Further Kinetic Evidence for the Energy Separation between Triplet and Singlet Methylene

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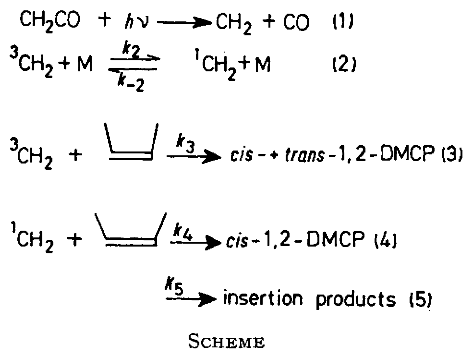
Summary An investigation of the reactions of methylene with *cis*-but-2-ene, in excess of nitrogen, as a function of temperature yielded results which are interpreted in terms of a high (*ca.* 38 kJ mol^{-1}) energy separation between triplet and singlet methylene.

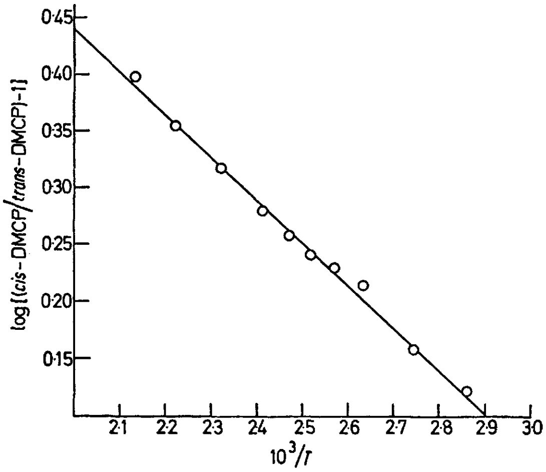
RECENT theoretical calculations[1] lead to a value of 46 ± 9 kJ mol^{-1} for the energy difference between the $^3B_1$ ground state and the $^1A_1$ first excited state of methylene (triplet $^3CH_2$ and singlet $^1CH_2$ methylene). A reinterpretation of earlier experimental data[2] yielded a lower limit of 34 kJ mol^{-1} for this separation in sharp contrast to much smaller values of 4—10 kJ mol^{-1} previously suggested.[3] This work represents another experimental approach to determine the value of the energy separation and also to attempt to understand in more detail one aspect of the much studied methylene–inert gas–but-2-ene system.

Mixtures of keten, *cis*-but-2-ene and nitrogen in the ratio 1 : 2 : 60 were irradiated with the unfiltered light of a super-pressure Hg lamp at temperatures ranging from 75 to



SCHEME

200 °C. The hydrocarbon products were completely analysed by gas chromatography [100 m capillary column (PPG) at 0 °C]. We have focussed attention on the ratio of *cis*- to *trans*-1,2-dimethylcyclopropanes; these compounds constituted *ca.* 50% of the reaction products with the pent-2-enes and 2-methylbut-2-ene as the other C_5 hydrocarbons. The simplified mechanism is shown in the Scheme.



Figure

If the isomer ratio produced by reaction (3) is taken as unity,[4] then the yield of *cis*-1,2-dimethylcyclopropane (*cis*-DMCP) arising from reaction (**4**) can be evaluated. There is much evidence[5] that many singlet methylene reactions have small or zero energies of activation and we assume here that k_4 has a zero energy of activation. Carr *et al.*[6] have shown that the value of k_{-2} is comparable with the rate of singlet methylene reactions with hydrocarbons, so that with the large excess of nitrogen, we may assume here that an equilibrium ratio of singlet to triplet methylene is maintained, which is not significantly perturbed by either reaction or its non-equilibrium production in the photolytic step.

We may derive the following:

$$\log[(cis\text{-DMCP}/trans\text{-DMCP}) - 1] = \log(2A_4/3A_3) - (E_2 - E_3)/2{\cdot}303\,RT$$

where E_2 is energy separation between the two states of methylene, E_3 is the energy of activation of reaction (3) and A_3 and A_4 are the Arrhenius pre-exponential factors for reactions (3) and (4) respectively. A plot of the l.h.s. of the equation against $1/T$ is shown in the Figure. From least squares analysis of these data we obtain $E_2 - E_3 = 7{\cdot}11 \pm 0{\cdot}21$ kJ mol^{-1} and $A_4/A_3 = 22{\cdot}7 \pm 1{\cdot}5$.

Since $E_2 > E_3$ the overall reaction exhibits increased stereospecificity at higher temperatures. Since chemical evidence indicates a reactivity of triplet methylene similar to that of the methyl radical we estimate E_3 as *ca.* 30·5 kJ mol^{-1}, the value for the addition of methyl to but-2-ene and hence $E_2 = 38$ kJ mol^{-1}. Although the uncertainty in the assumption of E_3 is reflected in this value, this work gives further chemical evidence for a 'high' value of E_2.

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