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# ONIUM SALTS AS CATALYSTS IN THE LIQUID-PHASE OXIDATION OF CYCLOHEXENE OR TETRALINE BY $N_2O$

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## Abstract

The liquid-phase oxidation of cyclohexene or tetraline with $N_2O$ was studied in various solvents in the presence of onium salts or without them. The onium salts exerted significant promoting effect on the reactions. The activation of the oxidant was studied by IR spectroscopy. It was found that the interactions of the ions in the onium salts and the polarised N–O bond further enhanced polarisation leading to an activation of the oxidant, thus, increasing the rate of oxidation.

**Keywords:** liquid-phase oxidation; $N_2O$ activation; onium salts; cyclohexene; tetraline; promoting effect.

## Introduction

$N_2O$ could be an environmentally benign oxidation agent, since upon providing the useful product(s) after oxygen transfer $N_2$ is only formed. However, it is a sluggish reactant in both gas-phase and liquid-phase oxidations: high pressures (53-120 bar) and high temperatures (150-250 °C) are required, for a recent review, see ref. [1]. Nevertheless, it is an oxidant of interest for the chemical industry as well [2, 3].

Research in this area is going on, recently, a chemoselective catalyst ($Ru^{IV}$-$Co^{III}$ oxides supported on $\gamma$-$Al_2O_3$) was developed for the oxidative preparation of aldehydes and ketones from saturated and unsaturated primary and secondary alcohols using $N_2O$. Still, the reactions only proceed under pressure (10 bar) and at relatively high temperature (110 ˚C) [4]. Under forcing conditions (200 ˚C or higher, 25 bar total pressure) cyclic alkenes could be oxidised to cyclic ketones [5] without promoters.

In our hands, however, the liquid-phase oxidation of cyclohexene or tetraline with $N_2O$ took place under mild conditions (70 °C, 1 bar) with appreciable rate in the presence of onium salts. The onium salts were proved to be necessary and choice of solvent was found to be critical. Kinetic investigations are detailed elsewhere [6], here we report on results acquired during studying the interactions between the oxidant, the onium salt and the solvent by IR spectroscopy.

## Experimental

The onium salts ($Hex_4NCl$ and $Me(Oct)_3NCl$), the solvents (chlorobenzene, acetonitrile, diethyl carbonate and $CCl_4$), cyclohexene and tetraline were the products of

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Aldrich Co and were used without further purification. The oxidant $N_2O$ (Ph. EUR 4 grade) was supplied by Linde Co. The $O_2$ content was < 0.03% by gas chromatography (5A molecular sieve column). The presence of traces of $O_2$ in $N_2O$ is an indication that not even traces of NO can be present, because NO would react with $O_2$ instantly.

The reactions were performed in the liquid phase at 70 °C at atmospheric pressure. Samples were withdrawn after 2 hours and the concentrations of the reactants and the products were determined by gas chromatography. Identification was performed using authentic samples of the compounds (both the products and the reactants).

For studying the possible interactions between the onium salt and $N_2O$ in various solvents a BIORAD Digilab FTS-65/896 spectrometer equipped with a DTGS detector was used. The resolution was 4 $cm^{-1}$ and 128 scans were collected for a spectrum. Changes in the positions and band areas of N-O stretching ($\nu_1$), the $\nu_2$ deformation and the N-N stretching ($\nu_3$) vibrations were monitored. Spectral evaluations were done with the WinIR package. Before measurements the solvents were purged with $N_2$ for 5 min to remove traces of $O_2$. Then, the $N_2$ atmosphere was fully replaced by $N_2O$, the gas burette was connected, the oxidant was allowed to dissolve at atmospheric pressure under intense stirring for 5-10 hours, and the gas uptake was noted.

The $N_2O$ stock solutions could be stored without notable change under a protecting $N_2O$ blanket (at atmospheric pressure) in a closed vessel for at least 1-2 days. However, the $N_2O$ concentration dropped immediately when the vessel was opened. To avoid $N_2O$ loss when these solutions were diluted or mixed with onium salt solutions and also when the IR cell was filled, the stock solution in the reactor was passed via a siphon fitted with a 3-way tap either to the IR cell, or to a 4 $cm^3$ mixing syringe. The syringe initially contained 2.00 $cm^3$ solvent or onium salt solution, to which 2.00 $cm^3$ $N_2O$ stock solution was added at atmospheric pressure. After thorough mixing, the IR cell was filled from the mixing syringe.

## Results and discussion

As far as reaction rates are concerned chlorobenzene and $CCl_4$ proved to be the best solvents (Table 1).

