

ductile, had a hardness of 150 Vicker's pyramid number compared with 115 Vicker's pyramid number for the initial material; (2) an X-ray powder pattern gave five lines for a face-centred-cubic of  $a_0 = 4.61 \text{ \AA}$  although the alloy should have been entirely hexagonal. All 23 other lines of this pattern did index as hexagonal with  $c/a$  ratio nearly that of the parent B-6 alloy. Strain in the cubic phase was shown by a lattice parameter lower than the expected  $4.72 \text{ \AA}$  from an equilibrium, fully hydrided, cubic B-6 alloy. The volume of the hydride with the smaller parameter was intermediate between the hexagonal B-6 lattice and the expected hydride, being additional evidence for a slow structural change of the hydrides back to the initial material.

In conclusion, it is seen that decomposition pressure hysteresis in the Zr-Hf-H system is intimately connected with a slow-diffusion process controlled by structural features, most likely of a martensitic nature. This connexion has been drawn recently for other than hydrogen systems, notably cobalt<sup>9</sup> and zirconia<sup>10</sup>. With an appreciation of the hysteresis phenomena, it was then possible to derive meaningful and consistent thermodynamic functions for the Zr-Hf-H system.

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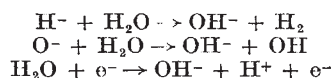
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## CHEMISTRY

### Hydroxyl Ions in the Mass Spectrum of Water Vapour

We have investigated the existence of stable primary OH<sup>-</sup> ions in the negative ion mass spectrum of water vapour. Mann, Hustrulid and Tate<sup>1</sup> specially looked for OH<sup>-</sup> ions in their mass spectrometric investigation of the ionization and dissociation of water vapour but found none. On the basis of this evidence Laidler<sup>2</sup> suggested extremely stable electronic configurations for the stable states of the OH<sup>-</sup> ion which would be strongly repulsive to an approaching hydrogen atom. The hydrogen would thus play no part in the electronic excitation.

However, Cottin<sup>3</sup> has carried out a similar investigation and has found three types of OH<sup>-</sup> ions; two of these are secondary products and are formed by electrons with energies between 5 and 12 eV. The ion which appears at 16 eV seems to be a primary ion. Cottin suggests that the three types of OH<sup>-</sup> ions are produced in the following way:

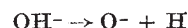


The pressure of water vapour in Cottin's work was about  $10^{-2}$  torr in the ion source and the formation of secondary ions is readily understood. The presence of the primary

ion could well have been due to collision stabilization of energy-rich states of OH<sup>-</sup>.

We have converted an A.E.I. MS2SG mass spectrometer for the investigation of negative ions by reversing the appropriate electrical connexions and increasing the sensitivity by using a 100-kMohm grid leak in the electrometer detector instead of the usual 20 kMohm. Source pressures were about  $10^{-4}$  torr to reduce any contribution from energy-rich states. OH<sup>-</sup> ions appeared at 17.5 eV and the OH<sup>-</sup> : O<sup>-</sup> ratio at 70 eV was 0.051. The negative ion mass spectrum of methanol has been investigated by Melton and Rudolph<sup>4</sup>, and we repeated this work to check the mass spectrometer and aid the identification of the OH<sup>-</sup> ions. The value for the ratio OH<sup>-</sup> : O<sup>-</sup> was 0.213 and we found 0.235. However, our ratio O<sup>+</sup> : O<sup>-</sup> from O<sub>2</sub> was about 280 while theirs was about 43. Thus there seems to be much more discrimination against negative ions in our mass spectrometer. This is probably because negative ions are generally formed with appreciable kinetic energy and the mass spectrometer discriminates against them. This discrimination varies from instrument to instrument, and it may be the reason why Mann *et al.* were not able to detect any OH<sup>-</sup> ions (particularly with pressures about  $10^{-4}$  torr in the analyser).

The formation of OH<sup>-</sup> means that the formation of O<sup>-</sup> in the electron impact dissociation of water can still be due to the dissociation of OH<sup>-</sup>. For the dissociation:



the appearance potential of O<sup>-</sup> is given by the relation:

$$A(\text{O}^-) = D(\text{OH}^-) - EA(\text{O}) + \Sigma_E$$

where  $D(\text{OH}^-)$  is the dissociation energy of OH<sup>-</sup>,  $EA(\text{O})$  is the electron affinity of O and  $\Sigma_E$  is the energy contribution from the kinetic and electronic states of O<sup>-</sup> and H. Now  $D(\text{OH}^-) = D(\text{OH}) + EA(\text{OH})$ , where  $D(\text{OH})$  is the dissociation energy of OH and  $EA(\text{OH})$  is its electron affinity. Substituting this in the aforementioned relation and using the values of  $D(\text{OH})$ ,  $EA(\text{OH})$  and  $EA(\text{O})$  given in the literature<sup>5-7</sup>, we get  $A(\text{O}^-) = 4.34 + 2.65 - 1.45 + \Sigma_E = 5.54 + \Sigma_E$ . Now  $A(\text{O}^-)$  for one of the O<sup>-</sup> species has been determined to be 7.4 eV. This leaves a not unreasonable amount of energy distributed between the different kinetic and electronic states of O<sup>-</sup> and H.

The appearance of OD<sup>-</sup> formed as a primary ion has been also observed by us. It appears at 18.1 eV and has an OD<sup>-</sup>/O<sup>-</sup> ratio of 0.065 at 70 eV.

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### Disproportionation of Halogenated Alkyl Radicals

WHEN 1,3-dichlorotetrafluoro acetone is photolysed, two CF<sub>2</sub>Cl radicals and a molecule of carbon monoxide are formed. The CF<sub>2</sub>Cl radicals combine to form 1,2-dichlorotetrafluoro ethane, and abstract chlorine atoms from the parent ketone to form dichlorodifluoro methane<sup>1</sup>; but, in addition to these products, a significant amount of 1,3-dichlorohexafluoro propane is found in the photolysis mixture. At first it was considered that this arose from a secondary photolysis of 1,4-dichlorohexafluoro acetone formed as a result of the chlorine abstraction reaction, but quantitative investigations<sup>2</sup> showed that it could not originate in this way.