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Concomitant Rearrangement of [^{15}N-NO_2]-*N*-(4-Fluorophenyl)-*N*-methylnitramine and *N*-Methyl-*N*-phenylnitramine

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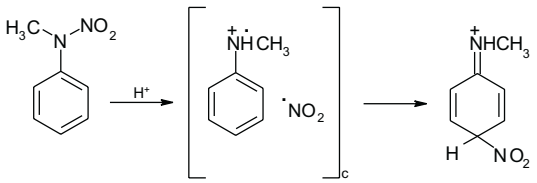
The aromatic rearrangements can be divided into two groups. The first one comprises rearrangements *sensu stricto* (benzidine, Claisen rearrangement *etc*.), following an intramolecular path. Wallach, Fischer-Hepp and other rearrangements proceeds on the intermolecular route involving dissociation and substitution. The common feature of most of these transformations is that they are acid catalysed, although at elevated temperature they proceed without an acidic catalyst [1]. The mechanism of nitramine rearrangement, presented on the scheme below, is peculiar.

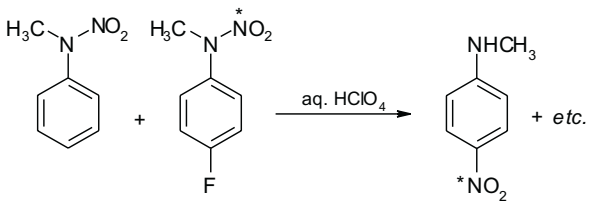


Homolytic cleavage of the N–N bond gives a radical and radical-cation captive in a *solvent cage*. Nitrogen(IV) oxide molecule migrates in the cage, responsible for the intramolecularity, to the *ortho* or *para* position forming σ-complexes, which are subsequently transformed into final products. Such a theory used to be considered as the reliable explanation of the mode of *N*-nitro group migration [2,3].

A *solvent cage* must be a construction of very specific properties. It must be stable and rigid enough to prevent escaping the migrating molecule. It must have a long life-time to enable migration to the distant *para* position. Finally, it must be loose and flexible, otherwise the displacement of the nitro group would be impossible. *N*-Methyl-*N*-phenylnitramine, the most frequently used model compound, rearranges in diluted aqueous solutions of strong acids, hence, the solvent cage must be built up of water molecules. It is well known, that nitrogen(IV) oxide reacts with water in a complex and exothermic reaction, forming nitric and nitrous acid. The properties of a hypothetical *solvent cage* seem to be contradictory, hence, we have studied once again all the papers, in which the mechanism of nitramine rearrangement is explained in terms of the *solvent-caged-pair* theory [4]. We have been looking for any evidence that a

solvent cage really exists and explanation what is it. Such data are not available, hence, this concept seems to be doubtful.

The term of *solvent cage* was devised by Franck and Rabinowitch to explain decreased quantum yields of photolytic reactions in solutions, in comparison with the same processes carried out in the gas phase. This is nothing more than an exemplification of the Franck-Condon rule. The molecules of a solvent, surrounding a pair of radicals, make difficult their separation by diffusion and facilitate dissipation of an excess energy by collisions. The *cage effect* can be responsible for the recombination of radicals [5], but cannot account for the intramolecularity of a rearrangement, which requires migration of the uncharged molecule on the distance of *ca*. 6 Å. Consequently, we have made some studies on the very beginning of the *solvent-caged-pair* theory. It is based on one experiment, which contradicts the results of some others. The rearrangements of primary and secondary arylnitramines in the presence of labelled nitrous or nitric acid provided the evidence of the intramolecularity, since the tracer was not incorporated [6,7]. However, the rearrangement of *N*-methyl-*N*-phenylnitramine in the presence of *N*-methyl-*N*-(4-fluorophenyl)-nitramine containing 13.6% of the tracer [^{15}N-NO_2] provided *N*-methyl-4-nitroaniline containing *ca*. 4% of the heavy isotope.



