UV Direct Photolysis of *N*-Nitrosodimethylamine (NDMA): Kinetic and Product Study

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Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

The ultraviolet (UV) direct photolysis of *N*-nitrosodimethylamine (NDMA) in aqueous solutions at pH 3 and 7 leads to dimethylamine, and nitrite and nitrate ions as the major degradation products. In addition, small amounts of formaldehyde, formic acid, and methylamine are formed. When the initial concentration of NDMA was 1 mM, only a 13% decrease in the total organic carbon (TOC) was measured at pH 7, whereas no significant change in the TOC was observed at pH 3. In the concentration range 0.01 – 1 mM NDMA, zero-order kinetics is obeyed, whereas first-order kinetics is followed at concentrations below 0.01 mM. The photolysis occurs much faster at pH 3 than at pH 7, which is explained by the difference in the quantum yields of the process at these two pH values. UV Direct photolysis is an efficient process for the removal of NDMA from contaminated waters, and electrical energy per order (E_{EO}) values as low as 0.3 – 0.5 kWh/order/m^3 were calculated for treatment of low concentrations of NDMA (0.001 mM).

Introduction. – *N*-Nitrosodimethylamine (NDMA) is not an industrially or commercially important chemical, but its occurrence in the human environment, as detected in outdoor air, surface waters, and soil, comes from its potential release from industries, such as tanneries, amine, pesticide, and detergent manufacturing plants, rubber and tire manufacturers, fish and food processing industries, malt beverage industries, dye manufacturers and cosmetics industries. It is also a hydrazine-decomposition intermediate. In water and soil, NDMA is formed by the reaction of widely occurring primary, secondary, or tertiary amines with nitrites. It has been found in groundwaters at levels as high as 10 ppb, and there is a growing concern with regard to health effects associated with exposure to NDMA.

Hepatotoxicity is the primary systemic effect of NDMA, and the mechanism of NDMA-induced liver damage may be related to the alkylation of cellular proteins [1]. Genotoxicity of NDMA *in vitro* and carcinogenity in various species of animals have been demonstrated in numerous studies over the past two decades.

Recent literature reports emphasize that both artificially generated UV light or natural sunlight are sufficient to enable NDMA to induce mutagenicity by methylation of DNA [2][3]. Consequently, NDMA has been assessed as a potential carcinogen in humans.

N-Nitrosodimethylamine does not currently fall under the U.S. EPA regulations, but it is listed as a priority pollutant on the *U.S. EPA National Priorities List*, and regulations and advisories are enforced in various states. At a 10^{-5} cancer risk level set

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by the U.S. EPA among the ambient-water-quality criteria, the corresponding level for NDMA would be 0.0014 µg/l, and the EPA drinking water standard at the same risk level would be 0.0007 µg/l [4]. The *Ontario Ministry of Environment*, Canada, established an interim drinking water standard for NDMA of 0.009 µg/l (9 ppt). The *California Department of Health Services* has set an interim control level of 20 ng/l (20 ppt).

It is known that *N*-nitrosamines are thermally stable in aqueous solutions. For example, it was found that their hydrolysis in aqueous HCl after refluxing for 24 h did not proceed beyond 10–12% [5]. Also, they are fairly resistant toward biodegradation, do not air strip or adsorb on activated carbon. However, they are photochemically labile, and, therefore, advanced oxidation technologies, based on irradiation with UV light, have been promoted for the removal of NDMA from contaminated waters.

The first study the NDMA photolysis was published in 1939, when *Bamford* [6] decomposed NDMA in the gas phase with both medium- and low-pressure Hg lamps. Several gaseous products, such as H_2, CH_4, N_2, $CH_2{=}CH_2$, and Me_2NH (DMA) were identified. Since then, several other studies on the photolysis of NDMA in the gas phase have been reported in the literature, and mechanistic pathways were attempted [7–9].

The acid-catalyzed photochemistry of nitrosamines in aqueous solution, including NDMA, has been thoroughly investigated by *Chow* and co-workers [10–13], whereas fewer studies on this subject have been conducted in neutral media [14] or in strong alkaline solutions [15]. *Ho et al.* [16] found a relatively strong pH dependence of the quantum yield for the direct photolysis of NDMA.

