

LABORATORY STUDIES OF TROPOSPHERIC NIGHTTIME CHEMISTRY USING FTIR

Francesco Cappellani, Jens L. Hjorth, Christian Lohse [†],
Claus J. Nielsen [‡], Giambattista C. Restelli and Henrik Skov [†]

Commission of the European Communities
Joint Research Centre - Ispra Establishment
I-21020 Ispra (VA), Italy.

The homogeneous vapour phase reactions between the nitrate radical, NO_3 , and propene, 2-methylpropene, 2-butene (Z and E), 2-methyl-2-butene and 2,3-dimethyl-2-butene have been studied by FTIR. Preliminary results from the study of these model compounds indicate that the major products of the tropospheric nighttime reactions between NO_3 and the naturally emitted terpenes are carbonyl compounds and that only small amounts of dinitrates are formed.

INTRODUCTION

The earth's atmosphere is conveniently divided into several distinct regions according to its temperature - altitude profile. In the troposphere, which is the lowest region of the atmosphere, the air temperature decreases with altitude. At 10 - 15 km above the earth's surface, the air temperature becomes stabilized and starts to increase slightly until a height of ca. 30 km. This layer, the stratosphere, is characterized by its high ozone concentration, by its even temperature, and by the absence of convective air currents. Hence, vertical transport through the stratosphere and between the troposphere and the stratosphere is very slow. Apart from the water vapour content, the lower atmospheric regions have a very uniform chemical composition. Dry air is (measured by volume) composed by ca. 78 % N_2 , 21 % O_2 , 1 % Ar, 0.03 % CO_2 and less than 0.005 % of all other chemical substances together.

Even without the influence of anthropogenic pollution, the troposphere is a complicated, dynamical physico-chemical system where a flow of chemical compounds either emitted from the earth or transported down from the stratosphere react, partly under the influence of sunlight. The reaction products are continuously removed from the troposphere by physical processes such as "dry" and "wet" deposition or by transport to the stratosphere.

The natural processes, that determine the concentration levels of trace gases in an unpolluted atmosphere are however being severely perturbed by the impact of manmade pollution. Table 1 gives some estimated figures for anthropogenic and natural emissions of important tropospheric trace gases (the estimates given for sulfur and non methane hydrocarbons, NMHC, are very uncertain). It is worth noticing that a major part of the naturally emitted NMHC consists of very reactive compounds such as isoprene and a number of terpenes. Although the total natural emission of a variety of reactive compounds exceeds the anthropogenic emissions it must be taken into account

[†] On leave from Department of Chemistry, University of Odense, DK-5230 Odense N, Denmark.

[‡] On leave from Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo 3, Norway.

that the manmade pollution sources are concentrated in the industrialized parts of the world, that form only a small percentage of the total. The consumption of fossil fuel for combustion, e.g. as estimated for the year 1976, was divided almost equally between North America, Europe and the rest of the world.

TABLE 1. Estimated global emissions of some important air pollutants [10^9 kg year⁻¹].

Pollutant	Total	Antropogenic	Natural
Sulfur containing compounds estimated as S	250	100	150
Carbon monoxide, CO	400-7750	250-1050	150-6700
NO _x estimated as NO ₂	130-235	65-110	65-125
Non methane hydrocarbons, NMHC	580	80	500

The pollutants emitted from antropogenic sources (the primary pollutants) such as SO₂, nitrogen oxide, hydrocarbons, CO etc. may be toxic themselves, but often the most aggressive pollutants are those formed by chemical reactions in the air (the secondary pollutants) such as ozone, PAN, nitric acid, and sulfuric acid. On the other hand, many harmful chemicals of antropogenic origin are oxidized in the troposphere to harmless substances. In order to analyze the complex source-receptor relationship in air pollution a detailed understanding of a variety of chemical as well as meteorological relationships is necessary. The understanding of the basic mechanisms in tropospheric chemistry has been developed only within the last twenty years and still much work needs to be done.

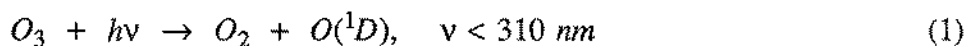
Computerized models that simulate the meteorology and the chemical kinetics involved in air pollution episodes have become an important tool applied in the efforts to abate air pollution, but they are obviously limited by the physical and chemical understanding of atmospheric processes and the quality of the input data. Therefore laboratory studies of rate constants and reaction mechanisms in atmospheric reactions are needed to provide the necessary information.

As mentioned above, the majority of the naturally emitted NMHC consists of isoprene and a number of terpenes. In spite of their importance in the tropospheric chemistry, the mechanisms of their oxidative degradation in the nighttime is not known in detail. Only two mechanistic studies of the thermal reaction between alkenes (represented by propene) and the important nighttime species NO₃ have been published /1,2/. Different methods were used in the two studies and the results were also widely different.

One of the main questions to be answered is whether the interaction between nitrogen oxides and unsaturated hydrocarbons leads to the formation of stable, unreactive nitrogen containing products, such as organic nitrates and HNO₃, or only to a reduction of NO₃ to NO₂. The present communication contains some of our preliminary results from FTIR studies of the nighttime reactions (initiated by the NO₃ radical) of the model compounds propene, 2-methylpropene, 2-butene (Z and E), 2-methyl-2-butene and 2,3-dimethyl-2-butene.

