

ADVANCED SUBSIDIARY GCE

CHEMISTRY B (SALTERS)

F332/ADVANCE NOTICE

Chemistry of Natural Resources: Advance Notice article

For issue on or after:

17 NOVEMBER 2010

Thursday 20 January 2011

Afternoon

Duration: 1 hour 45 minutes



NOTES FOR GUIDANCE (CANDIDATES)

- 1 This leaflet contains an article which is needed in preparation for a question in the externally assessed examination F332.
- 2 You will need to read the article carefully and also have covered the learning outcomes for Unit F332 (*Chemistry of Natural Resources*). The examination paper will contain questions on the article. You will be expected to apply your knowledge and understanding of the work covered in Unit F332 to answer these questions. There are 20 marks available on the paper for these questions.
- 3 You can seek advice from your teacher about the content of the article and you can discuss it with others in your class. You may also investigate the topic yourself using any resources available to you.
- 4 You will **not** be able to bring your copy of the article, or other materials, into the examination. The examination paper will contain a fresh copy of the article as an insert.
- 5 You will not have time to read this article for the first time in the examination if you are to complete the examination paper within the specified time. However, you should refer to the article when answering the questions.

This document consists of **8** pages. Any blank pages are indicated.

INSTRUCTION TO EXAMS OFFICER / INVIGILATOR

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Understanding our Changing Atmosphere

Adapted from 'Understanding our Changing Atmosphere'
Educ. Chem. 2007

Chemical processes occurring in the atmosphere determine current and future atmospheric compositions, which in turn affect climate, air quality, and the spread of pollution. What are these processes and can they help us understand the likely impacts of climate change upon atmospheric conditions?

William Bloss

While the bulk of our atmosphere is made up of nitrogen, oxygen, carbon dioxide and water vapour, atmospheric chemistry is dominated by reactions of trace constituents, specifically gas phase radicals, present in parts per million (ppm), billion (ppb) or even trillion (1 part in 10^{12}). Through chain reaction cycles, these highly reactive compounds control the levels of the more abundant species in the atmosphere.

Tropospheric chemistry

The basic chemistry of the first 10–15 km of our atmosphere, the troposphere, is dominated by the reactions of hydrocarbons with hydroxyl radicals ($\bullet\text{OH}$), see **Scheme 1**. Ozone (O_3) is broken down by sunlight, leading to high-energy oxygen atoms, which may be stabilised by colliding with nitrogen or oxygen molecules, or may react with water vapour to form two $\bullet\text{OH}$ radicals. The $\bullet\text{OH}$ radicals then react with hydrocarbons to form organic peroxy radicals ($\text{RO}_2\bullet$) – for example, $\text{CH}_3\text{O}_2\bullet$ is

formed when an $\bullet\text{OH}$ reacts with methane in the presence of dioxygen.

What happens next depends upon the availability of the nitrogen oxide radicals, $\text{NO}\bullet$ and $\text{NO}_2\bullet$ (collectively called ' NO_x '). The main source of NO_x is the combustion of fossil fuels – atmospheric scientists refer to low NO_x environments, e.g. the remote atmosphere over the Pacific Ocean, as 'clean' and high NO_x environments, e.g. cities, as 'polluted'.

In the presence of NO_x , organic peroxy radicals (e.g. $\text{CH}_3\text{O}_2\bullet$) can react with $\text{NO}\bullet$ (and dioxygen) to form $\text{HO}_2\bullet$ and methanal. $\text{HO}_2\bullet$ can react with another $\text{NO}\bullet$, forming $\text{OH}\bullet$ again. This can react with another methane and thus hydrocarbons are oxidised as part of a propagating chain. This is shown in **Scheme 1**. Notice that the $\text{NO}_2\bullet$ can be broken down by photolysis forming $\text{NO}\bullet$ (to take part in the cycle again) and oxygen atoms that can form more ozone.

