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The Emission Spectra of Hydrogen Atoms Produced from Methanol by Electron Impact

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The emission spectra of several fragmental species, especially of hydrogen atoms, produced by the electron impact (energy: 240 eV) of gaseous methanol and deuteromethanols have been investigated. The intensity ratios of the Balmer-β lines of the H and D atoms are *ca.* 2.9:1 for CH_3OD and *ca.* 1:1.8 for CD_3OH, indicating that the excited hydrogen atoms result from the O–H bond scission, as well as from the C–H bond scission, of the parent methanol molecules. The ratio of the scission probability of a C–H bond to that of the O–H bond is calculated to be 0.8, taking into account the correction of the isotope effect. It was concluded that the excited hydrogen atoms are produced by the primary process of fragmentation *via* a superexcited species.

The emission spectra of simple molecules under electron impact have been studied extensively by several investigators,[2–5] and information has been obtained on the lifetime of the excited species thus produced by the use of the spectrophotometric method.[6–8] However, few studies have dealt with the emission spectra of organic molecules.[9]

In the radiation-chemical reaction of methanol, the primary process is generally considered[10] to be the split-off of a hydrogen atom from the methyl group of a methanol molecule, Eq. (1a). This conception is based on various pieces of

$$\mathrm{CH_3OH} \begin{array}{ll} \nearrow \dot{\mathrm{C}}\mathrm{H_2OH} + \mathrm{H} & \quad (1a) \\ \searrow \mathrm{CH_3\dot{O}} + \mathrm{H} & \quad (1b) \end{array}$$

evidence; *e.g.*, the $\dot{C}H_2OH$ radical was found in irradiated solid methanol by the ESR method,[11] and the peak of the CD_2OH^+ ion appeared abundantly in the mass spectrum of CD_3OH.[12] Contradicting the above conclucion, however, one critical experiment[13] reported that, in the γ-ray radiolysis of CH_3OD, the amount of HD in the produced hydrogen reached 60%, and also a little D_2 appeared. This finding can be easily explained if the scission of the C–H and the O–H bonds is assumed to occur with the same probability in the primary process of fragmentation, but the result was later understood in terms of an ion-molecule reaction.[12] Most methods hitherto used identify only the products which have already been stabilized. Unlike these indirect methods, however, emission spectra under electron impact may give direct information as to the excited hydrogen atoms produced by electron impact.

In the present investigation, the emission spectra of the fragmental species produced from methonal and deuteromethanols by electron impact were observed, and the origin of excited hydrogen atoms was discussed on the basis of the isotopic ratio of the hydrogen produced.

Experimental

The electron-impact apparatus was described in a previous paper.[14] The acceleration voltage of the electrons was 240 V and the electron current was between 20 and 300 μA. The gas pressure was estimated at about 10^{-2}mmHg by the use of a Pirani gauge attached near the collision chamber.

The photoemission was observed in the direction perpendicular to the electron beam, and the gas flow, through a quartz window by means of a Shimadzu GE 100 grating monochromator equipped with an EMI-6256B photomultiplier.

The CH_3OH was obtained from Nakarai Chemicals, and the CD_3OD and CH_3OD, from Merck. The CD_3OH was prepared from CD_3OD *via* $(CD_3O)_2Mg$, and was distilled in a vacuum four times. In order to eliminate the mixing of hydrogen occluded in the wall of the apparatus, the sample gas was introduced into the reservoir and collision chamber and then removed by evacuation. This procedure was repeated until a constant spectrum was obtained.

Results

Figure 1 shows the emission spectrum obtained by the electron impact of CH_3OH in the region from 350 to 500 nm. Similar spectrum can be observed from CD_3OD. No bands of the excited methanol molecule, the CH_3 radical, the CH_2 radical, or their ions are found in the same wavelength region. The intense peaks in the spectrum belong to the Balmer series of the H atom and the comet-tail band system of the CO^+ ion. The Balmer-α (656.3 nm) was not observed because of the low sensitivity of the photomultiplier in the longer-