Mechanistic studies on the photolysis of NDMA indicated that the principal products are DMA and NO_2^- ions. Small amounts of N_2O, N_2, HCHO, methylidene-methylamine, amidoxime derivative, $MeNH_2$, and HCOOH can be also formed, but their levels are strongly dependent on the environment [11–14][17–24]. *Adeleke* and *Wan* found ESR evidence for nitric oxide as a primary product in the photolysis of NDMA in aqueous solution at room temperature [25], whereas *Jakubowski* and *Wan* identified the dimethylaminium radical as an intermediate radical species, by ESR spectra at 77 K [26].

Over the past decade, UV companies have installed several full-scale UV reactors in North America for treatment of NDMA in drinking water and in ground and wastewaters. The concentration of NDMA in the influents can be as high as 100 ppt in drinking water, 1.5 ppm in groundwater and 1,400 ppm in wastewater. Ozone alone or ozone/UV processes are totally inefficient in the degradation of NDMA [27]. Similarly, preliminary studies on the UV/H_2O_2 process applied to the NDMA removal indicated no significant improvement of that treatment compared to UV alone [28][29].

Even though some mechanistic pathways have been proposed in the literature for the direct photolysis of NDMA [12–14][30], to our knowledge, no thorough product or kinetic study, and/or organic carbon and nitrogen balances are reported in the literature.

Here, we report results on the kinetics and degradation products of the UV direct photolysis of NDMA at pH 3 and 7 in dilute aqueous solutions, and discuss briefly a reaction mechanism based on the identified and quantified intermediate by-products. The degradation profiles of NDMA and its intermediates are correlated with the organic carbon and nitrogen mass balances.

Results and Discussion. – The NDMA absorption spectrum exhibits a strong band with a maximum at $\lambda = 228$ nm ($\varepsilon = 7378$ M^{-1} cm^{-1} [31]), and a weak band with a smooth maximum at $\lambda = 332$ nm ($\varepsilon = 109$ M^{-1} cm^{-1} [31]). The first absorption band is regarded as a $\pi \rightarrow \pi^*$ intramolecular charge transfer, whereas the second is associated with an $n \rightarrow \pi^*$ transition band. When irradiated with UV light, the N–N bond is broken in the NDMA molecule, generating reactive radicals that are involved in further degradation processes. *Fig. 1* shows the absorption spectra of NDMA and NO_2^-/NO_3^- ions. The latter are among the major degradation by-products of NDMA, which, once released into the irradiated system, will compete for the light with the parent pollutant.

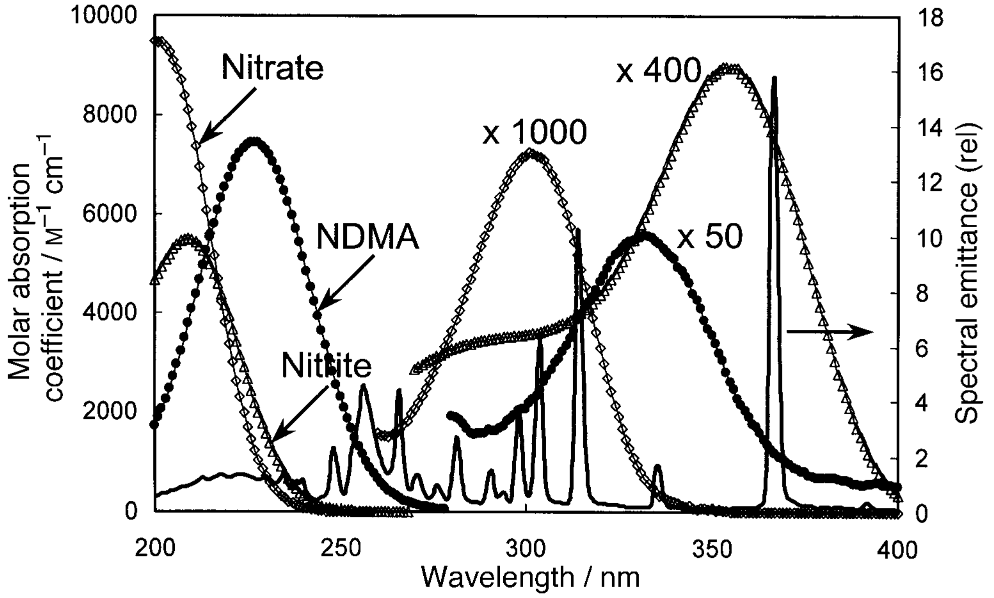


Fig. 1. *Absorption spectra of NDMA and its major degradation products, and the spectral distribution of the 1-kW medium-pressure Hg lamp*

Degradation Products during the UV Photolysis of NDMA. The irradiation of a *ca.* 1 mM aqueous NDMA solution at pH 3 led to a rapid decay of NDMA and the formation of DMA and NO_2^- ions as the major products. HCHO was a minor degradation product, which eventually was oxidized to HCOOH. NO_3^- Ions were generated along with the NO_2^- ions, but at a lower level. The decrease of the NO_2^- concentration after the removal of NDMA is associated with the increase of NO_3^- concentration through a photo-oxidation process. CH_3NH_2 is an expected degradation product of NDMA, as being formed in a 1:1 ratio with HCHO. However, its quantitative determination has not been attempted.

