MECHANISM OF THE BASE PROMOTED FRAGMENTATION OF CHLOROACETYLHYDRAZIDE

W. J. le Noble[*], S. Chang, J. Child, T. Ushijima, and J. Zias

Department of Chemistry, State University of New York

at Stony Brook, New York 11794

Summary: Experiments are described supporting the positions that the visible transient intermediate occurring during the fragmentation of chloroacetylhydrazide is the anion of acetyldiazene, and that the concurrent reduction is not a simple recombination reaction.

Several years ago, we proposed a new mechanism[1] for the base promoted fragmentation of chloroacetylhydrazide to give chloride and acetate ions, nitrogen and hydrazine. The reaction which had been discovered by Buyle,[2] has considerable promise as a source of diazene (diimide) in aqueous or alcoholic media,[3] and the detailed pathway therefore deserves to be known. The mechanism first proposed by Buyle and by Paulsen[4] (see scheme) was ruled out by our results,

which included a negative activation volume typical of a displacement reaction but not of a concerted fragmentation, a small rate effect by β-$\underline{N}$-dimethyl substitution, total inhibition by α-$\underline{N}$-methyl substitution, and a change in rate law from second order in buffered solutions to base independence at high base concentrations (stopped flow conditions; the pKa of the precursor acid was thus shown to be 11).

At high pH, a transient yellow color is observed which the stopped flow experiments reveal to have a λ_{max} of 325 nm and an ε_{max} of at least 1500. As candidates for the species responsible for this absorption, we ruled out (a) because its formation would not be expected to be slow, (b) because some known isolable α-lactams are colorless, (c) because independently produced ketene did not lead to the transient color upon injection into aqueous base, and (d) because the disappearance of the yellow color was first order and because the known (yellow!) diazene had been reported to be stable only below -170°, at least in the pure state. We proposed (e) and (f) as the only surviving alternatives.

Acetyldiazene (or the tautomeric α-diazoethanol) has been proposed as an intermediate in many reactions,[5] and much attention has also been paid to the properties and chemistry of diazene. We were therefore much interested in a report by Willis,[6] who generated solutions of diazene in liquid ammonia by passing hydrazine vapor through a microwave discharge: these solutions decomposed at only moderate rates (half life of the order of many minutes at -33°), and they did so with a first order rate law! Presumably, $\underline{E}$-(d) first isomerizes to the $\underline{Z}$-isomer in a rate controlling step. Thus, our arguments for ruling out (d) were invalid, and hence, further work was in order.

The possibility that the transient yellow intermediate is diazene was submitted to a direct test: mixing Willis' solutions with strong aqueous base should give rise to the same UV-visible spectrum as that produced in the stopped flow experiments. These solutions were generated by passing carefully dried and degassed hydrazine vapor for 10 minute periods through a microwave discharge. The excitation was achieved with an open reflecter antenna powered by a Raytheon microwave power generator model PGM-10 (2540 Mc, 385 watts). The condensate was freed from hydrazine by means of a rapid, low temperature vapor transfer distillation. The resulting yellow mixtures were shown in the manner reported by Willis and Back to contain between 100 and 400 micromoles of diazene. When these mixtures of diazene and ammonia were treated with 1M aqueous NaOH saturated with NaCl at -20°, the yellow color of the diazene was instantly discharged. A number of variations of this experiment were tried, such as passing gaseous diazene through the cold base; however, the results were uniformly the same: no yellow aqueous solutions resulted. Thus, Willis' species and ours are not the same.

In order to facilitate further study, we learned to carry out Buyle's reaction in saturated aqueous sodium chloride at pH 11-12 at -20°; the transient yellow color then builds up to a maximum intensity in a minute or two and remains visible for many minutes afterwards. This

result made it possible to consider the question whether the transient intermediate is the anion (f) or the neutral species (e): we attempted next to extract it from the cold aqueous solution with such solvents as methylene chloride and chloroform. In spite of the saturation with sodium chloride, not a trace of the colored species could be extracted, convincing us that it must be the ionic species (e). A quenching experiment was then done to learn more about the relation between the anion and the neutral species in equilibrium with it. A sudden reduction in pH to 2 or 3 discharges the color; when the solution is immediately made basic again, the yellow color is partially restored, but only slowly (see Fig. 1); clearly (e) is unstable under acid conditions, and the formation of new (f) at restored high pH depends on unconsumed starting material. These experiments were completely reproducible at 325 nm, a Carey 14 then being used to follow events. Attempts to trap the anion with methyl iodide or acetaldehyde have not led to success.[7]
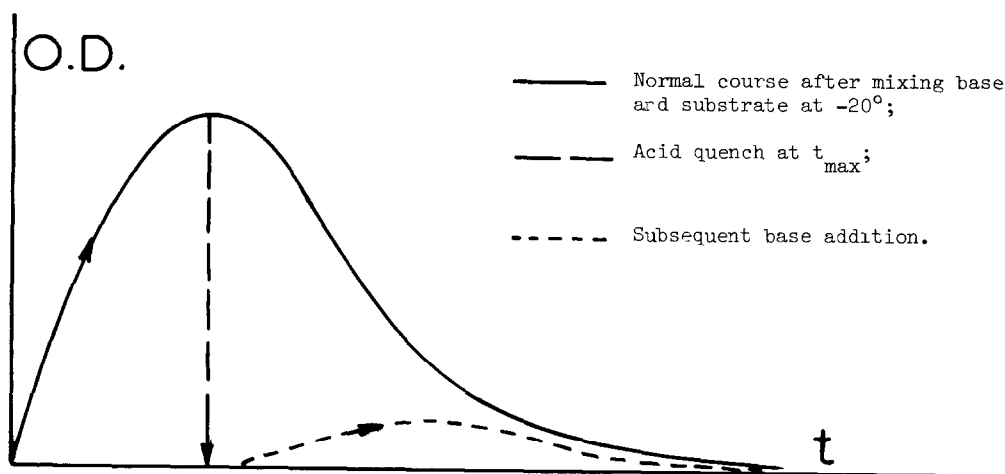