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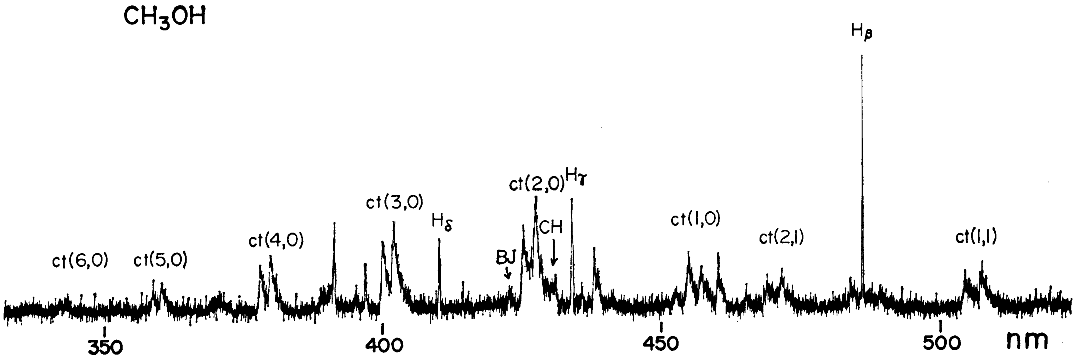

Fig. 1. Emission spectrum observed by electron impact of CH_3OH.
Acceleration voltage of electron: 240 V
H_β, H_γ, H_δ: Balmer series of hydrogen atoms
ct: CO^+ comet-tail bands
BJ: CO^+ Baldet-Johnson band

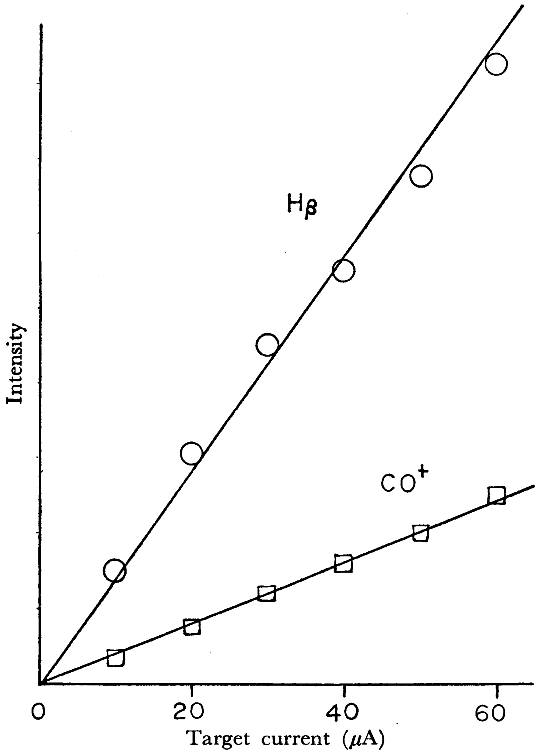

Fig. 2. Dependency of intensities of the H_β and the comet-tail (2,0) band on the target current; the pressure in the reservoir: 3 mmHg.

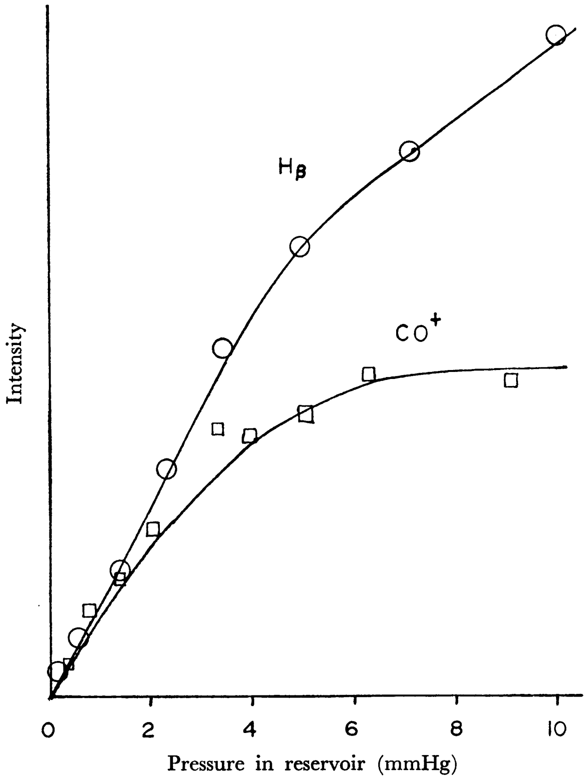

Fig. 3. Dependency of intensities of the H_β and the comet-tail (2,0) band on the gas pressure; the target current: 50 μA.

