# Formation of Diacetylene Ion ($A^2\Pi_u$) by Controlled Electron Impact on Unsaturated Molecules

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By the impact of an electron beam (100—450 eV) on aliphatic hydrocarbons ($C_2H_2$, $C_2H_4$, $C_4H_6$), cyclooctadienes, and aromatic molecules ($C_6H_6$, $C_{10}H_8$, $C_{12}H_{10}$, *etc.*) at about $10^{-3}$ Torr, the Schüler's T spectrum of diacetylene ion ($A^2\Pi_u$–$X^2\Pi_g$) was observed in the 505—570 nm region, in addition to the well-known systems of H(Balmer), CH(A–X), and $C_2$(Swan). Three different kinds of mechanisms for the formation of $C_4H_2^+$ (A) were derived from the dependence of the emission intensity on the electron-beam current and the gas pressure: (a) the primary excitation process ($C_4H_6$), (b) the secondary excitation process (aromatic molecules, cyclooctadienes), and (c) the dimerization excitation process ($C_2H_2$, $C_2H_4$). The intensity ratio ($C_4D_2^+/C_4H_2^+$) of the T spectrum from $C_6H_6$ and $C_6D_6$ was $0.83\pm0.04$ for the (0,0) sequence at 300 eV excitation.

Schüler and Reinebeck observed a new spectrum in low current discharges through a number of organic vapors (acetylene, benzene, naphthalene, *etc.*), usually in a carrier gas such as helium.[1] This spectrum was labelled "T". Calloman assigned the "T" spectrum to the diacetylene (1,3-butadiyne) ion, $C_4H_2^+(A^2\Pi_u—X^2\Pi_g)$, through isotopic studies and detailed analysis under a high resolution.[2]

Mass-spectrometric measurements have provided information on the mechanism of the formation of $C_4H_2^+$ under electron impact; this ion is produced through a primary collision of an electron with a molecule in the cases of aromatic molecules,[3] and through some ion-molecule reactions at high pressures in the cases of $C_2H_2$[4] and $C_2H_4$.[5] In addition, the dimeric ion, $C_4H_2^+$, has been found to be formed by ion-molecule reactions in the α-particle radiolysis of $C_2H_2$[6] and $C_2H_4$[7] and in the photoionization of $C_2H_2$,[8] and by the chemi-ionization reaction between excited- and ground-states of $C_2H_2$.[9] However, no studies have been carried out on the mechanism of the formation of $C_4H_2^+$ in the excited state.

The photometric measurement on the collision of an electron beam with a molecular jet is of great advantage for the investigation of the excitation, the ionization, and the dissociation processes and of the reactions of the species thus produced.[10–14] We have observed the Schüler's T spectrum by electron impact on aromatic molecules and aliphatic hydrocarbons.[11] It has been found that the excited $C_4H_2^+$ species were formed from naphthalene by a secondary collision of an electron with a primary product.[11] The purpose of this investigation is to elucidate the mechanism for the formation of $C_4H_2^+$ (A) under controlled electron-impact excitation (100—450 eV) on such organic vapors as aromatic molecules, cyclooctadienes, and aliphatic hydrocarbons.

## Experimental

The electron-impact apparatus and the experimental procedure are essentially identical with those described previously.[11] An electron beam of a variable energy (100—450 eV) and a variable current (1—3000 μA) passes through the collision chamber so as to collide with the sample gas introduced from a nozzle. The pressure in the collision region was estimated by a penning gauge to be of the order of $10^{-3}$ Torr when the sample gas was introduced and of the order of $10^{-5}$ Torr when it was shut off. The pressure in the gas reservoir measured by a mercury manometer was estimated to be proportional to that in the actual collision region.