Fig. 2 shows the time profiles of NDMA and its degradation by-products during the photolysis at pH 3. One observes that DMA reaches a maximum concentration of *ca.* 0.9–1 mM at the same time when NDMA was fully photodegraded, and it does not undergo any significant decay under further irradiation, since it does not absorb UV light. From the industrial point of view, this might be a problem, when UV direct

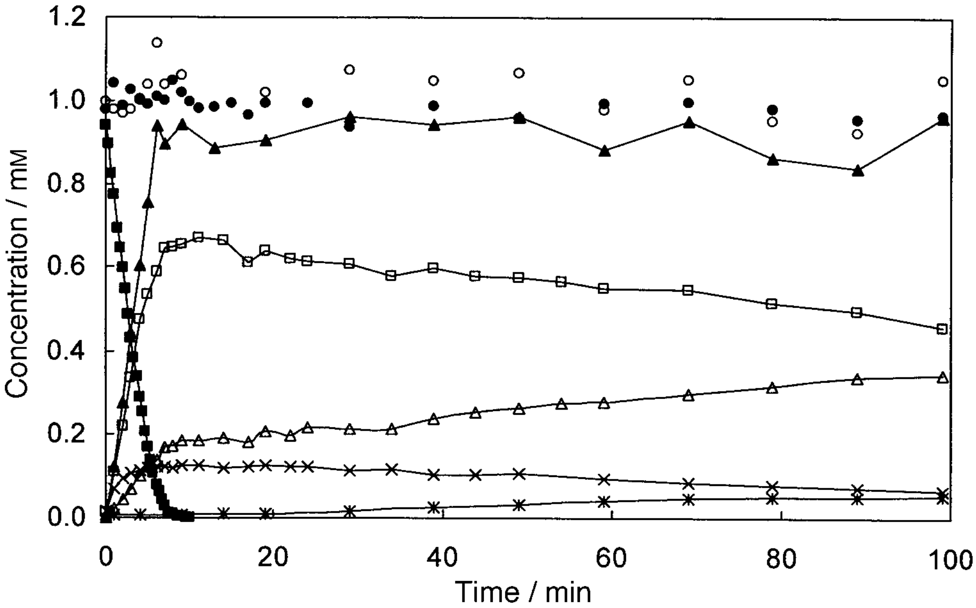


Fig. 2. *Time profiles of NDMA and its degradation products, and TOC mass balance during irradiation at pH 3.* ■: NDMA; ▲: dimethylamine; □: nitrite; △: nitrate; × : formaldehyde; ∗: formic acid; ○: calculated TOC/2; ●: measured TOC/2. The 'calculated' TOC represents the TOC in NDMA and degradation products.

photolysis is used to treat NDMA, since the persistence of DMA in the treated waters can possibly lead to the re-formation of NDMA [32].

As shown in *Fig. 2*, there is a good agreement between the calculated and experimentally measured total organic carbon (TOC) over the entire irradiation period, which suggests that the major organic compounds present in the irradiated system were properly identified and quantified. No significant decrease in the TOC level was observed, which is consistent with the resistance of DMA to the UV treatment.

The degradation of 1 mM aqueous NDMA solution at pH 7 proceeded much slower than at pH 3, which is expected given the difference between quantum yields determined at these pH values [16]. DMA and NO_2^- ions were quantified as the major products; HCHO was formed at a higher yield than in the case of photolysis conducted at pH 3. However, at pH 7, NO_3^- ions were exclusively generated by the photooxidation of NO_2^- ions, whereas at pH 3, as pointed out above, initially, they were formed simultaneously with NO_2^- ions as primary degradation products. That may suggest that the mechanistic pathways of the irradiated system are pH dependent. *Fig. 3* shows the time profiles of NDMA, degradation by-products, and the TOC.

