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Mendeleev Commun., 2007, **17**, 289–290

Mendeleev Communications

Synthesis of nitromethane from acetic acid by radiation-induced nitration in aqueous solution

Boris G. Ershov,* Andrei V. Gordeev, Gennady L. Bykov, Andrei A. Zubkov and Inessa M. Kosareva

A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 335 1778; e-mail: ershov@ipc.rssi.ru

DOI: 10.1016/j.mencom.2007.09.014

The γ-irradiation of solutions containing acetic acid, nitric acid and/or their salts produces nitromethane.

It is known[1,2] that nitration, that is, the incorporation of nitro groups into organic molecules, occurs on treatment with nitrating mixtures. The process involves various mechanisms, in particular, the radical mechanism. In the latter case, it is the $\cdot NO_2$ radical formed from nitric acid and nitrogen oxides that serves as the active nitrating agent. The reaction preferably occurs at elevated temperatures (above 180 °C) and high pressures.

In this study, we have discovered that ionizing radiation of aqueous solutions of acetic acid containing nitric acid and nitrates at room temperature results in nitration of acetic acid. The process occurs due to reactions of radicals resulting from radiolysis of the solution. The phenomenon discovered is practically important because treatment of spent nuclear fuel produces considerable amounts of liquid radioactive waste containing organic compounds, nitric acid and its salts. The fact that nitro compounds are formed upon irradiation of liquid radioactive waste may be important in determination of the safety of radioactive waste storage and treatment.

Nitrate–acetate mixtures (~10 ml) were placed in sealed glass tubes about 30 ml in volume and evacuated under irradiation. Solutions of nitric and acetic acids and their salts (reagent grade) were prepared using distilled water.

Solutions used for nitromethane analysis were prepared using methanol, sulfanilic acid, sodium nitrite (reagent grade), $Na_2HPO_4\cdot 7H_2O$ (reagent grade) and $NaH_2PO_4\cdot 2H_2O$ (reagent grade).

Irradiation was carried out on a GUG-120 setup with the ^{60}Co radioactive isotope. The dose rate was 4.5 kGy h^{-1}.

The composition and amount of gases were analysed with a Tsvet-5 chromatograph using a 2 m column packed with 0.4–0.8 mm grade silica gel. IR spectra were recorded using an M-80 spectrometer with an upgraded control and signal detection system.

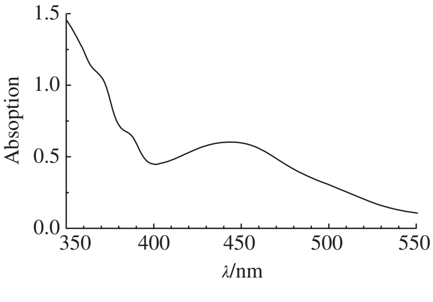

Figure 1 Optical absorption spectrum recorded during nitromethane analysis[3] in a γ-irradiated air-free solution containing 0.4 M AcOH and 0.6 M $NaNO_3$. The optical cell thickness is 0.5 cm. The absorbed dose is 0.5 MGy.

The composition of the liquid phase was analysed by UV spectroscopy using an M-40 spectrophotometer with an upgraded control and signal detection system.

Nitromethane was determined using the reaction with *p*-diazobenzenesulfanilic acid as reported elsewhere.[3] In addition, it was also analysed using IR spectroscopy and gas chromatography–mass spectrometry (GC-MS).

The results of this study confirm unambiguously that nitro compounds are formed upon irradiation of solutions containing nitric and acetic acids and their salts. The IR spectra of chloroform extracts from γ-irradiated solutions with various concentrations of AcOH, HNO_3 and $NaNO_3$ (absorbed dose of 0.2–0.5 MGy) showed, in comparison with a nonirradiated solution, additional bands at 1605, 1560 and 1380 cm^{-1} characteristic of the stretching vibrations of the N=O group in organic nitro compounds. The intensity of these bands increased if small amounts of nitromethane were added to the solution. On the other hand, the intensities of the other peaks remained almost unchanged. The formation of nitromethane is confirmed by GC-MS. The mass spectrum of the dichloromethane extract from irradiated solution of 0.4 M AcOH and 0.3 M $NaNO_3$ (absorbed dose of 1.5 MGy) revealed peaks with *m*/*z* 61 and 46, whose positions and intensities coincided with those of the peaks observed for nitromethane. These peaks belong to the $MeNO_2^+$ and NO_2^+ ions, respectively.