The photoemission of the excited species was measured in the visible region (400—660 nm) with a JASCO CT-50 monochromator equipped with a 1200 groove/mm grating blazed for 500 nm. The photons were detected by either an EMI 9558QB photomultiplier with a DC amplifier or an HTV R585 photomultiplier with an NF-PC545A photon counter. The isotope effect on the emission intensity of the T spectrum from $C_6H_6$ and $C_6D_6$ was measured by exchanging the reagent gases alternatively several times under identical conditions. The intensities were measured in the band area. The wavelength was calibrated by means of a low-pressure mercury lamp; its error was estimated to be within ±2 Å.

The gas samples used were of Research Grade from the Takachiho Trading Co. ($C_2H_2$ 99.6%, $C_2H_4$ 99.8%, 1,3-$C_4H_6$ 99.5%); the other compounds, of the best grade, were obtained from Wako Pure Chemical Ind. or the Kishida Chemical Co., except for $C_6D_6$, which was obtained from Merck. The samples were subjected to several freeze-pump-thaw cycles before use.

## Results

*Aromatic Molecules.* Most aromatic molecules show the photoemissions of the parent molecule ($S_1—S_0$) and a few fragment species in the 240—450 nm region under electron-impact excitation.[10–14] The spectra in the visible region (400—660 nm) are found to consist of various bands of fragment species. Typical spectra of $C_6H_6$ and $C_6D_6$ are shown in Figs. 1 and 2, in which most features of interest appear.

The sharp lines at 656 (not shown in Figs. 1 and 2), 486, 434, and 410 nm with high peak intensities are identified as the hydrogen Balmer serires ($H_{\alpha,\beta,\gamma,\delta}$ and $D_{\alpha,\beta,\gamma,\delta}$). The 4300 Å system ($A^2\Delta—X^2\Pi$) of the CH or CD radical and the Swan system ($d^3\Pi_g—a^3\Pi_u$) of $C_2$ are also identified. It should be noticed that, upon deuterium substitution, the intensities of the Balmer

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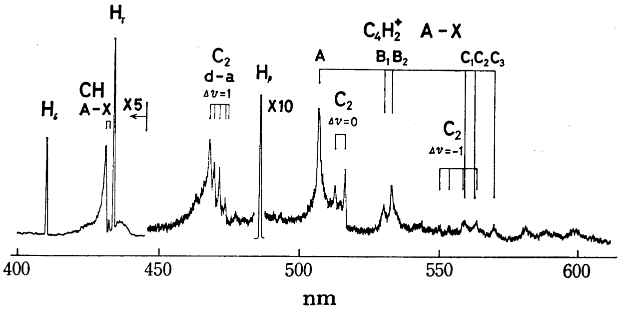

Fig. 1. Emission spectrum of $C_6H_6$ by controlled electron impact. Electron energy 300 eV, electron-beam current 1 mA, monochromator resolution 4 Å (FWHM).

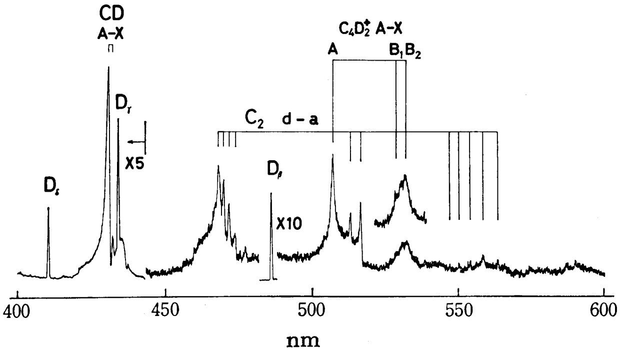

Fig. 2. Emission spectrum of $C_6D_6$ by controlled electron impact. Electron energy 300 eV, electron-beam current 1 mA, monochromator resolution 4 Å (FWHM). Upper spectrum of group B of $C_4D_2^+$ (A–X); electron energy 300 eV, electron-beam current 2 mA, monochromator resolution 3 Å (FWHM).

lines decrease, while those of the methylidyne radical increase.

