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VISIBLE EMISSION OF EXCITED FRAGMENTS FROM ACETYLENE IN THE ARGON FLOWING AFTERGLOW REACTION

KAORU SUZUKI* and KOZO KUCHITSU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113 (Japan)

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Summary

Visible emission spectra of the CH $A^2\Delta-X^2\Pi$, CH $B^2\Sigma^- - X^2\Pi$ and $C_2 d^3\Pi_g - a^3\Pi_u$ transitions were measured in the argon flowing afterglow reaction of acetylene. The emission intensities from these excited fragments decreased by one order of magnitude when positively charged species were eliminated from the discharged afterglow. Considerations of energetics suggest that argon ions in metastable states are the main active species which produce these excited fragments.

1. Introduction

Electronically excited fragments are produced from simple molecules by various methods of energy deposition, *e.g.* vacuum ultraviolet irradiation [1], electron impact [2] and reaction of metastable rare gas atoms [3]. The use of a reaction of metastable rare gas *ions* as an alternative source of energy is reported in the present paper, where electronically excited fragments are produced from acetylene. There have been only a few reports on the dissociative excitation of molecules by metastable rare gas ions: in the formation of $CH(A^2\Delta)$ from CH_3CN [4] and CH_nCl_{4-n} (n = 1 - 4) [5] and Cl(5p) from HCl [6] reported in our previous papers, argon ions in metastable states were deemed to be major active species.

Fragmentation of acetylene in the discharged flow of argon was first studied by Prince *et al.* [7]. They reported that under their experimental conditions a flame composed of the C_2 Swan bands and the CH 430 nm band was produced mainly by the reaction of neutral metastable argon atoms. However, their reaction mechanisms are questionable since they underestimated the contribution of the ions in the discharged flow and also their discussion of the reaction mechanisms has to be revised in the light of

*Present address: Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan.

more recent data on the dissociation energies. Accordingly, the present study aims at a more precise observation of the same emission spectra and a more quantitative understanding of the dissociation energetics.

2. Experimental

The flowing afterglow apparatus used in the present study is described in detail elsewhere [4]. Active species of argon were produced by microwave discharge (2.45 GHz, about 500 W). The acetylene gas (Matheson, purity 99.6%) at about 50 mTorr was admixed downstream. The pressure of argon at the reaction zone was about 0.6 Torr. The reaction flame was observed through a quartz window. A photon-counting apparatus was employed to detect the light through a Spex 1704 spectrometer with an HTV R585 photomultiplier. A grid was placed between the discharge section and the reaction zone, and a negative potential with respect to the wall potential was applied to the grid in order to investigate the effect of charged particles on the observed emission.

3. Results and discussion

A green reaction flame was observed. This strong emission was composed of the C_2 Swan system ($d^3\Pi_g - a^3\Pi_u$), the CH 430 nm ($A^2\Delta - X^2\Pi$) and 390 nm ($B^2\Sigma^- - X^2\Pi$) systems, and a broad band extending from about 400 nm to longer wavelengths, as shown in Fig. 1. Calculated minimum energies for formation of excited fragments by the dissociative excitation of acetylene are listed in Table 1.

3.1. The C_2 Swan system

The $\Delta v = 0$ and 1 transitions of the Swan system [13] were observed in the present experiment. When an electrostatic potential was applied to the grid, the Swan band decreased its intensity to about 10% as shown in Fig. 2. This shows that about 90% of the emission is caused by charged species in the flow of the argon afterglow. According to the experimental evidence

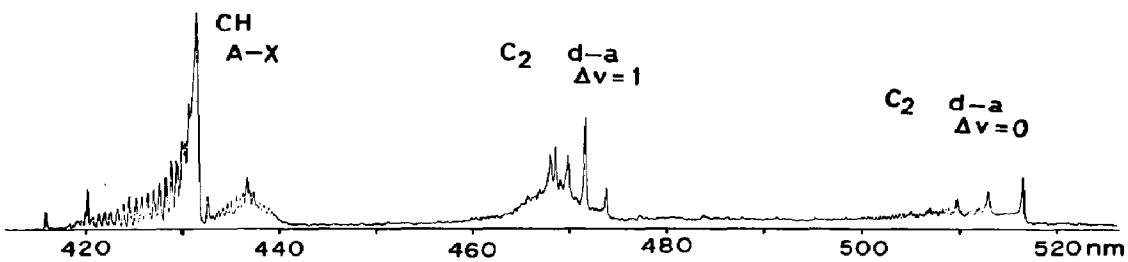

Fig. 1. Visible emission spectrum of excited fragments produced in the argon flowing afterglow reaction of acetylene.

TABLE 1

Minimum energies for formation of excited fragments by dissociative excitation of acetylene[a]

Dissociation products		E(eV)	Channel
C_2H_2 →	$C_2(d^3\Pi_g) + H_2$	8.6	1
	$C_2(d^3\Pi_g) + 2H$	13.1	2
	$C_2(d^3\Pi_g) + H_2^+$	24.0	3
	$C_2(d^3\Pi_g) + H + H^+$	26.7	4
	$CH(A^2\Delta) + CH(X^2\Pi)$	12.8	5
	$2CH(A^2\Delta)$	15.7	6
	$CH(A^2\Delta) + C + H$	16.2	7
	$CH(A^2\Delta) + CH^+$	23.9	8
	$CH(A^2\Delta) + C^+ + H$	27.5	9
	$CH(A^2\Delta) + C + H^+$	29.8	10
	$C_2H(\tilde{B}^2A) + H$	9.5[b]	11

[a] The following dissociation energies were used: D(HC–CH) = 9.89 eV [8], D(C–H) = 3.47 eV [9] and D(H–H) = 4.48 eV [9]. Excitation energies of $CH(A^2\Delta)$ and $C_2(d^3\Pi_g)$ were taken from ref. 8. Ionization potentials were taken from ref. 10. Our estimates for channels 1, 2 and 5 - 7 are the same as those reported by Beenakker and de Heer [17].
[b] Ref. 12.

