

dependent effect becomes relatively less important as the field is raised and disappears when fields of 5×10^2 v./cm. are reached. It must be regarded as field independent to a first approximation, or, as studies at the lowest fields show, as dependent on field to a very much smaller degree than is the conductance measured at longer pulse lengths, say $10 \mu\text{sec.}$, at higher fields.

Kraus' classic measurements² on dilute solutions of alkali metals in liquid ammonia were made in a cell with electrodes 0.7 mm. in diameter, the axes of which were separated by 1.5 mm., corresponding to a closest spacing of 0.8 mm., "by means of a bridge and telephone." If, as may reasonably be surmised, audio-voltages between 1 and 10 v. were employed, then the experimental conditions were very close to those under which we have found field-produced conductance increases of several per cent.

It is thus of compelling interest to examine in detail the frequency, field, and concentration dependence of the phenomena described above.

We have remarked somewhat similar phenomena in previous papers^{3,4} under circumstances where the field was not known. The novel results reported here result from improved technical manipulation of the solutions⁵ and are made possible by the construction of vacuum-tight conductance cells in which the field is as well known as in previous investigations of aqueous solutions.¹ The work is continuing.

(2) C. A. Kraus, *J. Am. Chem. Soc.*, **43**, 749 (1921).

(3) G. Lepoutre, N. Segard, and A. Patterson, *Ann. Soc. Sci. Bruxelles*, **69**, 5 (1955)

(4) G. Lepoutre and A. Patterson, *Compt. rend.*, **240**, 1644 (1955).

(5) P. Schettler and A. Patterson, *J. Phys. Chem.*, **68**, 2870 (1964).

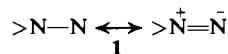
Paul D. Schettler, Andrew Patterson, Jr.
Sterling Chemistry Laboratory, Yale University
New Haven, Connecticut

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Diazenes from Angeli's Salt

Sir:

We wish to report that the reaction of aliphatic secondary amines with nitrohydroxylamine (introduced as Angeli's salt, Na_2ONNO_2)¹ is an especially simple and convenient source of diazenes (1). Evidence for



these short-lived species is provided by the marked parallelism between two sets of experiments, one involving base-catalyzed decomposition of arenesulfonyl derivatives of certain 1,1-dialkylhydrazines (a reaction known to proceed *via* diazenes)^{2,3} and the other revealing the action of Angeli's salt on the corresponding secondary amines. Structure and reaction conditions wield great influence over the fate of a diazene, with the result that it may pursue any of a variety of characteristic reaction pathways. The experiments were chosen to exploit this ability, and thus to maximize the significance of parallel behavior in the two series.

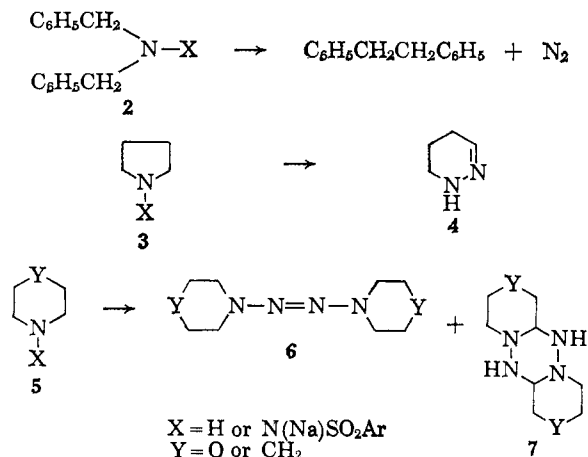
(1) A. Angeli, *Chem. Zentr.*, **67**, I, 799 (1896); H. R. Hunt, Jr., J. R. Cox, Jr., and J. D. Ray, *Inorg. Chem.*, **1**, 938 (1962).

(2) Cf. D. M. Lemal, F. Menger, and E. Coats, *J. Am. Chem. Soc.*, **86**, 2395 (1964), and references contained therein.

(3) W. H. Urry and C. Ikoku, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 25C; R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 174, 175 (1964).

