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Potential of electrophilic epoxide reactions for the monitoring of acid gases in the environment

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Abstract

Mineral and short-chain carboxylic acid vapours and NO_x gases were reacted with cyclohexene oxide (1,2-epoxycyclohexane) to quantitatively produce specific, thermally stable cyclohexyl derivatives. Subsequent analysis of these derivatives by gas chromatography with mass spectroscopy and flame ionisation detection afforded a multi analyte method for the assay of these gaseous acidic atmospheric species. Derivatisation was found to be quantitative for the derivatives tested and the method highly sensitive (to 0.3 mg/m³ for a 30 l sample), accurate, precise and free from apparent interferences. The technique has been applied to “acid stack gases” and a number of other acid rich atmospheres and the results obtained show good agreement with the single analyte wet chemical determinations indicating that the approach has considerable potential as a routine analytical method for measuring such atmospheric pollutants. The high specificity of the reaction mechanism and its potential for the analysis of analyte mixtures is illustrated in the assay of nitric acid and its acid anhydride, dinitrogen pentoxide.

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1. Introduction

Acidic gases and vapours are released from a wide range of industrial processes as primary emissions, or from the manipulation and treatment of wastes and power production [1]. In the UK and reflected in regulatory regimes elsewhere, increasing legislative control has been applied to the release of oxides of nitrogen, sulfur and carbon from both point and diffuse sources [2,3]. In addition, the acidic nature of

many species means that plant durability can be a costly consideration in the overall management of an industrial site. As a consequence, there is considerable interest and demand for techniques that reliably and cost-effectively allow the monitoring of released compounds.

Monitoring of gaseous emissions is generally performed either by continuous/remote analysis or by discrete sample collection. For common acidic gases, a number of continuous instrumental devices, indicator systems or discrete wet chemical analyses are available [4,5]. Typical devices include a wet-rotating annular denuder filled with an absorption solution connected to an ion chromatographic sys-

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tem. This system continuously measures air concentrations of HCl and HNO_x [6]. Absorption efficiency is often improved by the use of bubblers which allow high sample flow-rates with minimal pressure fall as opposed to standard impingers which limit flow-rate due to a pressure [7]. The monitoring method for acid gases will be dependent on the likely levels and need for regulatory control.

Reported herein is the study and evaluation of the potential of an organic derivatisation reaction for application in the quantification of important industrial feedstock and waste products, namely mineral acids—HF, HCl and HNO₃, associated acid gases and organic acids (Fig. 1). The system studied is based on the reaction of an electrophilic cyclic epoxide (cyclohexene oxide) with a variety of such acidic molecules.

Epoxides or oxiranes are more reactive than their ether analogues, mainly due to the high degree of bond strain present thus enabling reaction with many strong nucleophiles. Indeed it is well documented that many epoxides react with halohydrin acids to yield halohydrin derivatives and that strained cycloalkyl epoxides are especially reactive in this respect [7]. In practice epoxides are cleaved under acid conditions, the incipient oxonium ion undergoing subsequent attack by the parent nucleophile. It has been reported [8] on the basis of the stereochemistry, inversion occurring at the site of attack, that the reaction proceeds via an S_N2 mechanism though some acid solvolysis reactions proceed via an S_N1 mechanism proceeding via the formation of a carbocation intermediate. This derivatisation reaction was utilised by Colgan and Krull [9] when they reacted picric acid salts with cyclohexene oxide and analysed the resulting cyclohexyl-picryl derivatives by high-performance liquid chromatography (HPLC).

The current study was directed specifically at determining whether the epoxide chosen would

quantitatively react with organic as well as mineral acids. A further aim was to investigate mixtures of these acid components that were reacted to produce discrete cyclohexyl derivatives which through gas chromatographic analysis would afford a method for quantitative assay of these analytes and their mixtures.