TROPOSPHERIC DAYTIME CHEMISTRY

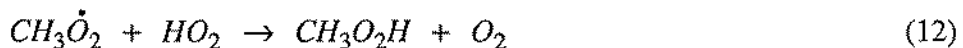
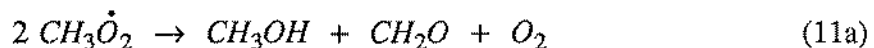
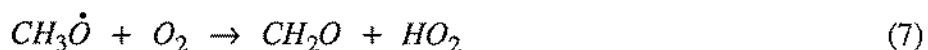
The oxidative degradation of volatile organic compounds in the troposphere is in the presence of sufficient NO_x (i.e. NO_2 and NO) combined with a build up of oxidizing substances. The most important of these is ozone. The OH radical, mainly formed by the photolytical cleavage of O_3 , has been found to play a pivotal role in these atmospheric processes.



A few other photolytical reactions, mainly of importance in the polluted troposphere, lead to the formation of OH radicals as well. Finally, OH is formed by reduction of hydrogenperoxy radicals:



The OH radicals react with most organic compounds either by hydrogen abstraction or by addition to π -bonds, thereby initiating oxidation. A typical sequence of reactions can be illustrated by the simplest hydrocarbon, methane:

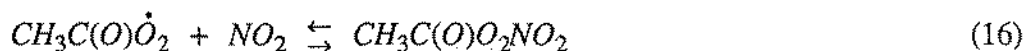
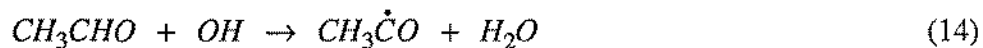


Step 4-10 show how the oxidation of methane to formaldehyde (that eventually will be photolyzed or react further with OH) is followed by formation of ozone via the oxidation of NO to NO_2 . The peroxy radical reactions 11-13 are, however, competing with reactions 6 and 8 and may dominate when the NO_x concentration is sufficiently small. In this case the tropospheric photochemistry will provide an ozone sink (due to reaction 1) and this seems actually to be the situation in some parts of the world.

In other parts of the world, particularly in vicinity of urban centres where antropogenic emissions of hydrocarbons and NO_x are large, there is a build up of ozone in the daytime and the

photochemical air pollution can be a severe problem with respect to damages to human health as well as plant crops.

Together with ozone a variety of noxious, but less abundant, products are formed. Presumably the most important among these is peroxy acetyl nitrate (PAN), formed by reactions 14-16:



Photochemistry is also a main cause of the oxidation of SO_2 to sulfuric acid and of NO_x to HNO_3 :



While the formation of HNO_3 under daylight conditions seems almost entirely due to the reaction between NO_2 and OH , the SO_2 oxidation proceeds via liquid phase reactions in droplets and "wet" aerosols as well.

TROPOSPHERIC NIGHTTIME CHEMISTRY

The daytime chemistry of the troposphere is mainly driven by the impact of sunlight. Hence, the formation of ozone and related products reaches a maximum around noontime and falls off to zero when the sun disappears. This does not mean that the chemical activity in the troposphere stops; the reactive species formed during daytime are still present and will continue to perform thermal reactions (like the reactions between ozone and olefins). Among these thermal reactions is the reaction between NO_2 and O_3 leading to formation of the highly reactive NO_3 radical:



In the daytime NO_3 is rapidly photolyzed but at nighttime it builds up significant concentrations. The few direct measurements of ambient concentrations of NO_3 that have been carried out until now show a range of concentrations from less than one ppt in the free troposphere in the Mid Pacific up to 355 ppt during an urban air pollution episode; typical concentrations measured in continental air suggest however a key role for the NO_3 radical in the chemistry of troposphere.

TABLE 2. Rate constants [$cm^3 \text{ molecule}^{-1} s^{-1}$] for the reaction between natural hydrocarbons and O_3 , OH and NO_3 . Data taken from Ref. 3.

Hydrocarbon	Ozone	OH	NO_3
Isoprene	$1.4 \cdot 10^{-17}$	$1.0 \cdot 10^{-10}$	$5.8 \cdot 10^{-13}$
α -Pinene	$8.4 \cdot 10^{-17}$	$5.3 \cdot 10^{-11}$	$5.3 \cdot 10^{-12}$
β -Pinene	$2.1 \cdot 10^{-17}$	$7.8 \cdot 10^{-11}$	$2.5 \cdot 10^{-12}$
Δ^3 -Carene	$1.2 \cdot 10^{-16}$	$9.0 \cdot 10^{-11}$	$1.1 \cdot 10^{-11}$
<i>d</i> -Limonene	$6.4 \cdot 10^{-16}$	$1.5 \cdot 10^{-10}$	$1.4 \cdot 10^{-11}$

