

OH Induced Denitration of Nitromethane*

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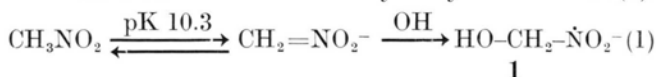
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Nitromethane, OH-radicaladdition,
Disproportionation, Denitration

Disproportionation dominates the second order reactions of the OH adduct to acinitromethane and leads to production of nitrite ion.

Hydroxyl radicals react with most organic compounds either by hydrogen abstraction or by addition. The addition of hydroxyl radicals to acinitromethane ($\text{CH}_2=\text{NO}_2^-$), which is the predominant form of nitromethane above pH 10, leads to the transient anion radical of hydroxynitromethane (1).



Radical 1 has been detected by the *in situ* radiolysis-ESR¹ and optical pulse radiolysis² methods in studies of basic nitromethane solutions.

From kinetic studies it was concluded that 1 decays predominantly in second order reactions². From the present investigation it becomes obvious that this decay proceeds largely *via* disproportionation. Subsequently the oxidized product decomposes and yields nitrous acid and formaldehyde. The observed yield of nitrite in irradiated alkaline aqueous solutions of nitromethane can be taken as a measure of the importance of this reaction.

The solutions under investigation were prepared from triply distilled water. They were 0.5 to $2 \cdot 10^{-3}$ M in nitromethane (Eastman Kodak spectrograde). The solutions were either saturated with highly purified N_2O in order to convert irradiation produced hydrated electrons into additional hydroxyl radicals³ or deoxygenated with highly purified nitrogen. The pH was adjusted either to pH 11.6 with KOH or to pH 6 with KH_2PO_4 buffer. A ^{60}Co γ -ray source (Gammacell 220

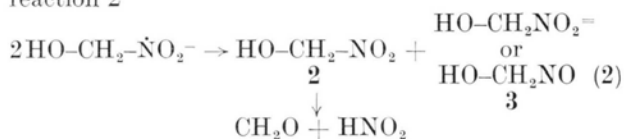
Table I. Yields of nitrous acid in irradiated aqueous solutions of nitromethane*.

	N_2 sat.	N_2O sat.	$\text{N}_2\text{O} + 1\% \text{O}_2$
pH = 11.6	1.35	2.6	4.2
pH = 6.0	0.3	0.25	0.3
pH = 11.6 + 0.1 M <i>tert</i> -butanol	0.11	0.15	1.03

* $5 \cdot 10^{-4} - 2 \cdot 10^{-3}$ M; dose $3.73-7.46 \cdot 10^{17}$ eV/ml.

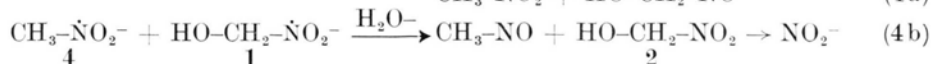
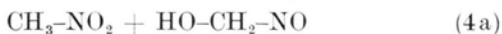
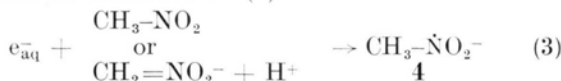
of Atomic Energy of Canada Ltd.) was used for irradiation. The total dose amounted to from 3.7 to $7.5 \cdot 10^{17}$ eV/ml. The irradiated solutions were analyzed spectrophotometrically for NO_2^- using the method of GRIESS-ILOSVAY⁴. The yields of nitrous acid are shown in Table I. The results show that the yield of NO_2^- is twice as high in N_2O saturated solution compared with deoxygenated solution, that it decreases if the solution contains *tert*-butanol which is known to be an effective OH scavenger⁵, that it is reduced in a neutral solution where according to the acid base equilibrium⁶ little acinitromethane is present and that it is also strongly affected by low oxygen concentrations.

The total yields of nitrite in either deoxygenated or N_2O saturated solution amount to approximately 50% of the initial OH yields of 2.8 and 6.0 respectively. This leads to the conclusion that disproportionation of radical 1 proceeds according to reaction 2



and yields an oxidized product (hydroxynitromethane (2)) which decomposes into nitrous acid and formaldehyde. The reduced product will very likely protonate and eliminate water to form hydroxynitrosomethane (3). No attempt was made to identify the organic products of these reactions.

In the absence of N_2O the hydrated electrons react with nitromethane or acinitromethane to form the anion radical (4).



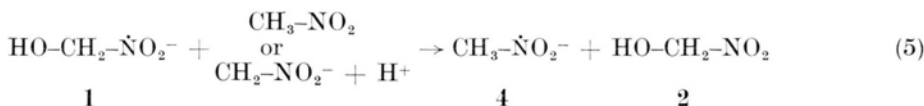
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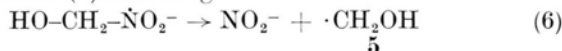
In this case disproportionation between 1 and 4 must also be considered.

Since $G(\text{NO}_2^-) = 1.35$ for the N_2 purged solutions it is concluded that reaction 4b is the important disproportionation step between 1 and 4. Electron transfer from radical 1 to nitromethane or acinitromethane according to reaction 5 can be neglected since only a very weak ESR spectrum of the



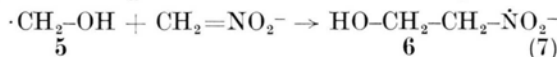
relatively long lived anion radical (4) is observed in a N₂O saturated solution¹.

ASMUS and TAUB² suggested that first order decomposition of 1 was of some importance. Decomposition of 1 into NO₂⁻ and hydroxymethyl radical (5) according to reaction 6



would lead to G(OH) = G(NO₂⁻) = 2.75 in N₂ and 6.0 in N₂O saturated solution and does not seem to contribute significantly. Direct oxidative denitration is known to occur for several aromatic and cycloaliphatic nitrocompounds where OH adds to a C=C double bond bearing a nitro group, *i.e.* nitrophenols⁷, 5-nitouracils and nitrofurans^{8,9}. No evidence was found for a similar direct denitration during the present study. The hydroxymethyl

radical (5) produced under the present conditions would add to acinitromethane according to reaction 7 and can be readily detected in the *in situ* radiolysis-ESR experiment when methanol is present¹.



The ESR experiments on nitromethane solution, however, give no evidence for radical 6 so that the production of radical 5 (and therefore reaction 6) cannot be important.

The very large effect of oxygen on the yield of nitrous acid indicates that oxygen oxidizes radical 1 to CH₂O and NO₂⁻ with high efficiency.

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