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NOTE

Mass Spectrometric Evidence for H_3O, HD_2O, and D_3O

Sworski (*1*) and Magee (*2*) have postulated that H_3O is an important intermediate in the radiolysis of aqueous solutions. In addition, Bernstein (*3*) has predicted from thermochemical considerations that hydrogen-excess radicals such as H_3O may be stable. Furthermore, many workers in the field of mass spectrometry have observed an ion beam at mass 19 which could not be explained on the basis of an isotopic contribution. This ion beam in previous studies (*4*) was attributed to either H_3O^+ formed by an ion–molecule reaction or F^+ from residual background.

Evidence is reported in this paper that the ion beam observed at $M/E = 19$ is in

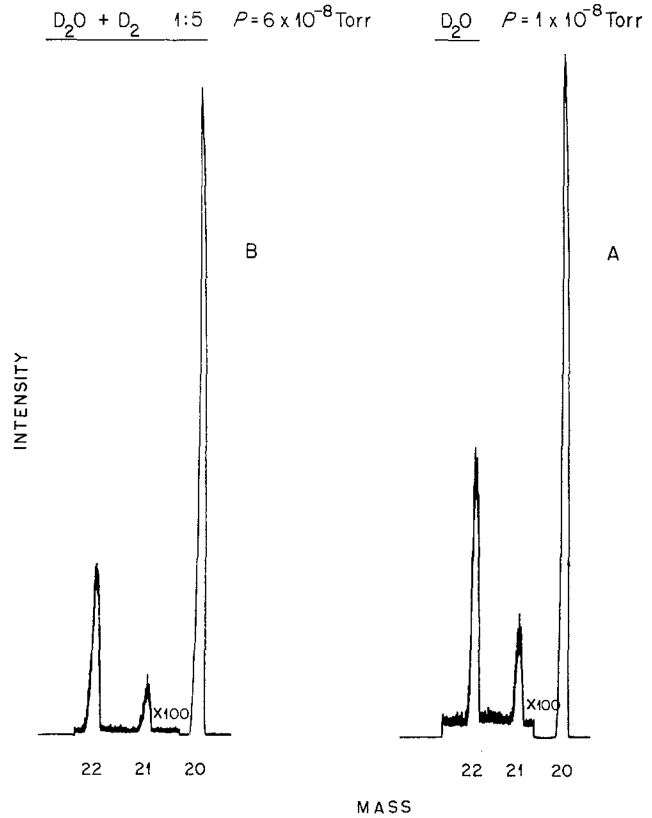

FIG. 1. Mass spectra showing evidence for HD_2O (mass 21) and D_3O (mass 22). In 1B, D_2 is added to the system and the abundance of HD_2O and D_3O, relative to D_2O (mass 20), is greatly reduced, suggesting a surface reaction.

