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]

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

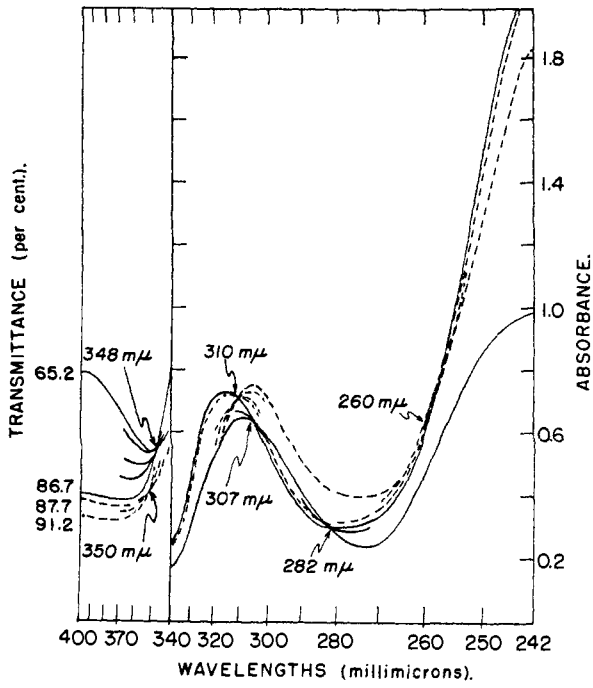
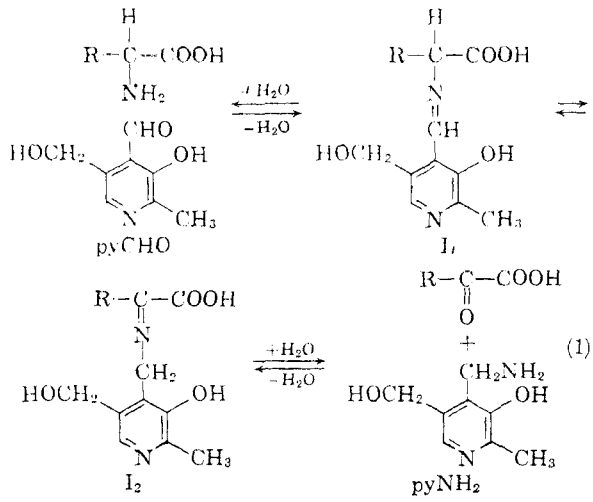


Fig. 1.—Spectral-time study for the reaction of pyridoxal (10^{-4} *M*) with phenylglycine (2×10^{-4}*M*) in the presence of imidazole (1.8 *M*) in water at pH 8.61 and a temperature of 30°. The tracing shows the shape of the absorbance curves and isosbestic points for the first (———) and second (- - - -) phases of the reaction.

Both the formation of I_1 and its conversion to I_2 should, *a priori*, be subject to general acid and or general base catalysis. Only weak bases are available to form the active site of the transaminase. Near neutrality the imidazolyl group of a histidine residue, due to its p*K*a′, would be the most effective



general base or general acid species available to the enzyme. On the basis of the reasoning presented above the influence of imidazole as a catalyst for the transamination of phenylglycine by pyridoxal was investigated. The transamination of pyridoxal by phenylglycine as catalyzed by imidazole was followed by periodically withdrawing aliquots from a continuously stirred (30°, in the dark under nitrogen) aqueous solution of pyridoxal hydrochloride (1.0 mmole), phenylglycine (1.0 mmole), imidazole hydrochloride (1.0 mmole), and imidazole (50 mmole) in 20 ml. of water. The concentration of keto acid in each aliquot was determined by its conversion to the 3-phenyl-2-oxyquinoxaline derivative.[7] The reaction was found to be *pseudo* first order in appearance of I_2 and to go to 30% completion at t_∞. No reaction occurred if the imidazole was replaced by a borate buffer (0.4 *M*) which provided the same pH conditions. These results show that imidazole and/or its conjugate acid catalyze (1).