Consider the "control" reactions (Chart I), the first of which has been reported previously. The diazene formed from 2 ($\text{X} = \text{N}(\text{Na})\text{SO}_2\text{C}_6\text{H}_5$) by loss of sodium benzenesulfinate decomposes to bibenzyl and nitrogen, apparently because the transition state is stabilized by benzylic resonance.⁴ Concerted fragmentation of the

Chart I



diazene derived from 3 ($\text{X} = \text{N}(\text{Na})\text{SO}_2\text{C}_6\text{H}_5$) into ethylene and nitrogen occurs in aprotic solvents.^{5,6} Interestingly, choice of a protic solvent such as water for the decomposition of 3 ($\text{X} = \text{N}(\text{Na})\text{SO}_2\text{-}p\text{-C}_7\text{H}_7$) results in *complete suppression of gas evolution*. Ring expansion to 2,3,4,5-tetrahydropyridazine (4),⁷ an example of the diazene-hydrazone rearrangement, is the dominant process (56% yield). The ability of hydroxylic solvents to catalyze tautomerization of a diazene to its 1,3-dipolar isomer, an intermediate in the rearrangement, has been discussed elsewhere.^{2,8} Pyrolysis of the morpholine and piperidine derivatives 5 ($\text{X} = \text{N}(\text{Na})\text{SO}_2\text{Ar}$) in diglyme gives the corresponding tetrazenes 6 and their decomposition products because no low-energy fragmentation pathway like that for the pyrrolidine derivative is possible. Again the switch to a hydroxylic solvent provides an opportunity for formation of the 1,3-dipolar tautomer of the diazene (8) isolated as its dimer 7.⁹

When dibenzylamine (2, $\text{X} = \text{H}$) reacted with Angeli's salt in aqueous dimethylformamide containing acetic acid, bibenzyl was produced in 70% yield (corrected for recovered amine). Addition of Angeli's salt (2 molar equiv.) to an aqueous solution of pyrrolidine (1 equiv.) and hydrochloric acid (2 equiv.) was accompanied by vigorous gas evolution due to decomposition of the salt; nevertheless, the tetrahydropyridazine 4 was formed in 68% yield. Morpholine and piperidine were each transformed by the action of Angeli's salt

(4) L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 4427 (1957).

(5) D. M. Lemal, T. W. Rave, and S. D. McGregor, *ibid.*, **85**, 1944 (1963).

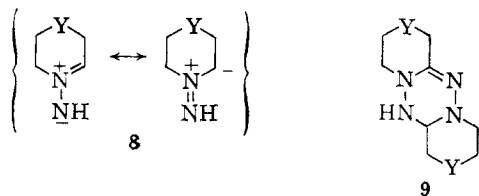
(6) Despite indications to the contrary, it is possible that decomposition of 2 and/or of 3 is totally concerted. Should this be true, merely an "incipient" diazene rather than a discrete diazene intermediate would be involved.

(7) Infrared, ultraviolet, and n.m.r. spectra of all new compounds were satisfactory, and correct carbon, hydrogen, and nitrogen analyses were obtained for all new compounds and/or their derivatives. Detailed evidence for all structures will be presented in a full paper.

(8) D. M. Lemal, C. D. Underbrink, and T. W. Rave, *Tetrahedron Letters*, No. 29, 1955 (1964).

(9) Yields of 7 from 5 ($\text{Y} = \text{CH}_2$, $\text{Ar} = \text{C}_6\text{H}_5$) were as high as 80%, those from 5 ($\text{Y} = \text{O}$, $\text{Ar} = p\text{-C}_7\text{H}_7$) were ~40%, and very little or no tetrazenes (6; $\text{Y} = \text{O}$, CH_2) was produced in typical runs.

and hydrochloric acid into at least three compounds: the tetrazenes **6**, their tricyclic isomers **7**, and dehydro derivatives of **7** (**9**).¹⁰ In an experiment not designed



to optimize yields, morpholine gave 34% of **6**, 10% of **7**, and 6% of **9**.

Thus a comparison of the two series of reactions represented in Chart I allows little opportunity for doubt that diazenes are generated when Angeli's salt acts upon secondary amines in the presence of acids. Whether or not the unstable nitroxyl (HNO), a known decomposition product of Angeli's salt,¹¹ is the attacking species is not yet entirely clear. This and other aspects of the reaction will be investigated further in our laboratory.

Acknowledgment. The authors wish to express their gratitude to Dr. Ray S. Dewey (Merck Sharp and Dohme), who first acquainted them with Angeli's work on amines. They are indebted also to Mr. Richard W. Harrington for skillful technical assistance and to the National Science Foundation and the National Institutes of Health for financial support.

(10) At the turn of the century A. Angeli discovered that sodium nitrohydroxylamate transformed secondary aliphatic amines, and piperidine in particular, into the corresponding tetrazenes (A. Angeli, *Chem. Zentr.*, 71, II, 857 (1900)). Later he reported the isolation of three additional compounds from the reaction with piperidine: N-aminopiperidine and two crystalline substances which roughly corresponded in properties to **7** and **9** (Y = CH₂), but which he formulated incorrectly (A. Angeli and V. Castellana, *ibid.*, 76, I, 1260 (1905)). It is noteworthy that he considered the possibility of diazene intermediates at that time.

