Indirect Determination of Molecular Chlorine by Fourier Transform Infrared Spectrometry

ZOLTÁN BACSIK,* NÓRA BALOGH, and JÁNOS MINK

Institute of Structural Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Pusztaszeri út 59–67, H-1025 Budapest, Hungary (Z.B., J.M.); and Research Institute of Chemical and Process Engineering, University of Pannonia, Egyetem u. 10, H-8200 Veszprém, Hungary (N.B., J.M.)

INTRODUCTION

Nowadays, Fourier transform infrared (FT-IR) spectrometry (both extractive and open-path techniques) is widely used for the detection of air pollutants[1–6] because the method is fast, reliable, and nondestructive. It is capable of detecting simultaneously all compounds except non-infrared active homonuclear diatomic molecules.

Molecular chlorine gas has many anthropogenic sources, including water treatment plants, chemical production facilities, ceramic brick industries, and paper production processes,[7–9] and it can also be formed in marine environments by reactions with sea salt particles.[10–13] Various sensors have been applied to detect chlorine, including chemical sensors based on semiconductor metal oxides.[14] Mass spectrometry also can be used for the determination of halogen molecules at atmospheric pressure.[10,15] A mist chamber and ion chromatographic detection has been employed to detect molecular chlorine indirectly at the parts per trillion (ppt) level.[16] Spectroscopic techniques (e.g., ultraviolet (UV), Raman) are also capable of measuring molecular chlorine directly. An artificial chlorine cloud was investigated by Edner et al.[17] by the differential absorption LIDAR (light detection and ranging) method.

Fourier transform infrared spectrometry has already been used to detect a homonuclear diatomic molecule. Larsen and co-workers[18] measured the concentration of oxygen in a gas cell by determining the concentration of ozone produced upon UV irradiation of the sample. The authors established a linear correlation between the concentration of oxygen in the original sample and the concentration of ozone produced by photolysis of the sample. The aim of the present work was to investigate whether it is possible to detect chlorine molecules by means of FT-IR spectrometry as predicted by Hanst.[19] If successful, a new analytical method can perhaps be developed based on this investigation.
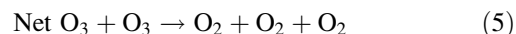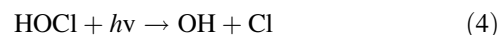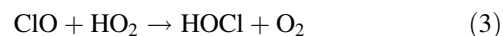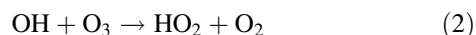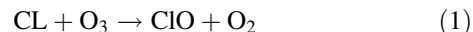
EXPERIMENTAL

A Bio-Rad FTS-185 series spectrometer and a multipass gas cell (Infrared Analysis Inc., Anaheim, CA) with a 25.7-m effective path length were used for the experiments. The special cell was equipped with a mercury UV-radiation source, whereby ozone and reactive radicals can be produced. The source of the radiation was a medium-pressure quartz mercury

lamp. This type of lamp emits one or two percent of its radiation in the 185 nm mercury line and about 90% in the 254 nm line, with the remainder in lines that fall in the near-UV and visible ranges. The 185 nm photons dissociate oxygen molecules and the resultant oxygen atoms react mainly with molecular oxygen to form ozone. The ozone can react with other molecules, or it can absorb the 254 nm photons and be photo-dissociated, giving oxygen atoms in the energetic singlet-D state. These energetic atoms react with water to produce hydroxyl radicals. The ultraviolet photons can also directly photo-dissociate pollutant molecules.[19]

The concentration of molecular chlorine gas was measured with a wide-range vacuum gauge (Kurt Lesker Co, KJL902074) connected to a vacuum system. Following introduction of a known quantity of chlorine gas and normal air (according to the analysis of the infrared spectra, this air contained 6650 ppm water vapor, 333 ppm carbon dioxide, 1.77 ppm methane, 0.32 ppm nitrous oxide, and 0.30 ppm carbon monoxide) at atmospheric pressure into the evacuated gas cell, the UV lamp was switched on after recording the first single beam spectrum. Next, a kinetic study was carried out during the photolysis: a spectrum was recorded every 15 s.

RESULTS AND DISCUSSION

Since there are many possible reactions (e.g., Eqs. 1–5) beyond ozone and reactive radical formation under the influence of the UV lamp, it is not practical to try to explain everything that could occur in the gas cell. In the course of the reactions, chlorine will be produced in atomic form and serve as a catalyst for ozone depletion. Some possible reactions are given here:[20,21]

$$CL + O_3 \rightarrow ClO + O_2 \tag{1}$$

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{2}$$

$$ClO + HO_2 \rightarrow HOCl + O_2 \tag{3}$$

$$HOCl + h\nu \rightarrow OH + Cl \tag{4}$$

$$Net\ O_3 + O_3 \rightarrow O_2 + O_2 + O_2 \tag{5}$$

The important point is that a band had to be identified that belongs to a molecule produced from the reaction of ozone or reactive radicals with molecular chlorine present in the sample gas. It was expected that the analytical band would be developed in a short time with an appropriate intensity and would not be overlapped with other bands in the spectra. From a preliminary investigation and bearing in mind the possible
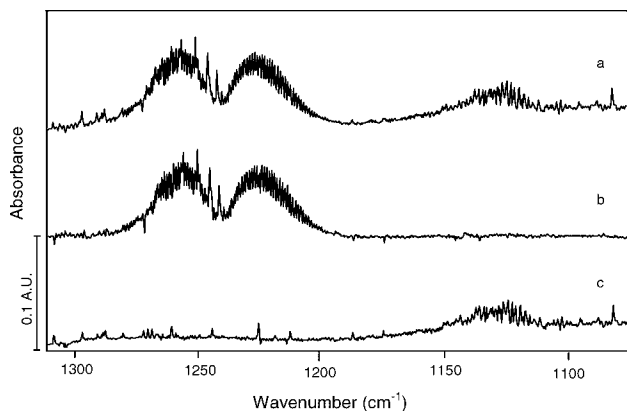
FIG. 1. Quantitative determination of hypochlorous acid. (*a*) Sample spectrum, (*b*) HOCl reference, and (*c*) sample spectrum after subtraction of HOCl reference.