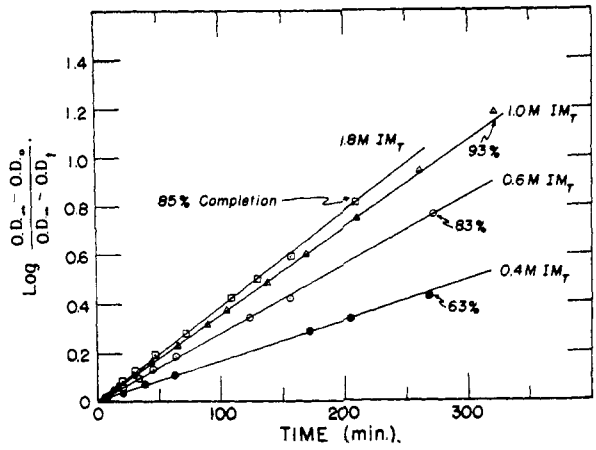


Fig. 2.—First order plots for the appearance of I_2 (as determined at 246 mμ) in the presence of varying concentrations of imidazole (pyridoxal and phenylglycine initially at 10^{-4} *M*; pH 8.61; μ 0.05 *M*; *T* 30°).

The detailed kinetics of the reaction were studied spectrophotometrically (Perkin–Elmer Model 350, with thermostated cells) between 400 and 235 mμ in water (pH 8.61, *T* 30°; μ 0.05 *M*) at concentrations of pyCHO and phenylglycine of 5×10^{-5} to 3×10^{-4} *M*. The results of a typical spectral-time study are presented in Fig. 1. The reaction may be divided into two distinct phases. In the initial phase pyCHO and amino acid are converted to an equilibrium mixture of pyCHO and amino acid, I_1 (low steady state) and I_2. For the initial phase true isosbestic points are obtained at 348, 307 and 282 mμ and a linear relationship exists between the decrease in absorbance at 395 mμ (pyridoxal) and increase in absorbance at 246 mμ (I_2). The finding of isosbestic points supports the contention of a low steady state concentration in I_1. Under conditions of equimolar concentrations of pyCHO and amino acid (10^{-4} *M*) and at all concentrations of imidazole the first phase of the reaction proceeded to *ca.* 54% production of I_2. The kinetics for phase one were found to be first order (to 60–95% completion, see Fig. 2) as anticipated for the general system (2)

(2) E. E. Snell, *Fed. Proc.*, **20**, (II) 81 (1961).
(3) W. T. Jenkins and I. W. Sizer, *J. Am. Chem. Soc.*, **79**, 2655 (1957).
(4) W. T. Jenkins and I. W. Sizer, *J. Biol. Chem.*, **234**, 1179 (1959).
(5) W. T. Jenkins, D. A. Yphantis and I. W. Sizer, *ibid.*, **234**, 51 (1959).
(6) W. T. Jenkins and I. W. Sizer, *ibid.*, **235**, 620 (1960).
(7) J. Buraczewski and L. Marchlewski, *Ber.*, **34**, 4008 (1901).

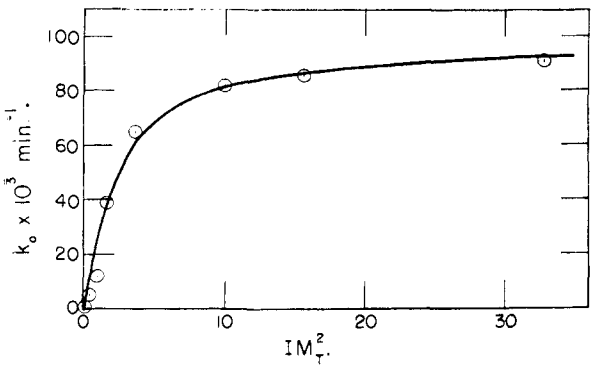


Fig. 3.—Plot of the observed first order rate constants (k_0) for the appearance of I_2 *vs.* the square of the concentration of total imidazole. The points are experimental and the curve is that obtained from equation 3.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} D \qquad (2)$$

where C is at low steady state. With increasing imidazole concentration k_0 proceeded from second order to zero order dependence in imidazole concentration (Fig. 3). Thus, Michaelis–Menten type kinetics are followed (3)

$$k_0 = \frac{0.95 \times 10^{-2}(IM_T)^2}{0.20 + (IM_T)^2} \qquad (3)$$

where k_0 is the observed rate of attainment of equilibrium and IM_T the total concentration of imidazole (*i.e.*, $IM_T = IM + IM^+H$). The results enumerated above suggest two alternative explanations for the imidazole catalysis: (a) saturation of I_1 by two molecules of an imidazole species followed by an intracomplex general base and/or general acid catalysis of the prototropic shift leading to I_2; and/or (b) the catalysis of the formation of I_1 involving two molecules of an imidazole species is rate determining at low IM_T concentration but at high IM_T concentration the non-catalyzed prototropic shift of I_1 to I_2 becomes rate determining and the reaction changes from second to zero order in IM_T. Replacement of pyridoxal by its morpholine imine does not unduly affect the over-all rate, suggesting that the rate-determining step is in fact the prototropic shift. Furthermore, the kinetic treatment is based upon the assumption of a rate-determining prototropic shift and has been found to predict accurately the effect of variation of the initial reactant concentrations upon the observed overall rates.