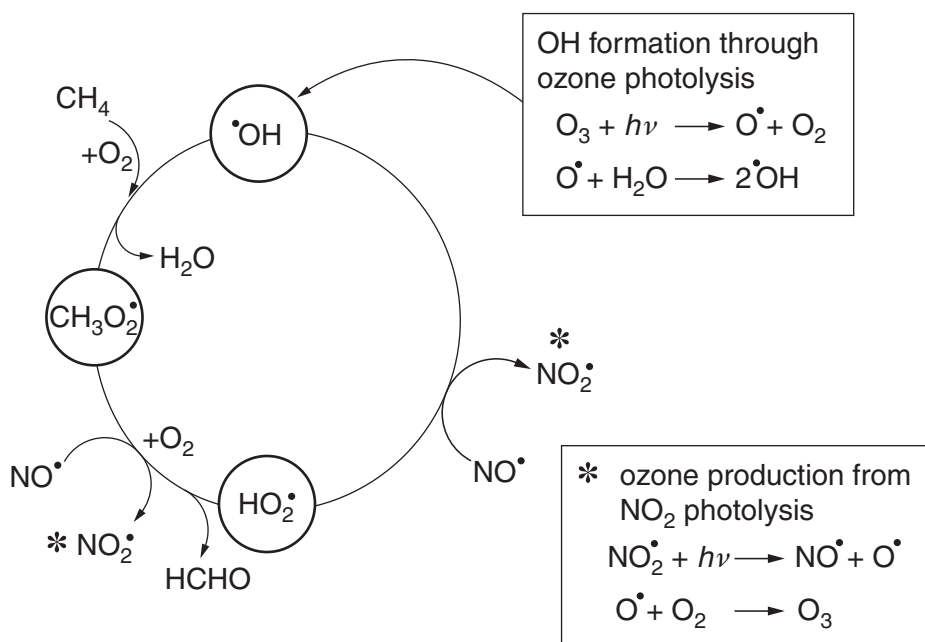
Impacts of tropospheric chemistry

The chemical processes shown in **Scheme 1** control many aspects of atmospheric composition: reaction with $\bullet\text{OH}$ dominates the removal of most pollutants emitted to the atmosphere, determining their lifetime and abundance. Tropospheric $\bullet\text{OH}$ levels thus regulate the self-cleansing ability, or oxidising capacity, of the atmosphere, and control the levels of greenhouse gases such as CH_4 . (Note CH_4 is the second most significant greenhouse gas after CO_2 ; CO_2 does not react with $\bullet\text{OH}$.)

This behaviour has been used advantageously in the case of hydrochlorofluorocarbons (HCFCs), such as CHF_2Cl , the hydrogenated replacements for chlorofluorocarbons (CFCs, such as CF_2Cl_2), introduced in the 1980s and 1990s to prevent stratospheric ozone loss. The $\bullet\text{OH}$ reacts with HCFCs by removing the H atom to form water, leaving an alkyl radical, which then undergoes further breakdown in the atmosphere. So HCFCs are removed in the lower atmosphere, while CFCs pass unimpeded to the stratosphere.

Tropospheric chemistry also affects air quality. Oxidation of hydrocarbons such as methane, carbon monoxide and larger molecules such as volatile organic compounds (VOCs) in the presence of NO_x leads to the production of ozone, see **Scheme 1**. This is important because ozone is both a greenhouse gas, contributing to climate change, and a major constituent of the photochemical smog observed over many cities during summertime, which is harmful to human and animal health, vegetation and certain materials such as plastics.

Current UK National Air Quality strategy suggests a target level of 50 ppb for ozone. Mild health problems, owing to ozone inhalation, may become noticeable for sensitive individuals at levels of 50–90 ppb, requiring them to spend less time outdoors, while at levels over 90–100 ppb asthma sufferers may need to increase their use of an inhaler. For comparison, ozone levels in remote environments may be 5–10 ppb, typical background UK levels are around 30 ppb, while levels in Los Angeles in the late 1970s reached up to 500 ppb. Thus by understanding tropospheric atmospheric chemistry we can put forward strategies to improve air quality, such as identifying particular compounds with a high ozone creation potential, whose emissions should be controlled.



Scheme 1 A simplified diagram representing tropospheric oxidation chemistry.

Simulation chambers and field experiments

Our understanding of atmospheric chemistry has been developed through a combination of laboratory studies, field measurements and computer modelling. Laboratory experiments are used to determine the molecular properties (reaction rate constants and photolysis rates) governing the fate of individual atmospheric species. The results are used to design reaction mechanisms for specific species, which are then used in computer models of atmospheric chemistry. Comparisons of such models with field measurements of concentrations in the ambient atmosphere are then used to test the model, and refine the reaction mechanism as necessary.



