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DISSOCIATIVE ELECTROIONIZATION STUDY OF ACETYLENE. THE PRODUCTION OF $CH(D)^+$ IN C_2H_2 AND C_2D_2

M. Davister and R. Locht.

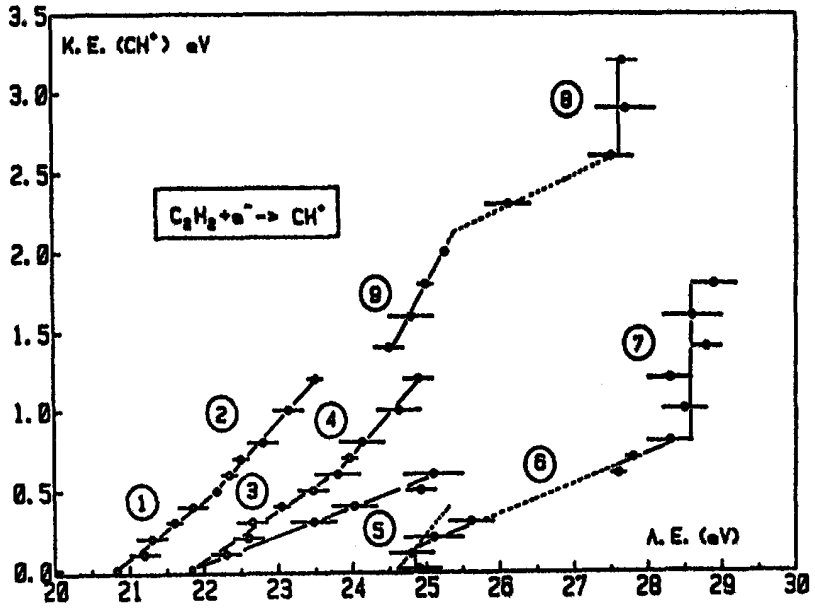
Département de Chimie Générale et de Chimie Physique, Université de Liège, Institut de Chimie, Bât. B6, Université de Liège, Sart-Tilman par B-4000 Liège 1, Belgium.

Very recently, the extensive investigation of the dissociative ionization of C_2H_2 , C_2D_2 and C_2HD by electron impact has been completed. All the dissociation channels were examined, including the formation of CH_2 and the decomposition of the doubly ionized states of C_2H_2 up to 50 eV electron energy. The doubly ionized molecular ion has been investigated in C_2HD.

In the scope of this abstract, e.g. only the results on the CH^+ -producing channel could be presented. The results obtained for the other decay channels, e.g. H^+ , extensively discussed in the recent literature, will be available at the meeting.

The experimental setup used during these measurements has already been described in detail elsewhere[1]. The C_2H_2 was a 99.98% pure sample (Linde), whereas C_2D_2 was 99% isotopically pure (M.S.D.). The sample pressure in the ionization region was 10^{-6} Torr. Translational energy spectra were recorded for impinging electron energies of 20-100 eV. Ionization efficiency curves of $CH(D)^+$ were measured between 16-50 eV for different retarding potential settings V_R , shifted by 100 mV steps. The aim of these measurements is to obtain the Kinetic Energy (KE) -versus-Appearance Energy (AE) plot shown in Fig.1. The slope of the straight lines, related to the dynamics of the decomposition, is expected to be 0.5 as far as only translational excess energy is involved in the process under consideration.

FIG.1: *Kinetic Energy (KE)-versus-Appearance Energy (AE) plot for CH^+ from C_2H_2 .*



As shown in fig.1, at least nine CH^+ -producing processes have been detected in the 20-30 eV electron energy range. From 30-50 eV electron energy three dissociation processes involve both $C_2H_2^+$ and $C_2H_2^{2+}$ ionic states. Below 35eV the process labelled (9) has to be ascribed to the acetone (1%) present in the C_2H_2 sample. In the same energy range essentially four mechanisms producing CH^+ with no or small amounts of KE are detected at 20.83 ± 0.05 eV, 21.74 ± 0.04 eV, 24.9 ± 0.3 eV and 33.8 ± 0.6 eV.

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Process (1) at 20.83 eV involves 50 ±12 meV total KE and is assigned to $C_2H_2^+$ ($B^2\Sigma_u^+$) → CH^+ ($X^1\Sigma^+$)+ CH($X^2\Pi$). The slope of 0.38 (0.23 in CD^+) indicates that the excess energy is partially converted (to an extend of 25%) into ro-vibrational energy. Process (3) at 21.74 eV (slope 0.3) could be assigned to $C_2H_2^+ \rightarrow CH^+$ ($a^3\Pi$)+ CH($X^2\Pi$) where one or both fragments carry translational and internal energy. Process (6) at 24.9 eV corresponds to the onset for the dissociation of $C_2H_2^+ \rightarrow CH^+$ ($X\ ^1\Sigma^+$) + C (^3P_u)+H (^2S_g). About 0.2 eV total KE is measured at the onset. The slope of 0.18 is assigned to excess energy conversion into translational (for 40%) and vibrational (for 60%) energy. The threshold at 33.8 eV, observed for V_R = 0.0-0.1 V, has to be ascribed to the onset for double ionization of C_2H_2. This is con firmed by the direct measurement of the double ionization energy of C_2HD.

The other processes will be discussed at the meeting. These results can partially be compared with those of Plessis and Marmet[2] .

References

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