

Kinetics of Oxirane Formation in the Reaction of Nitrate Radicals with Tetramethylethylene

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The kinetics of oxirane formation in the reaction of nitrate radicals with tetramethylethylene was investigated in a flow system at room temperature. Total pressure ranged from 5 to 1000 mbar. Using inert gas (He, N₂) tetramethyloxirane only was detected as reaction product. In the case of synthetic air acetone also is formed in dependence of the system pressure. With increasing pressure the oxirane yield decreases and the acetone yield increases. Under tropospheric conditions 20% tetramethyloxirane was found.

It is concluded that the oxirane observed results from the excited adduct formed in the electrophilic addition of the nitrate radical to the double bond. In the absence of O₂ the quenched adduct radical forms oxirane in a thermal reaction also.

Kinetic parameters were estimated.

Introduction

In recent years rate constants of nitrate radical reactions with alkenes were measured extensively by several groups [1]. Product studies, mostly with in situ FTIR detection of the products in smog chambers with air as pressure gas are available [2, 3]. Using this approach, substituted and unsubstituted carbonyl compounds, α,β -dinitroxy- and α,β -hydroxy-nitroxy-compounds were found in various ratios in dependence of the structure of the alkene reacted. More recently, oxirane formation was reported in the case of styrene and alkyl substituted monoalkenes in the low pressure range [4–6]. Earlier, oxirane observation (propene oxide) in such a system was reported in the studies of Hoshino et al. [7].

For reason of the poisonous nature of the oxiranes it is necessary to investigate the channels leading to these formation. In our studies we investigated at first the reactions of tetramethylethylene (2,3-dimethyl-2-butene). From further analysis of other alkenes informations of the influence of structure to the reaction products are expected.

Experimental Section

All experiments were carried out in a 2.13 cm i.d. quartz flow system at room temperature. MKS flow controller and Baratron pressure gauges are used. A vacuum system connected to a GC-MS/FID equipment (HP 5890) allowed the analysis of reaction products by both detectors simultaneously.

Nitrate radicals were generated in the tube by thermal decomposition of N₂O₅ which was synthesized by the method of Davidson et al. [8]. Before entering the tube N₂O₅ was premixed with the carrier gas, the other reactant was added through a moveable inlet. The reaction was terminated by injection of NO at a fixed port. In order to identify the compounds formed tetramethyloxirane (TMO) [9] and 2,3-dimethyl-2,3-dinitroxy-butane [10] were separately prepared.

Our equipment is suitable for analysis of stable substances. The detection limit of tetramethylethylene (TME) is

about $5 \cdot 10^{11}$ molecule cm⁻³ (FID). In the experiments performed the initial concentrations of TME varied in the range of (0.4–6.5) 10^{13} molecule cm⁻³ with a conversion of TME 15.1–100% and the reaction times of 0.1–8 s. Uncertainties of 5–10% in the measurements of the concentrations have to be taken into account. The system pressure ranged from 5 to 1000 mbar.

Results and Discussion

Tetramethyloxirane (TMO), acetone and small amounts of 2,3-dimethyl-2,3-dinitroxy-butane were identified by the mass spectrum of the reference substances and retention time, respectively, as products of the reaction of nitrate radicals with tetramethylethylene (TME) performed in various gases. The carbon mass balances varied from 93% in average in the case of reaction in synthetic air to about 100% using inert pressure gas. In summary of our experimental results the following simple reaction pattern is proposed, cf. Fig. 1. The numbering of the steps is equal to those of the rate constants.

Experiments in He and N₂

In the investigations performed in the absence of radical scavengers only TMO as a reaction product was obtained.

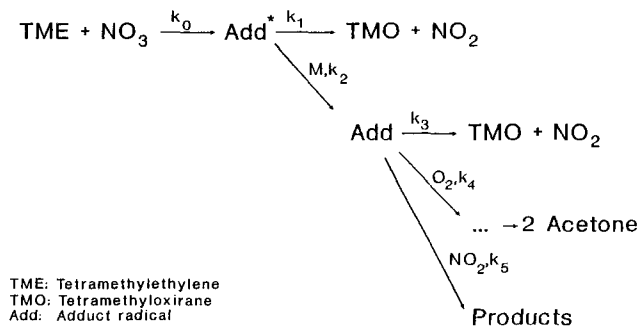


Fig. 1
Proposed reaction pattern

Up to 1000 mbar there is no pressure dependence of the TMO yield, cf. Fig. 2. From REMPI-studies under similar conditions in the low pressure range NO_2 formation is known [6]. NO_2 yields found are in agreement with our oxirane observations.