The strong band at 5069 Å and the doublet band at 5303 and 5331 Å in the spectrum of $C_6H_6$ are assigned to the Schüler's T spectrum of $C_4H_2^+$ ($A^2\Pi_u - X^2\Pi_g$).²⁾ In the spectrum of $C_6D_6$, the corresponding bands appear at 5064, 5285, and 5318 Å. The doublet band can be resolved more clearly with a higher resolution, because a shoulder at about 530 nm makes the spectrum broad, as is shown in Fig. 2.

The band at around 507 nm, which shows the smallest isotope shift, is assigned to the (0,0) sequence, which is designated as A.¹⁾²⁾ The bands at 530 and 533 nm, designated as $B_1$ and $B_2$, are assigned to the (0, $\nu_3''$) and (0, $2\nu_7''$) sequences. The shoulder at 530 nm in $C_6D_6$ is ascribed to other strong sequence bands of the group $B_2$, as was reported by Calloman.²⁾ The groups $C_1$ (0, $\nu_3''+2\nu_7''$), $C_2$ (0, $4\nu_7''$) and $C_3$ (0, $\nu_2''$) are observed in $C_6H_6$ at 559, 563, and 570 nm respectively, although the former two bands are partially overlapped on the (1, 2) and (0, 1) bands of the $C_2$ Swan system. The assignments of the vibrational modes are as follows: $\nu_2$ is symmetric C≡C stretching, $\nu_3$ C–C stretching and $\nu_7$ symmetric bending.

The relative intensity of the T spectrum from $C_6D_6$ to that from $C_6H_6$ is measured for group A under 300 eV —1 mA excitation. The $C_4D_2^+/C_4H_2^+$ ratio is found to be $0.83 \pm 0.04$.

The Schüler's T spectrum is observed for various aromatic molecules, such as benzene, hydrocarbons (toluene, *o*, *m*, *p*-xylenes, cumene, *p*-cymene, phenylacetylene, naphthalene and biphenyl), halides (fluoro-, chloro-, iodo-benzenes, *p*-chlorotoluene and benzyl chloride), and nitrogen derivatives (benzonitrile, aniline and 2-naphthylamine). Schüler and Reinebeck reported that the intensity of the T spectrum was greatly reduced by the substitution of Cl or $NH_2$.¹⁾ However, no such significant change in intensity can be found in chlorobenzene, aniline, and 2-naphthylamine in the present study. Meanwhile, oxygen derivatives (phenol, anisole, phenetol and benzophenone) and nitrobenzene do not show appreciable bands of $C_4H_2^+$, as in the case of phenol by discharge¹⁾; this is partly because the intense comet-tail system of $CO^+$ occupies the wavelength region of the strongest band of $C_4H_2^+$.

All the aromatic molecules described above give the bands of such fragment species as H(Balmer), CH(A-X), and $C_2$(d-a). Their intensities in $C_6H_6$ are found to be linear both to the electron-beam current and the gas pressure, as has partly been reported previously.¹⁰⁾ However, the band intensity of $C_4H_2^+$ in $C_6H_6$ is found to be proportional to the second power of the electron-beam current, although it is also proportional to the gas pressure, as is shown in Fig. 3. Similar results are obtained for H, CH, $C_2$, and $C_4H_2^+$ in most of the other aromatic molecules described above.

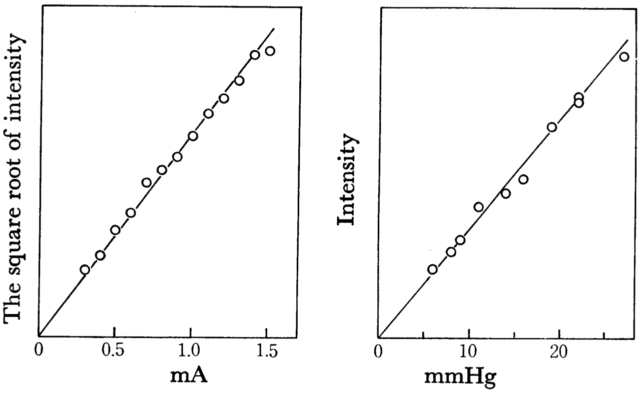

Fig. 3. Dependence of photoemission intensity (arbitrary units) of $C_6H_6$ on the electron-beam current (mA) and the pressure in the gas reservoir (mmHg).
Left; $C_4H_2^+$ (507 nm), electron energy 300 eV.
Right; $C_4H_2^+$ (507 nm), electron energy 300 eV, electron-beam current 300 μA.

