Emission Spectra Obtained by Low Energy Electron Bombardment of Methane and Chlorinated Methanes

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Spectroscopic studies of a molecular beam bombarded by a low energy electron beam were carried out for several simple organic molecules. The collision chamber resembled the ionization chamber of a mass spectrometer, and the electrons were accelerated at about 270 V. The spectrum of methane showed lines of excited hydrogen atoms and bands of excited CH radicals. The spectra of chlorinated methanes showed lines of excited chlorine atoms and bands of excited hydrogen chloride positive ions (HCl^{+*}) in addition. Even the spectrum of a mixture of methane and carbon tetrachloride revealed bands of HCl^{+*}. Dependence of emission intensities on target currents and gas pressures indicated the origin of the excited hydrogen atoms and CH radicals to come from direct fragmentation and the excited HCl^+ ions from a bimolecular process.

Mass spectrometric studies have provided information on the ionization and fragmentation of electron-bombarded molecules, but it is limited to the ionized species. Though, there are a few studies[2] on the neutral species, little is known on the excitation of molecules and their fragments in the ionization chamber. Thus, spectroscopic studies on the excited species in the ionization chamber would be of use.

The electric discharge method has been used to produce unstable species in combination with their spectroscopic detection in the discharge chamber and on the cathode. Though this method is very effective for analysis, the complicated character of the discharge is a major obstacle for detailed analysis of the mechanism of fragmentation and excitation of the species concerned. Horie, Nagura and Otsuka[3] investigated collisions between molecules and electrons with known velocities and observed an unusual distribution of the rotational energy of the fragment species OH, which was produced by the electron impact of H_2O or H_2O_2. An interpretation by a statistical model was reported.[4] Emission spectra of such simple molecules as N_2, CO, and CO_2 produced by electron bombardment were reported[5] and lifetimes of their excited species were measured by a similar method,[6] though only a few organic molecules were studied.

According to the quasi-equilibrium theory, fragmentation schemes of molecules in a mass spectrometer were interpreted,[7] while by use of a molecular orbital treatment, predictions as to the initial fragmentation were made by Hirota and his co-workers.[8] To clarify the mechanism of bond scissions and to justify the theoretical interpretation, knowledge of possible excited species and their behavior is of vital importance. Thus, we carried out spectroscopic studies of a molecular beam of some simple organic molecules bombarded by electrons.

Experimental

A molecular beam was crossed perpendicularly to collide with an electron beam in a chamber as shown in Fig. 1. A rhenium filament (e) was heated by a regulated DC power supply at about 6V and 3A. Two grids (c, d) were used to push the electron into a collision chamber (a). The collision chamber was kept at 220—270 V above the filament and had a slit of 20×2 mm, through which the electron beam was introduced. A target (b) was kept at 21 V above the chamber to collect the electrons. The sample gas was introduced from the bottom through several pin holes. In order to keep the filament and its surroundings in a high vacuum, a differential pumping system was used. Typical target and chamber currents used were 300 μA and 5 mA, respectively. The rate of molecular beam was estimated to be about 10^{19} molecules/min.

The light emitted perpendicularly both to the molecular beam and to the electron beam through a quartz window (g), 11 mm in diameter, was measured with a Shimadzu GE

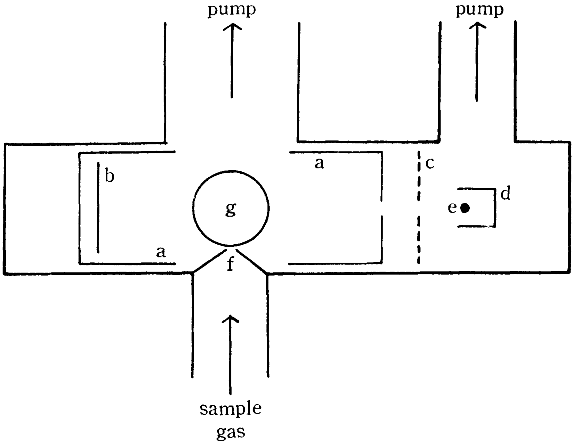

Fig. 1. Schematic diagram of the collision chamber: (a) collision chamber, (b) target. (c) grid 1, (d) grid 2, (e) rhenium filament, (f) pin holes, (g) quartz window.