It was assumed that the chemical activated (excited) adduct (Add*) leads to the oxirane (R1) [6]. Due to our results over a wide pressure range it is necessary to formulate an additional channel. Further investigations showed that this formation channel is suppressed in the presence of sufficient amounts of O_2 or NO_2 . It is concluded that the quenched adduct radical (Add) forms TMO also in a thermal reaction via (R3).

The oxirane yield was not affected by a large excess of N_2O_5 , high nitrate radical concentrations and for 100% conversion of TME. Under our experimental conditions the consecutive reaction



is negligible ($k_6 < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

In according with the reaction pattern two molecules NO_2 per molecule TME reacted are formed. From a maximum initial TME concentrations of $6.5 \cdot 10^{13} \text{ molecule cm}^{-3}$ $1.3 \cdot 10^{14} \text{ molecule cm}^{-3}$ of NO_2 are formed. Further studies with definite addition of NO_2 showed that concentrations lower than $10^{15} \text{ molecule cm}^{-3}$ are unimportant and in these cases channel (R5) is negligible.

Experiments in Synthetic Air

In these experiments oxygen is a collision partner as well as a scavenger. Acetone formation in the reaction of nitrate radicals with TME in synthetic air using smog chambers was reported by Niki et al. [11] and Hjorth et al. [3].

We found a strong pressure dependence of the product distribution, cf. Fig. 3. With increasing system pressure the TMO yields decrease. This behavior is expected if TMO is formed from the excited adduct (R1) and the quenched adduct reacts with the excess of oxygen (R4). In result from

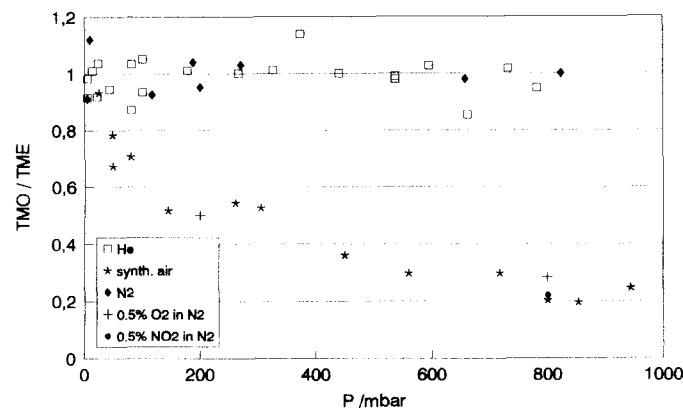


Fig. 2 Plot of oxirane yield (TMO/TME) vs. system pressure using various pressure gases and mixtures with radical scavengers

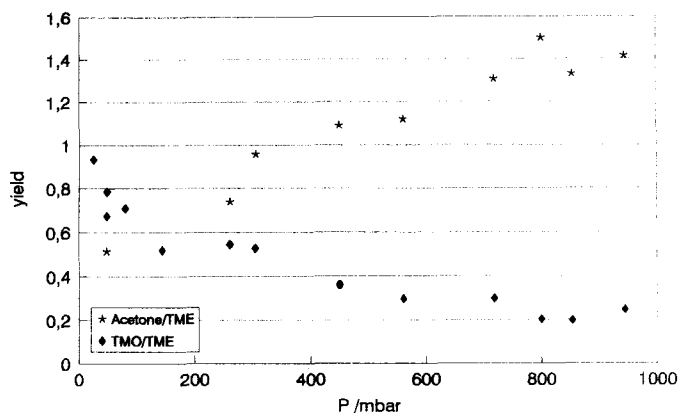
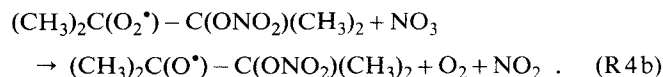
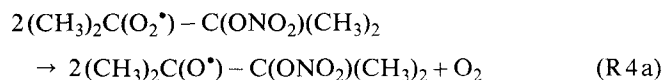


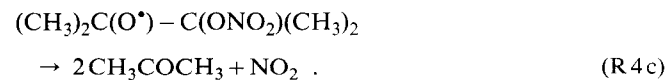
Fig. 3 Plot of product yields (TMO or acetone) vs. pressure of synthetic air (small amounts of 2,3-dimethyl-2,3-dinitroxy-butane are not considered)

FTIR-studies similar oxirane yields up to atmospheric pressure were reported [5]. Both experimental techniques show a TMO yield of about 20% for tropospheric conditions.

In order to explain the acetone yield found it is necessary that each peroxy radical formed in (R4) produces two molecules of acetone. Initially the peroxy radical has to be reduced to the corresponding oxy radical. Two possibilities are discussed in the literature: self reaction and reaction with NO_3 ; viz.



The oxy radical subsequently leads to acetone in a thermal reaction:



The consecutive reactions (R4a)–(R4c) are complete under our experimental conditions. Thus, reaction (R4) is in accordance with the acetone yield. This is also confirmed by the carbon mass balance.