A 'smog chamber' at the European Photoreactor (EUPHORE) in Valencia, Spain

'Smog chambers' or simulation chambers are used to study artificial atmospheres. The EUPHORE ('European Photoreactor') simulation chamber in Valencia, Spain, for example, comprises two 200m³ hemispherical reaction vessels, each about 4m tall, made from a (transparent) non-reactive polymer 'bag' 0.2mm thick. Each vessel has covers which can be raised to block sunlight, and houses a range of analytical instruments. Artificial atmospheric mixtures of a particular chemical system are introduced into the chambers and the photochemical reactions started by opening the covers and admitting sunlight. The resulting changing chemical composition is monitored.

Fig. 1, below, shows observed concentrations of NO₂ and NO (black lines) during an experiment to investigate benzene removal. This was obtained as part of the EXACT (Effects of the OXidation of Aromatic Compounds in the Troposphere) research project involving a consortium of scientists from European universities. The concentration of benzene falls because of its reaction with •OH, and the resulting increase in ozone levels through the reactions shown in **Scheme 1**. Also shown in the figure are the predictions (dotted lines) of an atmospheric model, the Master Chemical Mechanism, which agree well with the observations, giving us confidence in the reaction mechanisms.

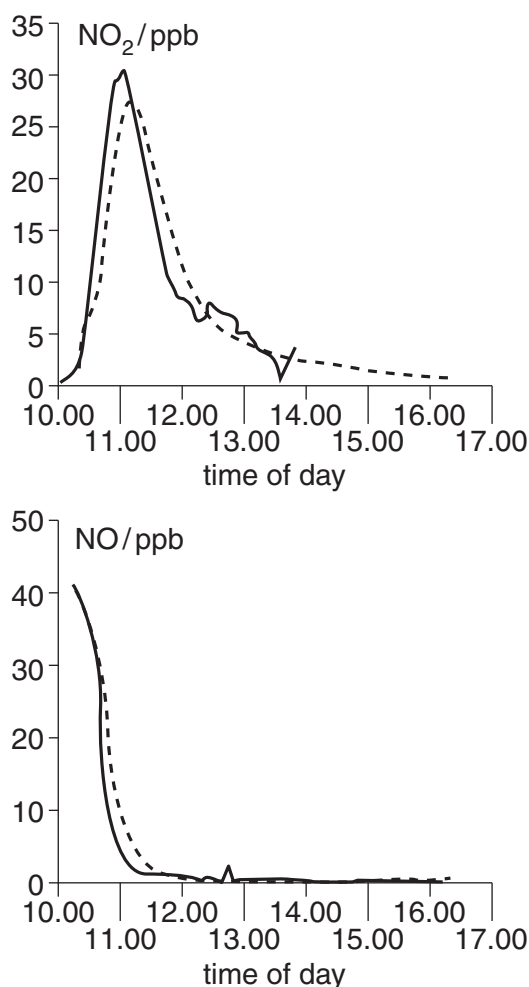


Fig. 1 Observed (black lines) and simulated (dotted lines) concentrations of NO₂ and NO during EUPHORE experiments

Another approach involves taking a range of measurements of as many of the atmospheric reactants as possible at a particular location over a short time, typically 4–6 weeks. This often involves teams of scientists from different institutions, specialising in a variety of measurement techniques. The data acquired are then compared with calculations and model predictions. Consider, for example, $\bullet\text{OH}$, one of the most highly reactive radicals. The lifetime of $\bullet\text{OH}$ is extremely short, typically 0.1–2s, in the lower atmosphere. Thus $\bullet\text{OH}$ concentrations are determined by local chemical production and loss, rather than transport, in other words $\bullet\text{OH}$ is not blown to a particular location from elsewhere. This behaviour allows us to use observations of very short-lived species like $\bullet\text{OH}$ to test our understanding of the chemistry. We suggest a chemical mechanism based upon our best knowledge, measure the levels of (comparatively) long-lived species such as O_3 , NO_x and VOCs, use the mechanism to calculate the levels of short-lived species based upon measurements of those with longer lifetimes, and compare the resulting calculations with measurements of $\bullet\text{OH}$ etc.

This approach eliminates the need to worry about the transport of atmospheric constituents by winds.

Model studies based upon our current understanding of atmospheric chemistry, and estimates of likely future emissions under various scenarios, predict the change in tropospheric ozone levels which might be expected in the future. Surface ozone levels at mid-latitudes are predicted to rise by approximately 30 ppb by 2100 – an increase which will lead to background ozone levels being comparable to the limits set in current air quality standards. If these predictions are borne out, people's health in polluted regions will be adversely affected – and the improvements in air quality observed in many Western nations over the past few decades may be reversed (as far as ozone is concerned) in the future.

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