wavelength region, whereas Balmer-β (486.1 nm), Balmer-γ (434.0 nm), Balmer-δ (410.2 nm), and Balmer-ε (397.0 nm) were clearly observed. The "ct" sign in Fig. 1 represents the comet-tail band (CO^+ $A\ ^2\Pi \longrightarrow X\ ^2\Sigma^+$), while the two numbers in parentheses following represent the vibrational quantum numbers of the upper and lower electronic states respectively. Furthermore, the Baldet-Johnson band (CO^+ $B^2\Sigma^+ \longrightarrow A\ ^2\Pi$) and the 430 nm band of the CH radical ($A\ ^2\Delta \longrightarrow X\ ^2\Pi$) are found.

The linear dependency of the intensities of the Balmer-β line and the comet-tail (2,0) band on the target current, as shown in Fig. 2, indicates that the excited species are produced primarily by a collison of a parent molecule with an electron. The dependency of the intensities of these peaks on the pressure in the gas reservoir is shown in Fig. 3. The pressure in the collision chamber was estimated to be higher than one seven-hundredth of the pressure in the gas reservoir. The intensities of the Balmer-β line and the comet-tail (2,0) band increase linearly with an increase in the gas pressure up to a certain pressure, but they increase more slowly above this pressure. The levelling-off of the intensities at higher gas pressures may be due to the collisional deactivation of the excited species, and not to the self-absorption of the emission. Similar behavior has also been reported for the emission spectrum of carbon monoxide by Rothe and McCaa,[15] who

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observed that the intensities of the emission bands of CO^+ increase rapidly up to *ca.* 5×10^{-2} mmHg in pressure and thereafter increase gradually, while the neutral CO bands (Herzberg and Angstrom) increase rapidly with an increase in the carbon monoxide pressure.

In order to find the absolute cross-section of the Balmer-β line from methanol, a mixture of a known composition of CD_3OD and CH_4 was bombarded by electrons, and the intensities of the Balmer-β emissions of the H and D atoms, which are separated by 1.3 Å, were measured. The cross-section of the Balmer-β emission from CD_3OD is determined to be *ca.* 4×10^{-19} cm^2 by normalization to the absolute cross-section of the Balmer-β line from CH_4 reported by Vroom and De Heer,[9] although the present cross-section may involve some error because of the relatively high pressure.

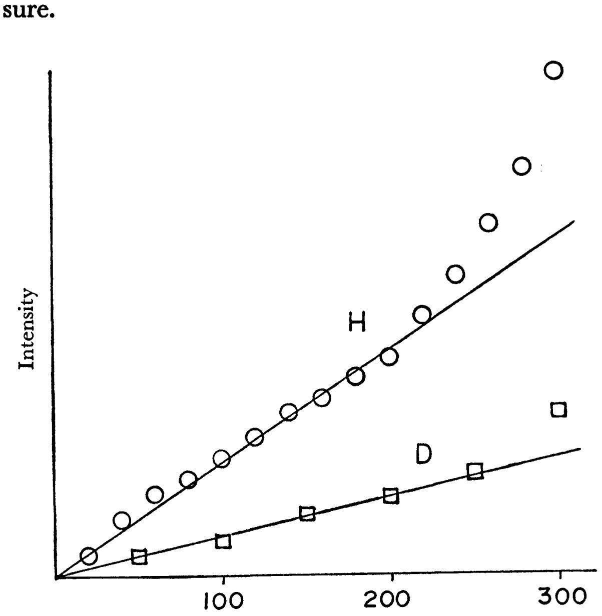

Fig. 4. Intensity of Balmer-β emission of H and D from CH_3OD; the pressure in the gas reservoir: 10 mmHg.