Following the attainment of equilibrium in I_2 the second and slower phase of the reaction is encountered in which equilibrium is attained between all species [*i.e.*, amino acid + pyCHO $\rightarrow$ $I_1 \rightleftarrows$ $I_2 \rightleftarrows$ $pyNH_2$ + keto acid]. The second phase is accompanied by an increase in absorbance at the isosbestic points for the first phase, appearance of new isosbestic points at 310, 350 and 260 mμ, decreased absorbance at 395 mμ (continuing decrease in pyCHO concentration) and decreased absorbance at 246 mμ (the absorbance by I_2 + pyCHO + amino acid at 246 mμ is greater than that of $pyNH_2$ + keto acid produced). The pH-dependence of the imidazole-catalyzed reaction, details of the kinetics and equilibrium constants and a discussion of the possible mechanism for catalysis will be submitted for publication shortly.

The present results open the door to the possible establishment in aqueous solution of similar model systems of the racemization, decarboxylation and C_α—C_β bond scissions of α-amino acids which are mediated by enzymes requiring pyridoxal phosphate as cofactor. Investigation of these possibilities is being actively pursued.

(8) This work was supported by grants from the National Institutes of Health and the National Science Foundation.

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THE MOLECULAR STRUCTURE OF $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$

Sir:

The reactions of acetylenes with metal carbonyls or other transition metal compounds have yielded a wide variety of organometallic complexes. Compounds of two general types have been prepared in which the acetylenes either (1) form new carbon–carbon bonds by polymerization or reaction with other ligands present or (2) complex to a metal without formation of new carbon–carbon bonds. The former group[1–5] includes compounds with metals bonded to organic ring systems (with or without incorporated CO groups); the ring system may be heterocyclic with a transition metal as the hetero atom.[5] To date the only known structures of the latter group of compounds,[6] in which acetylene remains as a distinct recognizable entity, have involved acetylenes which form metal complexes either via one[7] or two[8,9] μ-type bonds[10] or via two "bent" σ-bonds.[1,2a,11]

(1) G. E. Coates, "Organometallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960.

(2) (a) G. E. Coates and F. Glocking, "Organometallic Chemistry," edited by H. Zeiss, Reinhold Publishing Corp., New York, N. Y., 1960, pp. 458–463; (b) J. Chatt, P. L. Pauson and L. M. Venanzi, *ibid.*, pp. 492–498; (c) H. Zeiss, *ibid.*, pp. 411–417.

(3) D. W. A. Sharp, "Annual Reports on the Progress of Chemistry," The Chemical Society (London), **56**, pp. 140–143 (1959); **57**, pp. 147–148 (1960).

(4) P. L. Pauson, *Proc. Chem. Soc.*, 297 (1960).

(5) (a) W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Krüerke, D. A. Brown, G. D. S. King and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959); (b) W. Hübel and E. H. Braye, *ibid.*, **10**, 250 (1959); (c) E. H. Braye, C. Hoogzand, W. Hübel, U. Krüerke, R. Merényie and E. Weiss, "Advances in the Chemistry of the Coordination Compounds," edited by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, pp. 190–198; (d) G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5307 (1959).

(6) Transition metal acetylides or metal acetylene complexes with the acetylene possessing additional coördinating groups capable of interacting with a metal atom (*e.g.*, hydroxyacetylenes) are not included in this classification.

(7) F. L. Carter and E. W. Hughes, *Acta Cryst.*, **10**, 801 (1957); S. V. Bukhovets and N. K. Pukhova, *Zhur. Neorg. Khim.*, **3**, 1714 (1958); J. Chatt, L. A. Duncanson and R. G. Guy, *Chem. and Ind.*, 430 (1959); J. Chatt, R. G. Guy and L. A. Duncanson, *J. Chem. Soc.*, 827 (1961).

(8) H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, *J. Am. Chem. Soc.*, **78**, 120 (1956); W. G. Sly, *ibid.*, **81**, 18 (1959).

(9) J. F. Tilney-Bassett and O. S. Mills, *J. Am. Chem. Soc.*, **81**, 1757 (1959); M. Dubeck, *ibid.*, **82**, 502 (1960); J. F. Tilney-Bassett, *J. Chem. Soc.*, 577 (1961).