The study of atom reactions in gases by electron spin resonance

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Electron spin resonance provides a specific and sensitive method of studying paramagnetic free atoms in gases at low pressures. We are using this technique to study the reactions of free oxygen atoms and hydrogen atoms with simple hydrocarbons using an X-band superheterodyne spectrometer (Coates 1964; Brown 1966) with a TE_{102} mode cavity. With this arrangement, only atoms (which have magnetic dipole transitions) can be detected, the smallness of the magnet available has pre-
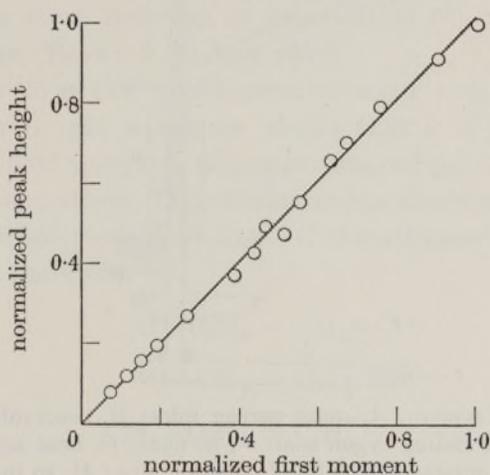

FIGURE 1. Plot of hydrogen atom peak height against first moment. Argon carrier at 2 mmHg.

vented the use of a cavity which was also suitable for the electric dipole transitions of diatomic radicals. Magnetic field modulation at 33 c/s is used and the signal recorded in differential form by phase sensitive detection at 33 c/s. Transitions of molecular oxygen are used to calibrate the sensitivity at regular intervals (Krongelb & Strandberg 1959; Westenberg & de Haas 1964), this calibration was checked by measuring the oxygen atoms produced in the stoichiometric titration of active nitrogen with known flows of nitric oxide. All the reactions studied to date are first order in free atom concentration, therefore only relative concentrations are needed except in determining the overall stoichiometry. It was found that the peak-to-peak height of the differential display and its first moment were strictly proportional to each other for both oxygen atoms and hydrogen atoms at constant total pressure (figure 1) providing the usual precautions were taken to avoid line distortion and power saturation. Nitrogen atoms, which give very narrow lines and have a long spin relaxation time, need particular care.

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The design and operation of the flow system call for some comment. A 10 mm diameter quartz flow tube is used with a fixed distance of about 1 m between the discharge and the measuring cavity (figure 2). For typical total pressures around 2 mmHg, a 50 W microwave discharge gives about 1 % of free atoms (i.e. 10^{-9} g atom cm^{-3} or 6×10^{14} atoms cm^{-3}). Concentrations of hydrogen atoms are measured down to 10^{-11} g atom cm^{-3} (6×10^{12} atoms cm^{-3}), the limit of detection being smaller than this by about a factor of 10. A movable probe permits the introduction of varying amounts of reactants at different points upstream from the measuring
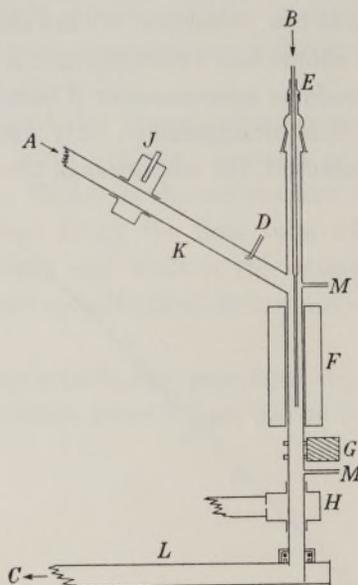

FIGURE 2. Diagram of flow system. A, main carrier inlet; B, reactant inlet; C, to pump; D, nitric oxide inlet; E, sliding tygon seal; F, furnace; G, heat sink; H, e.p.r. cavity; J, discharge cavity; K, quartz flow tube; L, copper tube; M, to pressure gauges.

cavity. The change of atom concentration at the cavity is then wholly due to the reaction being studied, and the loss of atoms by parallel processes such as re-combination on the walls of the flow tube is automatically cancelled, providing it and the reaction studied are both first order in free atoms (Clyne & Thrush 1963). This condition is fulfilled for the surface recombination of oxygen atoms and hydrogen atoms. The above relation holds even if the surface recombination is not uniform (Hartley & Thrush 1967). Since all runs can start from the same measured atom concentration irrespective of the reaction time and reactant concentration chosen, the reproducibility and drift of the spectrometer and flow system can be checked frequently. Under favourable conditions, spectrometer reproducibility approaches 3 %.