Figure 1 shows the optical absorption spectrum of a γ-irradiated aqueous solution containing 0.4 M AcOH and 0.6 M $NaNO_3$, after chemical analysis for nitromethane.[3] According to this technique, the reaction of nitromethane with *p*-diazobenzenesulfonic acid for 5–10 min produces an intense absorption band at 440 nm ($\varepsilon = 9\times10^3$ dm^3 mol^{-1} cm^{-1}) owing to the formation of 1-nitroformaldehyde-*p*-sulfophenylhydrazone. Figure 1 shows that absorption of this kind actually appears. The analytical reaction is selective;[3] other derivatives of *p*-sulfophenylhydrazone formed in reactions, *e.g.*, with nitroethane or nitropropane, and perhaps with other nitro compounds, show absorption at ≤395 nm.

In order to study the dose dependence of nitromethane accumulation, we used 0.4 M acetic acid and 0.3 M $NaNO_3$ solutions. Irradiation was carried out until the absorbed dose was 5 MGy, at which point the nitrate initially present in the system decomposed almost completely. The formal first-order decomposition rate of nitrate was calculated to be 5.4×10^{-7} dm^3 mol^{-1} s^{-1} (at a dose rate of 4.5 kGy h^{-1}). As nitrate was consumed, formation of nitromethane was detected in the solution. One can see (Figure 2) that the concentration of nitromethane in the solution increases with absorbed dose to reach a maximum (1.65×10^{-2} M) at about 3.5 MGy, after which its concentration decreases. Unlike

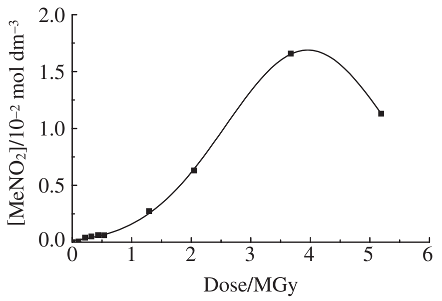

Figure 2 Nitromethane concentration as a function of absorbed dose during γ-irradiation of an air-free solution containing 0.4 M AcOH and 0.3 M $NaNO_3$.

nitrate decomposition of which can be tentatively described by a first-order rate equation, the kinetic curve of nitromethane formation is more complex. The initial section of the accumulation curve has a pronounced *s*-shape (Figure 2). This suggests that the formation of nitromethane is preceded by generation of an unstable intermediate, which is consumed during subsequent irradiation.

Nitromethane is formed in a concentration range from 0.2 to 1.6 M of each of the components, *i.e.*, acetic acid (or sodium acetate) and nitric acid (or sodium nitrate), both in acidic and neutral solutions.

Radiation-chemical transformations of dilute aqueous solutions result from reactions with ionic and radical species that are formed due to water decomposition under ionizing radiation. In general, this process can be expressed by the following equation:

$$H_2O \rightsquigarrow e^-_{aq}\ (2.7),\ {}^{\bullet}H\ (0.5),\ {}^{\bullet}OH\ (2.9),\ H_2\ (0.5),\ H_2O_2\ (0.7),\ H^+\ (2.7)$$

The resulting hydrated electron (e^-_{aq}) and hydrogen atom (H) have high reduction potentials (–2.7 and –2.3 V, respectively), whereas the hydroxyl radical (OH) has a high oxidation capacity (2.9 V).[4] The numbers in parentheses indicate the primary radiation-chemical yields of radiolysis products in bulk solution per 100 eV of absorbed energy for soft radiation types (γ-rays or fast electrons) with low linear energy transfer. A specific feature of acidic solutions that we studied is that the major part of hydrated electrons (e^-_{aq}) in the reaction

$$e^-_{aq} + H^+ \rightarrow {}^{\bullet}H, \qquad 2.3\times10^{10}\ dm^3\ mol^{-1}\ s^{-1}$$

are transformed to $^{\bullet}H$ atoms.