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100 grating spectrograph, equipped with a 1200 grooves/mm grating blazed for 5000 Å and with a 1000 mm collimator system. Photographic measurements were carried out with a Kodak Tri-X Pan Film in the 2500—7000 Å region for determination of wavelength and finer details of emission lines. An EMI 6256 B photomultiplier was used for photometric measurements, when the intensities were to be determined in the 2000—6600 Å region.

The wavelength was calibrated by a low pressure mercury lamp. The intensity was calibrated by a Toshiba standard tungsten lamp (1500°C). No features of water or of organic substances were observed in the spectra of nitrogen and of carbon monoxide, which were utilized to see the performance of the instrument. The mass spectrum was recorded on a Hitachi RMU-5 mass spectrometer. Methane used was a Research Grade product from Takachiho Trading Co., and other compounds were of the best grade available from Wako Pure Chemical Ind., except for CH_2Cl_2 which was from Nakarai Chemicals. All the samples were used after repeated degassing in a high vacuum.

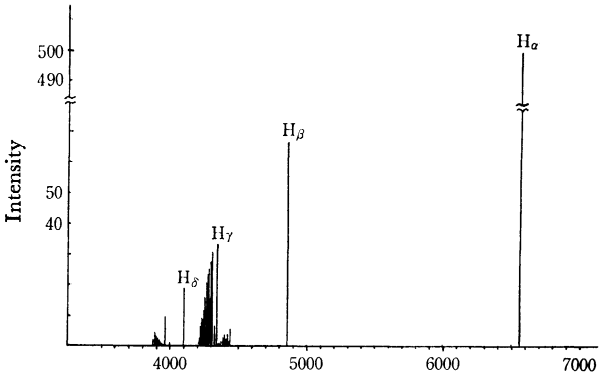

Fig. 2. Emission spectrum of methane bombarded by an electron beam.
260 V impact at 300—400μA.

Results and Discussion

A typical spectrum of methane is shown in Fig. 2. The very intense lines are the hydrogen Balmer series, which are denoted by H_α, H_β,$\cdots$. Six lines were clearly observed and their relative intensities were close to those in literature,[9] though the intensity of H_α line could not be determined accurately because of the poor sensitivity of the photomultiplier used at 6500 Å. The complicated features in the 3800—4500 Å region were assigned to CH (A→X) and CH (B→X) emission.[10] The detailed spectrum in 4200—4400 Å region is shown in Fig. 3. The assignments of vibrational and rotational bands were carried out with reference to literature.[11] A few very weak lines assignable to nitrogen were found, but no bands of CO.

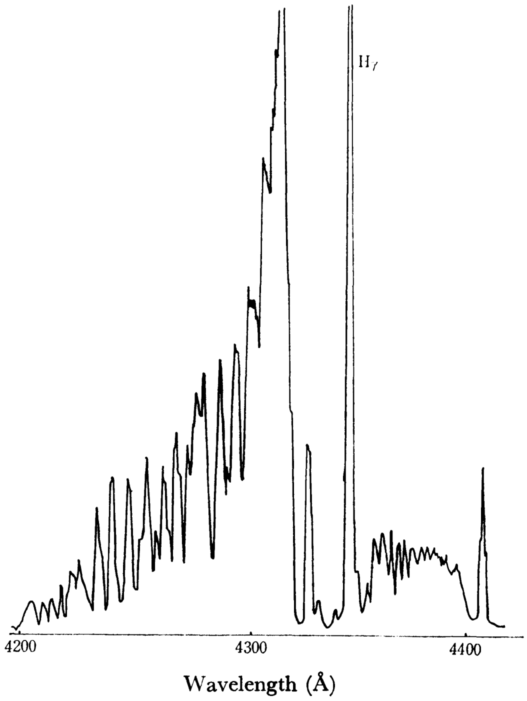

Fig. 3. Emission spectrum of methane in 4200—4400 Å region. 260 V impact at 700 μA. 200 μ slit.

