

silic acid,¹⁵ but the behavior of irradiated sRNA on these columns was clearly different from the controls. We are also unable to present additional information on the specificity of the cleavage.

This reaction is of particular interest in view of the recent reports on the photoinactivation of sRNA^{16,17} and the implication that either uridine or pseudouridine residues¹⁷ may be involved in this loss of activity. Further work on the mechanism of the photolysis of $\Psi 3'P$ and on the photolysis of sRNA is in progress.

Acknowledgment.—This work was supported by a grant from the United States Public Health Service (GM-072620-4).

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(18) Recipient of an Investigatorship of the Health Research Council of the City of New York under Contract I-200.

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RECEIVED AUGUST 11, 1964

Specifically Solvated Ion-Pair Intermediates in Nitrous Acid Deamination of an Axial Amine¹

Sir:

Nitrous acid deamination of equatorial amines gives substitution products of very predominantly retained configuration,² while axial amines have been reported to give steric results which range from complete retention, as in the case of $\delta\alpha$ -cholestan-3 α -ylamine,³ to very predominant inversion, as in the case of the structurally similar *trans,trans*-2-decalylamine (I).⁴ The non-stereospecific results obtained with *cis*-4-*t*-butylcyclohexylamine has led to the postulation⁵ that a free carbonium ion is an important reaction intermediate.

We now wish to demonstrate the value of a new technique for studying this type of reaction. It involves the determination of the proportion of alcohol and acetate in both the inverted and retained products of nitrous acid deamination of an amine in aqueous acetic acid mixtures of varying composition. When applied to the *axial* amine (I)⁷ this procedure provides the data shown in Table I.⁸

The results almost certainly preclude a "free carbonium ion"^{5,6} as the sole or even predominant inter-

(1) This work was supported by Grant AM 06419 from the National Institutes of Health and Grant B-19 from the Health Research and Services Foundation, Pittsburgh, Pa.

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(4) W. Hüchel, *Ann.*, **533**, 1 (1938).

(5) W. Hüchel and I. Heyder, *Ber.*, **96**, 220 (1963); a similar postulation has been put forth⁶ to explain the steric results in other *axial* cases.

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(7) This was prepared in pure form by ammonolysis of the epimeric tosylate; see J. L. Pinkus, G. Pinkus, and T. Cohen, *J. Org. Chem.*, **27**, 4356 (1962).

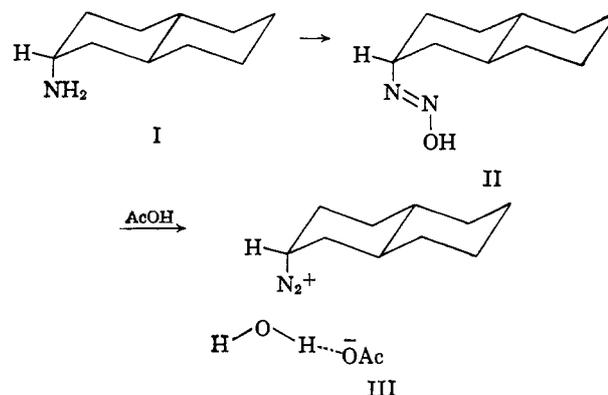
(8) Control tests established that olefins and alcohols are partially destroyed under the reaction conditions, but that the latter can be fully regenerated by ebullition of the reaction mixture with nitrogen until nitrous fumes are no longer evolved. Any nitrite esters formed by attack of nitrite ions on intermediates during the deamination reaction would be converted to alcohols by this procedure. However, nitrite ions are not expected to enter into the reaction significantly since acetate ions apparently do not do so (see below).

TABLE I
DEAMINATION^a OF I AT 30.0 \pm 0.1 $^\circ$

Mole % acetic acid	% Inversion ^b (% alcohol) ^c	% Retention ^b (% alcohol) ^d
3.4	79.5 (65.8)	20.5 (70.3)
25.0	50.1 (53.2)	49.9 (65.6)
49.9	42.1 (29.9)	57.9 (56.9)
49.9 ^e	42.9 (29.5)	57.1 (57.4)
49.9 ^f	39.7 (29.0)	60.3 (56.8)
75.0	39.4 (12.9)	60.6 (51.7)
100	40.3 (3.7)	59.7 (45.6)

^a Molar ratio of sodium nitrite to amine is 5. ^b % of substitution product. ^c % in inverted product; the remainder is acetate. ^d % in retained product; the remainder is acetate. ^e Sodium acetate (in same molar quantity as sodium nitrite) was added. ^f α -Deuterio-*trans,trans*-2-decalylamine.

mediate, since the ratios of alcohol to acetate in the retained and inverted products are different throughout the range and their variations with solvent composition differ greatly. These ratios in the product of retained configuration are remarkably insensitive to solvent composition, changing only from 0.84 to 2.37 as the molar ratio of water to acetic acid varies from 0 to 28.4. This provides strong support for the existence in this reaction of a specifically solvated diazonium acetate ion-pair intermediate (III).⁹ The bulk of retained product must arise by loss of nitrogen from III followed by rather nonselective attack of the internal water or acetate on the "front side" of the resulting carbonium ion.



Another striking fact is that the proportion of acetate in the inverted product is greater than the molar proportion of acetic acid in the solvent in each of the media used, except in acetic acid. The most dramatic example is in the case of 3.4 mole % acetic acid, in which 34% of the inverted product is acetate. The intramolecular inversion mechanism of White and Aufdermarsh¹¹ cannot explain this result over the whole range since the mechanism allows no greater proportion of acetate in the inverted than in the retained product. Indeed, an upper limit of about 8% (3.7 + 3.7 \times 54.4/45.6) can be placed on the proportion of inverted product formed by this mechanism in pure acetic acid. Neither is this due to attack of acetate ions¹² on the back side

(9) This type of intermediate (III), presumably formed by reaction of the diazohydroxide II or its precursor with acetic acid, has been postulated¹⁰ to account for the alcohol of retained configuration which is produced along with acetate in deaminations conducted in acetic acid. Our finding that a substantial proportion of the retained product is acetate, even in a solvent which contains very little acetic acid, is entirely consistent with this view.