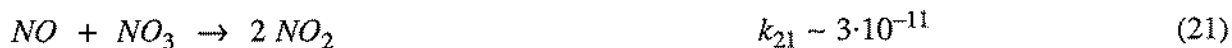
The rate constants for the initial reaction between the NO_3 radical and ca. 60 different compounds of environmental interest have been measured, /3/ (and references cited therein). In Table 2 are listed the rate constants for the reaction of a few of the naturally emitted hydrocarbons with ozone, OH and NO_3 . As is apparent, the rate constants for the reaction of unsaturated hydrocarbons with the NO_3 radical are much larger than those of ozone and almost comparable to those of the OH radical. The rate constants themselves do not reflect the importance of the NO_3 reactions in the tropospheric nighttime chemistry, the individual concentrations of the oxidizing agents have to be taken into consideration. The estimated lifetimes of the natural hydrocarbons with respect to the oxidizing species O_3 , OH (daytime) and NO_3 (nighttime), have been collected in Table 3. The lifetimes given in Table 3 were calculated assuming concentrations typical for "clean" and "polluted" tropospheres and they clearly show that the nitrate radical plays a very important role in the nighttime chemistry.

TABLE 3. Estimated lifetimes of some natural hydrocarbons [minutes] in "clean" and "moderately polluted" atmospheres. The lifetimes have been calculated using the rate constants in Table 2 and assuming the typical O_3 , OH and NO_3 concentrations given below.

Hydrocarbon	"Clean" atmosphere			"Polluted" atmosphere		
	Ozone	OH (day)	NO_3 (night)	Ozone	OH (day)	NO_3 (night)
Isoprene	1600	170	115	240	42	12
α -Pinene	270	320	13	40	80	1.3
β -Pinene	1075	220	27	160	54	2.7
Δ^3 -Carene	190	190	6	28	47	0.6
d-Limonene	35	115	5	5	28	0.5
[O_3]	30 ppb			200 ppb		
[OH]	0.04 ppt			0.16 ppt		
[NO_3]	10 ppt			100 ppt		

The ozone - NO_x nighttime system.

In a nighttime atmosphere containing only O_3 , NO_x , H_2O and air, the homogenous reactions controlling the individual concentrations, i.e. the reactivity, are:



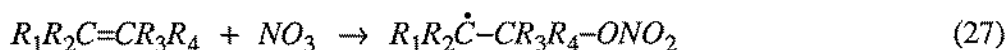
The oxidation of NO by O₂ is much too slow to be of importance at typical ambient concentrations. Likewise, the equilibrium reactions leading to N₂O₃ and N₂O₄ are without importance. The sum of these reactions is in effect a very slow removal of O₃ from the atmosphere during the nighttime and a very slow formation of HNO₃.

The heterogeneous reaction between N₂O₅ and water droplets is several orders of magnitude larger than the homogeneous reaction (26). Together with the daytime reaction (17), the heterogeneous water/N₂O₅ reaction presumably constitutes the most important sinks for NO_x in the troposphere.

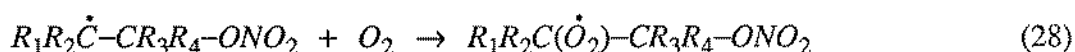
NO_x - alkene reactions

The possible reaction paths for the nighttime chemical degradation of alkenes by NO_x are given in the following. Some of the individual steps proposed are analogues to the known reactions of alkyl, alkoxy, and alkylperoxy radicals. Typical rate constants for the individual steps are collected in Table 4. The reactivities of NO, NO₂, NO₃ and N₂O₅ towards alkenes are very different. NO₃ reacts fast with the alkenes while NO₂ reacts very slowly and finally both NO and N₂O₅ so slowly that it cannot be measured. Although the NO₂ concentrations are at least an order of magnitude larger than the NO₃ concentrations in the natural and the polluted atmosphere the rate constants for the initial reaction NO₂/alkene are so much smaller than the corresponding NO₃ reactions, that they are of no importance.

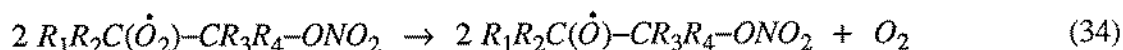
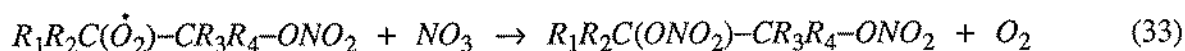
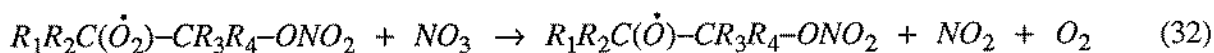
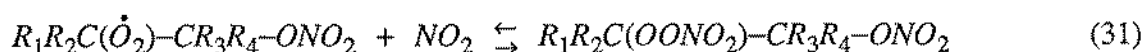
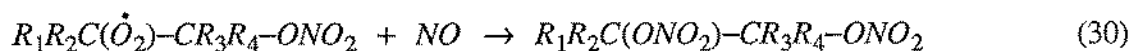
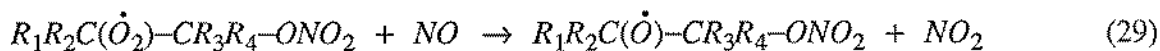
The primary reaction between the NO₃-radical and an alkene is an addition reaction (hydrogen abstraction from sp³ hybridized carbon is two to four orders of magnitude slower):