reactions, the deformation mode of hypochlorous acid (HOCl) at 1239 cm^{-1} should be suitable for this purpose (Fig. 1).

A reference spectrum of HOCl was constructed from an absorbance spectrum of the sample, cutting out the spectral range of 1080–1320 cm^{-1}. The shape of the HOCl band in this reference spectrum was checked by an artificial reference spectrum of HOCl made with the aid of software[22] using data from the HITRAN[23] database. The HOCl reference spectrum was subtracted from all the spectra measured during the photolysis and subtraction factors were plotted as a function of time. Linear trends were fitted to the first five points (Fig. 2). Sample spectra were recorded three times (three independent measurements of the chlorine concentrations with the vacuum gauge) for each point in the calibration. The measurements were fairly reproducible (see error bars in Fig. 3).

Plotting the calibration chlorine concentrations as a function of the gradients of the lines of HOCl concentration changes (the factual concentrations of HOCl were not determined, but the subtraction factors are directly proportional to the concentrations according to the Lambert–Beer law in this absorbance range), a linear relationship (Fig. 3) was established for the concentration range investigated (Eq. 6).

$$c_{chlorine} = 1190.7b - 3.248, \quad (R^2 = 0.989) \quad (6)$$

where $c_{chlorine}$ is concentration of chlorine (ppmv) and b is the gradient of the HOCl concentration change.
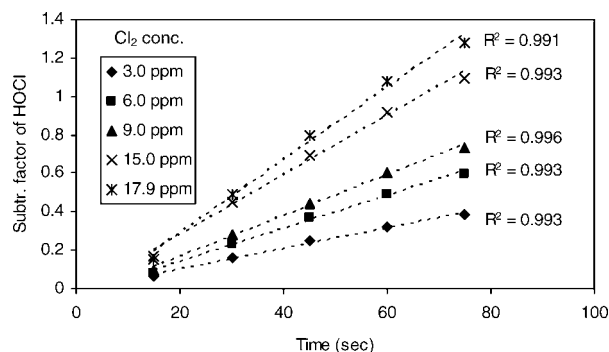

FIG. 2. Changes in HOCl subtraction factors (concentrations) during the first 75 s of the photolysis at different chlorine calibration concentrations.
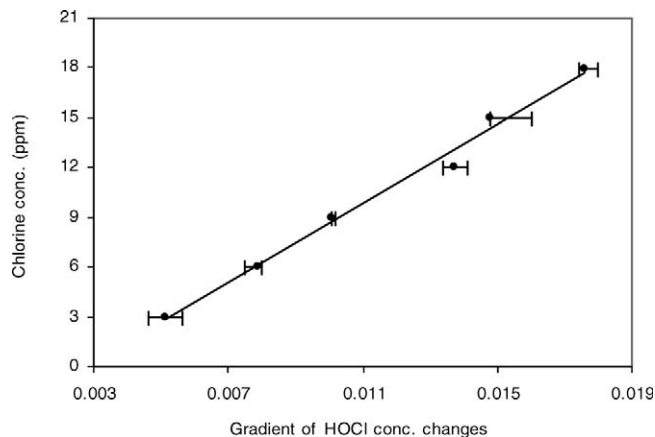

FIG. 3. Calibration chlorine concentrations as a function of the gradients of the lines of HOCl concentration changes. The error bars represent the minimal and maximal gradients determined from HOCl concentrations measured during the three independent experiments.

TABLE I. Calculated and measured (with the vacuum gauge) chlorine concentrations and the error of the developed method.

Gradient of the HOCl concentration change	Chlorine concentration determined from Eq. 6 (ppmv)	Measured chlorine concentration (ppmv)	Difference	Relative error (%)
0.0051	2.83	2.99	0.16	5.35
0.0079	6.16	5.98	0.18	3.01
0.0100	8.66	8.97	0.31	3.45
0.0137	13.06	11.96	1.10	9.19
0.0148	14.38	14.95	0.57	3.81
0.0176	17.71	17.94	0.23	1.28

CONCLUSION

By monitoring the concentration of HOCl, clear evidence was obtained for a correspondence with the original chlorine concentration in the gas cell. According to our investigation, unknown chlorine concentrations can be determined from the gradient of concentration change of the HOCl produced during the course of the photolysis reaction in the range of about 3–18 ppm, with an acceptable level of relative error (Table I). It has been shown that analysis of molecular chlorine by means of FT-IR spectrometry is therefore theoretically possible.

Our future work will be focused on an investigation of the applicability of the method over a wider concentration range and we will work out the exact chemometrics for measurement of molecular chlorine with analytical accuracy. It will also be important to investigate the influence of water (as a possible source of hydrogen for HOCl) and other compounds present in the sample gas and produced during the photolysis on the original chlorine concentration.[24–27]

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