

CHEMISTRY OF ETHYLENIMINE

II. On the Mechanism of the Oxidative Conversions of N-Aminoethylenimine

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The structure of the compounds formed by the oxidative conversions of N-aminoethylenimine (I) was established by the application of IR spectroscopy, PMR, gas-liquid chromatography, and independent syntheses. Basically the reaction proceeds with the formation of ethylideneaminoethylenimine (II); in addition to this, bisaziridine, acetaldazine, and the hydrazone of acetaldehyde are also formed.

During efforts to prepare pure N-aminoethylenimine (I), we observed that its rectification in the

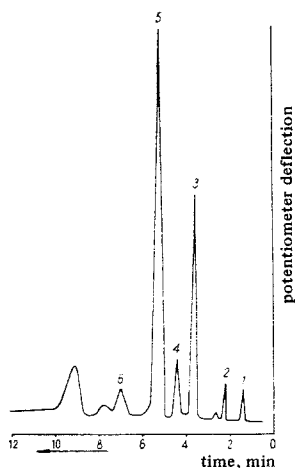


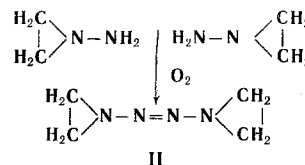
Fig. 1. Chromatogram of the products of the oxidative conversion of N-aminoethylenimine: 1) bisaziridine; 2) ethylenimine; 3) ethylideneaminoethylenimine; 4) acetaldazine; 5) aminoethylenimine; 6) acetaldehyde hydrazone.

presence of even traces of air was always accompanied by the formation of a series of by-products. Only by separating the mixture of by-products by preparative gas-liquid chromatography was it possible to identify them. This induced us to study the composition and structure of the products formed by the action of air on (I), and also to investigate the mechanism of the oxidative conversion of N-aminoethylenimine.

The oxidative reaction of hydrazine and its derivatives has been studied in detail and has been the subject of numerous papers published in the course of the last 10 to 20 years [1, 3]. Nevertheless there has been until now no data on the oxidation of (I).

To judge from the analogy of the oxidative reactions of symmetrically and unsymmetrically substituted hydrazine already studied [1, 2], it may be assumed that the first oxidative stage of (I) in the presence of atmospheric oxygen is the formation of a symmetrically substituted tetrazine (II). A further decomposition of

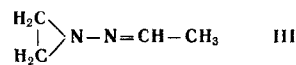
(II) leads to the formation of a series of products which are detected in the mixture formed by the oxidative conversion of (I).



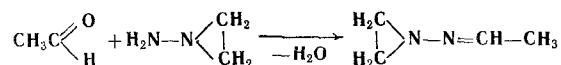
The oxidation of N-aminoethylenimine proceeds exceptionally smoothly. Upon merely standing in contact with air at room temperature, a deep-seated chemical transformation takes place, externally recognized by an initially yellow color which comparatively quickly changes to a dark-cinnamon hue. It should be remarked that when (I) is kept under nitrogen in a hermetically sealed ampul, it will remain for a long time without appreciable change.

As already stated, due to the extraordinarily easy oxidation of (I), its purification or its separation from the mixtures formed under the action of oxygen may be achieved only by the complete exclusion of all contact with air, preferably by analytical and preparative gas-liquid chromatography. The chromatographic analysis of the mixture of products formed by the oxidation of (I) indicates that this mixture is made up of 8 components (Fig. 1), among which the most abundant is (I). Efforts to separate (I) by rectification in a stream of argon in a highly-efficient column (80-85 theoretical plates) led to the selection of a fraction boiling at 81-82° C, in a quantity not exceeding 5% of the batch. As may be seen from Fig. 2, this fraction contains both compounds 3 and 5. The relative content of component 5 is 70%. The main portion (Fig. 3) is collected at 84-87°, and consists chiefly of component 3. Thus, by rectifying the oxidation products of (I), the percentage of 5 decreases, while the relative content of 3 increases. The rectification of this same mixture on solid alkali leads to the appearance in the high-boiling fraction (bp 94-105°) of new products, and their identification will be the subject of a separate paper.