Similar to the experimental data obtained at pH 3, a good TOC balance at pH 7 was found over the irradiation period, but a slight decrease of *ca.* 13% in the organic carbon was observed. CH_3NH_2 might be also an intermediate, but it was not quantified.

No depletion of the oxygen concentration in the solution was observed during the irradiation at either pH 3 or 7, which is consistent with the very low yield of mineralization.

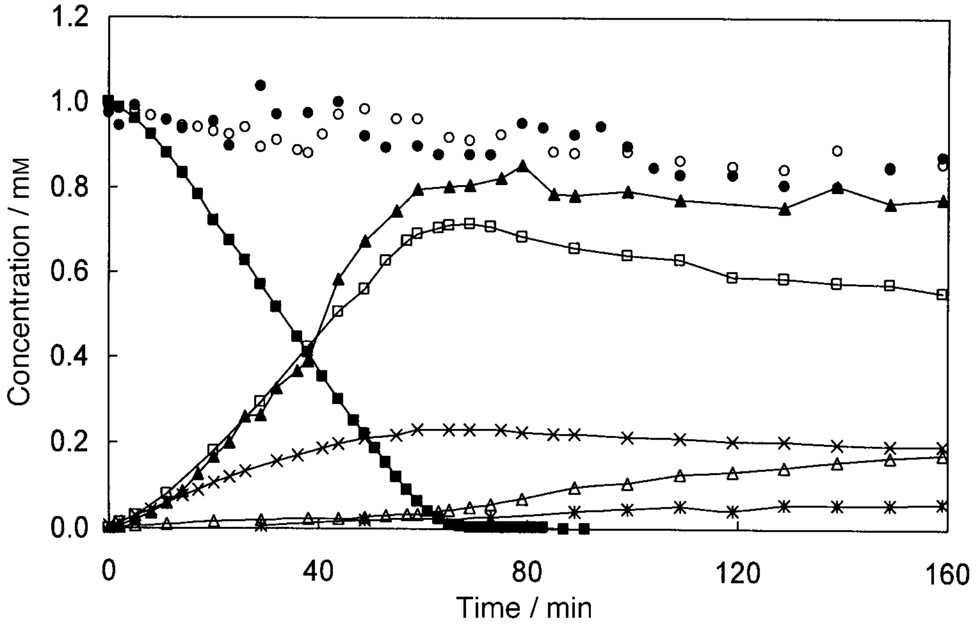


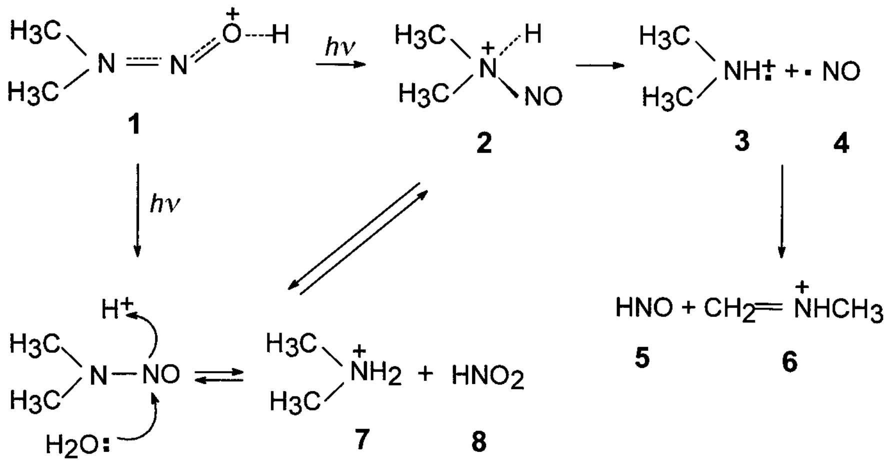
Fig. 3. *Time profiles of NDMA and its degradation products, and TOC mass balance during irradiation at pH 7.* ■: NDMA; ▲: dimethylamine; □: nitrite; △: nitrate; × : formaldehyde; ∗: formic acid; ○: calculated TOC/2; ●: measured TOC/2. The 'calculated' TOC represents the TOC in NDMA and degradation products.

A comparison between the total nitrogen concentration as calculated from the sum of the nitrogen content in the detected and quantified compounds in the irradiated system, with the initial concentration of nitrogen, as present in NDMA, reveals no change at pH 3, and a *ca.* 20% loss of nitrogen at pH 7. This is an additional indication that different reaction pathways are probably followed by the system, depending on pH. The loss of nitrogen at pH 7 might be accounted for mechanistically by the formation and stripping of nitrogen gases, such as N_2O, NO, and N_2, since no significant concentrations of nitrogen-containing organic compounds are missing from the analysis, as indicated by the TOC balance.

