Thermal Decomposition of *cis,anti,cis*-Tricyclo[3,1,0,$0^{2,4}$] hexane: Hot Molecule Effects

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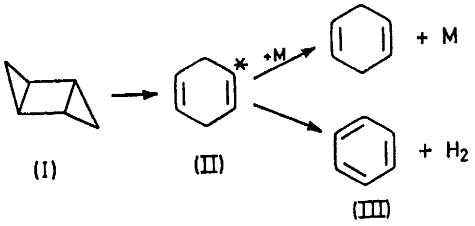
Summary At low pressures cyclohexa-1,4-diene formed from the thermal isomerization of tricyclohexane undergoes a hot molecule decomposition to benzene and hydrogen; theoretical calculations (RRKM) give a good description of the experimental results.

IN highly exothermic unimolecular isomerizations "hot" molecules are formed which may undergo further decomposition. This may lead to a variation of products with pressure and non-Arrhenius rate dependence. The situation can sometimes be recognised by the pressure dependence and the nature of the products[1] though ideally a quantitative unimolecular reaction rate theory calculation should be carried out.[2] We report here experimental and theoretical results for the thermal decomposition of a tricyclohexane and emphasise that the initial calculations were carried out not only before the experimental data were obtained, but even before Arrhenius parameters were available for the primary isomerization.

At 186·4° in the pressure range 0·3—10 Torr the thermal decomposition of *cis,anti,cis*-tricyclo[3,1,0,$0^{2,4}$]hexane gave a mixture of cyclohexa-1,4-diene (1,4-CHD), benzene, and hydrogen as the only products. The ratio of cyclohexa-1,4-diene to benzene was pressure dependent. The Table shows some values of this ratio as a function of pressure. The mechanism shown in the Scheme accounts for the findings. Cyclohexa-1,4-diene as initially formed (II) is a "hot" molecule owing to the exothermicity of the step (I) → (II). Such a scheme may be treated by the RRKM theory[2] with the following information; the Arrhenius parameters for step (I) to (II), and for (II) to (III), the enthalpy change corresponding to (I) → (II) and vibrational assignments for the two transition states involved. The rate constant for (I) to (II) at 186·4° was found to be $2{\cdot}05 \times 10^{-4}\,s^{-1}$ and an *A* factor of $10^{13\cdot9}$ was estimated on the basis of a biradical mechanism. This yields an energy of activation of 37·0 kcal mol^{-1}. The value for ΔH_{289} (I) → (II) was taken as 41·6 kcal mol^{-1} using methods of group additivity and estimates of ring strain based on analogous molecules. The Arrhenius parameters for (II) to (III) were available.[3] Vibrational assignments for reactants and complexes were made in the ususl manner.[4]

TABLE

log *p*/Torr	—0·55	—0·155	0·491	0·736	0·845	0·924
(1,4-CHD/benzene)$_{obs}$	0·183	0·555	2·63	4·62	6·03	7·59
(1,4-CHD/benzene)$_{calc}$	0·73	1·75	7·2	11·9	16	18



SCHEME

The Table shows the calculated ratio of cyclohexadiene to benzene. The agreement is good and a shift of the theoretical results by 0·45 log units (equivalent to changing the collision diameter from 0·6—0·35 nm) produces exact agreement. Analogous calculations for spiropentane require a pressure shift of 0·6 log units and "fall off" calculations for cyclobutene[5] require a shift of about 0·5 log units. Alternatively, essentially exact agreement may also be obtained if the estimated strain energy of tricyclohexane is increased by 4 kcal mol^{-1}.

Since the experimental work was completed, the Arrhenius parameters for the isomerization of (I) to (II) have been reported.[6] They are close to our estimated values, and calculated results using them are almost indistinguishable from the ones shown.

The present study demonstrates that methods of thermochemical kinetics and RRKM theory can be a predictive tool for hot molecule reactions requiring a minimum of experimental information, essentially one rate constant.

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