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Reactions of Methylene. V. The Effect of Inert Gases on the Reaction with Cyclopropane

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Methylene from the photolysis of diazomethane and ketene was made to react with cyclopropane in the presence of nitrogen and argon and the products analyzed for methylcyclopropane and the four isomeric butenes. The apparent lifetime of the activated methylcyclopropane was independent of pressure. Its variation when inert gases were introduced was interpreted as evidence for excess translational energy in methylene from diazomethane and evidence that methylene from diazomethane also possesses vibrational (or electronic) energy in excess of that from ketene.

Introduction

In the previous paper in this series,² data were presented on the reaction of methylene with propylene and cyclopropane and the rearrangement of the activated methylcyclopropane formed as a primary product. Trends in the lifetime of the activated molecules suggested that methylene from different sources may have different amounts of vibrational and translational energy. This conclusion was also reached by Frey³ in his work on the reactions of methylene with the butenes. Frey concluded that methylene from diazomethane possesses excess translational energy which can be removed by about twice as many collisions with an inert gas molecule as are required for reaction with a butene molecule. When this translational energy is removed, the relative rates of attack by methylene from diazomethane on the C-H and C=C bonds in butene are found to be the same as those of methylene from ketene.

Since Frey did all his inert gas experiments at high pressures, he was unable to observe the influence of the deactivating collisions on the lifetime of the activated molecule formed. The present work was undertaken to obtain data on this effect. Provided the relative efficiencies of cyclopropane and the inert gas in deactivating methylcyclopropane are known, the relative lifetimes of the activated molecules produced under various conditions can be calculated.

Experimental

Experiments were carried out at room temperature in the same apparatus as was used in the previous work.²

Prepurified nitrogen, distilled into the reaction vessel from a trap at -196° , and spectroscopically pure argon were used as inert gases. Cyclopropane (Matheson C.P.) was distilled in a Podbielniak column, the first and last thirds of the distillate being discarded. Ketene was prepared by pyrolysis of acetic anhydride, and diazomethane by reaction of N-methyl nitroso urea with aqueous potassium hydroxide.

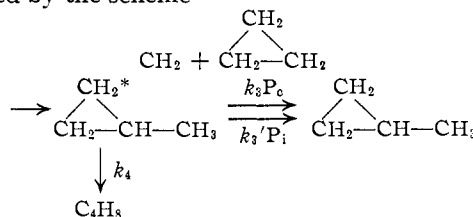
Diazomethane was photolyzed using polychromatic radiation of 3100 Å. and longer wave lengths; ketene was photolyzed using roughly monochromatic 3100 Å. radiation.

Mixtures of cyclopropane and diazomethane in a ratio of about 20:1 were diluted with nitrogen in ratios of 1:1 and 1:10 and with argon in ratio 1:10 and photolyzed until most of the diazomethane was gone. Mixtures of cyclopropane and ketene in a ratio of about 20:1 were diluted with nitrogen in ratio 1:10 and photolyzed until most of the ketene was gone.

The products were analyzed quantitatively by gas chromatography on a silver nitrate-glycol column for methylcyclopropane, 1-butene, *cis* and *trans* 2-butenes and isobutene. Experiments in which the ratio of C₃ to C₄ hydrocarbons was greater than 0.01 were discarded. Duplicate and triplicate analyses were performed when there was a large enough sample, and these agreed to within 5%. Because of the small yields of products, it was not possible to trap out the incompletely separated peak containing 1-butene and *cis* 2-butene and separate it on another column. Instead, the ratio of these two products was calculated from their relative peak heights. All other quantitative data were obtained by measuring areas.

Results

The reaction of methylene with cyclopropane to form activated methylcyclopropane and its subsequent rearrangement or deactivation can be represented by the scheme²



where k_3 is the rate of quenching of activated molecules by collision with cyclopropane (at partial pressure P_c) and k_3' is the rate of quenching by collisions with inert gas (at partial pressure P_i). A steady state treatment of this system results in the relation

$$k_4/k_3 = \left(P_c + \frac{k_3'}{k_3} P_i \right) B$$

where B is the ratio of total butene to methylcyclopropane in the products.

The distribution of butene isomers in the products is most significantly expressed in terms of the probability of transfer of a hydrogen atom in the rearrangement of methyl cyclopropane.² If the transfer of ring hydrogen to the adjacent carbons were completely random, the products of isomerization would be 40% 1-butene, 40% 2-butene and 20% isobutene. Deviations from this composition are a measure of non-random transfer. We denote the ring carbon to which the methyl group is attached by a, the two others by b and the relative probability of transfer of a hydrogen atom from carbon b to carbon a by α_{ba} , etc. These transfer probabilities α (unity for random transfer) are then determined by the butene composition:

$$\begin{aligned}
 \alpha_{ba} &= 2.5 \frac{(1\text{-butene})}{(\text{total butene})} \\
 \alpha_{1,2} &= 2.5 \frac{(\text{cis and trans 2-butene})}{(\text{total butene})}
 \end{aligned}$$

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(2) J. N. Butler and G. B. Kistiakowsky, *THIS JOURNAL*, **82**, 759 (1960).

