Variation of the Evolved Oxygen–Hydrogen Peroxide Ratio with Traversed Volume in the Discharged Water Vapour System

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VERY strong indications have been reported[1] that the species H_2O_4 (hydrogen superoxide) can be synthesized from hydrogen atoms and liquid ozone at the temperature of liquid nitrogen. The vitreous condensate prepared at −190° from water vapour dissociated in an electrical discharge is similar to the H-atom–ozone product in that it decomposes on warming to give hydrogen peroxide and oxygen and contains small concentrations of a frozen free-radical thought to be HO_2.[2] There are, however, two differences. First, the heats of decomposition of H_2O_4 in the two matrices differ by 9 kcal./mole, and this value is beyond the limits of experimental error.[3] Second, although the ratio of [moles evolved oxygen] to [moles hydrogen peroxide], R, for the H-atom–ozone condensate, prepared under certain conditions, is unity as required by the stoicheiometry of

$$H_2O_4 = H_2O_2 + O_2 \qquad [1]$$

it has always been very much less than unity for the discharged water condensate formed under conditions where large conversions of water into peroxide take place.[4] Even so, the evolved oxygen from this condensate was assumed to be formed by reaction [1] in the thermochemical calculations of reference 3.

We now report the results of some preliminary experiments, performed under conditions of low conversion, with the dissociated water vapour system in which the variation in peroxide yield and evolved oxygen yield with traversed volume (the volume between the discharge and the liquid air-cooled trap wall) was investigated.

The apparatus and the procedure used was similar to that described previously,[5] except that the high-voltage electrode connected to the Tesla coil consisted of a piece of aluminium foil (4 cm. wide) wrapped around the discharge tube. A second, similar piece of foil was wrapped around the tube 10 cm. upstream from the first and was grounded. The total power input to the Tesla coil was determined by means of an ammeter and voltmeter suitably connected into the primary circuit. The input voltage was varied by means of a Variac and the input current by adjustment of the gap-setting on the Tesla. Peroxide yield was determined by titration with standardized cerate solution and oxygen yield by pressure–volume measurements. The weights of the dilute peroxide solutions (up to about 1M-H_2O_2), produced when the condensate had been thermally decomposed, were also obtained.

The water vapour flow through the discharge tube was $0{\cdot}0806 \pm 0{\cdot}0006$ g. hr.$^{-1}$ ($4{\cdot}48 \pm 0{\cdot}02$ millimole hr.$^{-1}$). The total product weight, that is the weight of the dilute peroxide solution plus the weight of evolved oxygen, was found to be constant within the limits of precision of the weighing procedure, $0{\cdot}0796 \pm 0{\cdot}0016$ g. hr.$^{-1}$.

[1] N. I. Kobozev, I. I. Skorokhodov, L. I. Nekrasov, and E. I. Makarova, *Zhur. fiz. Khim.*, 1957, **31**, 1843.
[2] (*a*) R. Livingston, J. Ghormley, and H. Zeldes, *J. Chem. Phys*, 1956, **24**, 483.
(*b*) I. I. Skorokhodov, V. B. Golubev, L. I. Nekrasov, V. B. Evdokimov, and N. I. Kobozev, *Zhur. fiz. Khim.*, 1962, **36**, 47.
[3] D. A. Csejka, F. Martinez, J. A. Wojtowicz, and J. A. Zaslowsky, *J. Phys. Chem.*, 1964, **68**, 3878.
[4] "Chemistry of Discharged Water Vapour and Related Systems," M. Venugopalan and R. A. Jones, *Chem. Rev.*, to be published.
[5] R. A. Jones and S. S. Barton, *Canad. J. Chem.*, 1963, **41**, 1045.

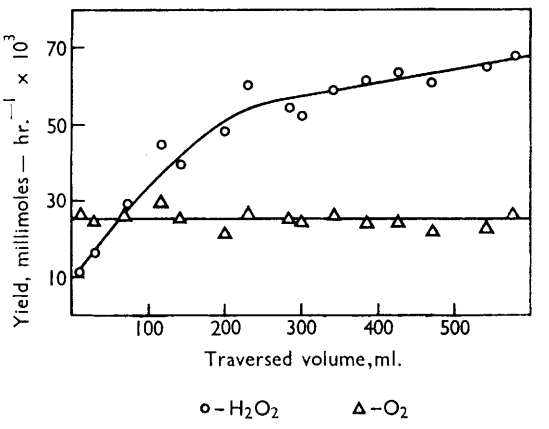
Thus about 1% of the products from the discharge passed through the trap and was lost to the atmosphere. The pressure at the inlet end of the discharge tube during the experiments was about 80 microns.

The data obtained at 10 watts input are shown in the Figure. The hydrogen peroxide yield increases with increasing traversed volume while the evolved oxygen yield remains constant. The value of R decreases continuously with increasing traversed volume from 2 to about 0·4.

The condensate was pale yellow below 230 ml. traversed volume and white at higher values. The yellow condensates became white on warming and finally liquefied with bubbling. The white condensates melted with bubbling.

When solid carbon dioxide–acetone was used to cool the trap no hydrogen peroxide nor evolved oxygen was obtained.

It is difficult, in this case, to ascribe the whole oxygen yield to reaction [1]; especially at the two lower values at the traversed volume where $R = 1$. Also the constant yield of evolved oxygen would imply a constant yield of H_2O_4, independent of traversed volume. It is possible that a contribution to the oxygen yield from the "water pump" action, described by Brackmann and Fite[6] must also be considered in cases where the gases impinging upon the cold surface contain large quantities of water.



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[6] R. T. Brackmann and W. L. Fite, *J. Chem. Phys.*, 1961, **34**, 1572.