# 放電フローへのUV-PES応用

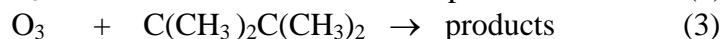D.E. Shallcross[1], J.M. Dyke[2] and M.Ghosh[2]

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The measurement of thermal gas-phase kinetic parameters in the temperature range of 200-300 K and in the pressure range from 1-760 Torr has particular importance for the Earth's atmosphere. Many reactions of atmospheric interest involve free radicals and therefore the rate coefficient of the reaction may display a complex temperature dependence and may also involve association channels that give rise to a pressure dependence also. The presence of radicals may also lead to multiple product channels. In order to model ozone depletion or air quality for example detailed information on these product channels is essential. Conventional approaches have focused on two direct techniques to measure rate coefficients, discharge-flow and flash photolysis. The discharge-flow technique involves generating reactants separately and bringing them together in a flowing gas mixture, the velocity of the flow dictates the reaction time between reactants mixing and reaching the detector. There is no restriction on the type of detector that can be used and their time response is not a drawback. The discharge-flow technique has until recently been restricted to low pressures (less than 10 Torr) and temperatures above 250 K due to flow profile disruption and loss of species to the walls. Flash photolysis involves the simultaneous generation of reactants from a light pulse acting on a suitable gas mixture, here fast response detectors are required and although temperature and pressure restrictions are far less the range of species that can be detected are more limited. Photolelectron spectroscopy (PES) is a scattering technique that permits the detection of all species in the reaction mixture. A high energy (21.22 eV, He Iα) radiation source (UV-PES) is used to eject photolelectrons from the gases present in the sample and these are energy analysed to produce a spectrum. The UV-PES detector is ideally suited for coupling with a discharge-flow tube, but has not until recently been accomplished. In this paper we describe the first results from coupling a UV-Photoelectron Spectrometer with a discharge-flow system to investigate the kinetics and products of two important reactions in the atmosphere.[1,2,3,4]

Fig. 1

$$Cl_2 \quad + \quad CH_3SCH_3 \quad \rightarrow \quad products \qquad (1)$$
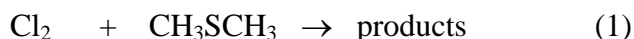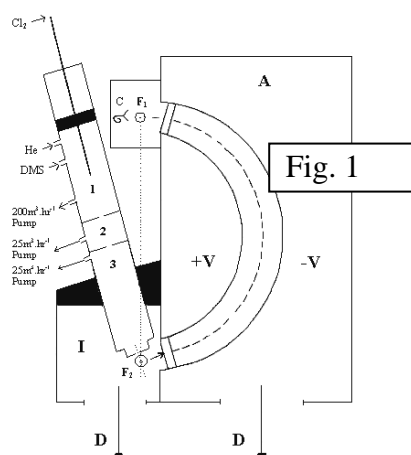
Reaction (1) between molecular chlorine and dimethyl sulphide (DMS) is of potential importance in the marine boundary layer where production of SO_2 from DMS oxidation can lead to cloud formation and directly impact on the Earth's climate through the CLAW hypothesis. Using the new instrument the overall kinetics of the reaction was determined at room temperature and low pressure was $k_1 = (3.4 \pm 0.7) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The analysis of the PES spectra revealed that the products of the reaction were HCl and CH$_3$SCH$_2$Cl and that a bound intermediate $(CH_3)_2SCl_2$ was involved in the reaction. Reaction (1) can occur at night and allow the build up of CH$_3$SCH$_2$Cl (as high as 50 ppt.) Further studies of the photochemistry of the product CH$_3$SCH$_2$Cl suggest that it can be photolysed during the day and cleave a C-S bond to yield CH$_3$S that can be readily oxidised to SO_2, thereby speeding up the oxidation of DMS and the production of SO_2.

$$O_3 \quad + \quad CH_2CH_2 \qquad\qquad \rightarrow \quad products \qquad (2)$$
$$O_3 \quad + \quad C(CH_3)_2C(CH_3)_2 \quad \rightarrow \quad products \qquad (3)$$

The ozonolysis of alkenes is a very important source of radicals in winter and at night in the troposphere and has been the subject of many studies. Reaction (2) and (3) were studied and apart from well known products such as HCHO, CO and CO_2 from reaction (2), O_2 ($^1\Delta_g$) and O_2 ($^3\Sigma_g$) were also observed at long reaction times shown in figure 2. The possible source of this excited oxygen arises from the decomposition of a secondary ozonide shown in figure3. Interestingly no O_2 ($^1\Delta_g$) is observed from reaction (3). Some suggestion why this might be are suggested.
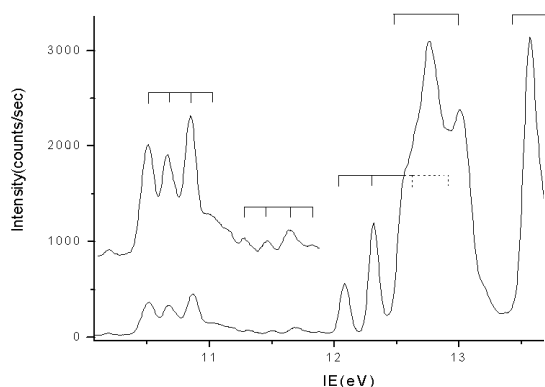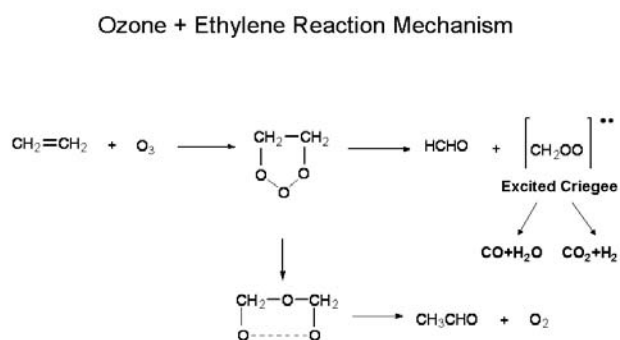
Figure 3: Schematic mechanism of ozone +ethylene

Figure 2: Photoelectron spectrum for O_3+ethylene

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3.. C. J. Percival etal. J. Photochem. Photobiol , **176**, 250 (2005).
4. H. D.E. Shallcross et al. *Atmos. Environ*.