*Cyclooctadienes.* The emission spectra of such cyclic dienes as 1,3- and 1,5-cyclooctadienes under electron-impact excitation were investigated to see whether these dienes showed the T spectrum, and if, they did, whether the difference in the conjugation of the two double bonds in these isomers affected the mechanism of the formation of $C_4H_2^+$ (A).

Both dienes are found to give the T spectrum with almost the same intensity, in addition to the band systems of H, CH, and $C_2$. The relationships between their intensities and the electron-beam current are identical with those of $C_6H_6$ for both isomers; the intensity of the $C_4H_2^+$ band is proportional to the second power, and that of the other bands to the first power, in the region of 400—1500 μA. However, the pressure dependence of the intensities was difficult to determine because of the low vapor pressures of cyclooctadienes.

*Aliphatic Hydrocarbons.* Acetylene, ethylene, diacetylene, and butadiene are known to give the strong T spectrum in the positive column of the discharge tube.[1,2] In the present study, this spectrum is observed for acetylene, ethylene, and 1,3-butadiene; besides this spectrum, these molecules show relatively strong bands of H, CH, $C_2$, and $CH^+$ (A–X). It should be noticed that the dimeric ion, $C_4H_2^+$, is obtained from $C_2H_2$ and $C_2H_4$ at low pressures of about $10^{-3}$ Torr. However, the intensity is so weak that only the strongest band at 507 nm is appreciable, with a high electron-beam current. Thus, there are significant differences in the intensities of the T spectrum; the order is generally: aromatic molecules>1,3-butadiene≈cyclooctadienes≫acetylene≈ethylene, as compared at 100—450 eV, 1 mA excitation.

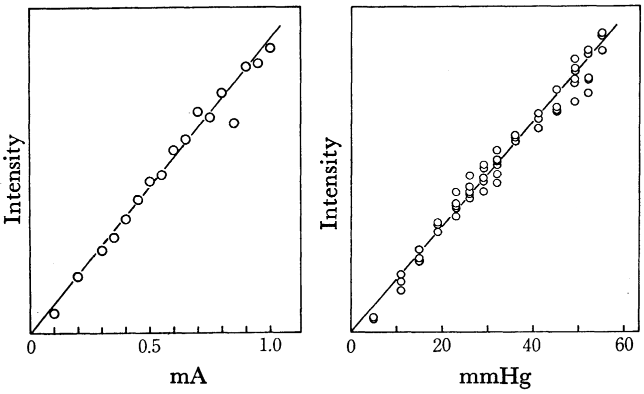

Fig. 4. Dependence of photoemission intensity (arbitrary units) of 1,3-$C_4H_6$ on the electron-beam current (mA) and the pressure in the gas reservoir (mmHg).
Left; $C_4H_2^+$ (507 nm), electron energy 300 eV.
Right; $C_4H_2^+$ (533 nm), electron energy 300 eV, electron-beam current 100 μA.

The current dependence of the intensity of the $C_4H_2^+$ band from 1,3-butadiene differs from that in the cases of the aromatic molecules; the band intensity of $C_4H_2^+$ as well as those of H, CH, $C_2$, and $CH^+$, is proportional to the first power of the electron-beam current and the gas pressure, as is shown in Fig. 4. In the cases of $C_2H_2$ and $C_2H_4$, similar quantitative measurements could not be carried out because of the weakness of the T spectrum and because of the band overlap of the group A with the tail band of the $C_2$ $\Delta v=0$ sequence.

## Discussion

The Schüler's T spectrum consists of the (0, 0) and (0, $v_i''$) sequences and the (0, 0) sequence is the most intense; thus, the Franck-Condon principle indicates that the molecular dimensions of this ion are not very different in the excited- and the ground-states.