We succeeded in separating by preparative gas-liquid chromatography the fraction boiling at 84-87°, and obtained 3 of its components in pure form. The elementary analysis of 3, the appearance of an absorption band at 1650 cm⁻¹ in its IR spectrum (an indirect proof of the presence of C=N), as well as its PMR spectrum allow us to assume that 3 is ethylideneaminoethylenimine.



This may be rigorously confirmed by the independent synthesis of (II) from (I) and acetaldehyde.



A comparison of the gas-liquid chromatographic, the IR spectra and the PMR spectra data of compound 3, separated from the mixture of products obtained by the oxidation of (I), with the properties of compound II, obtained by independent synthesis, fully confirms its identity with the compound of structure (II).

By studying the PMR spectrum of (II), it was established that the CH_3 -doublet (8.1–8.4 ppm) and $\text{CH}=\text{}$ quartet (2.26 ppm; $J_{\text{H}-\text{H}}$ 5.3 Hz) signals belong to the fragment $\text{CH}_3\text{CH}=\text{}$. Thus, for instance, in the acetaldazine molecule the corresponding chemical shifts amount also to 8.08 and 21.7 ppm. The PMR spectrum signal of the protons in the ethylenimine ring of molecule (II) is represented by a complex AA'BB' type multiplet and is partly overlapped by the CH_3 -protons doublet. The centers of the two multiplet fractions are

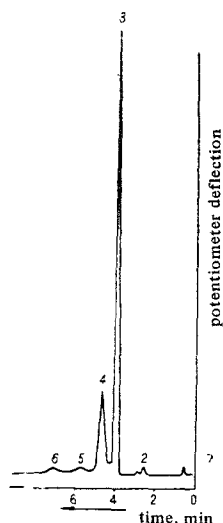


Fig. 2. Chromatogram of the fraction 81–82°: 3) ethylideneaminoethylenimine; 4) acetaldazine; 5) N-aminoethylenimine.

found at 8.33 and 8.15 ppm. The mean position of the resonance absorption of the ethylenimine ring, as known from its PMR spectrum, is found in the region characteristic for ethylenimine with a high-frequency inversion of the heteroatom (8.4–7.0 ppm). To the presence of a double bond at the nitrogen atom of the side chain of (II) is due to the possibility of delocalization of the heteroatom electrons. Therefore, inversion transitions in (II) should be sufficiently rapid already at room temperature. It may be assumed that the complex multiplet of the ethylenimine ring (II) protons owe their origin not to a difference between *cis*-*trans*-protons, as in slow inversion, but to the nonequivalence of the vicinal protons, linked with an anisotropic bond $\text{N}=\text{C}$ in the *syn*- or the *anti*-isomer of (II). The final choice between these two possibilities (slow inversion or anisotropic $\text{N}=\text{C}$ bond in the *syn*- or the *anti*-isomer) was achieved by a further complete analysis of

the PMR spectrum with the help of electronic computers.

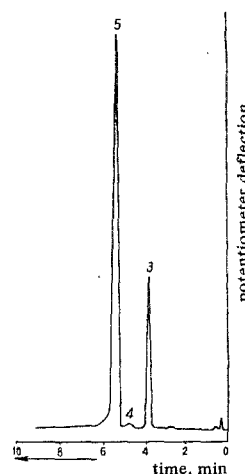


Fig. 3. Chromatogram of the fraction 84–87°: 2) ethylenimine; 3) ethylideneaminoethylenimine; 4) acetaldazine; 5) N-aminoethylenimine; 6) acetaldehyde hydrazone.

