them into water or molecular hydrogen, and thus suppresses to a certain extent the production of current.

A photosensitized decomposition of water could well account for experimental results published by other authors on photovoltaic phenomena in aqueous solutions[1-3] as well as on the acceleration of electrodeposition of hydrogen and oxygen by ultra-violet light[4-6].

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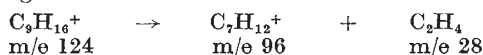[6] Hillson, P. J., and Rideal, E. K., *Proc. Roy. Soc.*, A, **199**, 295 (1949).

Effect of Geometrical Isomerism on the Behaviour of cis and trans Hexahydroindanes under Electron Impact

RECENTLY[1] I reported observations on the behaviour of *cis* and *trans* decalines under electron impact. It was shown that in these ionized stereoisomers an effect due to geometrical isomerism appears in two different ways. First, mass spectra, although qualitatively identical, show important differences between relative abundances of several main fragment ions. Relative abundances of molecular ions also differ and indicate a greater stability of ionized *trans* isomer. Secondly, from the point of view of energetics two results were obtained: (*a*) Ionization potentials measured for both isomers are the same, 9.61 ± 0.02 eV, within experimental uncertainties. (*b*) Appearance potentials of the two fragment ions first produced indicate that a lower energy is required to dissociate ionized *cis* isomer into fragments.
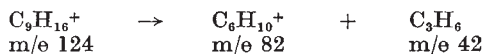
All these results can be interpreted in a satisfactory manner if it is noticed that the greater stability of ionized *trans* isomer parallels its greater thermodynamic stability which represents about 3 kcal/mole (ref. 2). An amount of energy of that order due to steric conformation is released in *cis* decaline when fragmentation occurs.

I wondered if a similar behaviour could still be observed in a case where the difference of thermodynamic stability between *cis* and *trans* isomers is smaller—the *cis* and *trans* hexahydroindanes (bicyclo-0,3,4-nonanes). Thermodynamic stability of *cis* isomer is only 1 kcal/mole smaller than that of *trans* isomer[3].

Similar experiments were performed on hexahydroindanes as on decalines. (*a*) Mass spectra were recorded for electron energies of a few volts above ionization potential, and relative abundances expressed as a fraction of total ionic current were calculated. (*b*) Ionization potentials of both isomers were determined as well as appearance potentials of the two main fragment ions, that is, $C_7H_{12}^+$ and $C_6H_{10}^+$, mass numbers 96 and 82, which are formed in the simplest way as shown in the following scheme:

$$C_9H_{16}^+ \rightarrow C_7H_{12}^+ + C_2H_4$$
$$m/e\ 124 \qquad m/e\ 96 \qquad m/e\ 28$$

and

$$C_9H_{16}^+ \rightarrow C_6H_{10}^+ + C_3H_6$$
$$m/e\ 124 \qquad m/e\ 82 \qquad m/e\ 42$$

Appearance potentials of three other important fragment ions, $C_7H_{11}^+$, $C_6H_9^+$ and $C_5H_7^+$, absent in mass spectra at 10 volts but present at 12 volts, have also been determined.

Relative abundances of ions are given in Table 1 for 12 and 10 volts electron energies.

Table 1. MASS SPECTRA OF *cis* AND *trans* HEXAHYDROINDANES AT 12 AND 10 V (PERCENTAGE OF TOTAL IONIC CURRENT)

Ion formula	$C_9H_{16}^+$	$C_7H_{12}^+$	$C_7H_{11}^+$	$C_6H_{10}^+$	$C_6H_9^+$	$C_5H_8^+$	$C_5H_7^+$
Mass No.	124	96	95	82	81	68	67
12 V							
cis isomer	19.9	31.3	2.3	26.1	8.5	1.0	2.5
trans isomer	28.5	26.3	3.3	22.3	3.7	1.3	6.1
10 V							
cis isomer	48.7	23.1	—	28.2	—	—	—
trans isomer	62.2	17.9	—	20.0	—	—	—

The figures in Table 1 show important differences between relative abundances of molecular ions and main fragment ions in *cis* and *trans* hexahydroindanes and indicate a greater stability of *trans* isomer as in the case of decalines.

Table 2 gives results obtained for ionization potentials (*IP*) and appearance potentials (*AP*) in the two isomers under the same experimental conditions as for decalines. Ionization efficiency curves have been treated by Warren's method[4].

Table 2. IONIZATION POTENTIALS OF *cis* AND *trans* HEXAHYDROINDANES AND APPEARANCE POTENTIALS OF MAIN FRAGMENT IONS (eV)

Formula and mass No. of the ion	*cis* isomer	*trans* isomer
$IP(C_9H_{16}^+)$ 124	10.13 ± 0.03	10.18 ± 0.03
$AP(C_7H_{12}^+)$ 96	10.96 ± 0.03	11.16 ± 0.03
$AP(C_7H_{11}^+)$ 95	11.71 ± 0.05	11.80 ± 0.05
$AP(C_6H_{10}^+)$ 82	10.79 ± 0.03	11.00 ± 0.02
$AP(C_6H_9^+)$ 81	11.99 ± 0.05	12.07 ± 0.04
$AP(C_5H_7^+)$ 67	12.21 ± 0.05	12.19 ± 0.03

From these results it turns out that, within experimental error, ionization potentials of *cis* and *trans* hexahydroindanes are the same. On the other hand, appearance potentials of the two principal fragment ions, $C_7H_{11}^+$ and $C_6H_{10}^+$, are different, the values being smaller for the *cis* isomer than for the *trans* isomer. For the other fragment ions investigated, no difference between appearance potentials could be detected.

As a consequence, the behaviour of *cis* and *trans* hexahydroindanes under electron impact appears quite similar to that found in *cis* and *trans* decalines. Although the difference between thermodynamic stabilities is very small in this case, only about 0.05 eV, there is a noticeable difference between the stabilities of ionized molecules as well as in the energetics of further decomposition of both isomers.

The results recorded here can be interpreted in the following way. (*a*) Relative thermodynamic stabilities are reflected in the behaviour of ionized isomers in the fundamental state. (*b*) An amount of energy of 1 kcal/mole provided by steric conformation is released in *cis* isomer when the molecule breaks down into masses 96 and 82, and used in the breaking process itself.

Similar cases of more complex systems are being investigated in this laboratory. I thank Prof. L. D'Or and the Fonds National de la Recherche Scientifique for advice and support.

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Hydrolysis of the Phosphorothioate Ion catalysed by Silicone Grease

WHEN preparing trisodium phosphorothioate from thiophosphoryl chloride and sodium hydroxide at 80° according to Åkerfeldt[1], it was observed that the yields became much smaller when the ground-glass joints of the apparatus used had been treated with silicone grease. In fact, in some cases no trisodium phosphorothioate could be isolated from the reaction mixture. In these instances liberal amounts of silicone grease had been used in lubricating the glass joints.

Thus it was observed that silicone grease in some way interfered with the reaction between thiophosphoryl