The mechanism of the formation of the excited species by electron impact can be discussed in terms of the dependence of the emission intensity on the electron-beam current and the gas pressure. Schüler and Reinebeck reported that they almost exclusively obtained the emissions of $C_2$, CH, and $H_2$ with high current densities in a discharge tube through various organic vapors ($C_2H_2$, $C_6H_6$, *etc.*).[1] Upon a decrease in the current, the diatomic bands became weak and the T spectrum came out. However, no quantitative measurements have been carried out on the changes in the intensity upon variations in the current density and the gas pressure.

In the present crossed electron-beam and molecular-jet method, most emitting excited species have been confirmed to be produced by a single collision of an electron with a molecule at low pressures;[10–14] such examples are excited fragments as H, CH, and $C_2$ in the present study, since their emission intensities are proportional both to the electron-beam current and to the gas pressure. Two kinds of exceptions have been pointed out:[13] (1) the excited CN, CO, and $CO^+$ species produced through the scission of two aromatic bonds (*e.g.*, $CO^+$ from dimethoxybenzenes[13]), and (2) the excited species produced through the formation of a new chemical bond (*e.g.*, $HCl^+$ from chlorobenzene[11]). The band intensities in these exceptional cases have often been found to be apparently proportional to the fractional power (1.0—2.0) of the electron-beam current. The deviation from the linearity can be interpreted by the competitive reactions between a one-electron process and a two-electron process, as was reported in the case of $CO^+$ from dimethoxybenzenes.[13] The formation of $C_4H_2^+$ (A), however, proceeds through either a one-electron process or a two-electron process; the mechanisms can be classified in the following three groups.

*(a) The Primary Excitation Process.* This process is applicable to 1,3-butadiene. The linear dependence of the emission intensity on the electron-beam current and the gas pressure shows that $C_4H_2^+$ (A) is produced through a unimolecular dissociative excitation induced by a collision with an electron and that the probability of collisional deactivation is negligible within its radiative lifetime:

$$1{,}3\text{-}C_4H_6 + e \longrightarrow C_4H_2^{+*}$$

where the asterisk denotes the emitting excited state of $A^2\Pi_u$. This result indicates that excited $C_4H_2^+$ ($m/e$=50) should be produced in the ionization chamber of a conventional mass spectrometer.

*(b) The Secondary Excitation Process.* Since the band intensity is proportional to the second power of the electron-beam current and to the first power of the gas pressure, the formation of $C_4H_2^+$ (A) from $C_6H_6$ proceeds through the two-electron and unimolecular dissociative excitation:

$$M + e \longrightarrow X$$
$$X + e \longrightarrow C_4H_2^{+*}$$

where M represents an incident molecule and where X stands for some kinds of intermediates. The possible intermediates are the ground state of $C_4H_2^+$, $C_4H_2$, and other larger neutral or ionic species. This process is also applicable to other aromatic molecules.

A number of mass-spectrometric measurements show that $C_4H_2^+$ is produced by the unimolecular decomposition of aromatic molecules.[3] Most of the $C_4H_2^+$ species thus produced in the ionization chamber are expected to be in the ground state.

*(c) The Dimerization Excitation Process.* One of the most prominent features of $C_2H_2$ and $C_2H_4$ in their photolysis and radiolysis is that these olefins are apt to polymerize mainly through consecutive ion-molecule reactions.[4-9] Hence, $C_2H_2$ and $C_2H_4$ may dimerize under the present experimental conditions. Meanwhile, since the T spectrum can be observed only at a high electron-beam current, two electrons should participate in the formation of $C_4H_2^+$ (A). These results lead to the conclusion that $C_4H_2^+$ (A) is produced from $C_2H_2$ and $C_2H_4$ through collisions of intermediates (neutral or ionic dimerization products) with another electron. The weakness of the intensity of the T spectrum in the present method indicates that the probabilities of such secondary reactions are much smaller than those in the discharge tube.