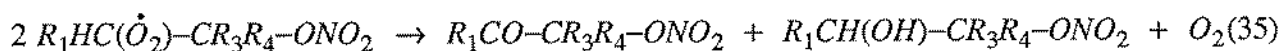
The resulting nitroxy-alkyl radical reacts immediately with the atmospheric oxygen to form a nitroxy-peroxy radical:



The further reactions of this nitroxy-peroxy radical in the atmosphere depends among other on the nature of the substituents R₁ - R₄. Assuming that only NO_x/O₂ are possible reaction partners, the following reactions may take place:

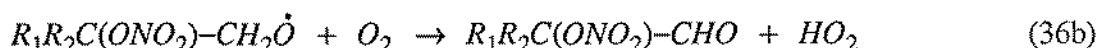


In the special case where R₁ or R₂ is hydrogen, the following reaction is possible:

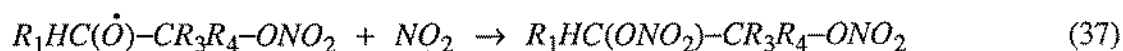


The dinitrates, formed by reactions (30) and/or (33) (and 38, see later), are fairly stable, in the sense that they only react very slowly with NO_x and water. The same is also true for the nitroxy alcohols and the nitroxy ketones/aldehydes formed by reaction (35). The nitroxy-peroxynitrate, formed by reaction (31), is also stable but in equilibrium with the nitroxy-peroxy radical and hence acts as a NO_2 -buffer.

The nitroxy-oxy radicals formed by reactions (29), (32) and/or (34) are unstable and react very fast either by isomerization (1,4/1,5-hydrogen shift), that leads to further addition of oxygen (eqn. 28) or by hydrogen abstraction by the atmospheric oxygen, which leads to the formation of nitroxy-ketones or nitroxy-aldehydes. In both cases the hydrogen peroxy radical is produced:



There is also the possibility for a reaction with NO_2 resulting in the formation of a dinitrate:



Finally, the oxy-nitroxy radical can decompose forming NO_2 and simple aldehydes or ketones:

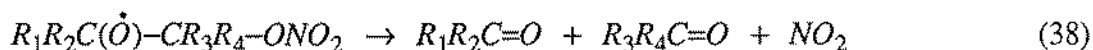


TABLE 4. Typical rate constants [$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] for the individual steps in the possible NO_x - alkene reaction mechanism.

Constant	Value	Constant	Value	Constant	Value
k_{27}	$10^{-15} - 10^{-11}$	k_{28}	10^{-12}	k_{29}	$10^{-12} - 10^{-11}$
k_{30}	$10^{-13} - 10^{-12}$	k_{31}	$5 \cdot 10^{-12}$	k_{31}	1
k_{32}	10^{-12}	k_{33}	?	k_{34}	$10^{-13} - 10^{-11}$
k_{35}	10^{-13}	k_{36}	10^{-15}	k_{37}	10^{-11}
k_{38}	$10^{-5} - 10^3$				

RESULTS

All of the alkene reactions with NO_3 and NO_2 led to formation of compounds having nitrate and pernitrate functional groups as brought in evidence by the characteristic absorption bands at ca. 850, 1280 and 1765 cm^{-1} for R-ONO_2 and at ca. 790, 1300 and 1725 cm^{-1} for R-OONO_2 corresponding to the $-\text{O-NO}_2$, the symmetric NO_3 , and the antisymmetric NO_3 stretching vibrations, respectively. Also carbonyl compounds, expected from reaction (38), could always be observed in the spectra. Another common feature for all of the reactions studied was the observation of a rapid build up of NO_2 in the initial stage of the process when both NO_3 and peroxynitrates were present in the reaction mixture.

In Fig. 1 are shown parts of the IR spectra obtained during the thermal reaction between propene and NO_3/NO_2 . For comparison, the IR spectrum of an authentic sample of one of the reaction products, 1,2-dinitroxypropane, has also been included in Fig. 1. The spectra are very similar to

those published previously /1/. In addition to the bands originating from N_2O_5 , HNO_3 and propene, strong absorptions corresponding to organic nitrate (845 and 1285 cm^{-1}) and pernitrate (790 and 1295 cm^{-1}) can be seen in Fig. 1. In the $1600 - 1800\text{ cm}^{-1}$ region are readily observed bands due to formaldehyde, acetaldehyde and to organic nitrate and pernitrate reaction products. After adding NO to the reaction mixture, whereby the organic pernitrate instantaneously was removed (see eqn. 29-31), the IR spectra revealed a band at ca. 1745 cm^{-1} of medium to weak intensity after spectral subtraction of formaldehyde and acetaldehyde. This band has been attributed to a carbonyl compound having an electronegative substituent in α -position. An analysis of the spectra demonstrates the presence of at least three different nitrate containing compounds: nitroxy-nitroperoxypropane, 1,2-dinitroxypropane and a nitroxy-carbonyl compound. Finally, the consumption of N_2O_5 (corrected for wall loss) is found to be larger than the sum of the HNO_3 production (reaction with water) and the consumption of propene.

