COMMUNICATIONS TO THE EDITOR

MERCURY PHOTOSENSITIZED INTERACTION OF ETHYLENE AND 2,2-DIDEUTERIOPROPANE

Sir:

In a recent publication,[1] Majer, Mile and Robb conclude that up to 30% of the isopentane formed in the 2537 Å. mercury photosensitized reactions of mixtures of ethylene and propane arises from a non-radical insertion reaction. The excited ethylene molecule is presumed to insert directly into the carbon-hydrogen bonds of propane in a manner analogous to the direct insertion of methylene into such carbon-hydrogen bonds.[2] The non-radical process for isopentane production was postulated from an analysis of effects of variation of mixture composition, pressure, and inert gases on the relative rates of formation of different products in terms of assumed reaction mechanisms. The existence of this molecular insertion reaction would be of considerable importance in considering studies of bimolecular reactivity of electronically excited olefins.

To verify the presence or absence of this insertion reaction experiments were performed under the conditions similar to those of the previous work[1] using 2,2-dideuteriopropane. Every isopentane molecule formed by an insertion process must be $C_5H_{10}D_2$, whereas isopentane produced in radical processes will probably originate in an isopropyl radical. This radical will then be monodeuterated. The ratio of $C_5H_{10}D_2$ to $C_5H_{11}D$ in the isopentane formed in radical processes will then depend on the relative probability of procuring a D or H atom in the later radical reactions.

Mixtures of 2.6 cm. ethylene and 1.4 cm. propane were saturated with mercury vapor at 0° and circulated through a photolysis vessel at 30°. Products were analyzed by gas liquid partition chromatography using a silicone oil on firebrick column. The iso- and *n*-pentane gas liquid partition chromatography peak homogeneities were checked by analyses using a silver nitrate in glycerol on firebrick column and by mass spectrometry. Reactant conversions were no more than 2%; those of the previous work ranged up to 8%.

Product analyses for runs with unlabeled propane were in general agreement with those reported[1]; the isopentane/*n*-pentane ratio was typically 5.0. Runs made with 2,2 dideuteriopropane (Merck of Canada, better than 98% isotopic purity) differed chiefly in a marked decrease in a few of the products which may be regarded as arising from isopropyl radicals. Thus the isopentane yield dropped and the isopentane/*n*-pentane ratio was 0.54 in runs with the deuterated propane. Mass spectrometric analyses of the isopentane gas liquid partition chromatography peak were in accord with those expected for monodeuterioisopentane. The m/e 74–73 ratio was less than 0.0075 ± 0.0075 after subtraction of the C^{13} isotope $m/e = 74$ peak which is 0.050 of the $m/e = 73$ parent peak. Thus it is concluded that there is less than 0.75% $C_5H_{10}D_2$ in the isopentane produced in the mercury photosensitized reactions of ethylene and 2,2-dideuteriopropane. Based on the larger isopentane yields obtained using undeuterated propane, the insertion of an excited ethylene molecule into a secondary carbon-deuterium accounts for less than 0.075% of the isopentane seen by Majer, Mile and Robb. This is certainly an upper limit since there has been no attempt to account for the $C_5H_{10}D_2$ produced in radical processes.

Allowing an isotope effect of a factor of ten, the ethylene insertion reaction in the secondary carbon hydrogen bond must therefore be less than 0.75% of the isopentane production. An isotope effect of 1.3 has been found for methylene insertion in secondary carbon-deuterium bonds,[3] and the factor of ten assumed for the isotope effect in ethylene insertion is probably extreme.

Hence it may be concluded that excited ethylene does not undergo one step insertion reactions to any appreciable extent. The decrease in isopentane yield and the observed improbability of $C_5H_{10}D_2$ formation by means of radical processes indicate a low level concentration of deuterated radicals in the system. A large isotope effect in the reaction $Hg^* + C_3H_6D_2 \rightarrow Hg + D + i\text{-}C_3H_6D$ is suggested. This will be investigated in more detail.

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[1] J. R. Majer, B. Mile and J. C. Robb, *Trans. Far. Soc.*, **57**, 1692 (1961).

[2] W. v. E. Doering and H. Prinsbach, *Tetrahedron*, **6**, 24 (1959).

[3] J. P. Chesick and M. R. Willcott, unpublished work.

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THE IMIDAZOLE-CATALYZED (NON-METAL ION MEDIATED) TRANSAMINATION OF PHENYLGLYCINE BY PYRIDOXAL. A REACTION OCCURRING AT AMBIENT TEMPERATURES BY WAY OF MICHAELIS-MENTEN KINETICS

Sir:

The only successful model systems for the enzymic catalysis of the transmination of α-amino acids by pyridoxal (reaction 1) in aqueous solution have involved metal ions (Cu^{++}, Al^{+++}, Fe^{++}, *etc.*) as catalysts. These reactions proceed at 100° and have been proposed to involve metal ion activation of the imine (I_1) formed between pyridoxal and amino acid.[1] In the enzymic catalysis metal ions may or may not be required.[2–6]

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[1] D. E. Metzler, M. Ikawa and E. E. Snell, *J. Am. Chem. Soc.*, **76**, 648 (1954).