The effects of variations in wavelength and irradiation times also are noteworthy. Both I and II do not absorb light having a wavelength greater than 3000 A. However, when the sample was irradiated for only a short time (~5 sec) with 2537-A light, cleavage occurred with the production of III and the corresponding carbonyl compound (IV or V), and subsequent irradiation with 3500-A light caused further photolysis, suggesting that sensitization was occurring. Photosensitizers such as benzophenone and acetophenone appeared qualitatively to give increased yields of III over those obtained in unsensitized photolyses. Such effects had not been observed earlier in previous work in solution.[1e]

These experimental data, besides confirming the previous postulation that methylene intermediates may be produced upon photolysis of oxiranes, also show that oxiranes provide another set of precursors for the epr study of methylenes, in addition to the diazo compounds[8] and bisazides[9] which have been used previously.

The mechanism by which the methylene is formed in the photolysis of these oxiranes is of some interest. The present work does not exclude a two-step homolytic process such as that formulated in Scheme II.

Scheme II
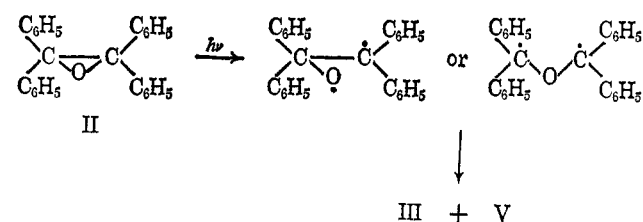
However, in epr studies in the magnetic field region where monoradicals or triplets with smaller spin-spin interaction (such as would be anticipated for VI) might exhibit resonance absorption, only a relatively weak signal was observed. Thus, one is tempted to conclude that if VI or VII is formed in a rigid glass, it has a rather short lifetime, and either reverts to II or fragments to III and V. Furthermore, in view of recent observations[10] on the solvolytic photochemical cleavage of cyclopropanes (a reaction which competes with the fragmentation to carbene) we should consider an ionic intermediate perhaps formed by initial heterolytic cleavage or in a later step from VI or VII. Further studies on the mechanism of the photolysis of oxiranes are continuing.[11]

(8) See ref 4b for bibliography.

(9) L. Barash, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, Sept 1965, p 54S; L. Barash, E. Wasserman, and W. A. Yager, to be published.

(10) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinnsson, C. S. Aaron, G. J. Boudreaux, and H. W. Griffin, *J. Am. Chem. Soc.*, 88, 5675 (1966).

(11) NOTE ADDED IN PROOF. According to P. Petrellis (unpublished results), diphenylcarbene is formed also in the photolysis of 2-methoxy-2,3,3-triphenyloxirane. The carbene was trapped in methanol as the methyl ether of benzhydrol. Methyl benzoate, the accompanying fragment, was isolated by glpc and compared with authentic material. The presence of III was detected by epr and luminescence studies. These data confirm and are consistent with the results of T. I. Temnikova and I. P. Stepanov, *Zh. Organ. Khim.*, 2, 1525 (1966); *Chem. Abstr.*, 66, 54820y (1967).

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Inversion of Positional Reactivity Order and Two Mechanisms of Hydrogen–Deuterium Exchange for Pyridine

Sir:

Considerable confusion has existed regarding the positional reactivity order of hydrogen–deuterium exchange for pyridine. Relative rates of deprotonation at positions 4, 3,5, and 2,6 are reported to be 10^3, 10^2, and 1, respectively, in ND_3–$NaND_2$ ($-25°$).[1] These deprotonations were said to proceed by way of an anionic intermediate resulting from the addition of amide ion to substrate. By contrast, pyridine is reported not to exchange in D_2O, while in D_2O–NaOD (220°) exclusive deprotonation at the 2,6 positions is said to result.[2,3]

We wish to present a clarified picture of H–D exchange for pyridine. We have evidence for an inversion in the relative positional reactivity order in aqueous solution and for the existence of two mechanisms of deprotonation. In DCl or D_2O pyridine undergoes exchange at measurable rates only at the 2,6 positions. In NaOD the protons at all positions exchange, but in the order 4 > 3,5 > 2,6.