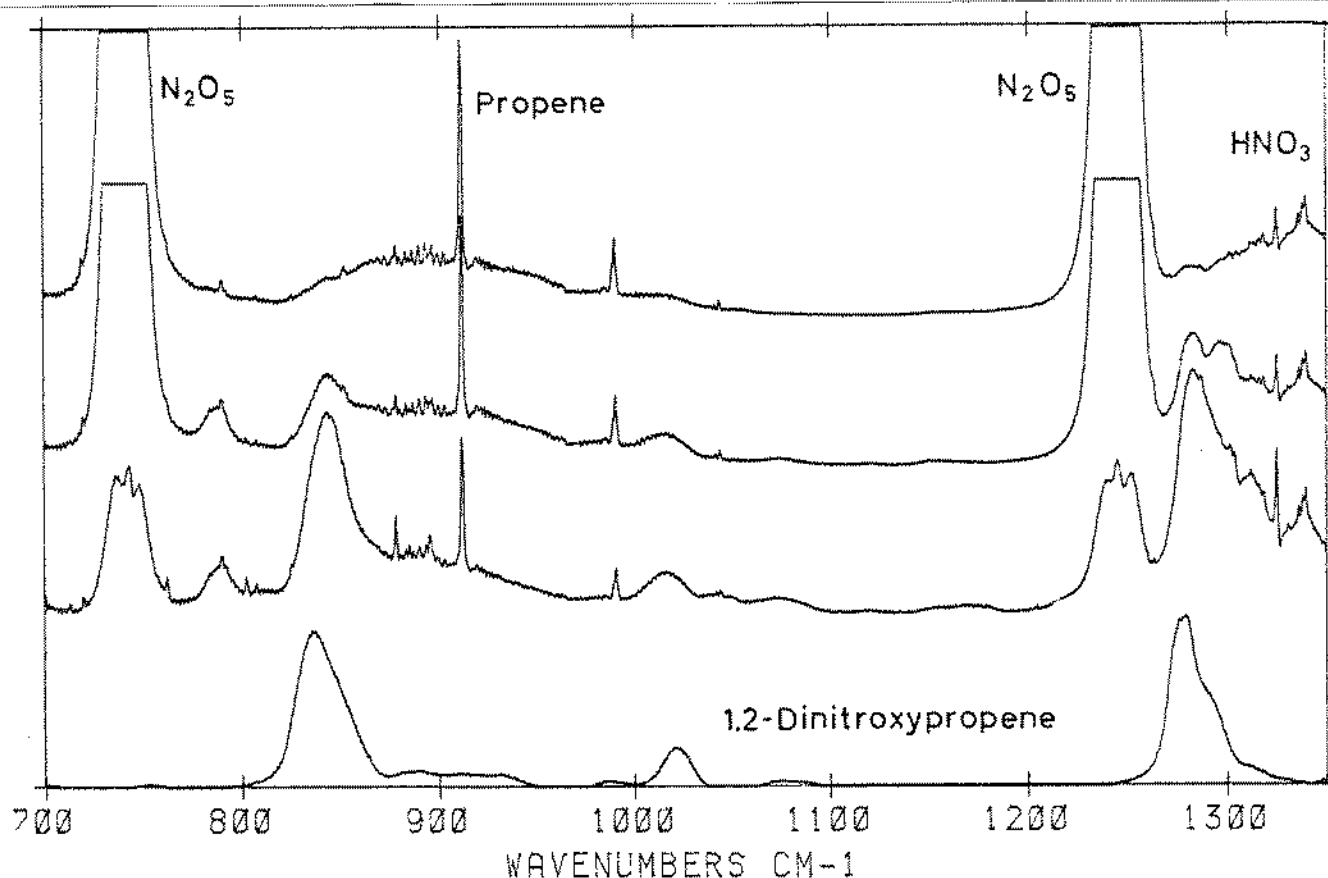


FIGURE 1. Infrared spectra ($700 - 1350\text{ cm}^{-1}$) of the reaction mixture propene, NO_2 and N_2O_5 . The spectra shown (from the top) were recorded: Immediately after mixing, after 6 min. reaction time and after 90 min. reaction time. The bottom spectrum is that of an authentic sample of 1,2-dinitroxypropane. Optical pathlength 80m, atmospheric pressure. Initial concentrations: propene 10 ppm, NO_2 4 ppm and N_2O_5 8 ppm.

The spectra of the reaction products from the reaction between *Z*- or *E*-2-butene with NO_3/NO_2 are almost identical. In Fig. 2 are shown some of the IR spectra obtained during the reaction. The IR spectrum of an authentic sample of 2,3-dinitroxybutane (*dl*) has also been included in Fig. 2. As can be seen from this figure, very strong bands similar to those observed in the reaction propene - NO_3/NO_2 appear. In addition to the bands originating from organic nitrate and pernitrate there are also bands corresponding to acetaldehyde and to an unidentified carbonyl

compound with absorption at ca. 1730 cm^{-1} . Most probably this carbonyl compound is 3-nitroxybutan-2-one.