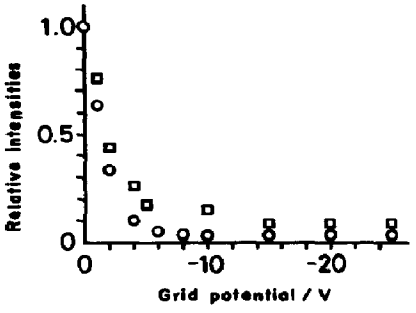

Fig. 2. Dependence of emission intensities (in relative scales) on the grid potential: □, $C_2 d^3\Pi_g - a^3\Pi_u$; ○, CH $A^2\Delta - X^2\Pi$.

given in previous reports for other molecules [4 - 6], metastable ions [14] $Ar^{+M}(^4D_{7/2}, {}^4F_{9/2,\ 7/2}, {}^2F_{7/2}, {}^2G_{9/2,\ 7/2})$ with available energies of 16.41 - 19.12 eV for $Ar^{+M} \rightarrow Ar^+(^2P_{3/2})$ and 32.17 - 34.88 eV for $Ar^{+M} \rightarrow Ar(^1S_0)$ can be regarded as candidates. All the channels listed in Table 1 for the $C_2(d^3\Pi_g)$ formation are energetically open if the active species are metastable ions. About 10% of the emission persisted even when the concentration of charged particles in the flow was reduced by a negative potential applied to the grid; this is probably a contribution from the reaction of the metastable atoms listed in Table 1 as channel 1. The fact that charged particles make a major contribution to the reaction contradicts the report of

Prince *et al.* [7], who considered that $C_2(d^3\Pi_g)$ radicals were mainly produced in the reaction with metastable argon atoms $Ar^M(^3P_{2,0})$ with excitation energies of 11.55 and 11.72 eV in channel 2. This process is evidently energetically unlikely.

The following existing reports suggest that $C_2(d^3\Pi_g)$ is produced favourably via states of the parent molecule to which optical transitions are forbidden: (1) the Swan system has not been observed in the photodissociation of acetylene by the krypton resonance lines [12, 15, 16] although channel 1 in Table 1 is energetically open; (2) electron impact on acetylene [11, 17] produced $C_2(d^3\Pi_g)$. Metastable argon ions can take part effectively in many of the optically forbidden processes, such as Ar^{+M} (quartet) to Ar^+ (ground state, doublet) (spin forbidden in the *LS* coupling scheme).

3.2. The CH 430 nm system

A negative potential applied to the grid reduced the emission intensity of this system (Fig. 2). This indicates that argon ionic species are also the main source for the production of $CH(A^2\Delta)$. All the channels listed in Table 1 for the production of $CH(A^2\Delta)$ (5 - 10) are possible for metastable argon ions Ar^{+M}.

Channel 5 with excitation by metastable argon atoms Ar^M was considered by Prince *et al.* [7] to account for the $CH(A^2\Delta)$ production. However, our observations indicate that this is not the case as do the present calculations of energetics (which show the proposed mechanism to be about 1 eV endoergic). Prince *et al.* also proposed the following alternative two-step mechanism:

$$Ar^* + C_2H_2 \rightarrow Ar + C_2H_2^+ + e \quad (12)$$

$$C_2H_2^+ + e \rightarrow CH(A^2\Delta) + CH(X^2\Pi) \quad (13)$$

This mechanism is consistent with the dependence of the emission intensity on the grid potential. However, additional energy of at least 1.4 eV must be supplied from the translational energy of the electrons. Therefore, this mechanisms is also unlikely.

A spin forbidden process in channel 5 was suggested by Tsuji *et al.* [11] who examined the shape of the excitation function near the threshold in an electron impact experiment. This process is probable in the Ar^{+M} reaction for the same reason as that discussed in the case of the formation of $C_2(d^3\Pi_g)$. Beenakker and de Heer [17] concluded from the Fano plot that optically allowed transitions were also important in the excitation transfer reactions 5 - 7. These transitions may also contribute to the production of $CH(A^2\Delta)$ where Ar^{+M} (doublet) can take part in the reaction.

3.3. The broad band

Even when a negative voltage was applied to the grid in order to reduce the charged species, the intensity of this broad band did not change appreciably. Therefore neutral metastable argon atoms Ar^M are the most probable source of excitation leading to this emission.

A similar broad emission band has been observed in the photodissociation [12, 15, 16] of acetylene by the krypton resonance lines and in controlled electron impact on acetylene [17]. This band was also reported in an earlier investigation of the argon afterglow reaction of acetylene [17]. The emitter of this band has been considered to be either $C_2H_2^*$ or $C_2H^*(B^2A)$ (where an asterisk represents an electronically excited state). The observation of this emission in the present study is compatible with either one of these species since metastable argon atoms have sufficient energy (11.55 and 11.72 eV) to produce species that can be produced by the krypton resonance lines (10.0 and 10.6 eV).

Acknowledgment

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