

LABORATORY FTIR STUDIES OF THE REACTIONS BETWEEN NO₃ AND ALKENES

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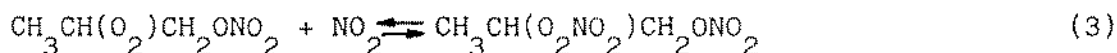
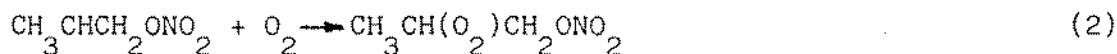
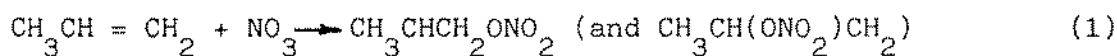
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1. INTRODUCTION

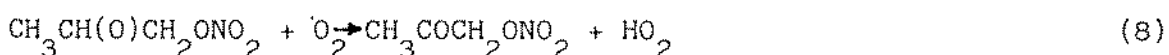
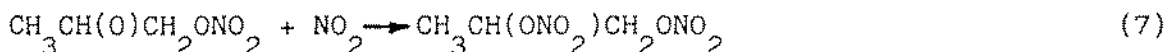
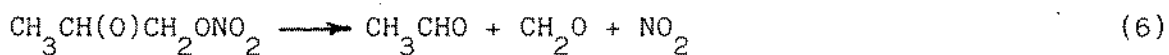
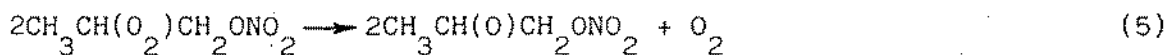
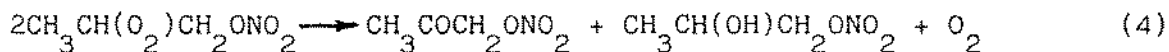
NO₃ radicals react with olefinic hydrocarbons with rate constants in the range 10⁻¹¹ (e.g. 2,3 dimethylbutene) to 10⁻¹⁶ (ethene); the biogenic terpenes seem to be particularly fast reacting (Finlayson Pitts and Pitts, 1986).

The product formation has been studied only in the case of propene (e.g. Oshino et al. 1978; Bandow et al. 1980; Shepson et al. 1985). The first reaction steps are found to be:

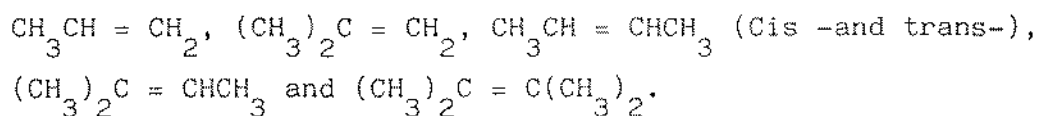


when the reaction takes place in air in the presence of NO₂. The subsequent reaction steps lead to the formation of formaldehyde, acetaldehyde, 1,2 propyleneglycol dinitrate, hydroxy-nitrate and nitroxy-carbonyl compounds. The previous studies, however, disagree on the nature of the nitrates and the main reaction pathways leading to their formation.

The proposed elementary reactions leading to the above-mentioned products are the following:



In the present work the product formation by reactions between NO₃ and alkenes in air in the presence of NO₂ is studied for a series of alkenes with different substitution around the double bond:

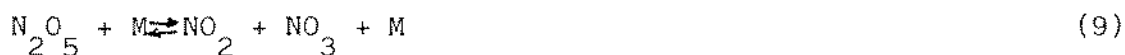


The formation of products is followed by FTIR with the aim of establishing the relative importance of the different reaction pathways and their dependence on the structure of the hydrocarbon.

2. EXPERIMENTAL TECHNIQUES

The experiments were carried out in a 480L cylindrical cell made of a 60 cm diameter 150 cm long Teflon coated Duran glass tube closed by Teflon coated aluminium flanges. The reaction chamber is equipped with a White type multiple reflection mirror system set to a total beam path of 80 m and connected to a Bruker 113 V FTIR spectrometer.

NO_3 was provided by the thermal equilibrium



N_2O_5 was introduced either by mixing NO_2 and O_3 in the reaction chamber or by adding it with a stream of air from a cold trap to the chamber.

The variations of concentrations of reactants and products were followed by recording a series of spectra at 1 cm^{-1} resolution.

3. RESULTS AND DISCUSSION

The course of a typical experiment is shown by the sequence of spectra in Figure 1. After the initial build-up of nitroxyperoxy-nitrate compounds (reactions 1-3), a slow decay of these and a build-up of carbonyl compounds is seen. Eventually the pernitrate bands disappear while bands showing the presence of organic nitrates remain.

The kinetics of the decay of the peroxyxynitrate intermediate was analysed in the case of 2,3 dimethyl-1-butene. In the situation where no N_2O_5 (and thus no NO_3) was present and NO_2 was large enough to remain essentially constant, the decay reaction was found to be second order in the pernitrate (and then also in the peroxyradical). This supports the hypothesis of reaction 6 and indicates that a possible wall decay must be of minor importance.

The pernitrate decay was found to be enhanced in the presence of N_2O_5 / NO_3 , which could be explained by a reaction between NO_3 and the

peroxyradical, e.g.



This was further supported by the observation that NO_2 was formed in larger amounts than could be explained by reactions 3 and 6.

A full identification of the organic nitrate compounds has not yet been done, but some qualitative information can be derived. Table 1 shows the yield of simple carbonyl compounds (e.g. acetone) and of organic nitrates (estimated as the area of the band at $\sim 850 \text{ cm}^{-1}$).