2. Materials and methods

2.1. Preparation of acid derivatives

The same general preparative method was used for preparation of all mineral acid derivatives. Changes were made to the method for preparation of carboxylic acid derivatives. All solvents (Aldrich, UK) were redistilled and dried with calcium chloride (Aldrich) and all glassware was oven dried for 24 h prior to use. The acids were supplied by Fluka except for N₂O₅ which was supplied by Nobel Explosives ICI, Ardeer, Stevenston, UK.

For preparation of the nitric acid, dinitrogen pentoxide, hydrochloric and hydrofluoric acid derivatives, the acids were dissolved in 50 cm³ of dichloromethane and cooled to about 0 °C. A solution of cyclohexene oxide (Aldrich) in dichloromethane (20%, v/v) was added slowly while stirring. The reaction mixture was then neutralised with sodium hydrogencarbonate. The dried (sodium sulfate) dichloromethane liquors were filtered and the solvent and excess cyclohexene oxide removed under vacuum to leave the product.

The acetic acid and propanoic acid derivatives were prepared in the same way only applying ultrasound to the reaction mixture for 20 min and using 40% (v/v) cyclohexene oxide in dichloromethane.

2.2. Characterisation of acid derivatives

The acid derivatives were characterised using infra-red (Perkin-Elmer 782, Perkin-Elmer 3600 data station), ¹H and ¹³C nuclear magnetic resonance (NMR) spectrometry (Jeol 90 MHz) and gas chromatography–mass spectrometry (GC–MS, Hewlett-Pac-

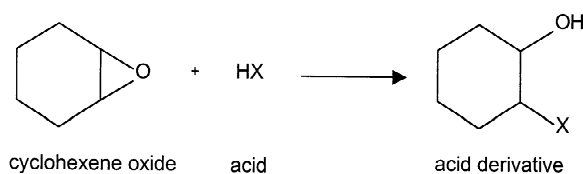


Fig. 1. Reaction of cyclohexene oxide with acids.

kard 5890 series II gas chromatogram coupled with a 5971 mass-selective detector).

For GC–MS analysis 1 μl of dichloromethane reaction liquor was injected in the split mode (20:1) with the MS system maintained at 280 °C and an injection temperature of 250 °C. A BP 20 column (30 m \times 0.25 mm, 0.33 μm) was heated from an initial temperature of 150 °C at 10 °C/min to a final temperature of 200 °C and held for 7 min. Helium was employed as carrier gas at a head pressure of 7 p.s.i. (0.6 ml/min, 29.3 cm/s; 1 p.s.i.=6894.76 Pa).

2.3. Applications

2.3.1. Qualitative analysis of a complex acid mixture

An acid mixture of HNO_3 (0.5 g), N_2O_5 (0.5 g) and HCl (0.1 g) was dissolved in 50 ml dichloromethane and a solution of 5 ml cyclohexene oxide in dichloromethane (20%, v/v) was added and allowed to react and analysed by GC–MS as described in Section 2.2.

2.3.2. Quantitative analysis of HCl in a fume cupboard atmosphere

Hydrochloric acid (4 M, 20 ml) was boiled on a hotplate in a fume cupboard for 10 min. The resultant fume cupboard atmosphere was sampled using a sample pump at a flow-rate of 1 l/min to draw air through an impinger containing cyclohexene oxide in dichloromethane (20%, v/v, 10 ml). A total of 30 l of air was sampled. A range of calibration standards (0.1–1000 mg/l) were prepared from the previously synthesised acid derivative. The reaction product was analysed by GC–FID using a HP 17 (10 m \times 0.25 mm, 0.33 μm) capillary column. A 1 μl sample was injected at 200 °C was heated from an initial temperature of 80 °C at 10 °C/min to a final temperature of 200 °C when the analysis was terminated. A carrier gas pressure of 4.2 p.s.i. (25.5 cm/s) was employed and the detector temperature was maintained at 220 °C.