The initial alkene - NO_3 reaction is much faster for 2-butene than for propene. In order to slow the reaction down, the NO_3 concentration was decreased by increasing the NO_2 concentration (see eqn. 22). As can be seen from the relative intensities of the $795\text{ (R-OONO}_2\text{)}$ and $845\text{ cm}^{-1}\text{ (R-ONO}_2\text{)}$ bands this also has the effect of increasing the amount of the intermediate nitroxy-nitroperoxy compound (eqn. 31)

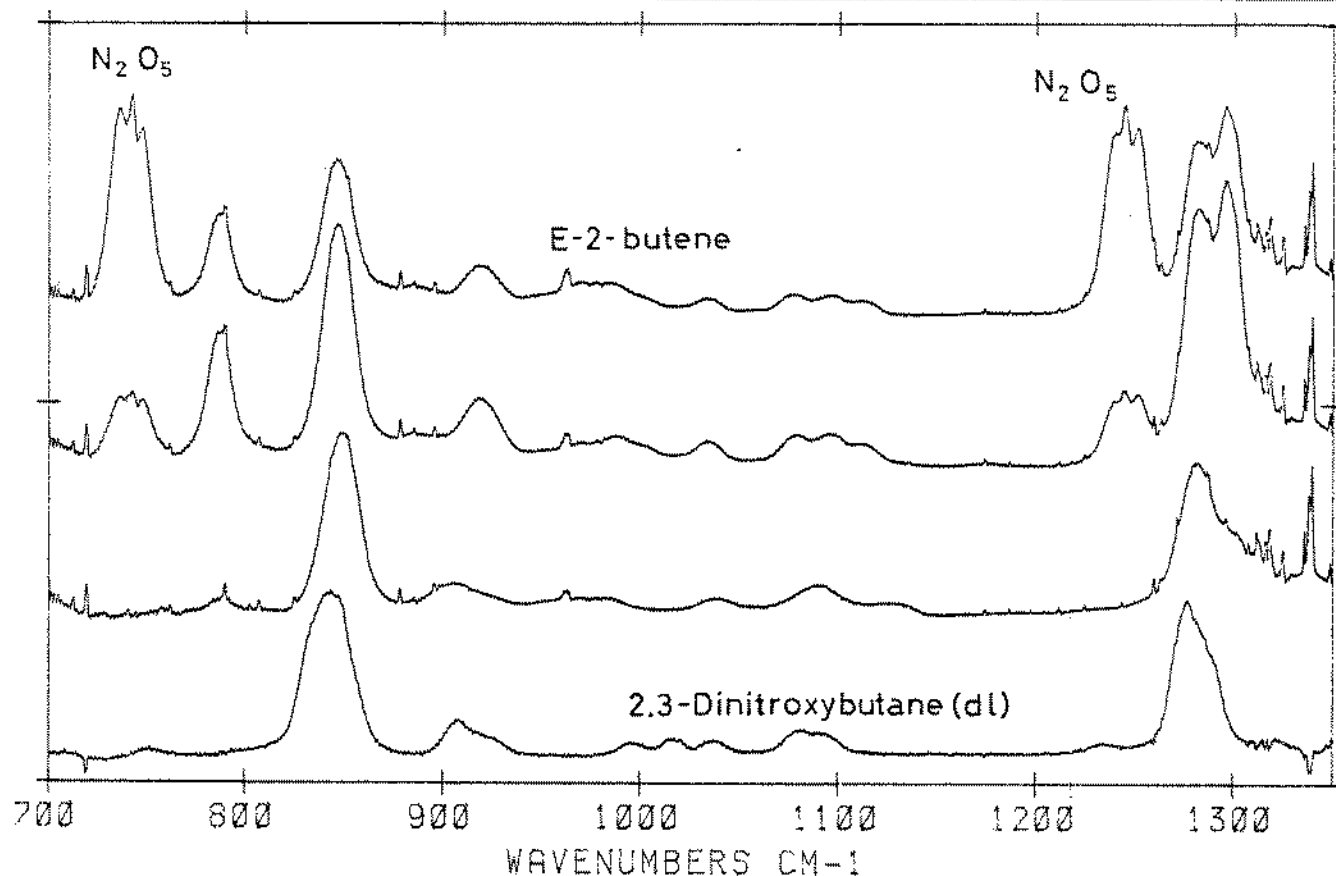


Figure 2. Infrared spectra ($700 - 1350\text{ cm}^{-1}$) of the reaction mixture E-2-butene, NO_2 and N_2O_5 . The spectra shown (from the top) were recorded: Immediately after mixing, after 6 min. reaction time and after 180 min. reaction time. The bottom spectrum is that of an authentic sample of 2,3-dinitroxybutane (dl). Optical pathlength 80m, atmospheric pressure. Initial concentrations: E-2-butene 10 ppm, NO_2 18 ppm and N_2O_5 7 ppm.

It can be seen directly from Fig. 2 that 2,3-dinitroxybutane is not the only organic nitrate formed during the reaction. In fact, less than 30 % of the total intensity of the nitrate bands at 845 and 1285 cm^{-1} appears to originate from the dinitrate.

Compared to the unbranched alkenes, the branched alkenes 2-methylpropene, 2-methyl-2-butene and 2,3-dimethyl-2-butene show a different product distribution in their reaction with NO_3/NO_2 . The most illustrative example of this is the extremely fast reaction between 2,3-dimethyl-2-butene and NO_3/NO_2 . The results from monitoring this reaction by IR spectroscopy are given in Fig. 3.

There are several interesting features in these spectra. First, the main reaction product appears to be acetone and there is only a small amount of organic nitrate among the final products.

