Measurement by Electron Spin Resonance of the Decay of Hydrogen Atoms in Flow Systems at High Pressures

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IN the past, measurements of hydrogen atom concentrations by electron spin resonance (e.s.r.) in gas-phase flow systems have been made at low pressures (< 10 torr) apparently because it is difficult to maintain high-frequency electric discharges at higher pressures. In the present work hydrogen atoms have been generated at a total gas pressure in the range 20—500 torr by passing a stream of pure hydrogen over a heated tungsten filament (*ca.* 1600° K). The e.s.r. spectrometer system described earlier[1] was used to measure the hydrogen atom concentration at various points downstream of the filament. (No appreciable broadening of the e.s.r. absorption line was observed as the total gas pressure was increased, which is in accordance with expectation[2] since line-broadening chiefly occurs because of collisions between hydrogen atoms and not between hydrogen atoms and other non-polar, non-paramagnetic molecules.)

The flow tube was a silica tube, 8 mm. i.d. and 180 cm. long, coated with polytetrafluoroethylene, and the decay curve for the hydrogen atom concentration was obtained by moving the e.s.r. detection cavity and magnet along the tube as described previously.[1] On the assumption that the main decay process is

$$H + H + H_2 \xrightarrow{k_2} H_2 + H_2$$

the value of the apparent second-order rate constant, k_2, was determined from the slope of the linear plot of $1/[H]$ against time. The values of k_2 (in terms of atom removal) obtained over the ambient pressure range 50—150 torr and for linear flow velocities of 1000—4000 cm.sec.$^{-1}$ are given in the Table. Reliable decay curves at pressures higher than 150 torr were difficult to achieve because of both the much lower absolute yield of hydrogen atoms (attributed to the short contact time with the tungsten filament) and the considerable heat carried down the tube as a result of the large gas-flow rates.

The mean value of k_2 from all the runs is $(3{\cdot}4 \pm 0{\cdot}5) \times 10^{15}$ cm.^{6} mole^{-2} sec.$^{-1}$ at room temperature (298° K) which is in good agreement with our values obtained at lower pressures ($\leqslant 10$ torr) in a clean quartz flow tube ($2{\cdot}7 \pm 0{\cdot}4 \times 10^{15}$ cm.^{6} mole^{-2} sec.$^{-1}$) and in a polytetrafluoroethylene-coated quartz tube ($4{\cdot}4 \times 10^{15}$ cm.^{6} mole^{-2} sec.$^{-1}$).

Values of k_2 obtained under various conditions of pressure and flow velocity

Run	Total mean pressure (torr)	Mean linear flow velocity (cm.sec.$^{-1}$)	$10^{-15}k_2$ (cm.^{6} mole^{-2} sec.$^{-1}$)
1	100	2030	3·70
2	99·5	2040	3·50
3	102	1985	2·97
4	99	2035	3·04
5	99·5	2040	2·97
6	100	2025	2·97
7	50·5	1975	4·26
8	81	1980	3·84
9	120·5	1990	3·04
10	150	2000	2·90
11	98	1081	3·08
12	98	2075	3·57
13	101	3180	2·97
14	100	4270	2·97
15	51	1065	3·64
16	50	2100	4·02
17	48·5	3320	4·09
18	50	4280	4·22

Runs 1—6 show repeatability at constant flow pressure.
Runs 7—10 show effect of pressure at constant flow (2000 cm.sec.$^{-1}$).
Runs 11—14 show effect of flow rate at constant pressure (100 torr).
Runs 15—18 show effect of flow rate at constant pressure (50 torr).

It is also in fair agreement with the recent value ($6\cdot8 \pm 1\cdot5 \times 10^{15}$ cm.^{6} mole^{-2} sec.$^{-1}$) obtained by Larkin and Thrush[3] using a different method of hydrogen atom detection. This agreement provides some justification for the assumption that the surface reaction, which is significant at lower pressures, can be neglected at higher pressures.

The surface recombination rate constant, k_1, for the present coated tube was determined by measuring the hydrogen atom decay at low pressures. The resulting values (0·5—2·0 sec.$^{-1}$) confirmed that the influence of surface recombination would be small at the higher pressures. However, the results in the Table show that k_2 increases slightly at 50 torr and this may indicate a small contribution from surface recombination. After a long exposure of the reaction tube to hydrogen atoms generated by the hot tungsten wire, the surface was found to become more reactive, presumably because of the deposition of trace amounts of tungsten.

Because the linear flow velocities (*ca.* 2000 cm. sec.$^{-1}$) have been greater than those used in previous flow tube experiments with e.s.r. detection (*ca.* 200 cm. sec.$^{-1}$), it is possible that the magnetic levels may not have been completely thermalized before the atoms passed into the microwave cavity.[4] However, the fact that the values of k_2 are not significantly larger than those obtained at much lower flow rates shows that, in the present experiments, thermal equilibrium of the spin levels is established before the atoms reach the cavity and that errors from incomplete thermalization are absent in both sets of experiments.

A further advantage of the measurement at relatively high pressures is that the kinetic analysis was simplified. Firstly the viscous pressure drop over the length of the reaction tube was always small (*ca.* 2%) compared with the mean pressure. Secondly, because the pressures were an order of magnitude higher than in the low-pressure experiments, the hydrogen atom diffusion rate was correspondingly lower and thus could be neglected. These reasons, together with the reduced contribution of surface recombination, justify the use of a simple second-order decay plot in analysing the results.

So far, attempts to increase the yield of hydrogen atoms (*ca.* 0·03% at 100 torr) by altering the temperature or the configuration of the tungsten filament have been unsuccessful. The filament consisted of a 10 cm. length of tungsten wire (0·013 cm. diam.; 40 SWG) which was coiled into an open helix about 0·3 cm. diameter. Optimum running conditions were obtained with a temperature of about 1600° K which required a dissipation of 60 watts in the filament.

The present work indicates a novel prospect for the use of e.s.r. to measure the concentration of hydrogen atoms at high ambient pressures and to study their reactions with other reactive species under these conditions.

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