The radiation-chemical processes that occur upon irradiation of aqueous solutions of both nitric acid and nitrates and, separately, acetic acid and acetates have been studied in considerable detail.[4,5] The ion radical products of water radiolysis (hydrated electron e^-_{aq}, $^{\bullet}H$ atom and hydroxyl radical $^{\bullet}OH$) react with dissolved compounds. In sufficiently general form, the radiation-chemical reactions in acidic nitrate–acetate solutions can be described by the set of reactions listed below.[4,5] In the case of acetic acid, these reactions generate the $^{\bullet}CH_2COOH$ ($^{\bullet}CH_2COO^-$) and $MeCO^{\bullet}$ radicals:

$$\begin{aligned}
&MeCOOH + {}^{\bullet}OH \rightarrow {}^{\bullet}CH_2COOH, && 1.4\times10^8\ dm^3\ mol^{-1}\ s^{-1};\\
&MeCOOH + H^{\bullet} \rightarrow {\cdot}CH_2COOH + H_2, && 3.5\times10^5\ dm^3\ mol^{-1}\ s^{-1};\\
&MeCOOH + e^-_{aq} \rightarrow MeCO^{\bullet} + OH^-, && 1.8\times10^8\ dm^3\ mol^{-1}\ s^{-1}.
\end{aligned}$$

In nitrate solutions, the reactive species include $^{\bullet}NO_2$ and $^{\bullet}NO_3$:

$$\begin{aligned}
&HNO_3 + {}^{\bullet}OH \rightarrow {}^{\bullet}NO_3 + H_2O, && 5.0\times10^5\ dm^3\ mol^{-1}\ s^{-1};\\
&HNO_3 + H^{\bullet} \rightarrow {}^{\bullet}NO_2 + H_2O, && 6.0\times10^6\ dm^3\ mol^{-1}\ s^{-1};\\
&HNO_3 + e^-_{aq} \rightarrow {}^{\bullet}NO_2 + OH^-, && 7.8\times10^9\ dm^3\ mol^{-1}\ s^{-1}.
\end{aligned}$$

Acetic and nitric acids and their salts in solutions compete in reactions with e^-_{aq}, $^{\bullet}H$ and $^{\bullet}OH$. The reaction rate constants presented above[4,5] allow us to give a quantitative estimate of their contributions to the radiation-chemical reactions of the solution components. Under the experimental conditions, the $^{\bullet}OH$ radicals are preferably (by more than 95%) involved in reactions with acetic acid to give $^{\bullet}CH_2COOH$ radicals, whereas e^-_{aq} and the $^{\bullet}H$ atoms are consumed (by almost 100%) for the reduction of nitric acid and the nitrite ion to give the $^{\bullet}NO_2$ radical.

The radical and ion radical species generated in the primary reactions react with each other and with dissolved compounds to give new radicals and the products.

An important role in the formation of nitromethane in nitrate–acetate solutions apparently belongs to the $^{\bullet}NO_2$ radical, which has strong oxidizing properties. It reacts with the $^{\bullet}CH_2COOH$ radical to give nitroacetic acid:

$${}^{\bullet}NO_2 + {}^{\bullet}CH_2COOH \rightarrow CH_2(NO_2)COOH, \qquad 2.0\times10^8\ dm^3\ mol^{-1}\ s^{-1}.$$

According to our calculations based on the diffusion-kinetic model of radiolysis of water and aqueous solutions,[6] the rate constant of this reaction can be estimated as 2.0×10^8 dm^3 mol^{-1} s^{-1}. Nitroacetic acid is an unstable compound. The double salt $KO_2NCHCOOK$ can be isolated from a solution in a pure state.[7] In neutral solutions, it undergoes decarboxylation to give more stable products, nitromethane and carbon dioxide:[8]

$$CH_2(NO_2)COOH \rightarrow MeNO_2 + CO_2, \qquad 2.5\times10^{-2}\ s^{-1}.$$

Presumably, acidic and alkaline solutions contain two tautomeric forms, O_2NCH_2COOH and $HO_2^{\cdot}NCHCOOH$, dissociation of which gives one- and two-charged ions, respectively. It has been found[8] that only the dissociated form of nitroacetic acid, that is, $O_2NCH_2CO_2^-$, is unstable. As a result, the observed decomposition rate of nitroacetic acid directly depends on its concentration in solution, which in turn depends on the pH value. It has been found[8] that the pK values for the first and second dissociation constants of nitroacetic acid are ~1.68 and 8.9, respectively. Therefore, nitroacetic acid is rather stable in acidic and alkaline solutions due to the low concentration of the dissociated form $O_2NCH_2CO_2^-$. Before the irradiation, the solutions studied had pH 2.5. Thus, nitroacetic acid formed as a result of radiation-chemical reactions in nitrate–acetate solutions decomposes to give nitromethane.

It was noted previously[4,5] that radiolysis of aqueous solutions of nitro compounds results in their decomposition. This study shows that they can also be formed due to the radiation-induced nitration of organic compounds. This fact is important for the ecological assessment of the safety of treatment and storage of liquid radioactive waste containing organic compounds and nitric acid.

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Received: 18th January 2007; Com. 07/2862