(3) H. M. Frey, *Proc. Roy. Soc.*, **A250**, 409 (1959); *ibid.*, **A251**, 575 (1959).

TABLE II

Inert gas	k_4/k_3 (atm.)	α_{ba}	α_{bb}	α_{ab}	<i>cis/trans</i>
Cyclopropane + diazomethane					
None	0.47 ± 0.02	1.21 ± 0.03	0.96 ± 0.03	0.65 ± 0.01	1.00 ± 0.05
Nitrogen 1:1	.40 ± .03	1.20 ± .04	.98 ± .04	.64 ± .02	1.02 ± .08
Nitrogen 10:1	.42 ± .02	1.29 ± .02	.95 ± .02	.52 ± .03	1.31 ± .07
Argon 10:1	.36 ± .03	1.35 ± .05	.86 ± .05	.57 ± .05	1.28 ± .08
Cyclopropane + ketene					
None	0.24 ± 0.06	1.02 ± 0.19	1.17 ± 0.16	0.62 ± 0.06	1.42 ± 0.46
Nitrogen 10:1	0.22 ± 0.03	0.90 ± 0.04	1.27 ± 0.04	0.66 ± 0.05	1.16 ± 0.12

instead of to zero at infinite pressure. Within the experimental error of our data the ratio B extrapolates to zero at infinite pressure.

In the previous paper of this series data was presented for the reaction of cyclopropane with diazomethane which showed that k_4/k_3 increased with pressure below 100 mm. This data was subsequently found to be erroneous because methylene attacks the C₄ products at different rates and the effect was eliminated by decreasing the diazomethane/cyclopropane ratio so that the C₅ products were less than 1% of the C₄ products. The curvature observed by Frey therefore is probably also due to experimental imperfection.

The ratio of *cis* 2-butene to *trans* 2-butene in the diazomethane experiments increases with increasing pressure, suggesting that *cis* is formed preferentially in the isomerization of methylcyclopropane and that it isomerizes to *trans* if it is not quenched by collisions. The low pressure limit of this ratio is never much below unity, whereas the high-pressure limit is around 1.2 without inert gas present and around 1.4 in mixtures where there is 10 times as much inert gas as reactants. The errors in the ketene experiments are larger than any trends of this type.

The probabilities of hydrogen transfer α do not appear to vary significantly with pressure.

Turning now to the averages presented in Table II, we see that if Chesick's values are used for k_3'/k_3 , the ratio k_4/k_3 for methylene from diazomethane decreases markedly (15%) on addition of a small amount of inert gas but does not further decrease significantly on addition of a large amount. Addition of inert gas does not alter k_4/k_3 for methylene from ketene within experimental error. These results may not be as accurate as the limits of error suggest, since the values obtained for k_4/k_3 in the 10:1 inert gas mixtures are quite sensitive to the choice of k_3'/k_3 .

It is possible to draw certain tentative conclusions from these results. Because k_4/k_3 for methylene from diazomethane decreases by about 20% on diluting to 1:1 with inert gas but does not decrease further on diluting to 10:1, we may conclude as Frey³ did that methylene from diazomethane contains excess translational energy and that the probability of the removal of this energy is about the same as the reaction probability. Since k_4/k_3 for methylene from ketene does not change on dilution to 10:1 by inert gas, it is likely that such excess translational energy is not imparted to methylene in the photochemical decomposition of ketene.

Further, since k_4/k_3 for methylene from diazomethane in the presence of 10:1 inert gas is still twice as high as k_4/k_3 for methylene from ketene, we might infer that methylene from diazomethane possesses vibrational or electronic energy in excess of that of methylene from ketene. Until much more accurate values for k_3'/k_3 are available, it is not possible to conduct experiments in extremely dilute inert gas mixtures to detect removal of some of the vibrational energy of methylene.

Addition of inert gas appears also to alter the composition of the butenes, although a simple qualitative explanation of this effect is not obvious. The *cis/trans* ratio at a given pressure increases somewhat (from 1.0 to 1.3) when inert gases are added. On the hypothesis that the initial *cis/trans* ratio is high but that *cis*-butene isomerizes unless quenched by collisions, it would be expected that the *cis/trans* ratio would decrease in the presence of inert gases, these being less effective than cyclopropane at quenching the "hot" molecules. This is the opposite of the effect observed; and indeed the change in *cis/trans* ratio may be due to an entirely different cause, as yet unknown.

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