

THE DECOMPOSITION OF VIBRATIONALLY EXCITED MOLECULES

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Abstract—Possible decomposition routes for vibrationally excited hydrocarbons are critically considered using a simple "symmetry" based model. It is shown that C—C bond rupture is characterised by a lower activation energy than the molecular cleavage of hydrogen, although the latter reaction is less endothermic. Other possible decomposition reactions of excited species are also considered.

INTRODUCTION

IN PRINCIPLE there are three ways in which a vibrationally excited paraffin molecule might decompose:

(1) by breaking a C—C bond; (2) by breaking a C—H bond; (3) by direct cleavage to smaller molecules.

Since C—H bond energies exceed C—C bond energies it is not surprising that (2) is not usually observed. Route (3) however will be considerably less endothermic than (1), and it is therefore of some interest to speculate on why the activation energies for such reactions should be so high.

DISCUSSION

By way of an example of route (3) let us consider the molecular cleavage of a hydrogen molecule from adjacent C atoms in a paraffin. The same type of argument will apply to the formation of any other molecular species from adjacent C atoms. A point along the reaction coordinate will correspond with the nuclear positions shown in Fig 1, two C—H bonds extended and with incipient H—H and C—C π bonds being formed. The situation is not without its local symmetry and the arguments of Woodward and Hoffman¹ can of course be applied directly. The simple correlation diagram is shown in Fig 2, (it is the same as for the disrotatory opening of cyclobutene—the general form expected for the in-phase cyclic interaction of four orbitals). If it is assumed that C(sp³), C(p) and H coulomb integrals are all the same and that C—H and H—H bond strengths are the same then the energy *vs* reaction coordinate curve is simply the dashed line in Fig 2. The height of the maximum is equivalent to the breaking of a single C—H bond. This very simple discussion therefore suggests that (1) will have the lowest activation energy and that (2) and (3) will have comparable, somewhat higher activation energies. Paraffins therefore tend to decompose by C—C bond cleavage.

Two further points of interest now suggest themselves:

- (I) suppose the paraffin molecule to be highly vibrationally excited, or
 - (II) suppose the cyclic interaction to involve six (or $4n + 2$) orbitals and not four (or $4n$).
- (I) If molecules can be made vibrationally excited to a degree E^* and there exist

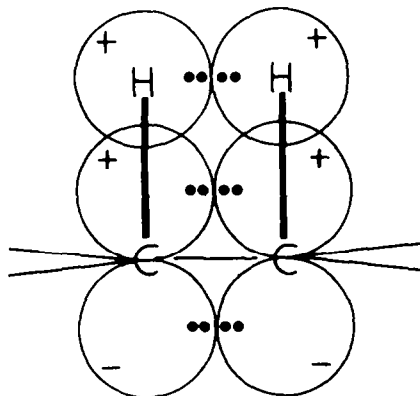


FIG 1. Portion of an excited alkane showing incipient $\text{H} \cdots \text{H}$ and $\text{C} \cdots \text{C}$ bond formation.

(—bonds to be broken, ... bonds to be formed)

decomposition routes characterised by activation energies E_1 , E_2 , E_3 , then the probability that decomposition will take place by route i will depend² upon $(E^* - E_i)$, and also upon a degeneracy factor (e.g. there would be only one C—C cleavage route for C_2H_6 but six C—H cleavage paths). Clearly the route of lowest activation

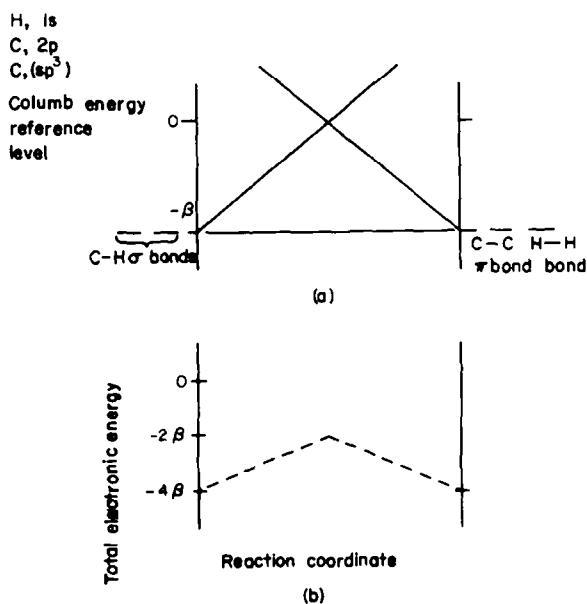
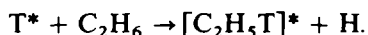


FIG 2. Schematic energy level diagrams for molecular cleavage of an excited alkane. The value of β is assumed to decrease to about 70% of its initial value at the mid point of the reaction and to return to its original value when the reaction is completed.

energy will be favoured, but less and less so as E^* gets greater and the differences between $(E^* - E_1)$ and $(E^* - E_2)$ etc diminish. Indeed should a single low energy pathway be in competition with a highly degenerate path there will be a value for E^* above which the yield for the high activation energy product will exceed that of the low energy product.