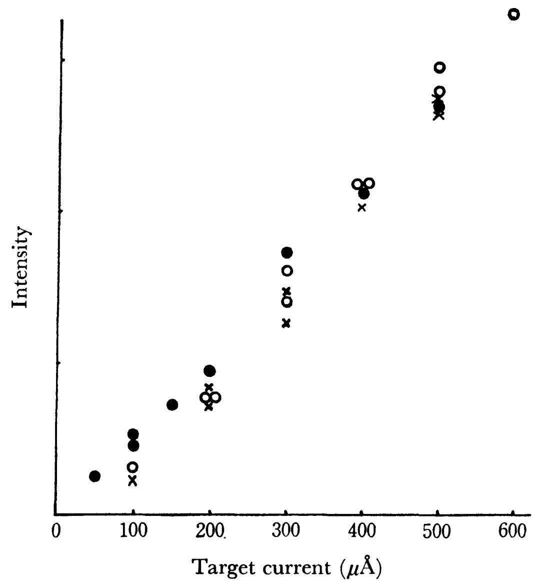

Fig. 4. Emission intensity *vs.* target current. H_β from methane at 4861 Å. For the sake of clarity, ten data were omitted below 50 μA, all of which lay on the same straight line. × 13.5 mmHg, ● 15 mmHg and ○ 18.5 mmHg in the gas reservoir.

Dependence of emission intensity on target current is shown in Figs. 4 and 5 for H_β (4861 Å) and for CH (4312 Å), respectively. The linear relationship was found in the region of 10—600 μÅ in both cases. The production of excited H atoms and excited CH radicals was, therefore, concluded to be a first-order reaction to the incident electrons, if it was assumed to be proportional to the target current. Dependence of emission intensities on gas pressures is shown in Fig. 6 for both H_β (4861 Å) and CH (4312 Å). The gas pressure was measured in the gas reservoir, where the pressure was assumed to be proportional to that in the collision chamber. The intensity of emission lines was in linear relation to pressure at lower pressures but the curves

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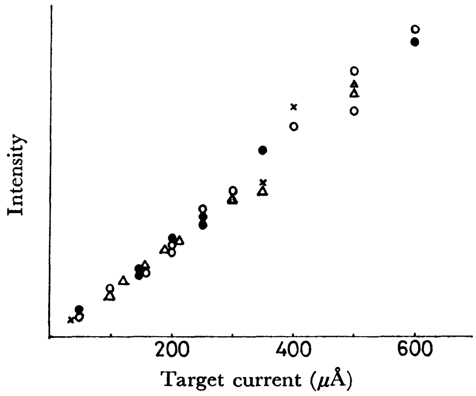

Fig. 5. Emission intensity *vs.* target current. CH* from methane at 4321 Å. For the sake of clarity, eight data were omitted below 60 μA, all of which lay on the same straight line. × 12.5 mmHg, ● 13.5 mmHg, ○ 17 mmHg and △ 21 mmHg in the gas reservoir.

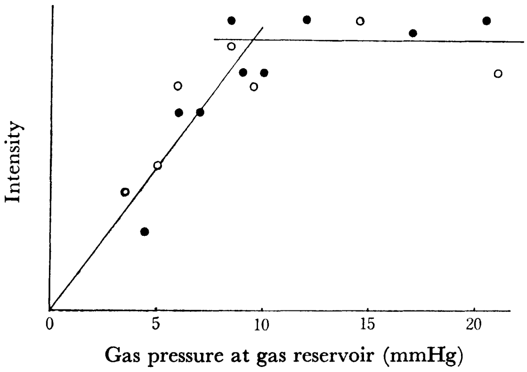

Fig. 6. Emission intensity *vs.* gas pressure. Target current was 10 μA. ○ H_β and ● CH*. Gas pressure indicated was measured not in the collision chamber but in the gas reservoir.

leveled off at a certain pressure, which was common to both H_β and CH and shifted to a lower value when the target current was increased. These results imply that collisional deactivation among excited species plays a dominant role, since the collisional deactivation between excited species and parent molecules should cause a shift to a higher value.

