

**"A Mass Spectrometric Study of the Species Involved in Carbon Deposition  
from R.F. Discharges in Carbon Containing Gases"**

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In order to gain direct evidence of the nature of the species involved in the radiolytic reaction between carbon dioxide and graphite in the presence of a number of additives (carbon monoxide, oxygen and methane) a study of the reactions occurring in radiofrequency discharges has been carried out. This paper is concerned with the results obtained in this study which are relevant to deposition processes.

Two experimental techniques have been used. The method of sampling neutral and ionic species from the 0.5 Mc/s rf discharge into an MS2R mass spectrometer has been reported previously (Evans and Jennings, Trans Faraday Soc. 61 2153 (1965)). A microbalance technique for studying deposition from a discharge in flowing gas has also been developed.

It was found that discharges in pure carbon dioxide gave no deposition but that deposition occurred from pure carbon monoxide and pure methane and from mixtures of these two gases. Deposition was also observed from certain carbon dioxide/carbon monoxide, carbon dioxide/methane, carbon monoxide/oxygen and methane/oxygen mixtures. Analysis of the results for carbon dioxide/carbon monoxide mixtures showed that the ions  $C^+$ ,  $C_2O^+$ ,  $C_3O_2^+$ , and possibly  $C_2^+$ , or their neutral precursors were probably involved in the deposition process and that the species  $CO_3^+$ ,  $CO_4^+$ ,  $C_2O_2^+$ ,  $C_2O_3^+$  and  $C_2O_4^+$  were probably not involved. Pure methane showed a complex ionic distribution with ions  $C_2H_5^+$ ,  $C_2H_3^+$ ,  $C_2H_4^+$ ,  $C_3H_4^+$ ,  $C_3H_5^+$ ,  $C_3H_3^+$  and  $CH_5^+$  dominant (Evans and Jennings, J. Phys. Chem. 70 1265 (1966)). Examination of the neutral and radical species suggested that the deposition process was due to a combination of ion-molecule and radical processes.

Experiments with methane/carbon dioxide, methane/carbon monoxide, methane/oxygen and methane/helium mixtures showed that the ion distribution was dependent on the nature of the reacting gases. Thus the ion distributions in depositing mixtures of pure methane, methane/carbon monoxide and methane/helium varied considerably. We deduced from the discharge studies that reactions of the sort



were important in our system and that the deposition from mixtures containing methane and oxygen involved reactions of  $CH_x$  formed in this way. In contrast the deposition from pure methane was more likely to involve ion-molecule reactions. The difference between the ion distribution in helium/methane and in methane could have been due to either a difference in the electron energy distribution in the discharge or to the probability of ion molecule reaction being reduced.

Examination of results for all gas mixtures showed that molecular oxygen ions were never present in significant proportion in depositing mixtures unless oxygen was an initial component of the system. This suggested that in our system molecular oxygen was formed mainly by recombination of oxygen atoms at the wall, and that the presence or absence of deposition depended on the relative supply of oxygen atoms and depositing species.

Studies of the rate of deposition on glass, alumina and graphite surfaces from pure carbon monoxide and pure methane showed that the rates of deposition were similar and were not greatly influenced by the nature of the surface. The rates of removal of deposits in a discharge in carbon dioxide were also similar and more rapid than the deposition rates by about an order of magnitude.

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