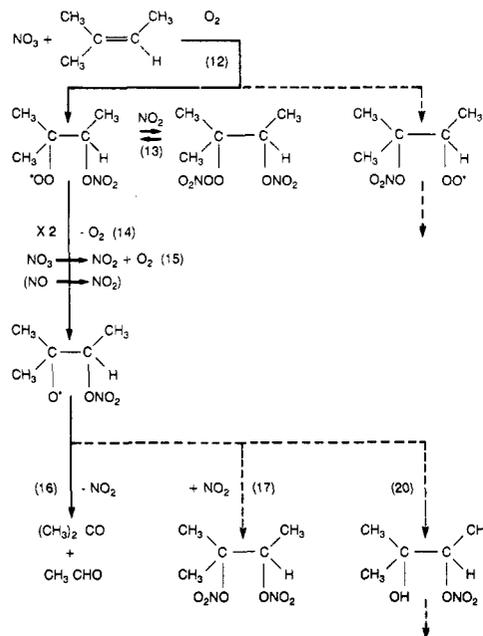
Figure 6. Proposed pathways for the reactions of the 2-methyl-2-but-ene–NO₃–air system. Minor reaction pathways are shown with dashed arrows. Numbers in parentheses refer to the reaction type as discussed in the text.
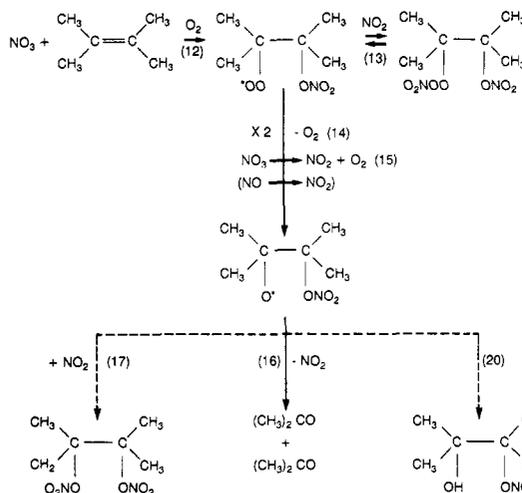
Figure 7. Proposed pathways for the reactions of the 2,3-dimethyl-2-butene–NO₃–air system. Minor reaction pathways are shown with dashed arrows. Numbers in parentheses refer to the reaction type as discussed in the text.

region 2680–2820 cm⁻¹ might indicate the presence of unidentified aldehydes. These species would derive from the alkoxy radical
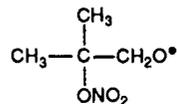
either immediately by H-atom abstraction by O_2 (reaction 19) or followed 1,4-H shift (reaction 20). No HO_2NO_2 could be detected since this pathway is certainly a minor one.

2-Methyl-2-butene. The proposed reaction mechanism in the case of 2-methyl-2-butene is shown in Figure 6. After the initial NO₃ addition, reactions 14 and 15 followed by reaction 16 are believed to be the main reaction pathway. The yield of unsubstituted carbonyl comopunds is about equal to or larger than in the case of the 2-butenes (see Table II). In fact no HO_2NO_2 was detected and the yield of organic nitrates was very low. A weak aldehyde band at 2740 cm⁻¹ leads also in this case to the suggestion of a minor route through 1,4-H shift (reaction 20).

2,3-Dimethyl-2-butene. The main reaction pathway is shown in Figure 7. The data of Tables II and IV showing relative high

yields of acetone and a low yield of organic nitrates support this reaction scheme. If only the reactions proposed in the case of propene by Shepson et al.[9] are considered, the 2,3-dimethyl-2,3-dinitroxybutane should be the only organic nitrate species formed. However, after abstraction of an authentic spectrum of this dinitrate from the product spectrum, infrared spectral features due to a nitrate group still remained, indicating the existence of another reaction pathway leading to organic nitrates. Further support to this hypothesis are as follows: the detection of a weak absorption at 2736 cm⁻¹, characteristic of aldehyde functional groups; the detection of traces of formaldehyde; a rapid decrease of the 2,3-dimethyl-2-butene concentration observed by addition of NO to the reaction mixture after the initial formation of the peroxynitrate intermediate which was most likely caused by OH radicals formed in the reaction between NO and HO_2.

These observations can only be justified if radicals of the type R–CH₂O₂• are formed as intermediates. This might occur by isomerization of the nitroxy alkoxy radical by 1,4-H shift (reaction 20) followed by reactions 22 and 23.
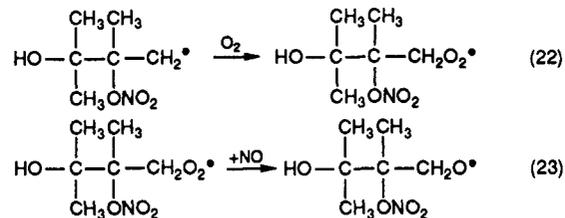
The alkoxy radical might form a nitroxy-substituted aldehyde by H-atom abstraction by O_2 (reaction 19) and formaldehyde together with another carbonyl species by decomposition (reaction 16).