The reactions were negligible or very slow in acetonitrile and diethyl carbonate. Moreover, these solvents were not transparent in frequency ranges important in studying $N_2O$ vibrations (see later), therefore, these systems were excluded from further considerations. The products in the remaining two solvents were cyclohexene oxide (chex-ox) and 2-cyclohexene-1-ol (chex-ol) from cyclohexene, α-tetralone (tetr-one) and α-tetralol (tetr-ol) from tetraline. Cyclohexene could be oxidised without onium salts in chlorobenzene and the products were the same as in the their presence. However, the reaction was much faster when onium salts were added. In $CCl_4$ only the alcohol could be detected and only in very minute amount without onium salts. Tetraline could not be oxidised in any of the solvents without onium salts. Oxidation of this compound was found to be selective. The oxo (tetr-one) compound was only formed in chlorobenzene, while exclusively alcohol (tetr-ol) was identified in $CCl_4$. It was also observed that oxidation was accelerated considerably in $CCl_4$ containing trace amounts of water.

Table 1
Product distribution (in mmol) in the liquid-phase oxidation of cyclohexene and tetraline with $N_2O$ after 120 min reaction time
quantities of cyclohexene (chex) and tetraline (tetr) are 19.744 and 22.078 mmol, respectively; amount of the onium promoter is 0.024 mmol at the beginning of the reaction

| Hydrocarbon | Catalyst | Chex-ox | Chex-ol | Tetr-one | Tetr-ol |
|---|---|---|---|---|---|
| Chlorobenzene | | | | | |
| Chex | – | 0.053 | 0.068 | – | – |
| Chex | $Hex_4NCl$ | 0.084 | 0.130 | – | – |
| Chex | $Me(Oct)_3NCl$ | 0.064 | 0.410 | – | – |
| Tetr | – | – | – | 0.000 | 0.000 |
| Tetr | $Hex_4NCl$ | – | – | 0.821 | 0.000 |
| Tetr | $Me(Oct)_3NCl$ | – | – | 0.499 | 0.000 |
| $CCl_4$ | | | | | |
| Chex | – | 0.000 | 0.020 | – | – |
| Chex | $Hex_4NCl$ | 0.019 | 0.302 | – | – |
| Chex | $Me(Oct)_3NCl$ | 0.009 | 0.164 | – | – |
| Tetr | – | – | – | 0.000 | 0.000 |
| Tetr | $Hex_4NCl$ | – | – | 0.000 | 2.585 |
| Tetr | $Me(Oct)_3NCl$ | – | – | 0.000 | 1.076 |

chex-ox – cyclohexene oxide, chex-ol – 2-cyclohexene-1-ol, tetr-one – α-tetralone, tetr-ol – α-tetralol

During the reaction the bonding system of $N_2O$ should change. Since the reaction rate is only appreciable in the presence of onium salts, the interaction between the ion pair and the $N_2O$ molecule should initiate this change. Infrared spectroscopy is an appropriate tool to detect it. The fundamental frequencies of $N_2O$ are collected in Table 2 in the gas phase as well as in the solvents used in this study. Fortunately, the solvents where the reaction rates were appreciable (chlorobenzene and $CCl_4$) are transparent in the frequency ranges of fundamental vibrations.

Table 2
Wavenumbers for the fundamental peaks of $N_2O$

| | Fundamental frequencies ($cm^{-1}$) | | |
|---|---|---|---|
| | N–N- stretch. ($\nu_3$) | N–O stretch. ($\nu_1$) | deform. ($\nu_2$) |
| | ←N—N→—<br>←O | ←N–<br>←N——O→ | ↑<br>N—N——O<br>↓ ↓ |
| Gas phase | 2224 | 1285 | 589 |
| Chlorobenzene | 2218 | 1281 | 583 |
| Acetonitrile | –[a] | 1284 | 586 |
| Diethyl carbonate | 2224 | –[b] | 585 |
| $CCl_4$ | 2218 | 1281 | 586 |

a – severely disturbed by the strong self-absorption of the solvent
b – could not be detected

It is to be seen that the frequencies do not change significantly on going from the gas phase to any of the solvents used. It was also observed that their positions remained the same when onium salts were present, however, the intensities of the $\nu_1$ fundamental vibration were very much altered with the addition of the onium salts, while the other two hardly changed.

Figure 1 allows the comparison of the IR spectra of the $N_2O$ solution with and without the onium salts and Table 3 summarises the ratios of the band areas at various onium salt concentrations for both promoters.

Data reveal that in chlorobenzene the $\nu_1$ band disappears and in $CCl_4$ greatly diminishes. At the same time, apparently nothing happens with the two other fundamental vibrations. These observations indicate that the N–O bond disruption is promoted by ion-pair formation between the cation of the onium salt and its counter ion at the O-end and the N-end of the N–O bond, respectively.