A number of mass-spectrometric studies of the ion-molecule reactions of $C_2H_2$ by electron impact[4] and α-particle radiolysis[6] occurring in the ionization chamber at elevated pressures show that the major secondary reactions of the primary ions at about $10^{-3}$ Torr are the formation of $C_4H_3^+$ and $C_4H_2^+$ as follows:

$$\begin{aligned} C_2H_2^+ + C_2H_2 &\longrightarrow C_4H_2^+ + H_2 && (1)\\ &\searrow C_4H_3^+ + H && (2)\\ C_2H^+ + C_2H_2 &\longrightarrow C_4H_2^+ + H && (3)\end{aligned}$$

Meanwhile, Koyano *et al.*[9] have reported that $C_4H_3^+$ and $C_4H_2^+$ are formed by the chemi-ionization reaction between excited- and ground-states of $C_2H_2$ at 5—50 × $10^{-3}$ Torr. Since the energy-loss spectra of $C_2H_2$ above 8.0 eV at incident electron energies of 40 and 50 eV have been reported to agree well with the UV spectrum,[15] dimeric ions may be produced *via* chemi-ionization under electron-impact excitation. However, no evidence for chemi-ionization induced by electron impact has been reported in the mass-spectrometric studies.[4] Consequently, the $C_4H_3^+$ and $C_4H_2^+$ formed through the ion-molecule reactions of (1)—(3) would be important intermediates. Besides them, some neutral dimerization products (*e.g.*, $C_4H_2$ and $C_4H_4$), as has been shown by VUV photolysis at high pressures,[16] are possible intermediates of $C_4H_2^+$ (A).

The mechanism for the formation of $C_4H_2^+$ (A) from $C_2H_4$ is probably similar to that from $C_2H_2$. Possible intermediates are the predominant secondary ions observed in the mass-spectrometric studies[5] (*e.g.*, $C_4H_5^+$ and $C_4H_7^+$) and such neutral species as $C_4H_2$ and $C_4H_4$.

The T spectrum can be observed from the non-conjugated cyclic diene as well as from the conjugated one. The formation of $C_4H_2^+$ (A) is confirmed to proceed through a two-electron process, (b) or (c), independent of the conjugation of the two double bonds. Since the intensity of the T spectrum from cyclooctadienes is much stronger than that from $C_2H_2$ and $C_2H_4$, and since the possibilities of the secondary reactions are expected to be smaller than those in the cases of $C_2H_2$ and $C_2H_4$, the corresponding mechanism for cyclooctadienes is concluded to be (b). The intermediates are probably alike, because no significant difference is found in the intensities of the T spectra of the two isomers.

The reason for the loss of the T spectrum in the oxygen derivatives (PhOH, $PhOCH_3$, $PhOC_2H_5$, and $(Ph)_2CO$) and nitrobenzene, all of which give strong $CO^+$ emissions, may be partly that another fast dissociative process, probably CO or $CO^+$ elimination, competes with the $C_4H_2^+$ (A) formation in the first or the second reaction of the (b) mechanism.

The isotope effect on the relative intensity of the T spectrum from $C_6H_6$ and $C_6D_6$ should originate from the contributions of the competitive processes of the excitation, the ionization, the dissociation, and the photoemission. The competition between dissociation and preionization in the superexcited states has been pointed out as being responsible for the isotope effect of the hydrogen Balmer emission by electron-impact excitation.[17-21] However, the increase in the intensity of the methylidyne radical upon deuterium substitution established in the present study seems to contradict such an interpretation. It, rather, seems to be caused by the slower rate of the competitive dissociation process, the cleavage of the C-D bond. Thus, the competition of various dissociation channels in the superexcited states plays an important role in determining the isotope effect in such a large molecule as benzene; this effect should also participate in the isotope effect of the diacetylene ion. In addition, differences in various non-radiative decay rates from the excited states of diacetylene ion induced by changes in the vibrational frequencies should be taken into account. Since unidentified secondary processes are involved in the reaction, a detailed interpretation of the isotope effect requires further investigation.

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