For studies at elevated temperatures, the reaction zone of the flow tube is surrounded by a furnace and a heat sink is clipped to the flow tube immediately before the cavity. Experiments using the temperature dependent air afterglow or nitrogen afterglow as indicator confirm that the temperature of the gases follows very closely that of the walls, as calculated from their low heat capacities and high thermal conductivities.

REACTIONS OF OXYGEN ATOMS

Oxygen atoms were obtained in the absence of molecular oxygen by titrating active nitrogen by nitric oxide,

$$N + NO = N_2 + O. \tag{1}$$
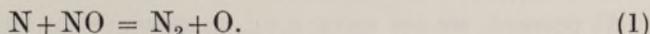
When these are reacted with paraffin hydrocarbons the initial steps are almost certainly

$$O + RH = R + OH, \tag{2}$$

followed by the very rapid second step (Clyne & Thrush 1963)

$$O + OH = O_2 + H. \tag{3}$$

Subsequent reaction between an oxygen atom and the alkyl radical will yield H or OH. Such schemes will give an overall production of 0·5 to 0·67 hydrogen atoms per oxygen atom removed as observed in the reaction between oxygen atoms and methane (Brown & Thrush 1967).

The initial step (2) is too endothermic to occur with acetylene: study of this reaction by electron spin resonance shows that 0.95 ± 0.08 hydrogen atom is formed and 0.55 ± 0.05 acetylene molecule removed per oxygen atom consumed at low acetylene concentrations. This eliminates the above mechanism and the formation of C_3H_4 at high acetylene flows shows that methylene radical must be involved. The mechanism is therefore

$$O + C_2H_2 = CH_2 + CO, \tag{4}$$

$$O + CH_2 = CO + 2H, \tag{5}$$

together with $$CH_2 + C_2H_2 = C_3H_4. \tag{6}$$
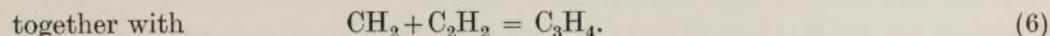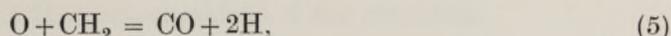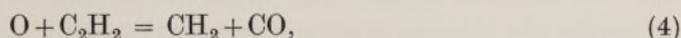
In these experiments we obtained $k_4 = (9.2 \pm 0.4) \times 10^{10}$ cm³ mole⁻¹ s⁻¹ and $k_5 = (2.7 \pm 1.0)k_6$ at 298 °K (Brown & Thrush 1967). The agreement with a recent mass-spectrometric value of $(9 \pm 2) \times 10^{10}$ cm³ mole⁻¹ s⁻¹ (Sullivan & Warneck 1965) and a photochemical value of $(11 \pm 1) \times 10^{10}$ cm³ mole⁻¹ s⁻¹ (Saunders & Heicklen 1966) is excellent, particularly when it is remembered that the stoichiometry of the overall reaction is needed to calculate the rate constant from our data. The 2:1 stoichiometry for consumption of O and C_2H_2 was also observed in the mass-spectrometric study by Arrington, Brennen, Glass, Michael & Niki (1965), but their rate constant of $k_4 = (5.3 \pm 1.7) \times 10^{10}$ cm³ mole⁻¹ s⁻¹ is not in good agreement with the other three values.

REACTIONS OF HYDROGEN ATOMS

We have studied the addition of hydrogen atoms to ethylene (Brown, Coates & Thrush 1966; Brown & Thrush 1967) and obtained a value of $k_7 = (1.2 \pm 0.1) \times 10^{11}$ cm³ mole⁻¹ s⁻¹ for the second-order addition of hydrogen atoms to ethylene at 298 °K

$$H + C_2H_4 = C_2H_5. \tag{7}$$
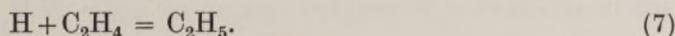
This value agrees excellently with the Arrhenius expression $k_7 = 3 \times 10^{13} \times \exp(-3180/RT)$ cm^3 mole^{-1} s^{-1} deduced by Baldwin, Simmons & Walker (1966) from various competitive reactions of hydrogen atoms. Previous direct studies of reaction (7) have given somewhat discordant results (Thrush 1965).

At present, we are using e.s.r. to measure simultaneously the concentrations of hydrogen and deuterium atoms in the reaction of D with C_2H_4 at low pressures. Under these conditions redissociation of unstabilised C_2H_4D radicals yields almost exclusively $H + C_2H_3D$.

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