Reaction between RO₂• and NO₃. The decay of the peroxynitrate intermediate formed by the reaction between 2,3-dimethyl-2-butene and NO₃ in air was found to be faster in the presence of N_2O_5; the final products, on the contrary, appeared to be the same. It is suggested that the enhanced decay has to be attributed to a reaction of the type

$$RO_2^\bullet + NO_3 \rightarrow RO^\bullet + NO_2 + O_2 \qquad (11)$$
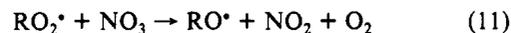
similar to that recently reported[18]

$$HO_2 + NO_3 \rightarrow HO + NO_2 + O_2$$
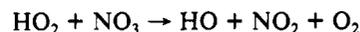
The rate constant of the reaction between the 2,3-dimethyl-2-nitroxy-3-peroxybutane radical and NO₃
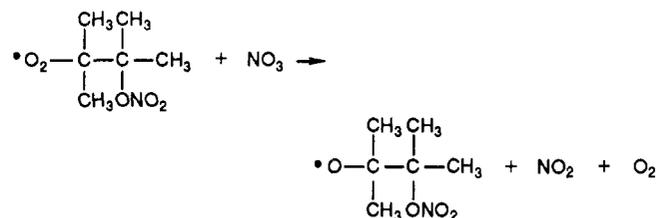
was estimated by fitting the experimental data for the decay of the peroxynitrate using the FACSIMILE software package.[19]

The decay of the peroxynitrate was considered to be due to the combined effect of reactions 11 and 24:

$$RO_2NO_2 \xrightarrow{\text{wall}} \text{products} \qquad (24)$$

Other reactions were considered to be unimportant.

The equilibrium constant for reaction 13
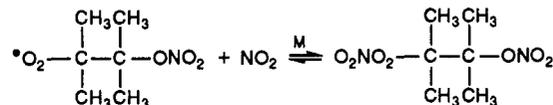
was assumed equal to $K_{13} = 1.5 \times 10^{-12}$ molecule⁻¹ cm³, a value

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(18) Mellouki, A.; Le Bras, G.; Poulet, G. *J. Phys. Chem.* **1988**, *92*, 2229.

(19) Chance, E. M.; Curtis, A. R.; Jones, I. P.; Kirby, C. R. UK Atomic Energy Research Establishment, Harwell (Report), 1977; AERE-R 8775.

based on the data for the dissociation of propyl peroxynitrate and the recombination of ethyl peroxy radicals with NO_2.[8]

The rates of reactions 14 and 24 were estimated from the data of three runs where the hydrocarbon concentration was in excess with respect to N_2O_5. k_{14} was determined as $(8.4 \pm 1.0) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} while k_{24} was variable ($\simeq 10^{-4}$ s^{-1}).

A best fit of k_{11} and k_{24} for the data of the three runs with excess N_2O_5 was thus obtained by letting k_{14} be fixed at the previously determined value. Under typical experimental conditions with excess N_2O_5, the rate of reaction 11 was considerably faster than that of reaction 14; e.g., for RO_2NO_2 = 1 ppm and N_2O_5 = 3 ppm, the measured rate of reaction 11 was about 5 times faster than that of reaction 14. k_{11} was found equal to $(4.8 \pm 0.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} while k_{24} was left variable ($\simeq 10^{-4}$ s^{-1}). The uncertainty limits indicated are 1 standard deviation of the values obtained from the different runs.

The uncertainty in the assumption of an approximate value for K_{13} and the other approximations done makes this calculation a rather rough estimate of k_{11} and we regard it as an order of magnitude value only.

The result appears close to the reaction rate constant of 2.3 $\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} recently determined by Crowley et al.[20] for the analogous reaction

$$CH_3O_2{}^\bullet + NO_3 \rightarrow \text{products}$$

Conclusions

The NO_3 radicals react with alkenes in air in the presence of NO_2 to form unsubstituted carbonyl compounds, nitroxycarbonyl compounds, nitroxy alcohols, and dinitrates.

The distribution of the products appears dependent on the alkyl-substitution pattern at the double bond, with the less substituted and unbranched alkenes giving the highest yields of organic nitrates. For the 2-butene and 2,3-dimethyl-2-butene reactions it was found that the dinitrate constituted only a small fraction of the total yield of products, even when the NO_2 concentration was several tens of ppm. Also for the other alkenes the reaction schemes which are supported by the experimental data suggest that the NO_2 concentration has in general little influence on the formation of organic nitrates under the experimental conditions applied. This means that the ratio between unsubstituted carbonyl and organic nitrate products obtained in this study should be representative also for ambient (tropospheric) conditions.

Evidence was found for a reaction between NO_3 and organic peroxy radicals, which in the case of 2,3-dimethyl-2-nitroxy-3-peroxybutane radical was estimated to proceed with a rate constant of about 5×10^{-12} cm^3 molecule^{-1} s^{-1}.

Isomerization of the alkoxy radicals by 1,4-H shift was also found to be a minor but not negligible pathway in the general reaction scheme.

Note Added in Proof: After submission of this paper, another paper was published (Barnes, J.; Bastian, V.; Becker, K. H.; Tong, Z. *J. Phys. Chem.* **1990**, *94*, 2413) where the mechanisms of the reactions of NO_3 with *trans*-2-butene and with isobutene are discussed.

(20) Crowley, J. N.; Burrows, J. P.; Moortgat, G. K.; Poulet, G.; Le Bras, G., submitted for publication in *Int. J. Chem. Kinet.*

(21) Atkinson, J.; Aschmann, S. M.; Winer, A. M.; Pitts, Jr., J. N. *Environ. Sci. Technol.* **1985**, *19*, 159.