The linear relations lead to the conclusion that the excited hydrogen atoms and the excited CH radicals were produced by a mechanism of direct excitation and fragmentation as follows:

$$CH_4 + e \longrightarrow CH_4^* \longrightarrow H^*, CH^* \cdots$$

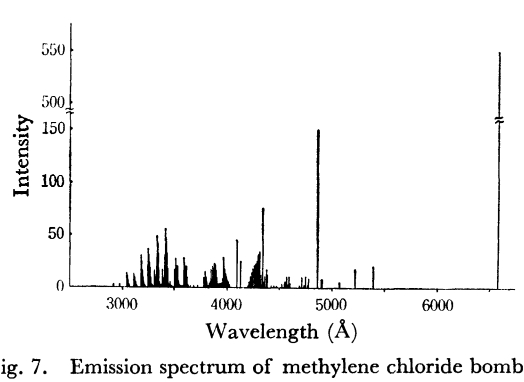

Fig. 7. Emission spectrum of methylene chloride bombarded by an electron beam. 260 V impact at 400—600 μA.

The emission spectra of chlorine derivatives of methane bombarded by an electron beam showed some additional features. The spectra of methyl chloride, methylene chloride and chloroform looked alike. A typical spectrum of methylene chloride is shown in Fig. 7. The strongest lines are assigned also to the hydrogen Balmer series, but the relative intensity of H_β to H_α in this case was found to be larger than that of methane. Emission bands of CH radicals (A→X and B→X) were also observed and are similar to those of methane.

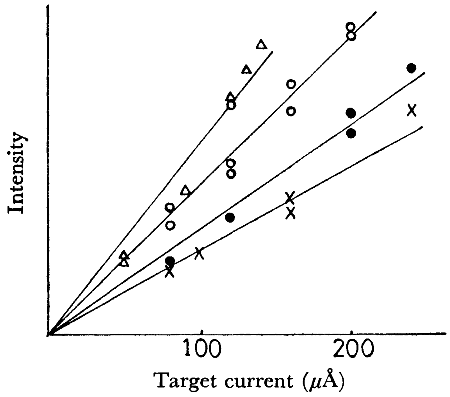

Fig. 8. Emission intensity *vs.* target current. H_β from methylene chloride at 4861 Å. × 5.5 mmHg, ● 10.5 mmHg, ○ 14.5 mmHg and △ 20 mmHg in the reservoir.

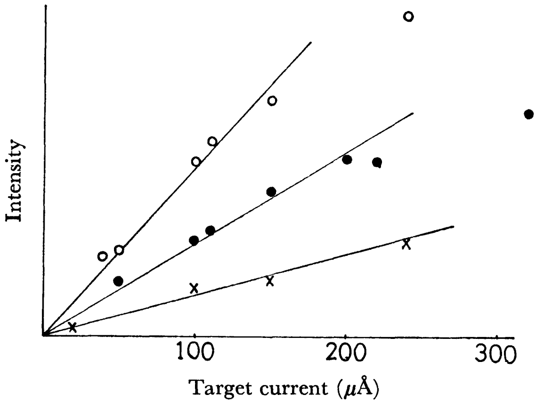

Fig. 9. Emission intensity *vs.* target current. CH* from methylene chloride at 4312 Å. × 6 mmHg, ● 9.5 mmHg and ○ 17.5 mmHg in the gas reservoir.