Besides identifying product 3, which proved to be ethylideneaminoethylenimine, we were also able to establish the structure of the remaining components of the mixture formed by the oxidative decomposition of (I), as shown in the chromatograph (Fig. 1). They were: 1-bisaziridine, 2-ethylenimine, 3-ethylideneaminoethylenimine, 4-acetaldazine, 5-N-aminoethylenimine-6-hydrazone of acetaldehyde. As constantly occurring impurities, we also detected small quantities of nitrogen, ammonia, and hydrazine.

To judge from the identified products of the oxidative decomposition of N-aminoethylenimine, the mechanism of this reaction may evidently be conceived as

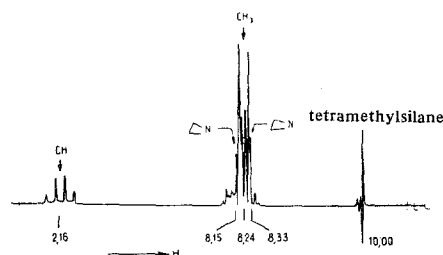
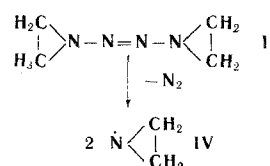


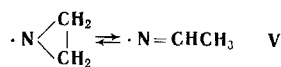
Fig. 4. PMR spectrum of ethylideneaminoethylenimine.

a complete radical reaction, initiated by the radicals formed by the decomposition of (II):

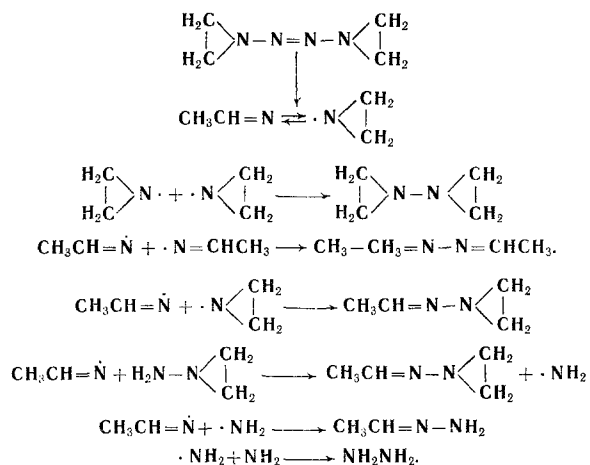


It is quite possible that the ethylenimine radical (IV) rearranges itself to form radical (V), according

to the scheme:



The recombination of radicals (IV) and (V) and their reaction with the original N-aminoethylenimine explains the formation of products 1, 2, 3, 4, and 5, detected by gas-liquid chromatography (Fig. 1).



EXPERIMENTAL

The separation of (II) from the reaction mixture was achieved on a preparative chromatography apparatus PGK-3, using an automatic fraction collector. The stationary phase E-301 amounted to 25% on modified INZ-600, fraction 0.5-0.25 mm. The column was 8 m long

and 18 mm in diameter. The detector was of the flame-ionization type in a bypass to the collector. Carrier gas was nitrogen. Volume flow was 600 cm³/min; thermostat temperature 80° C; vaporization temperature 120° C.

The identification of the compounds separated by preparative chromatography was carried out on a Tsvet-1 chromatograph. Detector-catharometer. The stationary phase was 25% of E-301. PEG-1200, 10%; polyethylenimine M-1200 on 545 celite, 15%; and also adjacent columns. Thermostat temperature 80°; evaporation temperature 120°; J 250 mA; carrier gas, helium. Volume flow, 46.6 cm³/min.

Ethylideneaminoethylenimine (II) was synthesized by a method to be described later. Bp 87°; d₄²⁰ 0.8749; N_D²⁰ 1.4410. Found, %: C 56.80; N 33.50; H 9.45; MR_D 25.432. Calculated for C₄N₂H₈, %: C 57.10; N 33.75; H 9.55; MR_D 25.28.

The physical constants of the other identified products 1, 2, 4, and 6 correspond to those found in the literature. The IR spectra were recorded in a UR-10 spectrophotometer.

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