TABLE I	α	β	$\overline{[\text{NO}_2]}$ (ppm)
$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	0.1 - 0.2	0.8 - 0.9	8 - 12
$\text{CH}_3\text{CH}=\text{CHCH}_3$	0.7 - 1.3		7 - 13
$\text{CH}_3\text{CH}=\text{CH}_2$	0.8 - 1.1	0.1 - 0.2	6 - 24
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	0.6 - 1.4	0.3 - 0.5	4 - 15

Yield of organic nitrates and of simple carbonyl compounds vs consume of hydrocarbon;

$\alpha = (\text{integrated } -\text{ONO}_2 \text{ band at } \sim 850 \text{ cm}^{-1}) / \overline{[\text{hydrocarbon}]}$

$\beta = (\text{yield of simple carbonyl compounds}) / \overline{[\text{hydrocarbon}]}$

The most pronounced difference seen in Table 1 is that between 2,3-dimethyl-2-butene and the remaining hydrocarbons, the nitrate yield for 2,3-dimethyl-2-butene being relatively low. This can be explained by the lack of H-atoms adjacent to the double bond in 2,3 dimethyl-2-butene, which precludes reactions 6 and 8. Another possible explanation could be a different stability of tertiary, secondary and primary alkoxy radicals; the 2,3-dimethyl-2-butene reaction can only lead to the formation of tertiary alkoxy radicals. The importance of H-abstraction reactions is, however, brought into evidence also by the observation that the organic nitrate yield was found to be not significantly correlated to the NO_2 concentration in the propene experiments. Reaction 7 then must be of little importance and the organic nitrates found should be formed mainly via reactions 4 and 8, when H-abstraction reactions are possible.

References

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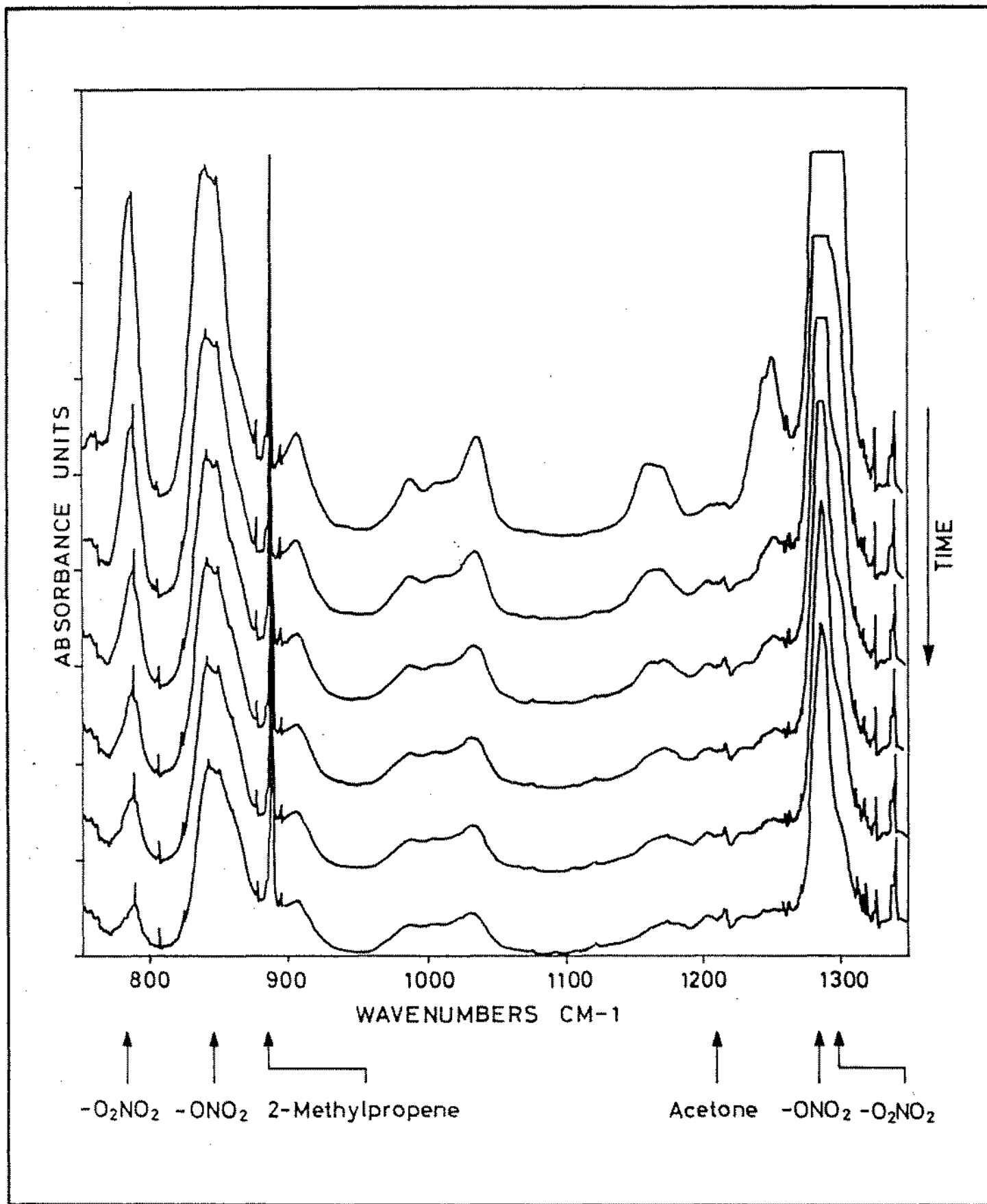


Fig. 1. Sequence of spectra recorded with 20 min. interval during the reaction of 2-methylpropene with NO_3 in zero air in the presence of NO_2 . The bands attributed to O_2NO_2 and ONO_2 groups and that of acetone are indicated.