

deionized water which had been boiled to remove dissolved gases. In Figs. 2 and 3 the variation of T with P for both liquids is shown.

Each curve can be considered to consist of three regions. For small values of P the value of T increases linearly with P indicating an absence of cavitation throughout this range. In the second region the curve departs from linearity and finally, in the third region, becomes horizontal. In this third region the recorded value of T has reached a limiting value \hat{T} which we interpret as the maximum or "critical" tension which the liquid can withstand, that is, the value that always induces cavitation. The second region of the curve indicates cavitation of a more sporadic nature, that is, cavitation occurring at certain isolated points in the liquid at tensions somewhat below \hat{T} . The end of the first linear portion in the curve for tap water shows that such sporadic cavitation can occur at a tension of about 7 atmospheres. The corresponding value for the boiled water is about 9 atmospheres. The critical tensions are $\hat{T} = 8.5$ atmospheres for ordinary tap water, and $\hat{T} = 15.0$ atmospheres for boiled deionized water. The higher value in the second case is what one would expect as the removal of much of the dissolved gas would increase the ability of the liquid to withstand tension.

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Cyclotron Resonance Studies of Chemi-ionization in the $O + C_2H_2$ Reaction

DURING an investigation into the kinetics of the $O + C_2H_2$ reaction in a flow system by electron spin resonance (ESR) spectroscopy (unpublished results of J. N. B. and R. S. T.) an intense signal with an effective g value of 2.00 was detected. The following evidence showed that it was the result of cyclotron resonance of free electrons. The signal appeared with a TE_{012} cavity, with electric lines of force perpendicular to the d.c. magnetic field, but not with a cavity operating in the TE_{102} mode. The application of a d.c. potential to tungsten electrodes inserted upstream of the cavity reduced the signal and produced a measurable current but did not affect the ESR signals. The signal was up to 10^7 times more intense than that of the normal radical electric dipole transition and was characteristically broad and unsymmetrical with a g value of 2.00 (refs. 1 and 2). The signal versus reaction time profile was similar in shape to those reported³ for the system using Langmuir probe and mass spectrometer detection.

Because the electron concentration will equal the concentration of ions, the technique can be used to study the kinetics of chemi-ionization. Atom, radical and ion concentrations can be measured simultaneously and there is no interference with the flow, such as can occur with the probes and sampling orifices which have been used previously. Furthermore, the volume within which measurements are made is better defined.

The kinetic studies have shown that the rate of ionization is proportional to $[O]_0$, at constant $[C_2H_2]_0$ and total pressure. At a fixed $[O]_0$, the rate is roughly proportional

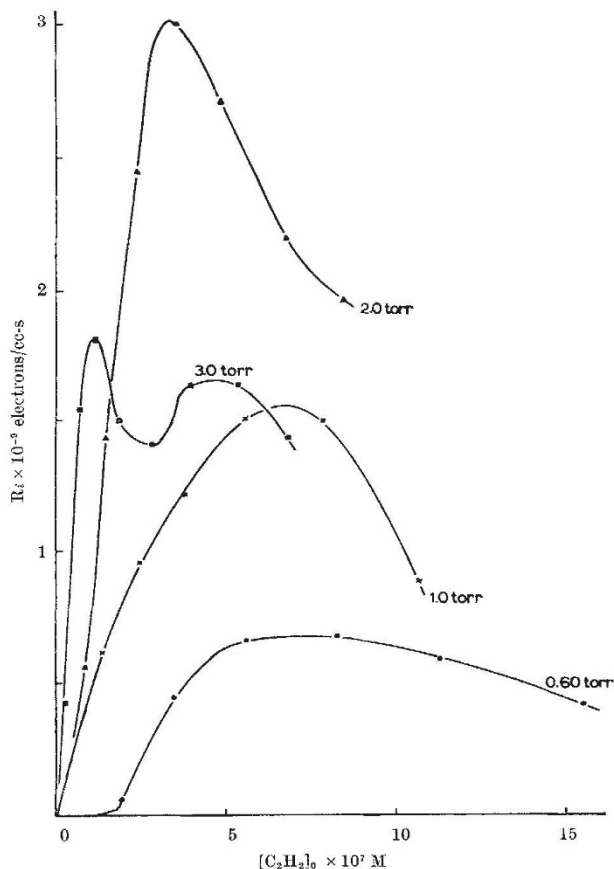
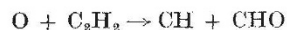


Fig. 1. The variation of rate of production of electrons with acetylene concentration at various total pressures. $[O]_0 = 7.35-8.0 \times 10^{-8}$ M.

to $[C_2H_2]_0$ up to $[C_2H_2]_0 \approx 10[O]_0$ and to total pressure up to 2-3 torr (Fig. 1). This provides strong evidence that the rate-determining step is either the primary reaction



or a parallel reaction to it, such as



and is not dependent on secondary reactions such as



Coupled with the results of previous investigations^{3,4}, it seems likely that the common precursor to the major ions CHO^+ , $C_3H_3^+$ and $C_4H_5^+$ is CH^* and that the excited state is not the $^2\Delta$ state observed in chemiluminescence experiments which shows higher order dependences^{4,5} than observed here. It seems that the use of emission measurements in the interpretation of chemi-ionization mechanisms is open to criticism.

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