In order to determine the emission probabilities of the Balmer-β radiation of hydrogen atoms from the methyl group and the hydroxyl group separately, the intensity ratios of the Balmer-β emissions of the H and D atoms from CH_3OD and CD_3OH were determined. Figure 4 shows the intensities of the Balmer-β emissions of H and D from CH_3OD against the target current. The curves deviate upwards from the linear lines above a certain target current, indicating the contribution of some excited hydrogen atoms produced by collisions with two or more electrons. The intensity ratio of the Balmer-β line of H to that of D resulting from the bombardment of CH_3OD is about 2.9 in the linear part of Fig. 4, whereas that of D to that of H from CD_3OH is about 1.8. The disagreement of the above ratios for CH_3OD and CD_3OH indicates the existence of an isotope effect.

Assuming that the bond scissions of the methyl and hydroxyl groups are independent of each other, and that their isotope effect is equal in size in both groups, the following two conclusions can be drawn from the above results. First, the emission probability of D is less than that of H by *ca.* 20%, a value which is comparable to the isotope effect observed for CH_4 and CD_4.[9] Second, the probability of the production of the excited hydrogen atom from the methyl group is less by *ca.* 20% than that from the hydroxyl group per each hydrogen atom, taking into account the correction of the isotope effect.

Discussion

In the radiolysis of methanol, it was previously concluded, as has been mentioned above, that the primary process of fragmentation is a C–H bond scission.[10] This conclusion, supported by several experimental results, seems reasonable on the basis of the difference in the bond energies of the C–H and O–H bonds, the former having the smaller bond energy by 7.5 kcal/mol.[16] Nevertheless, the present measurement of the production of excited hydrogen atoms shows that a bond scission of the O–H bond is as probable as that of a C–H bond. However, this study is concerned only with the production of the excited hydrogen atom, and not with that of the hydrogen in the ground state. Therefore, the contribution of the excited hydrogen atoms to the overall production of hydrogen atoms is not established by the present experiment.

The emission probabilities of hydrogen atoms from the methyl and hydroxyl groups are of nearly the same magnitude; those from methanol and methane are also found to be comparable. These findings are interesting with regard to the result on some hydrocarbons that the number of excited hydrogen atoms produced in a particular energy level is practically independent of the hydrocarbons.[9]

Table 1. Energies for reactions

Reaction	Energy (eV)	Ref.
$CH_3OH \longrightarrow CH_3\dot{O}+H$	4.3	16
$CH_3OH \longrightarrow \dot{C}H_2OH+H$	4.0	16
$CH_3OH \longrightarrow CH_3OH^++e$	10.83	19
$H\,(n=1) \longrightarrow H\,(n=4)$	12.75	

The excited hydrogen atom must be produced *via* a superexcited methanol molecule, as was pointed out by Platzman *et al.*,[17,18] because the sum of the bond energy of the C–H or O–H bond and the excitation energy of a hydrogen atom is greater than the ionization energy of methanol, as is shown in Table 1. The autoionization and dissociation of the superexcited molecule compete, and the isotope effect exists only in the dissociation process, which is affected by the nuclear mass difference. Hence, the superexcited molecule containing a heavier isotope has, in general, a smaller probability of dissociation. The isotope effect of the Balmer emission from methanol mentioned above is, therefore, reasonable.

Since the intensity ratio of the Balmer line of H to

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that of D had to be measured at pressures as high as 10^{-2} mmHg because of the weak intensity of the lines, the secondary effects which affect the intensity ratio, such as collisional deactivation or self-absorption, might occur in the present system. However, further discussion along these lines could not be made because of the present lack of quantitative data on these effects.

Conclusion

By the electron impact of methanol, various excited fragments, such as the H atom, the CO^+ ion, and the CH radical, were produced, but no larger excited fragments, no excited parent molecule, and none of the corresponding ions could be found in the spectral range from 350 to 500 nm.

It was concluded that the excited hydrogen atom resulted from the scission of the O–H bond as well as from that of the C–H bond, and that the probabilities per bond of the above two processes were of nearly the same magnitude, if the isotope effect is considered. It is not certain, however, if this process is as important as the one which produced the hydrogen atom in the ground state, so that the present finding may not contribute much to clarifying the total split-off processes of the hydrogen atom from methanol.

By a comparison of the Blamer-β emission for CH_3OD and CD_3OH, an isotope effect of about 20% was preliminarily estimated for the dissociative excitation for the H and D in the molecules, the former having the larger cross-section. This effect can be explained by a process including superexcitation.

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