Dissociative excitation of molecules by electron impact

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A study is reported of dissociation by electron impact of CH_4, CH_3Cl, CH_2Cl_2, and $CHCl_3$ molecules into excited H, CH($A\,^2\Delta$), and (Cl^+) fragments. It is shown that the cross section for the formation of H* is almost constant for all the molecules and is close to the corresponding dissociation cross sections of aliphatic hydrocarbons. The cross sections for the formation of CH*($A\,^2\Delta$) and $(Cl^+)^*$ increase when the hydrogen atom is replaced by chlorine in the molecule.

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Experiments on the dissociative excitation of complex hydrocarbon molecules by electron impact have shown that the cross section for the formation of the H* fragments is almost the same[1–3] or shows small changes for different molecules.[4] For other fragments, such as CH* or C_2^*, the cross section for dissociative excitation is generally found to decrease with increasing number of atoms in the molecule.[1,3,4] This reduction in the probability of formation of particular fragments during the dissociation of molecules with increasing number of atoms per molecule is sometimes explained by an increase in the number of possible dissociative processes and, hence, by a reduction in the probability that a particular process will take place.[4,5]

In the present research, our aim has been to verify the effect of a different number of possible dissociation processes on the probability of formation of particular fragments. In order to establish a clear-cut situation, we investigated the dissociation of molecules with the same number of atoms and studied the formation of the same fragments. We chose the CH_4 molecule, in which the hydrogen atom was successively replaced by the chlorine atom, and we measured the cross sections for the formation of the excited fragments CH*, H*, and $(Cl^+)^*$. In this way, the total number of possible dissociation processes remains constant but there is a considerable change in the number of possible dissociation processes involving the formation of a particular fragment.

The experimental arrangement and the method of measuring the excitation cross sections were described previously in[6]. The gas pressure in the collision chamber was measured by a Knudsen manometer which was calibrated against a McLeod gauge for each gas. All the measurements were carried out in the region of single collisions ($P \leq 2\times10^{-3}$ Torr, $J \leq 500$ μA). The uncertainty in the measured excitation cross sections was ±30%.

The emission spectra of the CH_3Cl, CH_2Cl_2, and $CHCl_3$ molecules under electron bombardment were investigated in the region between 3900 and 6000 Å, and were found to be similar. In addition to the emissions observed in the methane spectrum,[7] i.e., the emissions from CH* ($A^2\Delta - X^2\Pi$ and $B^2\Sigma - X^2\Pi$), and the Balmer series of hydrogen, the spectra of these molecules were found to contain a number of multiplets due to $(Cl^+)^*$. Table I lists the cross sections for the excitation of the various emissions in the molecules under investigation at electron energy $E = 4$ keV. We also list the results on the dissociative excitation of methane obtained previously.1)

Analysis of our results leads to the conclusion that there are three different tendencies in the variation of the probability of dissociation into different fragments as one passes from the CH_4 to the $CHCl_3$ molecules. These can be seen by considering the cross sections for the formation of different excited fragments.

1. The cross sections for the formation of the excited hydrogen atom during the dissociation of the CH_4–$CHCl_3$ molecules remain practically constant even though the number of hydrogen atoms in the parent molecules is reduced from 4 to 1, so that there would appear to be a reduction in the number of possible dissociation processes leading to the formation of the H* fragments. The observed differences between the H* excitation cross sections lie within experimental error. A similar result has been obtained for the dissociation of the molecules of hydrocarbons.[1–3,7]

2. The cross sections for the formation of the excited ion $(Cl^+)^*$ are very different in the dissociation of different molecules, and for all the Cl II multiplets

TABLE I.

λ, Å	Transition	$\sigma\cdot10^{21}$ cm²			
		CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$
4315	CH $A^2\Delta - X^2\Pi$	99	139	223	480
4861	H_β	33	40.0	34.6	28.3
4340	H_γ	10	14.0	12.4	13.0
4101	H_δ	4.2	6.6	6.0	3.8
4740	ClII, $3d''\,^1D^0 - 4p''\,^1P$		0.9	1.2	2.8
4768.7	ClII, $4s''\,^3P^0 - 4p''\,^3D$		1.0	1.4	3.3
4794	ClII, $4s\,^5S^0 - 4p\,^5P$		6.6	9.4	21.4
4810			4.5	6.5	14.7
4819.5			3.1	4.5	10.2
4896.9	ClII, $4s'\,^3D^0 - 4p'\,^3F$		3.7	5.3	12.9
4904			3.1	4.5	11.0
4917			2.1	3.0	7.3
5070	ClII, $4s'\,^3D^0 - 4p'\,^3D$		2.4	4.3	9.5
5099			1.7	3.0	6.7
5217.9	ClII, $4s\,^3S^0 - 4p\,^3P$		2.7	8.6	16.1
5392	ClII, $4s'\,D^0 - 4p'\,^1F$		weak	3.2	7.5
5423	ClII, $3d\,^5D^0 - 4p\,^5P$		»	2.6	6.1
5443			»	2.1	4.9
5457			»	1.3	3.2

