SYNTHESIS, REACTIVITY AND STRUCTURE OF NITRODIAZOACETIC ACID

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Summary: Nitrodiazoacetic acid was prepared and its structure determined by low temperature X-ray crystallography. There is good agreement between the experimentally determined structure and that calculated at the ab initio rhf/3-21G level of theory. The acid is stable in neat trifluoroacetic acid and less stable in neutral non-polar solutions. In neutral polar solutions it undergoes rapid decarboxylation to yield nitrodiazomethane.

Our interest in nitrocarbenes as reactive intermediates prompted our investigation of nitrodiazomethane as a source of nitrocarbene.¹ Schollkopf and coworkers described the synthesis of nitrodiazomethane from t-butyl nitrodiazoacetate and trifluoroacetic acid/diethyl ether.² They reported no information regarding the presumed intermediate, nitrodiazoacetic acid (1), which apparently decarboxylates under the reaction conditions. Nitrodiazomethane is reported to be a white crystalline compound which decomposes at 550 C.

We have undertaken a detailed study of this reaction and have found that the white crystalline compound which was reported as nitrodiazomethane is actually nitrodiazoacetic acid. Nitrodiazoacetic acid has mp of 48 - 530 C (dec); ir (CDCl3) 2160, 1755, 1515, 1320 cm⁻¹. Chemical proof of structure is based on its conversion to the known methyl nitrodiazoacetate³ in 82% yield using an ethereal solution of diazomethane. Additionally, we have obtained a single crystal Xray structure of nitrodiazoacetic acid.⁴ Because of the acid's thermal instability, the X-ray data were collected at -60⁰ C. The structure of nitrodiazoacetic acid was calculated using ab initio molecular orbital theory and the 3-21G basis set with the Gaussian 82 program.⁵ A comparison of the experimentally determined structure and that calculated is shown in Table 1.



a. Numbers in parentheses are estimated standard deviations .

The decarboxylation of nitrodiazoacetic acid is extremely solvent dependent. It remains intact for many hours in dry trifluoroacetic acid/diethyl ether (1:2) and is extremely stable in neat trifluoroacetic acid. In diethyl ether or methylene chloride solutions it has a half life of about 2 hours. In very polar solutions such as water, methanol or acetonitrile, the decarboxylation reaction is complete in minutes.

By analogy to the decarboxylation of nitroacetic acid⁷, we propose that it is the ionized form of the acid which undergoes decarboxylation. Consistent with this hypothesis is the fact that addition of a catalytic amount of triethylamine to a methylene chloride solution of nitrodiazoacetic acid initiates rapid decarboxylation. This behavior is exactly opposite to that observed for ethyl diazomalonate, which is stable as its carboxylate salt but decarboxylates under acidic conditions.⁸



There are several examples of other stable diazo acids reported in the literature.⁹ The one common feature of all these is that they have an electron withdrawing group attached to the diazo carbon.

Nitrodiazomethane may be recovered from the decarboxylation reaction in nearly quantitative yield by evaporation of the solvent. Nitrodiazomethane is a yellow oil which solidifies between 0 and 8^o C. Both nitrodiazoacetic acid and nitrodiazomethane are extremely shock sensitive and have detonated spontaneously on many occasions. Both should be treated as powerful explosives. We recommend that less than 50 mg of material be prepared at any one time, since this is still enough material to completely destroy a 25 ml round bottom flask.

The spectral data for nitrodiazomethane match those reported by Schollkopf and coworkers.² This is undoubtably due to the facile decarboxylation of nitrodiazoacetic acid in polar solutions.

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