The production of such highly excited species is not easy by conventional means but can be brought about by reactions with translationally excited atoms produced either by atomic beams or by nuclear recoil. Using the latter technique, with tritium atoms ($\text{He}^3(n, p)\text{H}^3$) it is possible to produce excited paraffin molecules by the process



Not all the labelled ethane molecules formed in this way are highly excited and most of those that are, decompose to two methyl radicals³. However, the energy of the recoil tritium atom cannot be controlled at its point of reaction, so that a wide range of excitation energies is to be expected in recently labelled molecules. Those with the highest energies might well decompose by routes (2) or (3) rather than (1). Thus the small observed yields of $\text{C}_2\text{H}_4\text{T}^4$ and $\text{C}_2\text{H}_3\text{T}^5$ would be explained. Avdonina *et al.*⁶ observed that the yields of small labelled alkanes and alkenes, with the same number of C atoms, were in the same ratio no matter from which larger alkane they had been formed. This suggested a common origin in a highly excited fragment alkane molecule which could either be moderated or cleave out molecular hydrogen (or decompose by breaking a C—C bond but these radicals could not be distinguished from those from other molecules). Similar unimolecular decompositions to molecular products can explain the location of tritium atoms in isobutene formed as a result of the reaction of recoil tritium with neopentane. If it is supposed that two H atoms can be more or less simultaneously displaced then $(\text{CH}_3)_3\text{C}.\text{CHT}^*$ will result. This radical, if excited, will decompose to $(\text{CH}_3)_2\text{C}=\text{CHT}^*$; isobutene wholly labelled at the olefinic site. But Rowland⁷ has shown that tritium is to be found equally at the methyl and methylene positions. A result which can be explained by assuming the molecular decomposition of excited neopentane-t to methane and isobutene. Results of this type can most easily be understood if it is assumed that pathways (1) (2) and (3) are all open for highly vibrationally excited paraffin molecules and that the activation energies for (2) and (3) are comparable and not much greater than for (1).

(II) If it were possible to find a system whose geometry permitted reactions as shown in Fig 3 to take place then either symmetry¹ or pseudo-aromatic⁸ arguments would predict a low activation energy—probably lower than for simple C—C cleavage. Seeking model systems is complicated by the presence of the double bond which would facilitate the cleavage of an α - β C—C single bond by stabilizing the α electron through allylic resonance. A direct comparison in one molecule of C—C and H_2 cleavage might not therefore be possible.

The reactions of recoil tritium with *cis*- and *trans*-butene-2 molecules^{9,10} lead to small (and more or less equal) yields of labelled 1,3 butadiene. This product might be expected exclusively from the *cis*-configuration (as in Fig 3) but if the molecule, to undergo this elimination, needs energy in excess of that to perform the *cis/trans* isomerisation then no especially high yield is to be anticipated from the *cis*-isomer, the ability to undergo *cis/trans* isomerisation would also tend to destroy the rather

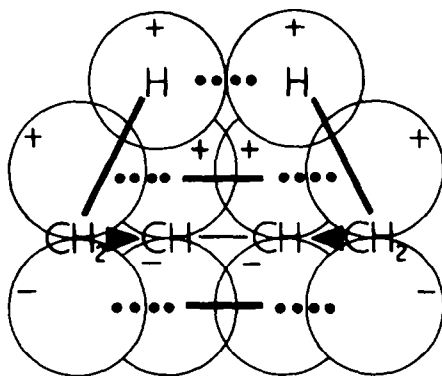


FIG 3. Formation of $\text{H}_2 + 1,3$ butadiene from excited cis but-2-ene.
(—bonds to be broken, . . . bonds to be formed)

special configuration necessary for this reaction to take place, hence the low yield. The reactions of hot tritium atoms with cyclohexene and cyclopentene have not yet been studied, but significant yields of cyclo-1,3-hexadiene-t and cyclo-1,3-pentadiene-t might well be found.

An actual example of a 6-centre transition complex may have been observed by Cipollini and Stocklin.¹¹ In their studies of the reactions of recoil tritium with ethane they noticed that the presence of methyl chloride considerably enhanced the yield of ethylene. If an excited, recently labelled ethane molecule were to collide with a methyl chloride molecule the situation shown in Fig 4 might result. Since this involves the cyclic, inphase interaction of six orbitals, three bonding orbitals will result ("aromatic"), with the creation of a reaction pathway characterised by a low activation energy. Thus ethylene, methane and hydrogen chloride would easily be formed as the products of such a collision (and the tritium atom could be found in any of these three products). Cipollini and Stocklin found that the enhanced yield of ethylene was greatest at low pressures—indicating a pressure sensitive intermediate, in agreement with the type of complex shown in Fig 4.

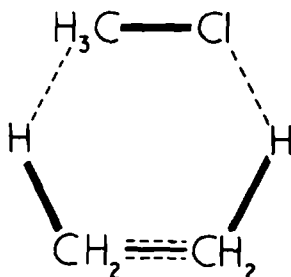


FIG 4. Orbital interactions in the methyl chloride assisted decomposition of excited ethane.

CONCLUSION

The predilection for C—C bond cleavage in vibrationally excited paraffin molecules, rather than the less endothermic breakdown to a smaller molecule and an olefin, is explained by means of orbital symmetry arguments. These arguments suggest that the activation energies for molecular cleavage routes and C—H cleavage should be about the same. This is supported by the decomposition products observed from high excited molecules produced by the recoil tritium labelling reaction. Similar arguments suggest that the cyclic interaction of six orbitals should facilitate decomposition to molecular products. Possible examples are discussed. It would be of interest to see if more examples of reactions of this type could be found and positively identified.

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