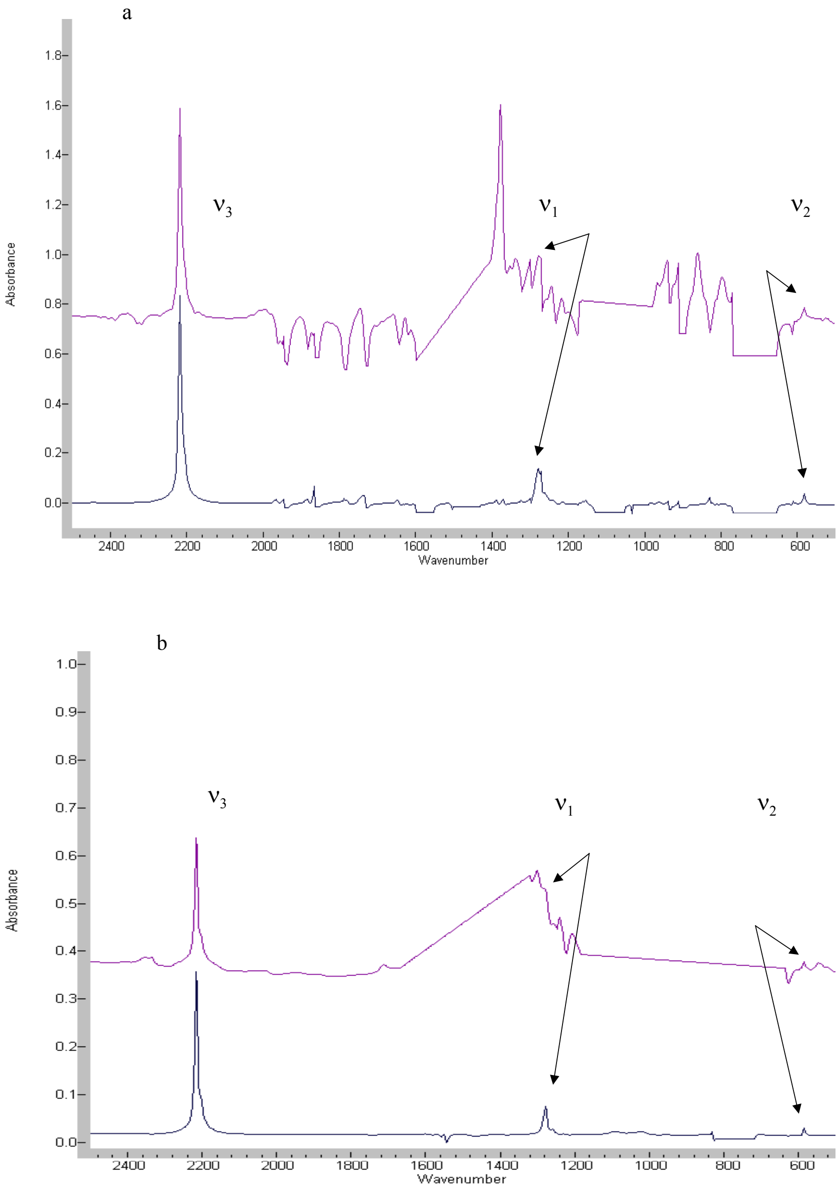


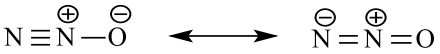
Fig. 1. IR spectra for $N_2O$ with (upper curve) and without onium salts (lower curve) in (a) chlorobenzene and (b) $CCl_4$

Table 3
Ratios of fundamental $N_2O$ IR band areas in the presence of promoter onium salts or without them using various solvents

| Promoter | Concentration (mol/dm$^3$) | Ratio of band areas | |
|---|---|---|---|
| | | $A_{\nu 3}/A_{\nu 1}$ | $A_{\nu 3}/A_{\nu 2}$ |
| in chlorobenzene | | | |
| – | 0 | 9.6 | 40.0 |
| $Hex_4NCl$ | 0.153 | –[a] | 46.6 |
| $Me(Oct)_3NCl$ | 0.153 | –[a] | 48.9 |
| in $CCl_4$ | | | |
| – | 0 | 6.0 | 40.3 |
| $Hex_4NCl$ | 0.155 | 20.3 | 48.1 |
| | 0.197 | 15.0 | 50.0 |
| $Me(Oct)_3NCl$ | 0.0214 | 24.0 | 48.0 |
| | 0.143 | 19.1 | 51.0 |

a – the $\nu_1$ band disappeared

The resonance theory representation of $N_2O$ (Scheme 1) places charges even onto the undisturbed molecule.



$$N\equiv\overset{\oplus}{N}-\overset{\ominus}{O} \longleftrightarrow \overset{\ominus}{N}=\overset{\oplus}{N}=O$$

Scheme 1. Limiting structures for $N_2O$ according to resonance theory

The inner nitrogen holds the positive charge in either limiting structure, while the negative charge can be located either on the terminal nitrogen or the oxygen. Thus, the anionic part of the onium salt surely will interact with the inner nitrogen, while both ends might interact with the cation. Since change was only found with the $\nu_1$ fundamental vibration, therefore it is safe to state that the cation interacts with the oxygen.

In the reaction mixture (where the hydrocarbon, the onium salt, the solvent as well as $N_2O$ are present) the terminal nitrogen somehow interacts with the double bond or one of the double bonds of these molecules. This interaction ceases by the end of the reaction since $N_2$ evolution occurs and at the same time or close to it the products are formed.

## Conclusions

The experimental results indicated that the interactions between the cation and the counter anion of the onium salts with the N–O bond in $N_2O$ significantly contribute to the activation of the molecule. The activated moiety reacts in the oxidation reactions of cyclohexene as well as tetraline under mild conditions.

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