(10) E. H. White and J. E. Stuber, *J. Am. Chem. Soc.*, **85**, 2168 (1963).

(11) E. H. White and C. A. Aufdermarsh, *ibid.*, **83**, 1179 (1961).

(12) These are produced during the deamination and by the reaction of excess nitrite ions with acetic acid.

of a reaction intermediate, since the addition of enough sodium acetate to ensure at least a doubling of acetate ion concentration leads to no change in product composition.

The composition of the inverted product could be accounted for by a proton abstraction from the diazonium ion by the internal acetate ion of III to form a diazoalkane, which could react fairly stereospecifically with acetic acid (but not with water) to form the more stable, inverted acetate. However, this is ruled out by the finding that the α -deuteriodecalylamine gives about the same product composition as the protium compound.¹³

The explanation for the failure of the more nucleophilic water molecules to attack the cationic intermediates more readily than do acetic acid molecules is probably related to the great nonselectivity of the intermediate "hot" carbonium ion.¹⁴ It also appears likely, in accord with the views of other workers,^{6,11} that substantial nucleophilic participation by solvent in the loss of nitrogen does not occur, since water should be much more effective than acetic acid in this process.

These results also provide a partial explanation for the much greater degree of retention observed upon the deamination of 5α -cholestan- 3α -ylamine in 23 mole %¹⁵ acetic acid in water³ than in the deamination of I in 3.4 mole %¹⁵ acetic acid.⁴ For reasons as yet unknown, the degree of inversion increases sharply with water content in the more aqueous solvents.

The technique used here appears to offer great promise as an informative probe in mechanistic studies of nitrous acid deaminations and, hopefully, of other solvolysis reactions.

(13) The isotope effect would be expected to reduce the importance of the diazoalkane path and to decrease the yield of inverted acetate.

(14) D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2866 (1957).

(15) 23 mole % and 3.4 mole % correspond respectively to 50 and 10 volume %.

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RECEIVED AUGUST 4, 1964

Pulse Radiolysis of Gases¹

Sir:

The technique of pulse radiolysis^{2,3} has been used with considerable success to observe the optical absorption spectra of transient species and to determine the rate constants for elementary reactions in the radiolysis of liquid systems.⁴ We have now extended this technique to the study of gaseous systems. In the pulse radiolysis of rare gas-naphthalene systems, we have observed the triplet state of naphthalene. In a kinetic study of irradiated oxygen we have determined the absolute rate constant for the reaction of oxygen atoms with molecular oxygen to form ozone.

The general experimental technique is similar to that used for liquids and has been described in detail.³ In the present work, a stainless steel cell, permitting high pressures, was used with the 14-Mev. electron beam and pulses of 0.4 to 5 μ sec. The cell, 13 cm. in

inside length, had a front window of aluminum, 1 mm. thick. The rear window, through which the analyzing light beam passed, was of high purity silica, 0.5 in. thick. A thin mirror inside the cell at the front was used with either two or four reflections, giving a light path of 26 or 52 cm.

The naphthalene system irradiated consisted of 10 to 30 atm. of xenon and about 0.1 mm. of naphthalene. A transient absorption spectrum was observed, consisting of three bands centered at 3984, 3772, and 3430 \AA ., with half-widths of about 60–70 \AA . and relative optical densities at the maxima of 1.0, 0.4, 0.15, respectively. This spectrum is assigned to the triplet state of naphthalene on the basis of the good agreement of the wave lengths, relative intensities, and half-widths of the bands with the three bands of greatest intensity observed by Porter⁵ in the flash photolysis of naphthalene vapor and assigned to the triplet state. Two weaker bands observed by Porter were not seen because of the low concentration of triplet.

Within our time resolution of about 0.5 μ sec., the naphthalene triplet seems to be formed instantaneously. There are several possible modes of formation of the triplet, one of the more likely of which is direct electron impact by subexcitation electrons⁶ in this two-component system.

The decay of the triplet was observed spectrophotometrically after the electron pulse by monitoring the bands at 3984 and 3772 \AA . The decay appears not to follow a simple first- or second-order rate law. Under the conditions of the experiment, the decay had an approximate half-time of 3 to 6 μ sec. followed by a longer decay of 10 to 20 μ sec. The decay kinetics are being investigated.

The ozone formation reaction (eq. 1) was investi-



gated over an oxygen pressure range of 7 to 130 mm. with argon present at pressures up to 100 atm. The Ar, in these experiments, was taken as the third body, M. The reaction was monitored at 2600 \AA . where the ozone has a suitable absorption band.⁷ The pulse duration was 0.4 and 1 μ sec. The formation rate curves obey a first-order rate law. These curves were generally analyzed starting at about 1.5 μ sec. after the electron pulse and had half-times of about 0.7 to 7 μ sec. The experimental results obtained, as well as calculations based on considerations of reactions of ionic and excited species likely to be responsible for the production of oxygen atoms, seem to indicate that the formation of oxygen atoms is negligible 1 μ sec. after the end of the pulse.

The data obtained give $k_1 = (0.7 \pm 0.3) \times 10^{14}$ (cc. mole⁻¹)² sec.⁻¹ at 25°. This value, obtained by a technique which is completely different from previous investigations, may be compared with recent values obtained in other ways. Measurements of ozone decomposition and equilibrium considerations,^{8–10}

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