Negative Ion Formation in the Atomic Oxygen – Acetylene Reaction

PREVIOUSLY[1,2] we have reported on the production of positive chemi-ions in low-pressure atomic oxygen–acetylene reactions. Now we have also observed large concentrations (estimated as 10^{11}–10^{12} c.c.$^{-1}$) of negative ions in this system and have concluded that they are formed predominantly by electron attachment processes. This medium thus offers a much-needed new opportunity for the examination of electron attachment and charge transfer phenomena and the reactions of negative ions with positive ions and neutral species. Both the 'natural' ions of the reaction environment and those ions formed in the presence of additives can be investigated.

The same mass spectrometer atomic-diffusion flame apparatus used for positive-ion studies was used in this investigation after electronic modifications for negative-ion operation[3]. An atomic oxygen stream, produced in a side tube by subjecting a 96 per cent helium–4 per cent oxygen mixture to a 2,450-Mc/s, 125-W microwave discharge, diffused into the central portion of a 12-in.-diam. 'Pyrex' cross through which C_2H_2 flowed. The resulting reaction zone was oxygen-atom rich in the early stages of the reaction (near the O-atom inlet) and hydrocarbon rich farther downstream. The reaction pressures were 1–10 torr and the temperature varied from a maximum of 700° K near the centre of the reaction zone to near room temperature far out in the 'Pyrex' cross.

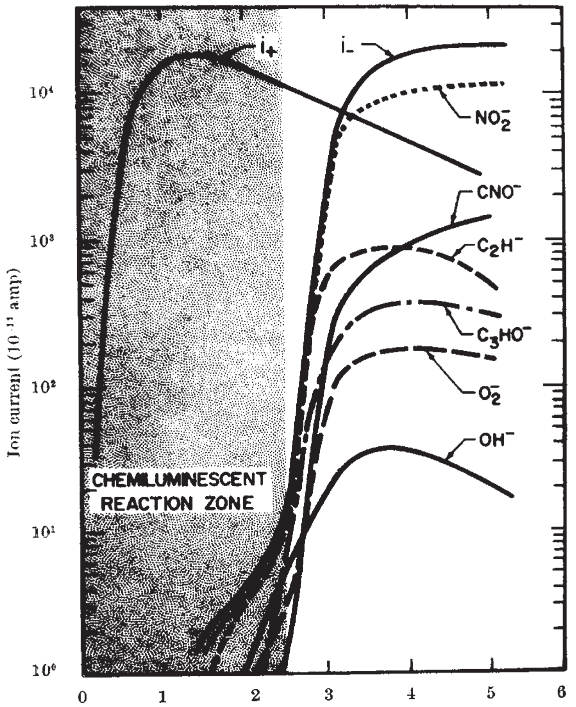

Fig. 1. Ion profiles. The magnitude of individual currents is not directly comparable to that of total current. i_+ and i_- indicate total positive and negative ion currents, respectively. C_2H_2 flow, 17·0 c.c. (S.T.P.) sec^{-1}; helium flow, 14·5 c.c. (S.T.P.) sec^{-1}; oxygen flow, 0·6 c.c. (S.T.P.) sec^{-1}

The negative ions observed include masses 16, 17, 24, 25, 26, 32, 42, 46, 49, 53 and 59. The hydrogen content of these ions has been determined in experiments where C_2H_2 was replaced with C_2D_2. Masses 17, 25, 53 and 59 all contain one hydrogen atom apiece; mass 49 may be a mixture of two species having one and five hydrogen atoms, respectively. The other ions contain no hydrogen. Commensurate with these results, the ions observed have been tentatively designated as the following: O^-, OH^-, C_2^-, C_2H^-, CN^-, O_2^-, CNO^-, NO_2^-, C_4H^- (and possibly $CH_5O_2^-$), C_3HO^- and $HCNO_2^-$. The presence of nitrogen-containing ions in large relative concentrations is indicative of the well-known high electron affinities of their parent compounds, which are present as impurities only. Addition of halocarbons to the acetylene stream results in atomic halogen ions becoming dominant; addition of SO_2 yields large quantities of SO_2^- (or S_2^-) and some S^-.

Some individual ion current profiles are shown in Fig. 1, together with total positive and negative ion current profiles; the magnitude of individual currents is not directly comparable to that of total currents. The maxima in these total ion current profiles are approximately equal, but their relative magnitude in the luminous zone indicates that the negative charge carriers there are mainly electrons. Negative ions become important charge carriers only in the gases surrounding the reaction zone, indicating that they are formed predominantly by attachment processes. Concentrations of O^-, C_2^- and CN^- were too small, relative to OH^- and C_2H^-, respectively, to allow us to take meaningful profiles. Masses 49 and 59 are present in maximum concentrations comparable to O_2^- and C_3HO^-, respectively. Large relative concentrations of heavier ions up to at least mass 130 have also been observed. Little effort has been given thus far to identification of these ions because of poor mass spectrometer resolving power at higher mass numbers. These heavier ion species, however, maximize further from the O-atom inlet than do most of the lighter ion species. They are, therefore, thought to be the products of ion-clustering processes.

It is interesting to compare the results obtained here to those obtained in low (1–10 torr)[3] and atmospheric pressure[4] C_2H_2-O_2 combustion flames. The low-pressure combustion shows relatively small negative-ion to positive-ion ratios and a preponderance of lighter ions. The atmospheric pressure flames behave much like the present system, which shows that both electron attachment and ion clustering are favoured by lower temperatures and higher pressures. The same observation with regard to clustering can be made for the positive ions in these three systems[2,5].

Fite and Rutherford[6], working with afterglows in atmospheric gases, reported the presence of significant quantities of CO_3^- and (NO_2^-·H_2O), due to carbon and water impurities. There are no detectable quantities of these ions in the present system, notwithstanding the presence of carbon, NO_2^-, and at least some H_2O; water has been found to be a minor reaction product[7], and its presence here is also substantiated by the observation of an H_3O peak[1,2].

A new mass spectrometer is being built to examine the discussed processes in further detail in electrical discharge flow systems of the Wood-Bonhoeffer type[1,2].

This work was sponsored by Project *SQUID* which is supported by the Office of Naval Research, Department of the Navy, under contract *Nonr* 3623(00), *NR*-098-038.

WILLIAM J. MILLER
A. FONTIJN

AeroChem Research Laboratories, Inc.,
P.O. Box 12, Princeton,
New Jersey.

[1] Fontijn, A., and Baughman, G. L., *J. Chem. Phys.*, **38**, 1784 (1963).
[2] Fontijn, A., Miller, W. J., and Hogan, J. M., in *Tenth Symp. (Intern.) Combustion* (The Combustion Institute, Pittsburgh, to be published 1965).
[3] Calcote, H. F., Kurzius, S. C., and Miller, W. J., in *Tenth Symp. (Intern.) Combustion* (The Combustion Institute, Pittsburgh).
[4] Feugier, A., and van Tiggelen, A., in *Tenth Symp. (Intern.) Combustion* (The Combustion Institute, Pittsburgh).
[5] Knewstubb, P. F., and Sugden, T. M., *Seventh Symp. (Intern.) Combustion*, 247 (Butterworths, London, 1958).
[6] Fite, W. L., and Rutherford, J. A., *Disc. Faraday Soc.*, **37** (to be published).
[7] Glass, G. P., comment in *Tenth Symp. (Intern.) Combustion* (The Combustion Institute, Pittsburgh).