

## A New Method for the Measurement of Molecular Singlet Oxygen Concentrations in the Gas Phase

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**Summary** A method for the measurement of singlet oxygen concentrations in the gas phase is described based on the fall in pressure in a gas flow containing

singlet oxygen when cyclohexene is introduced and the excess of cyclohexene and peroxide products are trapped.

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WE report a new method for measurement of molecular singlet oxygen [ $O_2(^1\Delta_g)$ ] concentrations in the gas phase. The well known reactivity of singlet oxygen towards double bonds has been used to trap the excited species. Cyclohexene was chosen as the organic reactant because of its kinetic behaviour<sup>1</sup> and price, and because it is heavy enough to be trapped easily. Precision can be increased by using much more expensive compounds such as tetramethylethylene or 2,5-dimethylfuran.<sup>2</sup> We have used a microwave discharge to produce, in a flow of oxygen, singlet molecules by means of a highly efficient cavity. Atomic oxygen is removed by introducing mercury vapour into the flow before the discharge tube. The HgO produced is deposited as a film on the walls and no mercury atoms remain in the gas phase. Under these conditions ozone cannot be produced.

A flow containing  $O_2(^3\Sigma^-_g)$  and  $O_2(^1\Delta_g)$  is passed through a battery of liquid nitrogen traps. The excess of energy is thereby removed from the singlet molecules and they return to their electronic ground state. The efficiency of this quenching was studied by following, after passage through the traps, the decrease in intensity of the red chemiluminescence arising from bimolecular collisions between singlet oxygen molecules.<sup>2</sup> The quenching can easily be made 100% efficient. After passage through the traps the pressure ( $P_1$ ) is measured; the  $O_2(^1\Delta_g)$  molecules are converted into their ground state to ensure that only molecules in the same state entered the pressure gauge. Differences in ionisation potential, or catalytic recombination on the filament, even though small, could affect the measurement in an unspecified way. With these precautions,  $P_1$  is the total pressure of the two species.

Gaseous cyclohexene is next introduced. It reacts with singlet oxygen to give peroxides, and an excess is used to ensure that no free singlet molecules remain and to increase the reaction rate. Reaction products and the excess of cyclohexene are removed from the gas phase by the liquid nitrogen traps, and measurement of the pressure now gives a lower value  $P_2$  because of the removal of the singlet

oxygen molecules. The difference  $P_1 - P_2$  gives the partial pressure of singlet oxygen. As this value is small (only a few percent of the total pressure) the gauge is coupled to a recorder.

The apparatus consists of a reaction vessel 2 m long  $\times$  35 mm diameter connected to the oxygen stream, and, *via* a flask (a), to another flask containing cyclohexene which had been thoroughly degassed by several freeze-pump-thaw cycles. Flask (a) can be used as a reservoir of cyclohexene, or as a regulator, with the flask containing cyclohexene in permanent contact with the rest of the apparatus so that measurements are made in a steady flow of cyclohexene. At the other end of the reaction chamber a double arm battery of liquid nitrogen traps is used to ensure efficient trapping; the two arms must be symmetrical to avoid perturbations in the flow. The traps are connected to the vacuum gauge, and, *via* a 10 l regulating flask, to a vacuum pump. If the pressure increases permanently when cyclohexene is introduced into a flow of oxygen in its ground state, the trapping is not efficient enough. There may be a temporary increase in pressure, however, due to perturbations in the flow. Measurements must be made under steady-state conditions.

We have compared this method with the easiest to handle and most accurate of the method presently available, that based on the 634 nm bimolecular emission. Our method uses much cheaper apparatus and is quicker (*ca.* 2 min per measurement *vs. ca.* 8 min for the spectroscopic method with the same gas flow under the same conditions). The spectroscopic method gives only relative concentrations whereas the present method gives absolute values. In a test experiment at 7 Torr total pressure we obtained values for the partial pressure of singlet oxygen of 0.44, 0.39, 0.31, and 0.21 Torr as the power to the microwave discharge was decreased, compared with relative values of 1:0.86:0.72:0.48 with the spectroscopic method.

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<sup>3</sup> C. Dupret, B. Vidal, and P. Goudmand, *Rev. Phys. appl.*, 1970, 337.