Short Communication

Carbene formation during H_2 elimination from excited cyclo-octane molecules

L. WOJNÁROVITS, T. SZONDY, E. SZEKERES-BURSICS and G. FÖLDIÁK

Institute of Isotopes of the Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 77 (Hungary)

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1. Introduction

During vacuum UV photolysis and radiolysis of liquid *n*-alkanes and C_5 - C_{10} cycloalkanes, part of the main product, hydrogen, is formed by unimolecular elimination [1 - 5]. The unimolecular contribution to the total hydrogen is 80% - 90% in 7.6 or 8.4 eV photolysis and about 20% - 30% in radiolysis. The yield of unimolecular H_2 elimination can be calculated by subtracting the fraction produced via hydrogen atoms from the total hydrogen. The hydrogen atom fraction is estimated from the dimer yields as outlined in refs. 3 and 4. Okabe and McNesby [6] and other researchers [7, 8] have suggested that this detachment occurs predominantly from a single carbon atom (1,1 elimination) via a carbene intermediate that rapidly transforms to alkene. However, other workers have considered a 1,2 elimination mechanism [9, 10] that yields alkene and H_2 directly.

In our earlier studies significant amounts of cross-bridged bicyclic products in addition to alkene were observed during H_2 elimination from cyclo-octane [2 - 4] and from cyclodecane [2, 4] in liquid phase radiolysis and 7.6 eV photolysis. Similar products were also found in the thermal decomposition of tosylhydrazone sodium salts of larger cyclic (higher than C_6) ketones under aprotic conditions (the aprotic Bamford–Stevens reaction) where the proposed intermediates, the carbenes, are believed to undergo transannular insertion to produce cross-bridged bicycloalkanes in highly stereospecific reactions [11, 12].

The aim of the present paper is to provide further evidence in support of H_2 detachment by 1,1 elimination from excited alkane molecules. A comparison of the product distribution obtained in radiolysis and photolysis with that of the decomposition of tosylhydrazone salts appears to be a suitable tool for this purpose.

2. Experimental details

Cyclo-octanone *p*-tosylhydrazone (melting point 137 - 140 °C) was synthesized in the usual way [13]. The sodium salt was prepared *in situ* by

adding excess sodium ethoxide or sodium hydride to the hydrocarbon solution, and the carbene was generated by photolysis using a high pressure mercury lamp with a Pyrex filter. The solutions were mixed for 1 h under an argon atmosphere before photolysis and were kept under argon during the photolysis.

The details of the radiolysis technique [2, 3] and of the photolysis with a bromine lamp (7.6 eV) [3, 4] are described elsewhere. The distribution of the products was also investigated by irradiation at 7.1 eV with an electrodeless nitrogen lamp (Suprasil quartz window) filled with nitrogen and argon mixed in a 1:3 ratio at a pressure of 100 Pa.

3. Results and discussion

The relative yields of the products formed by the unimolecular elimination of H_2 (Fig. 1) are given in Table 1. These results were obtained by γ radiolysis and vacuum UV photolysis of neat cyclo-octane and by UV photolysis of the tosylhydrazone sodium salt in a cyclo-octane solvent. Comparison of the data reveals that the relative yields are similar, and hence the hypothesis of 1,1 elimination is not disproved by the experimental results. However, a fortuitous coincidence cannot be ruled out.
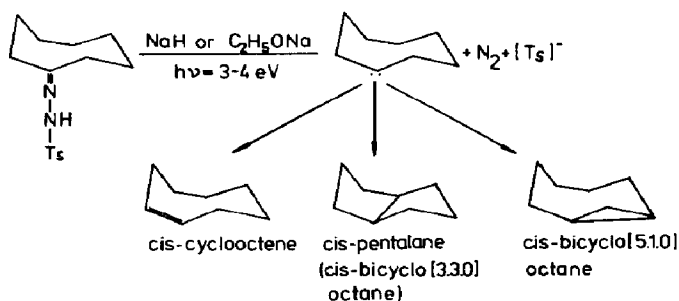

Fig. 1. Elimination scheme.