Under our conditions no evidence for the formation of the nitroperoxy-nitroxy compound $((\text{CH}_3)_2\text{C}(\text{O}_2\text{NO}_2) - \text{C}(\text{ONO}_2)(\text{CH}_3)_2)$ was found. This species was frequently detected in FTIR-studies in the reactions of nitrate radicals with different alkenes [1–3].

Definite Addition of O_2 and NO_2

Experiments were also performed with definite traces of O_2 and NO_2 in N_2 as pressure gas and with NO_2 in synthetic air at 800 mbar and 200 mbar. Fig. 4 shows the result

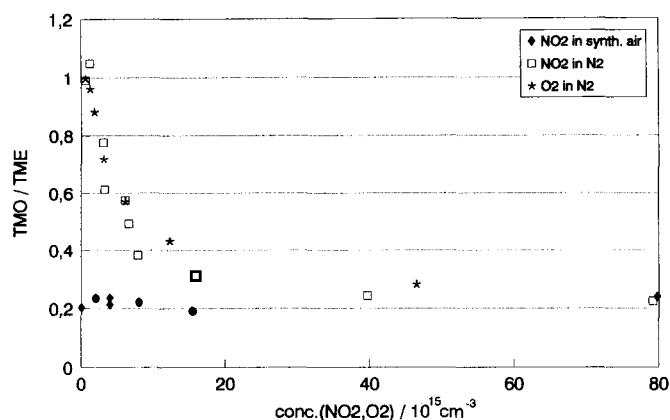


Fig. 4
Plot of oxirane yield vs. concentration of added radical scavenger (O_2 or NO_2) at 800 mbar

at 800 mbar system pressure. In all cases in N_2 using scavenger concentrations lower than 10^{15} molecule cm^{-3} no noticeable influence was observed. With increasing scavenger concentration, however, the TMO yield decreases and converges to the value approximately observed in synthetic air at this pressure, cf. Fig. 2. O_2 as well as NO_2 react with the quenched adduct radical ((R4) and (R5)) in competition to the oxirane formation via (R3). As expected, increasing NO_2 amounts in air do not show an effect.

Kinetic Parameters

Using the reaction pattern above ratios of rate constants were estimated by nonlinear regression analysis. In the case of the investigations in synthetic air (cf. Fig. 3) the channels (R3) and (R5) are negligible. The oxirane yield is given by:

$$\frac{[TMO]}{[TME]_{\text{reacted}}} = \frac{1}{1 + k_2[M]/k_1}, \quad [M] \rightarrow \text{synth. air}$$

and $k_2/k_1 = (1.75 \pm 0.19) \cdot 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$. The values $k_2[M]/k_1$ correspond to common S/D data (stabilization/decomposition). With the gas kinetic collision frequency of $5.12 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [12] applied for k_2 it is possible to estimate the unimolecular rate constant $k_1 = 2.9 \cdot 10^9 \text{ s}^{-1}$. In nearly the same way and by using the known k_2/k_1 ratio, the rate constant ratios k_4/k_3 and k_5/k_3 were estimated from experimental data with O_2 or NO_2 in N_2 as pressure gas at 800 mbar respectively, cf. Fig. 4. A compilation is given in Table 1. The errors given are one standard deviation.

From the ratios k_4/k_3 and k_5/k_3 the ratio $k_5/k_4 = 1.5 \pm 0.7$ is estimated. The rate constants of the reaction of the 2,3-dimethyl-3-nitroso-butyl-2 radical with NO_2 and O_2

Table 1
Compilation of ratios of rate constants (R) obtained

	$R/\text{cm}^3 \text{ molecule}^{-1}$	P/mbar	carrier gas
k_2/k_1	$(1.75 \pm 0.19) \cdot 10^{-19}$	25–944	synth. air
k_4/k_3	$(1.30 \pm 0.34) \cdot 10^{-16}$	800	N_2
k_5/k_3	$(2.01 \pm 0.74) \cdot 10^{-16}$	800	N_2
k_5/k_4^*	1.5 ± 0.7	800	N_2

*) dimensionless quantity.

are approximately the same. Baulch et al. [13] determined the rate constant ratios of the reaction of primary and secondary alkyl radicals with NO_2 and O_2 , respectively. Values of 14.7 ± 0.6 (prim.) and 4.5 ± 0.2 (sec.) were found for n-butyl radicals. Our result of 1.5 ± 0.7 in the case of the tertiary alkyl radical (2,3-dimethyl-3-nitroso-butyl-2 radical) is in a good agreement with the trend expected.

The present investigations of the system nitrate radical/TME are a case study. Our experimental results in the case of other substituted alkenes show that a generalization of these results is not possible. More information will be presented in a forthcoming publication [14].

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