Secondly, the nitrate band at ca. 855 cm^{-1} is situated almost ten wavenumbers higher than in the other compounds studied. Finally, in the region around 1300 cm^{-1} there appears only one band whereas two are expected. We tentatively explain these observations by the crowded situations in both the intermediate product 2-nitroso-3-nitroxyperoxy-2,3-dimethylbutane and in 2,3-dinitroso-2,3-dimethylbutane. We would expect the *anti* configurations to be favoured and the two molecules to be *pseudo* centrosymmetric and centrosymmetric, respectively, and only the *ungerade* vibrations to be IR active.

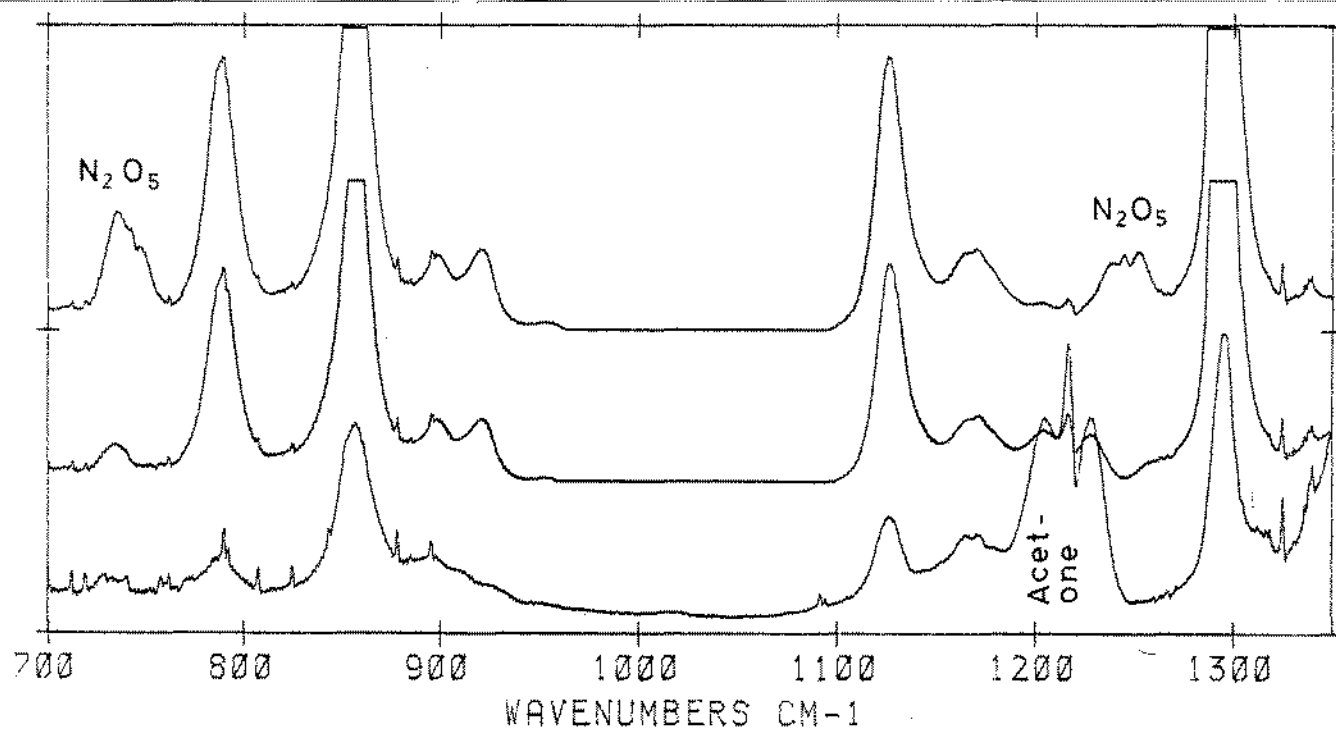


FIGURE 3. Infrared spectra ($700 - 1350\text{ cm}^{-1}$) of the reaction mixture 2,3-dimethyl-2-butene, NO_2 and N_2O_5 . The spectra shown (from the top) were recorded: Immediately after mixing, after 5 min. reaction time and after 140 min. reaction time. Optical pathlength 80m, atmospheric pressure. Initial concentrations: 2,3-dimethyl-2-butene 10 ppm, NO_2 5 ppm and N_2O_5 11 ppm.

The first three steps of the reaction mechanism are evidently (27) and (28) followed by the equilibrium (31) forming the nitroso-nitroperoxypropene. There are two routes to the formation of a nitroso-carbonyl compound, either directly from the nitroso-peroxy radical (35) or via the nitroso-oxy radical (36a,b). In the former case there should also be a production of a hydroxyl compound, which we so far have not been able to detect in the spectra. In the latter case the nitroso-carbonyl compound is accompanied by a production of HO_2 which we assume would react with NO_2 and NO_3 to form pernitric acid, HOONO_2 , and nitric acid, respectively. It appears necessary to obtain authentic samples of the possible nitroso-carbonyl and nitroso-hydroxyl compounds in order to be able to distinguish between reactions (35) and (36). The excess consumption of N_2O_5 during the reaction indicates that the steps (32) and/or (33) are important.