Dependence of emission intensities on target current is shown in Figs. 8 and 9 for H_β (4861 Å) and for CH (4312 Å), respectively. Since the intensities were in linear relation to target current, the production of excited H atoms and excited CH radicals can be concluded to be of the first order to the incident electrons. The identical argument as for methane could be applied further to the production of H* and CH* from chlorinated methanes, since the behavior of emission intensities was similar.

The most remarkable characteristic in this spectrum is shown by the bands which appear in the 2900—4000 Å region. Doublet splitting of vibrational structures is clearly observed. A detailed spectrum is shown in Fig. 10. The bands, together with vibrational and rotational structures, were assigned to HCl^+ (A→X)

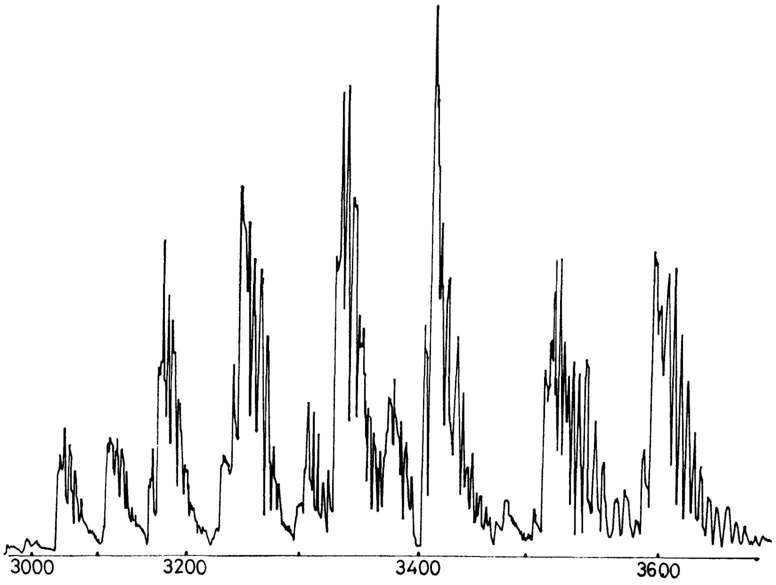

Fig. 10. Emission spectrum of methylene chloride in 3000—3700 Å region. 260 V impact at 400—600 μA.

according to the results by Brice and Jenkins,[12] and Norling.[13] The bands observed were in order of intensity: (1,0) at 3334 Å and 3410 Å, (2,0) at 3180 Å and 3245 Å, (0,0) at 3515 Å and 3595 Å, and (0,1) at 3863 Å and 3965 Å and also the (3,1) and (3,0) bands. The (1,1) (2,1) (2,2) and (4,0) bands could be pointed out. In comparison with the electrical discharge of HCl,[12] HCl^+ was found to be vibrationally excited.

The linear relations between the intensities and the amount of incident electrons as observed in the case of H and CH were not observed for HCl^+. It seems unlikely that H and CH and HCl^+ were produced by a similar mechanism. No strong peak was observed at $m/e=36$ (HCl^+) in the mass spectrum of methylene chloride; the intensity of HCl^+ was 3.5% of that of the strongest CH_2Cl^+. Since the pressure is much lower in the mass spectrometer, this suggests that HCl^{+*} would not be produced by direct fragmentation of methylene chloride, and HCl^{+*} observed in the present study would come from a bimolecular process.

The emission spectra of 1,1,1-trichloroethane and of a one-to-one mixture of methane and carbon tetrachloride were observed by the photographic method. In both cases, the bands of HCl^+ were clearly observed and looked identical to those of CH_2Cl_2. Similarity of the fine structure of HCl^+ suggests that the origins of HCl^+ were common for all parent species. From this and the result of mass spectroscopy on methylene chloride, it can be concluded that the excited hydrogen chloride positive ions were produced by a bimolecular process. Cashion and Polanyi[14] investigated the reaction,

$$H + Cl_2 \longrightarrow HCl + Cl$$

They observed that the product HCl was in vibrationally excited states. In the present study, the vibrationally excited HCl^+ might be produced by a related mechanism.

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