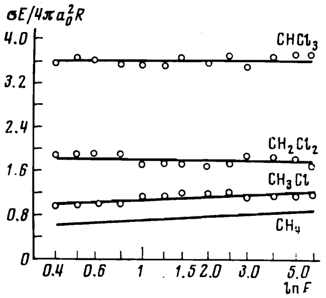

FIG. 1. Dependence of $\sigma E/4\pi a_0^2 R$ on $\ln E$ for CH*($A^2\Delta - X^2\Pi$) during the excitation of different molecules by electron impact.

that were investigated the change was found to be practically the same. The cross section for dissociative excitation of CH_2Cl_2 with the formation of $(Cl^+)^*$ is greater by a factor of 1.4–1.8 as compared with CH_3Cl, whereas the corresponding factor for $CHCl_3$ is 3–4. A direct correlation is observed in this case between the number of possible dissociation processes and the cross section for the formation of the fragment $(Cl^+)^*$ during dissociation.

3. An opposite tendency is observed in the case of the excited fragment CH* ($A^2\Delta$). Between CH_4 and $CHCl_3$, the cross section for the excitation of the CH* ($A^2\Delta - X^2\Pi$) emissions is found to increase monotonically by a factor of nearly 5.

Thus, it follows from our results that the number of possible dissociation processes does not necessarily determine the probability of dissociation into particular fragments although a definite correlation is observed in some cases (for example, in Cl^+). The observed increase in the cross sections for the excitation of CH* ($A^2\Delta$) when the hydrogen atom is replaced by the chlorine atom may be due to the lower energy of dissociation with the formation of CH* because the C–Cl bond energy (3.5 eV) is less than the C–H bond energy (4.4 eV).[8] However, this conclusion requires further verification. In general, the cross section for the formation of different fragments is determined by the distribution of excitation energy received from the exciting particle within the parent molecule, and by the properties of the unstable excited states of the molecules.

We have measured the excitation functions at electron energies of 0.4–6 keV for CH* ($A^2\Delta - X^2\Pi$), H_β, and a number of Cl II multiplets in the case of all the molecules under investigation. For CH_3Cl molecules, the excitation functions corresponding to the Cl II multiplets could not be determined because of their low intensity. As in[7], the resulting excitation functions were analyzed in terms of the Bethe–Born theory[9,10] to elucidate the role of dipole and optically forbidden transitions in the excitation of unstable molecular states. The H* excitation cross section was found to be inversely proportional to the electron energy for all the molecules under investigation, and this was found to be the same as the dependence for the hydrocarbons,[1-3] i.e., optically forbidden transitions play the main role in the excitation of unstable molecular states of the chlorine derivatives of methane, the dissociation of which results in the appearance of H* (just as for methane).

Figure 1 shows graphs of $\sigma E_{el}/4\pi a^2 R$ as a function of $\ln E_{el}$ for the CH* ($A^2\Delta - X^2\Pi$) emission in the case of the dissociative excitation of the above molecules. In this expression, a_0 is the first Bohr radius and R is the Rydberg energy. As can be seen, the dependence of $\sigma E_{el}/4\pi a_0^2 R$ on $\ln E_{el}$ for CH* has the greatest slope in the case of excitation of CH_4. The slope is smaller for CH_3Cl, and is practically zero for CH_2Cl_2 and $CHCl_3$. The slope of these lines is related to the sum of optical oscillator strengths of dipole transitions. Consequently, the contribution of dipole transitions to the excitation of unstable molecular states, which yield CH* on dissociation, decreases with increasing number of Cl atoms in the molecule, although the cross section for the excitation of CH* ($A^2\Delta$) increases.

On the other hand, in the case of photon excitation, the dipole transitions have the greatest probability, and the probability of formation of CH* ($A^2\Delta$) should therefore undergo a substantial reduction as the number of Cl atoms in the molecule increases. This cannot as yet be verified because we have no data on measured quantum yields during the photodissociation of these molecules.

The dependence of $\sigma E_{el}/4\pi a_0^2 R$ on $\ln E$ for the Cl II multiplets in the case of the $CHCl_3$ and CH_2Cl_2 molecules has an essentially positive slope which indicates that allowed transitions play the determining role in dissociative processes resulting in the formation of the excited fragment $(Cl^+)^*$.

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1) Our results reported in[7] for methane are now known to be too high because of errors in pressure calibration.

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