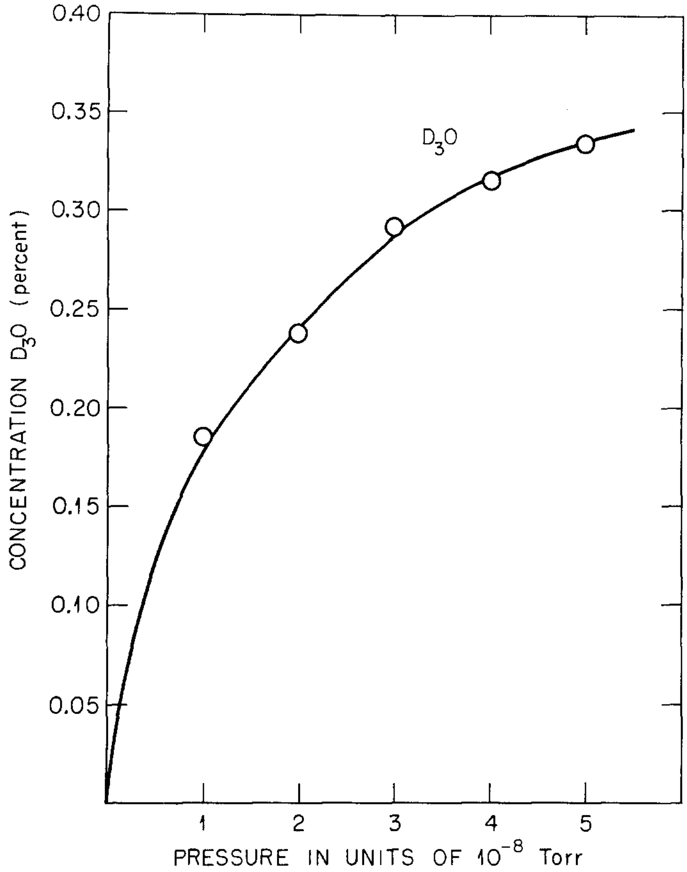

FIG. 2. Abundance of D_3O in D_2O as a function of pressure in a stainless steel ion source.

fact H_3O^+; the progenitor is neutral H_3O which is formed by a heterogeneous reaction on the walls of the ion source.

This study was carried out with two different instruments, a research mass spectrometer (*5*, *6*) with a stainless steel ion source and a conventional mass spectrometer with a copper ion source. Samples of either H_2O or D_2O were introduced into the instruments in the pressure range of 10^{-9} to 10^{-8} torr for the experiments. An actual scan of the mass 20 through 22 range with D_2O in the instrument is shown in Fig. 1A. The ions, HD_2O^+ (21) and D_3O^+ (22) were not observed in the absence of the ionizing electron beam or at very low electron energy. Qualitative appearance potential measurements showed that the ionization potential of D_3O was about 1 eV lower than that of D_2O. Wall reactions of D_2O^* (g) to form D_3O^+ (g) as discussed by Marmet and Morrison (*7*) appear to be ruled out in this study because of the low concentration of D_2O^*. Furthermore, the walls were made negative with respect to the ion repeller to prevent the possible evolution of ions from the surface as noted by Martin (*8*).

A second possible origin of the ions, ion–molecule reactions with D_2O^+ or some other abundant ion from D_2O, is eliminated by the following considerations. A simple calculation showed that under our experimental conditions and pressure range of from 2 to 30 $\times$ 10^{-9} torr the abundance of secondary ions from ion–molecule reactions was many orders of magnitude too low to explain the observed abundance of the new species. In addition to this evidence, the intensity ratios, HD_2O^+/HDO^+ and $D_3O^+/$

D_2O^+ were measured as a function of the electric-field strength within the ionization chamber. No change in these ratios was observed for changes in the electric-field strength from about 0 to 20 V cm^{-1}. This observation proves that HD_2O^+ and D_3O^+ were not produced by ion–molecule reactions since the abundance of secondary ions is sensitive to changes in the electric-field strength within the ionization chamber. A third possible origin of the ions, dissociative ionization of a dimer evolving from the surface, although apparently unlikely, could not be ruled out in the present study.

The intensity of D_3O^+ was reduced by about a factor of 2 when D_2 was added at a pressure of 5×10^{-8} torr, thus suggesting that the D_3O was formed on the surface (Fig. 1B).

The absolute abundance of the new species could not be accurately determined because the ionization efficiency curves are not known. Nevertheless, we obtained an approximate value (within an order of magnitude) by assuming equal cross sections for ionization by 75-eV electrons for the species with two hydrogens and the species with three hydrogens. The abundance of D_3O is shown as a function of pressure for a stainless steel ion source in Fig. 2 over the range of from 1×10^{-8} to 5×10^{-8} torr. This abundance was reduced by about a factor of 2 when O_2 at a pressure of 1×10^{-8} torr was introduced into the system, further confirming that the D_3O was formed on the surface. The pressure dependence of H_3O in the copper ion source behaved differently, decreasing with increasing pressure over the pressure range 10^{-9} to 10^{-8} torr.

Evidence from these experiments is consistent with the formation of neutral H_3O by a surface reaction. The lifetime, with respect to spontaneous decomposition, of H_3O in the gas phase must be at least 10^{-6} sec (transit time from the surface to the electron beam).

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