Isotope Effect in Dissociative Resonance-Electron-Capture (DREC) by Methylacetylene

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A pronounced isotope effect was observed on $(M\text{-}X)^-$ ion formation (X indicates a hydrogen or deuterium atom) in DREC by three deutero-protio isomers of methylacetylene (CH_3CCH, CH_3CCD and CD_3CCH), using a conventional ion source and a single focusing mass spectrometer.

A Hitachi RMU-6 mass spectrometer was used after modification for measurement of the negative ion as described previously,[1] except that in the present work the sensitivity of the ion detection increased to 5×10^{-19} A by the 10 stage Ag-Mg electron multiplier.

The ionization efficiency curves of $(M\text{-}X)^-$ ions produced from CH_3CCH, CH_3CCD and CD_3CCH by electron impact are shown in Fig. 1. Ion current in the energy range of resonance is linearly proportional to the sample pressure in the ionization chamber up to about 5×10^{-5} mmHg. As shown in Fig. 1, all $(M\text{-}X)^-$ ions have the same first appearance potential (2.75 ± 0.2 eV) and the apparent half width (1.2 eV) within experimental error. Thus, all $(M\text{-}X)^-$ ions in which a acetylenic or methylenic hydrogen atom is lost, are formed by the spontaneous decomposition of the similar compound-negative-ion state (CX_3CCX^{-*}). The relative intensity of $(M\text{-}X)^-$ ions produced in DREC is shown in Table 1. Using the values in Table 1 and assuming that the cross-sections for CX_3CCX^{-*} formation are independent of deuterium contents in the molecules, the ratios of the probabilities of DREC are obtained as follows: (1) $P_{ah}/P_{mh}=3.27$, (2) $P_{ad}/P_{md}=3.11$, (3) $P_{ah}/P_{ad}=13.2$ and (4) $P_{mh}/P_{md}=12.6$, where P_{ax} and P_{mx} express the probability of loss of an X atom by DREC at acetylenic and methylenic position, respectively. It is concluded that in DREC by methylacetylene (a) the probability of the loss of an acetylenic H (or D) atom is about three times greater than that of a methylenic H (or D) atom, and (b) the isotope effect in scission probability of the C-X bond in DREC is about a factor 13 greater in the C-H bond than in the C-D bond in either acetylenic or methylenic C-X bond. Recently, the very large isotope effect in DREC has also been observed on the methane[2] and the hydrogen molecule[3]. Further discussion of the results and details of this study will be published later.

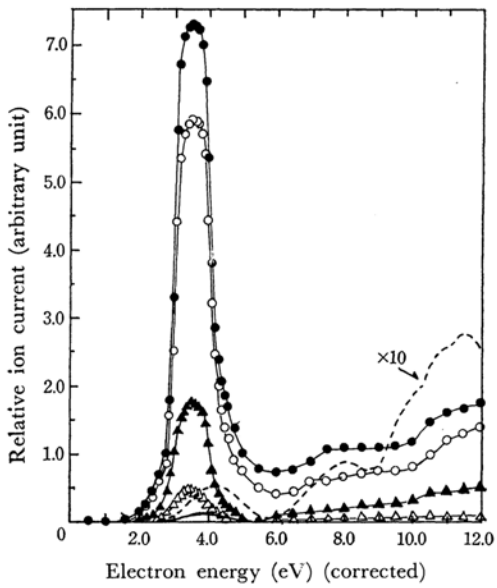

Fig. 1. Ionization efficiency curves of the $C_3X_3^-$ ions from methylacetylene-d_0, 1-d_1 and 3-d_3 by electron impact.
●, $C_3H_3^-$ (d_0); ○, $C_3D_3^-$ (d_3); ——, $C_3D_2H^-$ (d_3); ▲, $C_3H_2D^-$ (d_1) and △, $C_3H_3^-$ (d_1). Dashed curve show the ionization efficiency curve of $C_3H_2^-$ ions from the d_0 compound. All ion current have been normalized to unit pressure.

TALBE 1. RELATIVE INTENSITY OF $(M\text{-}X)^-$ IONS PRODUCED FROM DEUTERO-PROTIO ISOMERS OF METHYLACETYLENE BY DREC

Molecule	*M/e*	Ionic formura	Relative intensity
CH_3CCH	39	CH_3CC^- and CH_2CCH^-	100
CH_3CCD	39	CH_3CC^-	6.0%
CH_3CCD	40	CH_2CCD^-	24.3
CD_3CCH	42	CD_3CC^-	79.7
CD_3CCH	41	CD_2CCH^-	1.9%

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2) T. E. Sharp and J. T. Dowell, *J. Chem. Phys.*, **46**, 1530 (1967).

3) G. J. Schulz and R. K. Asundi, *Phys. Rev. Letters*, **15**, 946 (1965); *Phys. Rev.*, **158**, 25 (1967).