The reaction was performed in a large excess of perchloric acid (0.5 M), in the presence of sulphamic acid (0.05 M); the concentrations of the substrates were 0.0005 M. In fact, the presence of the tracer in the product molecule was not certified; *N*-methyl-4-nitroaniline was isolated, combusted to elemental nitrogen and analysed by the mass spectrometry [8,9]. We believe that Ingold's mechanism of the nitramine rearrangement (the *cartwheel* theory) [10] is correct, migration of the NO_2 molecule in a *solvent cage* is impossible, hence, we have re-examined White's results, using direct spectroscopic methods. Our aim was to confirm that *N*-methyl-4-nitroaniline is formed through the cross-nitration. There are, however, some other possibilities:

– *N*-Methyl-4-nitroaniline is formed from *N*-(4-fluorophenyl)-*N*-methylnitramine with the elimination of the fluorine atom; the *ipso*-substitution was observed in the case of bromo and chloro derivatives [11].
– Interchange of the nitro groups occurs between the substrates molecules in a reaction of unknown mechanism, but independent from the rearrangement.
– Nitramines can react as nitrosating agents, hence, *N*-methyl-*C*-nitroanilines are usually accompanied with significant amounts of *N*-methyl-*N*-nitroso derivatives [12]. Their separation is difficult, hence, we wanted to confirm that the tracer exists as the *C*-nitro and not as *N*-nitroso group.

The substrates were obtained according to the previously described method [13]. They were rearranged under acidic conditions and corresponding *N*-methylnitroanilines were isolated as pure compounds. Their ^{15}N-NMR spectra are given in Table 1.

Table 1. Nitrogen NMR spectra (in DMSO); the chemical shift are given in ppm *vs*. nitromethane as the external standard, long range F–N coupling constants are given in brackets.

Compounds	Amine nitrogen	Nitro groups
N-Methyl-*N*-phenylnitramine	–202.1	–27.9
N-Methyl-*N*-(4-flurophenyl)-nitramine	–203.3	–26.6
N-Methyl-2-nitroaniline	–309.0	–8.1
N-Methyl-4-nitroaniline	–306.0	–10.0
N-Methyl-4-fluoro-2-nitroaniline	–309.8 (1.5 Hz)	–10.4 (2.0 Hz)

The labelled substrate, *viz*. [^{15}N-NO$_2$]-*N*-methyl-*N*-(4-fluorophenyl)-nitramine was obtained by nitration with [^{15}N-NO$_2$]-n-butyl nitrate, prepared from nitric acid of 98% isotopic purity. The nitramine was rearranged in the presence of the equal amount of *N*-methyl-*N*-phenylnitramine with the natural isotopic abundance. The reaction conditions were exactly the same as employed by White [9]. The reaction mixture was neutralised and extracted, the crude product was examined by ^{15}N-NMR spectroscopy. To our surprise, the doublet corresponding to *N*-methyl-4-fluoro-2-nitroaniline was accompanied by two singlets characteristic of 4-nitro- and 2-nitro-*N*-methylaniline. Relaxation delay of 120 s was allowed between successive pulses and the signals were integrated. Their relative intensities were 83, 9 and 8% respectively. The tracer was found mainly in the parent molecule, but its content in *N*-methylnitroanilines was much higher than the natural isotope abundance. The products were not formed from the labelled *para*-fluoro nitramine; it was found that expulsion of the fluorine atom does not occur during the rearrangement. Interchange at the substrate stage was also excluded; the ^{15}N-NMR spectrum of the recovered substrates indicated, that the tracer was not transferred to *N*-methyl-*N*-phenylnitramine. Formation of *N*-nitroso derivatives of the rearrangement products was not observed, due to the low concentration of the substrates. The results suggested that migration of the *N*-nitro group is, at least in part, intermolecular.

According to the *cartwheel* theory, the *N*-nitro group migrates in the nitrito (ONO) form ([3,3]-sigmatropic shift). The σ-complexes, in which the substituent is bound to a tetrahedral carbon atom, are transformed into the final products by expulsion of *C*-proton and nitrito-to-nitro isomerization. The CIDNP effect, observed in the rearrangement of [^{15}N-NO$_2$]-*N*-(2,6-dichlorophenyl)-nitramine, indicated that the C–NO$_2$ bond was formed by recombination of radicals [14]. The last step of the nitramine rearrangement may occur in the *solvent cage*, since it does not require a far distant migration. The escape of NO$_2$ radical from the *cage* is responsible for the CIDNP effect and cross-nitration observed in the reported experiment.

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