Quantitative GC analysis was undertaken by injecting 1 μl of standard or sample in split mode (20:1) with injection and detector temperatures set at 200 °C. A HP 20 column (10 m \times 0.25 mm, 0.33 μm) was heated from an initial temperature of 80 °C at

10 °C/min to a final temperature of 200 °C. Helium was employed as carrier gas at a head pressure of 4.2 p.s.i.

2.3.3. Quantitative analysis of NO_x in a nitrator stack atmosphere

The NO_x atmosphere generated inside a nitrator stack of a nitrocellulose production unit was sampled (Nobel Explosives ICI). A scrubber solution of 1% hydrogen peroxide in water was used to oxidise the NO_x present to nitric acid on contact with water. Cyclohexene oxide in dichloromethane (20%, v/v, 15 ml) was added and the layers interspersed by shaking vigorously for 5 min. The organic layer was isolated, dried (sodium sulfate) and final volume adjusted to 25 ml with dichloromethane. The solution was then analysed by GC–FID using the conditions described in Section 2.3.2 only using an initial oven temperature of 120 °C.

3. Results

The acid derivative products were fully characterised by means of GC–MS, IR and ^{13}C -NMR and the relevant spectroanalytical data are summarised in Table 1.

GC–MS data showed the nitric acid and dinitrogen pentoxide derivatives as having single sharp chromatographic peaks and corresponding mass spectra which are consistent with the fragmentation patterns for the expected product structures (Fig. 2). The GC–MS profile for the hydrochloric acid, acetic acid and propanoic derivatives all showed two peaks with identical mass spectra. This suggested these products were a mixture of stereoisomers in agreement with the ^{13}C -NMR analysis. The m/z values obtained from each of the mass spectra are consistent with the fragmentation patterns for the expected product structure in each case. GC–MS analysis of the hydrofluoric acid derivative was impractical due to the viscous and involatile nature of this derivative. However, analysis of this compound may be possible by HPLC due to a strong absorption band at 230 nm.

Infra-red spectroscopy clearly identified the functional groups present in each of the acid derivatives. Each of the derivatives displayed a strong peak at about 2900 cm^{-1} which was assigned as C–H

Table 1
Summary of derivative characterisation

Acid derivative	Mean reaction yield (%) ^a	<i>t</i> _R (min)	GC–MS characteristic ions	IR (cm ⁻¹)	¹³ C-NMR δ (ppm)
Nitric acid	95 (5)	3.6	116, 97, 81, 70	3400, 2900, 1600	25, 25.3, 30.3, 33.8, 71.9, 88.6
Dinitrogen pentoxide	92 (4)	2.8	144, 98, 46	2900, 1600	23, 29, 80
Hydrochloric acid	89 (5)	5.5 and 5.6	134/136, 116/118, 97/98, 81/82	3400, 2900, 750	24, 26, 33, 35, 67, 75
Hydrofluoric acid	89 (8)	*		3400, 2900	
Acetic acid	81 (7)	5.8 and 6.6	158, 141, 115, 98, 43	3400, 2900, 1700, 1250	164, 165, 170
Propanoic acid	76 (7)	6.9 and 7.7	173, 155, 115, 98, 57	3400, 2900, 1700, 1250	Three peaks at 170

*Analysis not possible by GC due to involatile nature of derivative.

^a Figures in parentheses represent the standard deviation of six replicate derivatisation reactions (*n*=6).

stretching due to the cyclohexane ring in each case. A peak at 3400 cm⁻¹ was present for each of the derivatives with the exception of dinitrogen pentoxide derivative. This peak was assigned as an O–H vibration due to the hydroxyl group. The fact that the dinitrogen pentoxide derivative had no O–H group present and a peak at 1600 cm⁻¹ due to an R–O–NO₂ group suggested that the dinitrate derivative had been formed.