The differences in the product distributions implicate that the NO_3 radical adds to the less substituted carbon atom at the double bond. Hence, reactions like (36b) are unlikely to be important. It also means that we can classify the reactions studied according to the branching of the alkene. For the unbranched alkenes (propene and 2-butene) the reactions (35) and/or (36a) are likely to be important. For the branched alkenes (2-methylpropene, 2-methyl-2-butene and 2,3-dimethylbutene)

the formation of nitroso-oxo or nitroso-hydroxy compounds are unlikely to be of importance. Many of the naturally emitted terpenes belong to this class of alkenes.

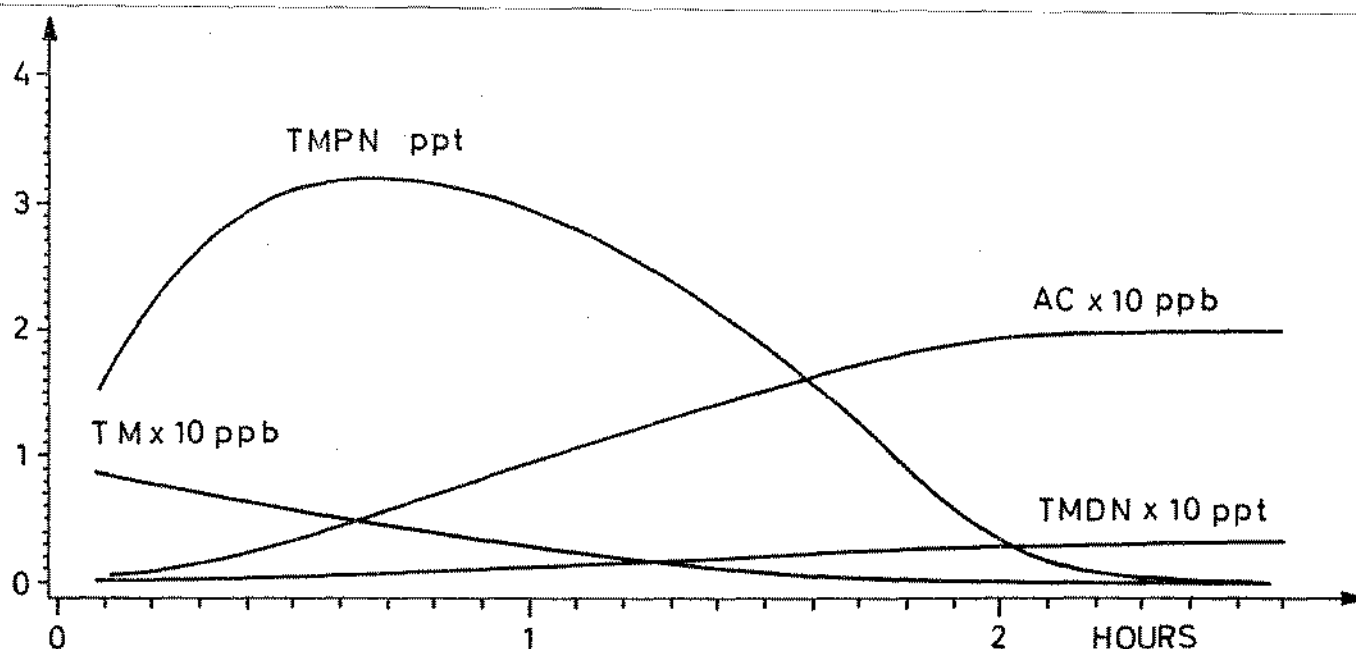


FIGURE 4. Simulation of the kinetics of the 2,3-dimethyl-2-butene reaction with NO_x under rural air conditions. Abbreviations: TM, 2,3-dimethyl-2-butene; TMPN, 2-nitroso-3-nitroperoxy-2,3-dimethylbutane; TMDN, 2,3-dinitroso-2,3-dimethylbutane; AC, acetone.

Models have been set up in order to extrapolate the observed kinetic behaviour of the alkene - NO_3/NO_2 reactions to realistic atmospheric conditions. In the case of 2,3-dimethylbutene the reactions (35) and (36) can be excluded, and a simple model, based on the reaction scheme presented previously, provides an acceptable simulation of the observed kinetics of the reaction under laboratory conditions. This model has then been applied to a fictitious rural air situation, where 0.1 ppb of 2,3-dimethylbutene is found together with 5 ppt NO_3 , 1 ppb NO_2 , 3 ppt N_2O_5 , 1 ppt NO and 30 ppb O_3 . The result is shown in Fig. 4; less than 0.1 % of the reacting nitrogen oxides are found as organic nitrate, the main product of the reaction being acetone and NO_2 . The major part of the terpenes are expected to follow the same reaction pathway and thus give rise to a reduction of NO_3 to NO_2 rather than to a removal of NO_x from the troposphere.

References

- /1/ Bandow, H., Okuda, M. and Akimoto, H.: J. Phys. Chem. 84(1980)3604.
- /2/ Shepson, P.B., Edney, E.O., Kleindienst, T.E., Pittman, J.H., Namie, G.R. and Culpitt, L.T.: Environ. Sci. Technol. 19(1985)849.
- /3/ Finlayson-Pitts, B.J. and Pitts Jr., J.N.: Atmospheric Chemistry, Wiley-Interscience (1986) New York.