TABLE 1

Distribution of the products of radiolysis and photolysis in the liquid phase at room temperature

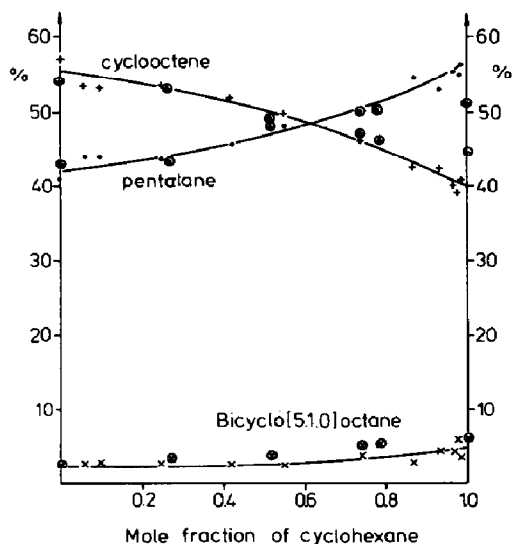| Method	cis-cyclo-octene (%)	cis-pentalane (%)	cis-bicyclo[5.1.0]octane (%)
Cyclo-octane radiolysis	59 ± 7	38 ± 4	3 ± 0.5
Cyclo-octane photolysis (7.1 eV)	55 ± 2	43 ± 2	2 ± 0.5
Cyclo-octane photolysis (7.6 eV)	57 ± 2	41 ± 2	2 ± 0.5
Photolysis of tosylhydrazone sodium salt in cyclo-octane solvent	54 ± 7	43 ± 6	3 ± 1

Fig. 2. Distribution of products in the 7.6 eV photolysis of cyclo-octane–cyclohexane mixtures (+, cyclo-octene; ●, pentalane; ×, bicyclo[5.1.0]octane) and the decomposition of tosylhydrazone (⊕, cyclo-octene; ⊙, pentalane; ⊗, bicyclo[5.1.0]octane).

In the 7.6 eV photolysis of liquid cyclo-octane–cyclohexane mixtures at room temperature the relative yields of products formed by unimolecular H_2 detachment from cyclo-octane depend markedly on the composition of the mixture (Fig. 2). Because of the low photon energy it is unreasonable to assume that more excited states of cyclo-octane act as precursors of the unimolecular H_2 elimination, with each excited state having a different probability of forming cyclo-octene, pentalane and bicyclo[5.1.0]octane. A more probable explanation is that changes in the composition of the liquid produce different conformations of the cyclo-octane molecules [14] and hence stereoselective transformations occur. The influence of the solvent was also investigated in the photolysis of the tosylhydrazone salt whose "physical" stage of decomposition is different from that in the 7.6 eV photolysis of cyclo-octane–cyclohexane mixtures. However, if the carbene intermediate hypothesis is correct, the precursors of the "chemical" stage are similar. Of course the presence of the tosylhydrazone group can affect the liquid structure around the reacting molecule and thus a discrepancy between the two sets of experiments does not preclude the existence of a common carbene precursor. However, if the lifetime of the carbene during which the decomposition products can escape from the cage is more than 100 ps or the presence of the tosylhydrazone group only moderately affects the liquid structure around the cyclo-octane group, the results of the two sets of experiments may be similar.

The similarity of the results can be seen in Fig. 2, and thus the assumption that the precursors of cyclo-octene, pentalane and bicyclo[5.1.0]octane are different in the two cases implies the fortuitous coincidence not only of two ratios but also of two curves. It need not be emphasized that the

probability of such a coincidence is very small. Thus our results offer a strong argument in support of the 1,1 elimination hypothesis.

4. Conclusions

The distribution of the products of unimolecular H_2 elimination from excited cyclo-octane molecules in the liquid phase is consistent with the assumption that the detachment takes place from a single carbon atom with an efficiency close to 100%. The carbene thus produced rearranges mainly to cis-cyclo-octene and cis-pentalane and to a lesser extent to cis-bicyclo[5.1.0]-octane. The composition of the cyclo-octane–cyclohexane mixtures has a marked effect on the ratios of the carbene rearrangements to the individual products.

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