For kinetic runs in acidic solution, pyridine and aliquots of DCl were mixed, sealed in glass tubes, and heated (218°). Analysis of the recovered pyridine by nmr showed exchange only at positions 2,6. The pseudo-first-order rate constants,[4] k, for this exchange are expressed as a function of acidity in Figure 1.[5] The resulting curve indicates that the rate of exchange at position 2 or 6 increases as the amount of unprotonated pyridine increases. The rate then levels and approaches that in neutral D_2O. We suggest that the mechanism for this exchange involves attack of deuterioxide ion on pyridinium ion to give ylide I. This ylide then captures a deuteron to produce exchanged pyridine (path 1). Support for this path is found in separate experiments with N-methylpyridinium chloride in D_2O. At 218° measurable exchange

(1) I. F. Tupitsyn and N. K. Semenova, *Tr. Gos. Inst. Prikl. Khim.*, 49, 120 (1962); *Chem. Abstr.*, 60, 6721c (1964).

(2) Y. Kawazoe, M. Ohnishi, and Y. Yoshioka, *Chem. Pharm. Bull.* (Tokyo), 12, 1384 (1964).

(3) We are unable to repeat these observations.

(4) Although deprotonation takes place consecutively at positions 2 and 6, for example, all rate constants in this work represent values for deprotonation at a single position. It follows from the usual kinetic treatment of consecutive, first-order reactions such as

$$H\text{-}2,\ H\text{-}6 \xrightarrow{2k} H\text{-}2,\ D\text{-}6 \xrightarrow{k} D\text{-}2,\ D\text{-}6$$
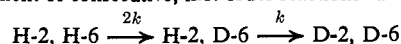
that the rate constant, k, for reaction at a single position is given by the expression $\ln ([H\text{-}2, H\text{-}6] + [H\text{-}2, D\text{-}6]/[H\text{-}2, H\text{-}6]_0) = -kt$. The concentration ratio in this expression was determined directly by nmr.

(5) That log [pyridine]/[pyridinium ion] provides a measure of solution acidity follows from the expression pD = log [pyridine]/[pyridinium ion] + pK_a. The pK_a value is known only approximately under the conditions of our experiments, but the ratio of free to protonated substrate is accurately known from the concentrations of pyridine and DCl employed.
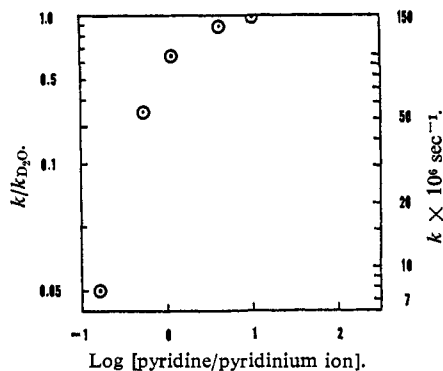
Figure 1. Log–log plot for the rate of hydrogen–deuterium exchange for pyridine at positions 2,6 in D_2O at 218° as a function of acidity. Left ordinate gives the ratio of the rate of exchange in pyridine–pyridinium ion mixtures to the rate of exchange in neutral water. Right ordinate indicates the observed rate constant. Total concentration of pyridine in all forms is 1.1 M.

occurs at only the 2,6 positions and is inhibited by decreasing the deuterioxide ion concentration.[6]
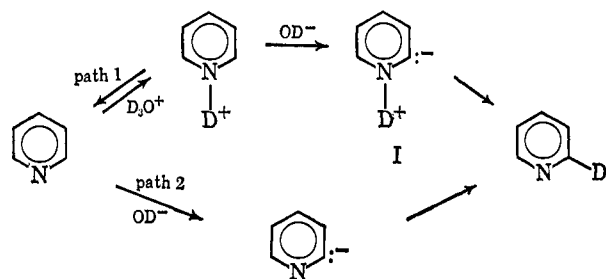
There is considerable precedent for ylide I. Such an intermediate is said to result during the decarboxylation of pyridine-2-carboxylic acid and of the betaine N-methylpyridine-2-carboxylic acid.[7] The dipolar intermediates which result during similar decarboxylations have been trapped.[8,9]

