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ISOTOPE EFFECT ON PROPYLENE FORMATION FROM DIMETHYLCARBENE

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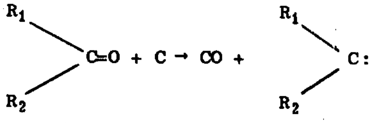
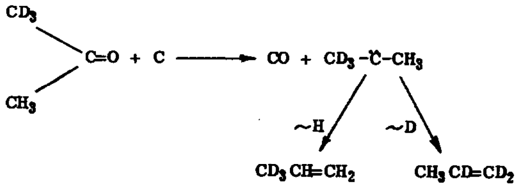
At present, very little is know about the isotope effects of intramolecular carbene reactions. A recent study[2] by Kirmse and co-workers has shown that when alkyl carbenes are generated from the photolysis of the diazocompounds at 25°, the hydrogen-deuterium isotope effects for intramolecular olefin and cyclopropane formation are both in the range of 1.1 to 1.4.[3] We have determined the intramolecular isotope effect for olefin formation in an alkyl carbene below -170°.

The observation[4] that carbon atoms react with ketones and aldehydes during their codeposition at a liquid nitrogen cooled surface to produce alkyl carbenes and carbon monoxide has made possible an examination of the low temperature chemistry of these species. The compound chosen for this study was 1,1,1-trideuterioacetone, which would



$$R_1R_2C{=}O + C \rightarrow CO + R_1R_2C{:}$$

deoxygenate to 1,1,1-trideuteriomethylmethylcarbene. The intermediate carbene could then produce two isomeric propenes, the 1,1,2-trideuteriopropene from deuterium migration and 3,3,3-trideuteriopropene from hydrogen migration.[5]



When 1,1,1-trideuterioacetone and carbon vapor are cocondensed on a liquid nitrogen cooled surface under a vacuum (10^{-5}mm Hg)[6] the major products were carbon monoxide and trideuteriopropene. Analysis of the trideuteriopropene by mass spectroscopy allows a calculation of k_H/k_D from the ratio of the $C_2H_3^+$ and $C_2D_3^+$ ions. The value of k_H/k_D obtained in this manner is 1.7. The ratio of the CD_3^+ and CH_3^+ ions is also a measure of k_H/k_D and has a value of 1.9 in this system; however, the lower intensities of the methyl peaks and the presence of traces of H_2O (m/e = 18) in the mass spectrometer make the methyl derived value less reliable. The 1,1,1-trideuterioacetone[7] used was at least 90 mole % labeled as named with the major impurity being about 5 mole % 1,1-dideuterioacetone. The k_H/k_D values are not corrected for this nor was any consideration of secondary isotope effects on the fragmentation of propylene included since they are not expected to alter the result significantly.

The assignment of the temperature of the reaction as less than -170° is based on the fact that reactions of carbon vapor may be run with propene and propane without encountering "dripping" of the matrix during the codeposition.[8] We have also noted[3] that the carbon monoxide liberated during deoxygenation does not become trapped in the frozen matrix but is liberated during the codeposition process. For this reason we feel the reaction occurs during the establishment of the frozen matrix. This cooling is very rapid and using the melting points of propene and propane (-185.2° and -189.9°) as references, it appears that the carbene should be present in its free state at no more than -170°. Assuming the value of -170° as the temperature of the reaction, the value of k_H/k_D at 25° may be estimated as 1.2. This value is in agreement with Kirmse's value of 1.16.[2] The relative insensitivity of the corrected value to temperature changes is illustrated by the fact that the k_H/k_D value measured in this work would not become 1.3 until -60°;[9] for this reason, elaborate corrections were not attempted.

On the basis of the evidence presently available, it would appear that the temperature corrected value of the intramolecular isotope effect is a workable criteria for the intermediacy of free carbenes. It has been observed[2] that when metal ions are used to catalyze the thermal decomposition of diazocompounds, the value of the intramolecular isotope effect increases to 1.6. An intramolecular isotope effect for cyclopropane formation from a "carbenoid" intermediate has been reported[10] and the values vary from

1.44 to 1.98 at 25° depending on the halogen ion present. Therefore, the observation of an intramolecular isotope effect for a suspected carbene reaction greater than 1.4 may be taken as an indication of a complexed carbene, a lower value implicating a free carbene intermediate.

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place. However, in the case of dimethylcarbene, the rearrangement is known to be faster than addition to olefin under the reaction conditions (see ref. 3) while carbenes which do not possess an intramolecular mode of product formation react readily with olefins under the reaction conditions to give cyclopropanes; see P. S. Skell and J. H. Plonka, J. Am. Chem. Soc., **90**, 2160 (1970).

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