Fig. 1. The normal formation and decay of the absorption at 325 nm, and the effects of quenching. Note that t_{max} is the same in both cycles.

We report one additional experiment that bears on the origin of a low yield (of the order of 20%) of acetylhydrazide as a by-product. Buyle pictures it as being formed from the fragmentation products, but this seems hardly likely as the hydrazide eventually must be completely hydrolyzed under these conditions. In our scheme, this compound could form via reduction of (f) by the diazene (d). The following labelling experiment shows that the acetylhydrazide is indeed formed without the CN bond being broken.

When the reaction is carried out in the presence of an equivalent of CD_3COOH, the hydrazide isolated contains no deuterium (^{1}H nmr in chloroform shows equal areas under the methyl and hydrazide peaks). To make sure that the deuterium had not been exchanged out of either the
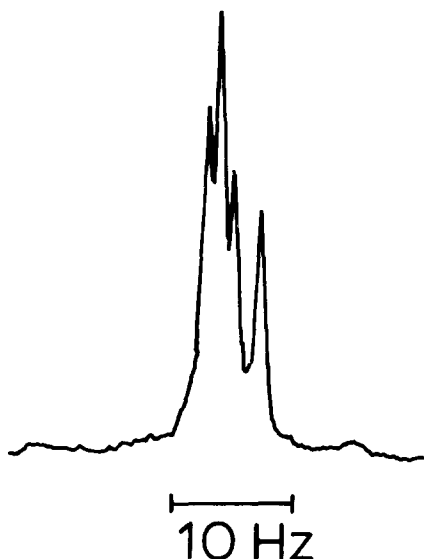
10 Hz

acetate or the hydrazide, the reaction was next carried out with natural acetic acid in D_2O. Under these conditions, acetylhydrazide-d_1 is formed:[8] the integregation is now 2:3, and the acetyl absorption is a 1:1:1 triplet with J_{HD} = 2.2 Hz. A minor singlet superimposed is due to light hydrazide formed with the exchangeable protons in the substrate and base added; see Fig. 2. Clearly, no major amounts of acetylhydrazide-d_2 are present. These two experiments show that the minor reduction product is not formed from acetic acid. Instead, it is formed from a precursor in which the C-N bond is still intact: (e) is the best candidate for this. We conclude that all known observations concerning Buyle's reaction are accommodated by our scheme.

Fig. 2. The methyl pmr region of the $CH_2DCON_2H_3$ formed in Buyle's reaction in D_2O. The $CH_3CON_2H_3$ peak is accounted for by dilution of the deuteron pool with exchangeable protons introduced as part of the experiment. Its slightly off-center position is an isotope effect.

REFERENCES AND FOOTNOTES

1. W. J. le Noble and Y. S. Chang, _J. Am. Chem. Soc._, 94, 5402 (1972).

2. (a) R. Buyle, A. Van Overstraeten, and F. Eloy, _Chem. Ind. (London)_, 839 (1964);

   (b) R. Buyle, _Helv. Chim. Acta_, 97, 2449 (1964).

3. S. Bank, private communication.

4. (a) H. Paulsen and D. Stoye, _Chem. Ber._, 99, 908 (1966); (b) H. Paulsen, "The Chemistry of Amides," J. Zabicky, Ed., Wiley, New York, N.Y., 1970, Chapter X.

5. R. Ahmed and J. P. Anselme, _Tetrahedron_, 28, 4939 (1972).

6. C. Willis, R. A. Back, J. M. Parsons, and J. G. Purdon, _J. Am. Chem. Soc._, 99, 4451 (1977) and earlier work quoted there.

7. Both reagents quench the yellow color, but no products with the C-N bond intact could be isolated.

8. The isolation procedure removes the nitrogen-bound deuterium.

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