(11) Cf. P. A. S. Smith and G. E. Hein, *J. Am. Chem. Soc.*, 82, 5731 (1960), and references contained therein; J. Veprek-Siska, V. Pliska, F. Smirous, and F. Vesely, *Collection Czech. Chem. Commun.*, 24, 687 (1959).

(12) National Science Foundation Cooperative Fellow, 1963-1964.

David M. Lemal, Terence W. Rave¹²

Department of Chemistry

The University of Wisconsin, Madison, Wisconsin

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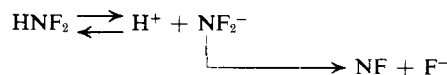
Evidence for the Difluoramide Anion

Sir:

Difluoramine, HNF₂, has been found to possess weak acid properties, and evidence has been obtained for the existence of the difluoramide anion, NF₂⁻. When HNF₂ became readily available by virtue of its direct synthesis,¹ an investigation of its dissociation was undertaken.

We have found the stability of HNF₂ in buffered aqueous solutions to decrease as pH or temperature increases, the principal decomposition products being N₂F₂ and N₂O. Furthermore, when the potentiometric titration of aqueous HNF₂ solutions with aqueous base was stopped short of the end point, the potentials drifted to lower pH. These results are consistent with the dissociation of HNF₂ and then relatively slow decomposition of the resulting anion.

(1) J. P. Freeman, A. Kennedy, and C. B. Colburn, *J. Am. Chem. Soc.*, 82, 5304 (1960).



The fluorazene formed in the anion decomposition would be the precursor of the N₂F₂ and N₂O isolated. Also, the postulated fluorazene has been shown to be the probable reactant in deamination reactions of difluoramine,² as well as a decomposition product of the electronically excited difluoramino free radical.³

Additional evidence for the difluoramide anion and its relative instability was provided by polarographic data. Difluoramine in aqueous solution undergoes a four-electron reduction at mercury electrodes at potentials more cathodic than -1.0 v. vs. s.c.e. It was expected that the reduction of NF₂⁻ would only occur at potentials beyond solvent reduction, while the reduction potential for undissociated HNF₂ was accurately predicted from a correlation of reduction potential with structure⁴ for a large number of difluoramino compounds. When base was added, the difluoramine reduction wave diminished and finally disappeared when base was in excess. If the solution was re-acidified rapidly, the wave reappeared but the diffusion current was somewhat diminished, the decrease in diffusion current being proportional to the time the solution stood before re-acidification.

A conductometric study of the dissociation of HNF₂ was carried out under carefully controlled conditions, but the results were inconclusive, since the data could also be explained by decomposition of less than 1% of the HNF₂ to fluoride. However, when conductometric titrations of aqueous HNF₂ solutions with NH₄OH solutions were performed rapidly, a distinct equivalence point was observed.

Finally, it was determined that aqueous solutions of difluoramine can be oxidized easily both electrochemically and chemically. The electrooxidation at a rotating platinum working electrode was observed in this laboratory as early as June 1961, and is a one-electron process. The homogeneous oxidation with ferric ion yielded tetrafluorohydrazine, N₂F₄, of high purity. The rate of the oxidation with ferric ion decreased rapidly with decreasing pH, which supports the proposal that NF₂⁻ rather than undissociated HNF₂ is the species being oxidized. It is interesting to note that although N₂F₄ has been prepared by a number of methods,⁵ each of the published processes suffers from one or more of the disadvantages of low yield, difficultly separated product mixtures, or high temperature requirement. In addition to the simplicity and high purity of product obtained, the oxidation of NF₂⁻ is made even more attractive for the production of N₂F₄ by the relatively easy preparation of HNF₂ by aqueous fluorination of urea.⁶

Caution is advised in working with these compounds.

(2) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *ibid.*, 85, 97 (1963).

(3) C. L. Bumgardner and M. Lustig, *Inorg. Chem.*, 2, 662 (1963).

(4) K. J. Martin, unpublished data.

(5) C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, 80, 5004 (1958); R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Inorg. Nucl. Chem.*, 14, 299 (1960); *Chem. Eng. News*, 38, 85 (1960); J. W. Frazer, *J. Inorg. Nucl. Chem.*, 11, 166 (1959); S. I. Morrow, D. D. Perry, M. S. Cohen, and C. Schoenfelder, *J. Am. Chem. Soc.*, 82, 5301 (1960); E. A. Lawton and J. Q. Weber, *ibid.*, 81, 4755 (1959).

(6) E. A. Lawton, E. F. C. Cain, D. F. Sheehan, and M. Warner, *J. Inorg. Nucl. Chem.*, 17, 188 (1961); V. Grakauskas, Abstracts of 140th National Meeting of the American Society, Chicago, Ill., 1961.