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DYNAMICS OF PHOTODISSOCIATION*

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1. Strictly linear triatomics

The prototype of all polyatomic photodissociation processes is the linear triatomic. Such a molecule is described by only two internal coordinates and thus is the only molecule amenable to a detailed state-to-state theoretical treatment. There is a problem, however. Stable linear triatomics have either 10 electrons (HCN) or 16 electrons (ICN, HgI_2, CO_2 and N_2O) and according to Walsh's rules the first excited upper states of these molecules are bent and would require additional coordinates for their description. Relief from this dilemma is furnished by going to a higher state in which the dissociation process

$$\text{A–B–C}(^1\Sigma) + h\nu \rightarrow \text{A}(^1\text{S}) + \text{B–C}(^1\Sigma)$$

takes place. Here both the ground and the excited states are rigorously linear.

We measured the translational energy distribution of $S(^1S)$ atoms generated from OCS at 157 nm. The measured translational energy distribution implied that the CO molecules were produced in vibrational states $v = 4$ - 8 with a peak at $v = 6$. OCSe was dissociated at 193 nm but only a minority of the selenium atoms were in the ^1S state and the translational energy distribution was less informative.

2. Cadmium dimethyl

Cadmium dimethyl ($Cd(CH_3)_2$) was chosen because *a priori* it should furnish a good example of linear three-body dissociation and the CH_3 radical speed distribution should reflect the mechanism of the bond breaking, *i.e.* simultaneous or sequential. Surprisingly, the total kinetic energy was only 1 - 2 kcal mol^{-1}. The investigation showed strong fluorescence from the $Cd(^3P_1)$ state so that virtually all the available energy was released as electronic energy.

3. s-Triazine

s-Triazine ($C_3H_3N_3$) was photodissociated at 248 and 193 nm into three HCN molecules. At 248 nm the kinetic energy distribution was extremely broad, stretching from 5 to 77 kcal mol^{-1}, implying an equally broad distribution in internal energy. At 193 nm the fragments moved very slowly with only a few kilocalories per mole of kinetic energy. An average HCN molecule has more than 30 kcal mol^{-1} of internal (mainly vibrational) energy. The striking difference between these two distributions is explained by postulating that the equilibrium structure of the triazine in the state excited at 248 nm is only slightly ex-

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TABLE 1

Molecule	D_0 (kcal mol^{-1})	$h\nu$ (kcal mol^{-1})	E_{AVL} (kcal mol^{-1})	E_E (kcal mol^{-1})	$\langle E_T \rangle$ (kcal mol^{-1})	$\langle E_V \rangle$ (kcal mol^{-1})	$\langle E_R \rangle$ (kcal mol^{-1})
OCS	72	185	113	63	14	36	0
C_2H_4S	85	148	63	26	11	48	≈0
$Cd(CH_3)_2$	61	148	87	87	≈1	≈0	≈0
H_2O_2	50	148	98	0	94	≈0	≈4
$C_3H_3N_3$	38	115	77	0	30	47	≈0
		148	111	0	6	105	≈0
$CSCl_2$[a]	64	115	51	0	16	35	≈0
$CSCl_2$[b]	114	148	34	0	17	17	≈0

[a] $CSCl_2 \rightarrow Cl + ClCS$.

[b] $CSCl_2 \rightarrow CS + 2Cl$.

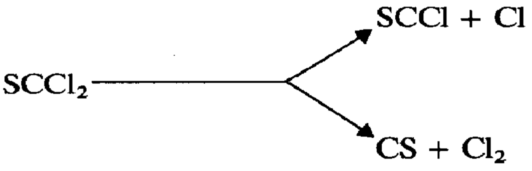
panded but that when excited at 193 nm triazine becomes greatly expanded and distorted.

4. Hydrogen peroxide

Hydrogen peroxide (H_2O_2) was dissociated both at 193 nm and at 248 nm into two OH radicals. Laser-induced fluorescence showed that the OH radicals were all in their vibrational ground states. At 193 nm the rotational distribution was found to extend from $K = 0$ to (at least) $K = 20$ but was peaked at $K = 0$. As seen in Table 1 almost all the available energy appears as translational energy largely because the center of mass of the OH radical is so close to the oxygen atom. The wide range of K values is ascribed to the large amplitude of the torsional motion of the parent molecule.

5. Thiophosgene

Thiophosgene ($CSCl_2$) is a "poor man's formaldehyde". (It has a much higher extinction coefficient and therefore requires less delicate apparatus for detection of its fragments.) At 248 nm we found, among others, CSCl and Cl_2 fragments, showing that both the processes



$$SCCl_2 \rightarrow SCCl + Cl \quad (1)$$

$$SCCl_2 \rightarrow CS + Cl_2 \quad (2)$$

occur although it appears that the quantum yield for process (1) is 0.8 ± 0.1. An impulsive spectator model is consistent with the observed average translational energy of 16 ± 2 kcal mol^{-1}.

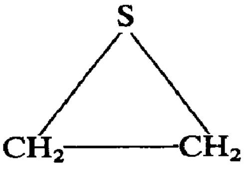
At 193 nm either process (2) or

$$SCCl_2 \rightarrow CS + 2Cl \qquad (3)$$

occurs. Laser-induced fluorescence showed that the CS fragments were rotationally excited and had a vibrational distribution peaking at $v = 3$. The vibrational excitation is explained on the basis of the differences in the CS bond length between the ground and excited states of $CSCl_2$, and the rotational excitation is explained on the basis of the non-planarity of the upper state.

6. Ethylene sulfide

Ethylene sulfide



was chosen because, if its C_{2v} symmetry is maintained during dissociation, no energy is released into rotation. At 193 nm a fairly broad distribution of translational energies was observed whose average value was 11 kcal mol^{-1}. This is consistent with a model in which the S atoms are produced "suddenly" in the ^1D state. The C_2H_4 part of the molecule is extended and bent with respect to ethylene so the suddenly produced ethylene is strongly vibrationally excited.

7. *Summarizing remarks*

In a photodissociation the excess of photon energy $h\nu$ over the dissociation energy D_0 is called the available energy (minus the small amount of thermal energy in the parent molecule) E_{AVL}. Table 1 presents a condensation of the experimental results in which no translational energy distributions are given but only the average translational energy release $\langle E_T \rangle$. From these and laser-induced fluorescence data, distributions over electronic, vibrational and rotational degrees of freedom were inferred.

There are diatomic-like polyatomics, *e.g.* H_2O_2, in which virtually all the energy release is in translation. In contrast, for $Cd(CH_3)_2$ virtually all the energy release is in electronic energy. In $C_3H_3N_3$ the energy release at 193 nm is almost all in vibration but at 248 nm is more evenly divided between translation and vibration. C_2H_4S and OCS exhibit a more even distribution of available energy into electronic, vibrational and translational degrees of freedom. $CSCl_2$ has three different sets of products. In short, the individual nature of molecules forbids generalizations about their upper potential surfaces.