In another series of experiments pyridine and D_2O–NaOD were heated in a Monel bomb (198 ± 3°).[10] Pyridine, recovered in good yield, was analyzed for positional deuterium content by nmr using t-butyl alcohol as an internal standard. Rates of exchange at all positions showed dependence on deuterioxide ion concentration. At low base concentrations the rates of exchange at position 2 were much greater than at 3 or 4. At high base concentration, in contrast, the 4 position exchanged most rapidly, followed by 3, and then 2. Rate constants for each position are compared by a graphical method in Figure 2. A slope in these plots gives the ratio of rate constants for exchange at two positions.[11] Such a plot for the rate of exchange at position 4 vs. exchange at 3 has a slope of 1.3; therefore, k_4/k_3 is 1.3. Data from several

(6) Another possible mechanism, in which pyridine removes a proton from a C–H center of a pyridinium ion, can be eliminated by the shape of the pD–rate curve. This mechanism demands a rate maximum when [pyridine] and [pyridinium ion] are equal. This maximum is not observed.

(7) P. Haake and J. Mantecón, J. Am. Chem. Soc., 86, 5230 (1964), and references cited therein.

(8) For a list of examples of the Hammick reaction see E. P. Oliveto, "Pyridine and Its Derivatives," Part III, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, pp 207–208.

(9) H. Quast and E. Frankenfeld, Angew. Chem. Intern. Ed. Engl., 4, 691 (1965).

(10) Glass tubes could not be used with basic solutions at these temperatures because of severe etching.

(11) S. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 98–99.
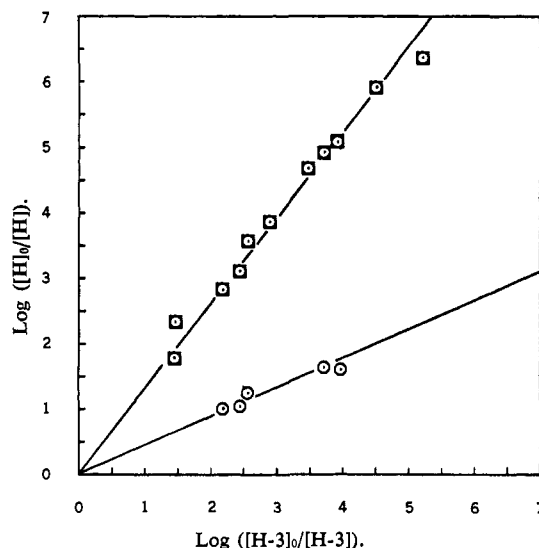
Figure 2. Log–log plot for the rate of hydrogen–deuterium exchange for pyridine in D_2O–NaOD at 198°. The ordinate expresses the inverse mole fraction of hydrogen remaining in either the 2,6 (circles) or 4 (squares) positions and the abscissa gives the inverse mole fraction of hydrogen remaining in the 3,5 positions. Approximate half-life for position 2 in 1.0 M NaOD is 0.9 hr.

determinations at different base concentrations were employed. Similarly k_3/k_2 is 2.3. For this latter comparison only data from runs in 1 N NaOD were used in order to minimize the effect of reaction at positions 2,6 by path 1. Relative rates of exchange of unprotonated pyridine at positions 4, 3, and 2 are 3.0, 2.3, and 1.0, respectively.

There can be little doubt about the positional reactivity order of base-catalyzed exchange for pyridine. We have found a similar order in t-butyl alcohol and in methanol at much lower temperatures. Exchange in liquid ammonia also follows the same pattern.[1] Furthermore, the rate of exchange for 3-chloropyridine at position 4 is much greater than at 2 in both methanol and liquid ammonia.[12]

The mechanism for exchange in basic solution most likely involves removal of a proton from pyridine by deuterioxide ion. The resultant pyridyl anion then abstracts a deuteron from solvent to form exchanged product (path 2). This mechanism is similar to that for exchange of chloropyridines in CH_3OD–CH_3ONa or NH_3–$NaNH_2$.[12]

That two pathways exist for exchange at position 2 while only one mode is dominant for positions 3 or 4 is readily understandable. Zwitterionic intermediates which would result from deprotonation of a pyridinium ion at position 3 or 4 have much less coulombic stabilization than ylide I.[13]

(12) J. A. Zoltewicz and C. L. Smith, J. Am. Chem. Soc., 88, 4766 (1966).

(13) The rate of decarboxylation of N-methylpyridine-2-carboxylic acid is about three powers of ten larger than that for the other two isomeric acids.[7]

(14) Arts and Sciences Fellow, 1966–1967.

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Communications to the Editor