Degradation Pathways in the UV Direct Photolysis of NDMA. The broad-band irradiation from the medium-pressure Hg lamp makes possible both types of electronic excitation in the NDMA molecule, *i.e.*, $\pi \rightarrow \pi^*$ ($\lambda_{max} = 228$ nm) and $n \rightarrow \pi^*$ ($\lambda_{max} = 332$ nm). The primary step consists in the photocleavage of the N–N bond (170 kJ/mol), with the generation of the corresponding dimethylaminium radical and NO, in a 'solvent cage' [33]. The generated radicals can recombine in the cage, reforming the original NDMA molecule, or can escape from the cage, leading to various products. *Polo* and *Chow* [11] proposed a simplified mechanism for the photodegradation of NDMA in weakly acidic aqueous solutions, as shown in *Scheme 1.*

Two distinct pathways are proposed for the decay of the excited state of NDMA. One implies the hydrolysis of the excited state, leading to the protonated form of DMA (**7**; $pK_a = 10.73$) and HNO_2 (**8**). The second assumes the rearrangement of the excited state of NDMA to the *N*-nitrosodimethylammonium ion (**2**), followed by dissociation

Scheme 1. *Primary Processes in the NDMA Photodegradation in Aqueous Solution*



to the dimethylaminium radical (**3**) and NO radical (**4**). HNO (**5**) and N-methylidenemethylamine (**6**) are generated as a result of the reaction of radicals **3** and **4** in the solvent cage [33][34]. The only stable species in *Scheme 1* are DMA and HNO_2/NO_2^- ions, which were identified and quantified in this study as the major degradation products of NDMA, both at pH 3 and 7.

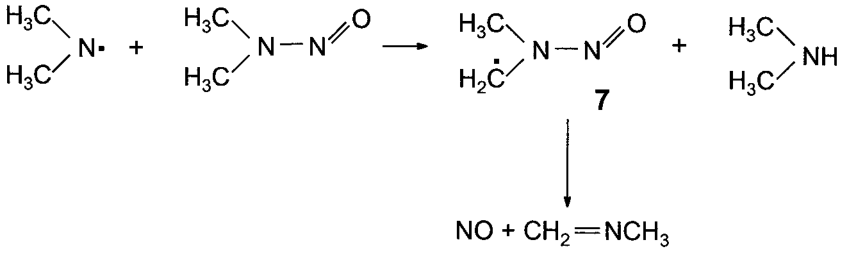
Further reactions of the above species can be postulated to explain the photodegradation products of NDMA observed in this work. These reactions are given in *Scheme 2*.

Scheme 2. *Generation of the Intermediate By-Products during the Photolysis of NDMA in Aqueous Solution*

$$\underset{\mathbf{6}}{CH_3\text{-}N{=}CH_2} + H_2O \xrightarrow{H^+} CH_3\text{-}NH_2 + HCHO$$

$$2\,\underset{\mathbf{5}}{HNO} \longrightarrow (HNO)_2 \longrightarrow H_2O + N_2O$$

$$HCHO + O_2 \xrightarrow{h\nu} HCOOH$$



The acid-catalyzed hydrolysis of the immonium compounds to the corresponding carbonyl and amine compounds is known in the literature [13][14]. Therefore, this can be a route toward the formation of HCHO and CH_3NH_2 in the irradiated system in a 1:1 ratio. HCOOH can be generated through the slow oxidation of HCHO. Similarly, NO_2^- ions are slowly oxidized to NO_3^- ions; once formed in the system, these ions will compete for the light with NDMA, reducing the effectiveness of the treatment, especially when starting with a high concentration of parent pollutant.

The dimethylaminyl radical is almost unreactive toward oxygen [7][17], but it readily reacts with H-atom-donating compounds by H-abstraction, forming the corresponding amine. It has been proposed that the dimethylaminyl radical may abstract a H-atom from another NDMA molecule, leading to DMA and the C-centered radical **7**, which rearranges to methylidenemethylamine **6** by losing the NO fragment [21][22].

No attempt was made to measure the nitrogen-containing gases, but their generation may explain the decay of the organic nitrogen content during the photolysis at pH 7.