An R–O–NO₂ group was also identified for the nitric acid derivative suggesting the hydroxy nitrate derivative had been formed. In addition to the C–H and O–H groups present the HCl and HF derivatives displayed peaks at 750 and 1100 cm⁻¹, respectively, corresponding to C–Cl and H–F bending vibrations. The IR spectra of the acetic acid and propanoic derivatives were very similar, both showing strong absorptions at 1700 and 1250 cm⁻¹ which were

assigned as C=O and C–O bonds, respectively, suggesting that both molecules were ester derivatives.

Further information on the structure of the acid derivatives was gained through the ¹³C spectra obtained for the derivatives. In agreement with the expected structures of the nitric and hydrochloric acid derivatives six ¹³C signals were detected indicating the presence of six different carbon environments. The dinitrogen pentoxide derivative gave rise to three ¹³C signals agreeing with the symmetrical structure of the proposed cyclohexane-1,2-dinitrate product.

The ¹³C spectrum of the acetic acid and propanoic acid derivatives were very similar. Three carbonyl peaks were present which suggested the products were mixtures. Two of the peaks were believed to be stereoisomers in each case as the peaks were very intense and in close proximity. The other peak was believed to be a side product in each case such as cyclohexane diacetate/dipropanoate. Limited information was obtained about the structure of the hydrofluoric acid derivative, as the ¹³C spectrum was too complex due to coupling with the fluorine atom.

The information gathered from IR, ¹³C-NMR and GC–MS allowed tentative structures to be assigned for each of the acid derivatives (Fig. 3). As the hydrofluoric acid derivative could only be characterised by IR the proposed structure is assigned tentatively.

3.1. Acid mixture

Fig. 4 shows the GC trace associated with the acid mixture. The peaks at 2.8 (1) and 3.6 (2) are

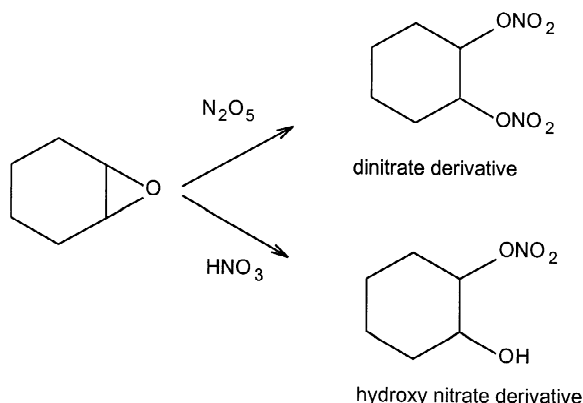


Fig. 2. Differentiation of nitric acid and dinitrogen pentoxide with cyclohexene oxide.

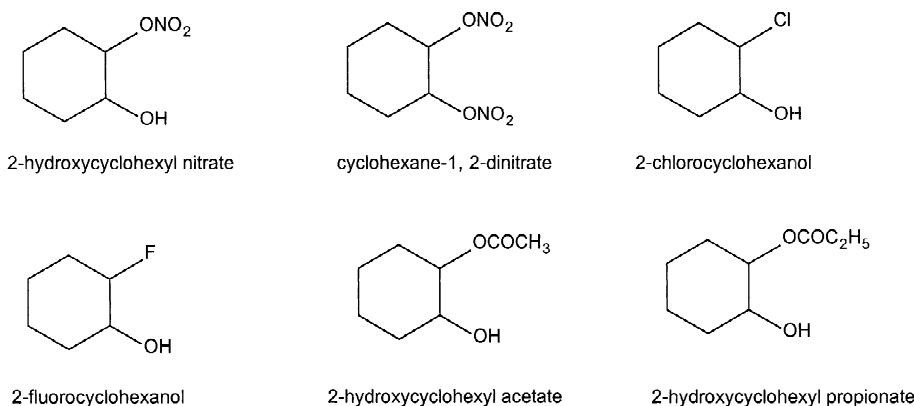


Fig. 3. Derivative structures proposed by GC–MS, IR and ^{13}C -NMR.

consistent with dinitrogen pentoxide and nitric acid derivatives, respectively. The peaks at 5.5 (3) and 5.6 (4) min were identified as stereoisomer peaks of hydrochloric acid. Mass spectra and retention times of these peaks were consistent with those of individual standards.

3.2. Quantitative analysis of HCl in fume cupboard atmosphere and method linearity

A plot of acid derivative peak areas (nitric and hydrochloric acids) against standard derivative concentrations gave excellent linear response with r^2 values of 0.999 and 1, respectively (analysis of variance, ANOVA, $P < 0.05$) with a detection limit of 1 mg/l in each case for FID (signal:noise ratio

$\geq 3:1$). This corresponds to an atmospheric detection limit for the HCl derivatives of 0.3 mg/m^3 for the application described in Section 2.3.2. This calibration line was used to measure the concentration of HCl in the fume cupboard atmosphere and was found to be 81.8 mg/m^3 .

The detection limit is comparable with analysis by ion chromatography and has several advantages over such conventional analysis such as the ability to analyse anhydride derivatives and mixtures of acids.

3.3. Quantitative analysis of NO_x in a nitrator stack atmosphere

The NO_x concentration determined as NO_2 in the stack atmosphere was calculated as 3.25 g/m^3 (4.45 g/m^3 was produced as HNO_3). Wet chemical analysis performed at the same time by ICI, Greenock resulted in a value of 3.16 g/m^3 for NO_2 . Therefore the titrimetric and derivatisation methods gave a 97% agreement. The low scrubber sample volume taken from the HCl atmosphere and relatively large chromatographic peak produced indicated that much lower concentrations of atmospheric NO_2 could actually be analysed. Evidently, confidence in the validity of the technique will increase through analysis of a range of samples by both laboratories.

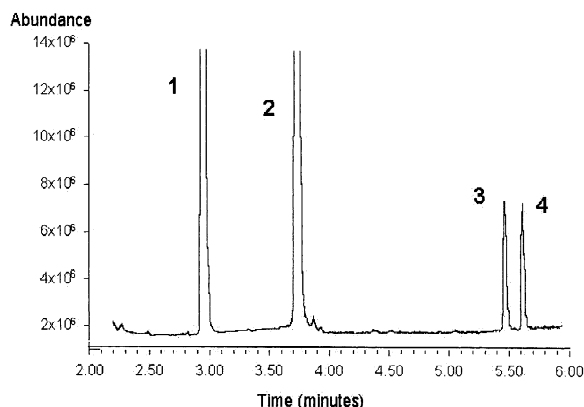


Fig. 4. Chromatographic trace of complex acid mixture.

4. Conclusions

This study has characterised several specific de-

rivatives of some common mineral and carboxylic acids. The derivatising technique used overcame most of the problems associated with conventional methods of acid analysis. The method is highly versatile due to the specificity of the reaction allowing analysis of acid mixtures and their anhydrides. The mineral and carboxylic acids investigated were found to react quantitatively with cyclohexene oxide all giving linear calibration plots from 0.1 to 1000 mg/l (FID).

The high specificity of the reaction mechanism makes it an attractive system to study mixtures of analytes. An example of the specificity of the reaction is illustrated in the reaction of nitric acid and its acid anhydride, dinitrogen pentoxide. A mixture of the anhydride and acid will react with cyclohexene oxide to produce different acid derivatives. The simultaneous analysis of an anhydride and its acid in the atmosphere is therefore possible.

All acid derivatives produced were of good thermal stability for analysis by gas chromatography apart from the HF derivative. Analysis of the HF derivative may be possible by HPLC due to a strong UV absorption band at 230 nm.

The atmospheric detection limit of 0.3 mg/l (2-chlorocyclohexanol) compares favourably with other methods such as ion chromatography and the excellent linearity of the reaction indicates the potential of the method for trace level analysis of environmental atmospheric gases. The limit of detection could be greatly improved by sampling a larger volume of air. The sampling of the acid-rich laboratory atmosphere created demonstrates the possible applicability of the reaction to urban atmospheres.

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