Kinetics of the UV Direct Photolysis of NDMA. The decay of NDMA in aqueous solutions of pH 3 and 7, under irradiation with a medium-pressure Hg lamp, was investigated over a wide range of concentration (0.001 – 1 mM). Depending on the initial concentration, the NDMA decay obeyed either zero- or first-order kinetics. In all cases, the degradation of NDMA was followed for more than one order of magnitude.

Figs. 4 and *5* illustrate the kinetic behavior of NDMA solutions, at pH 3 and 7, respectively.

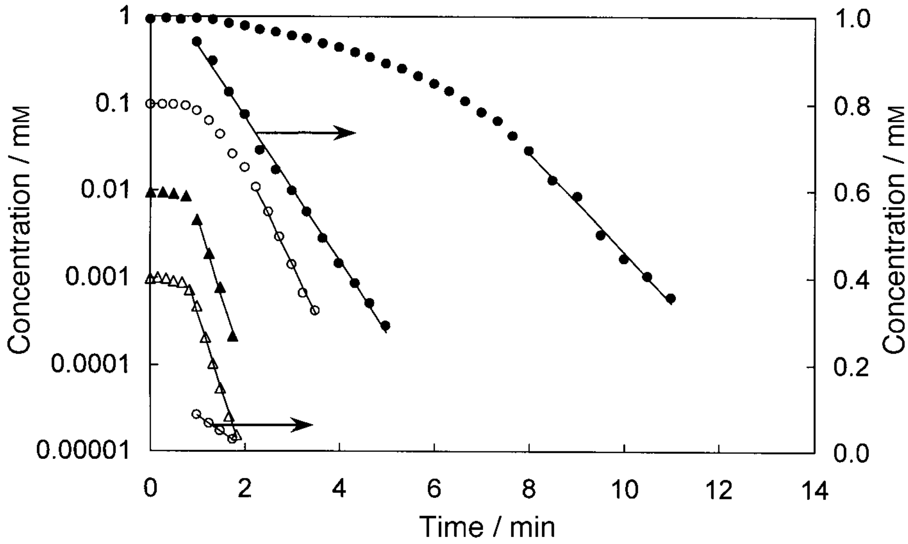


Fig. 4. *Kinetics of the NDMA photolysis at pH 3*

One observes that for similar initial concentrations, the rate of degradation of NDMA is significantly faster at pH 3 than at pH 7. This can be explained by the difference between the quantum yields at these pH values, namely 0.25 and 0.13,

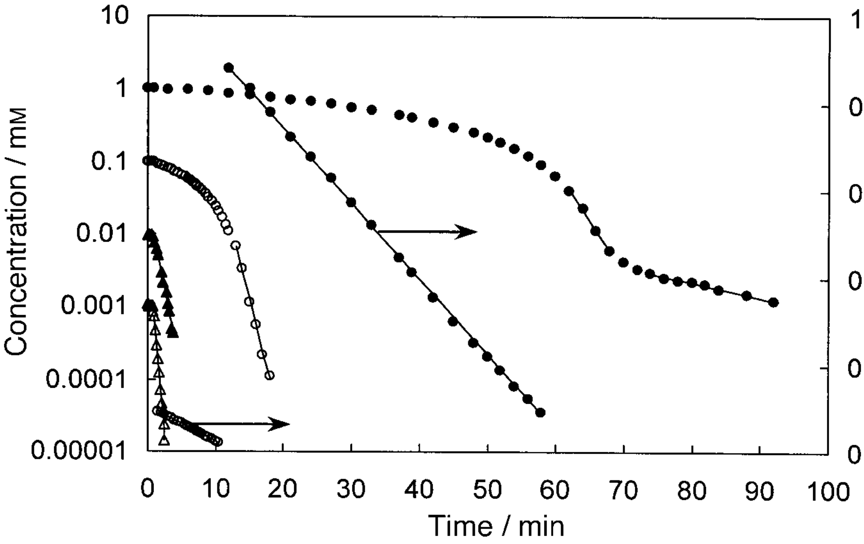


Fig. 5. *Kinetics of the NDMA photolysis at pH 7*

respectively [16], and possible NDMA-reformation mechanisms in neutral solutions. The *Table* summarizes the kinetic data and gives the efficiency of the UV process, as expressed by the figure-of-merit '*Electrical Energy per Order*' (E_{EO}), introduced by *Bolton et al.* [35]. The *Electrical Energy per Order* (kWh/order/m^3) is defined as the electrical energy [kWh] required to bring about the degradation of a contaminant by one order of magnitude in 1 m^3 of contaminated water or air.

Table. *Summary of the Kinetic Data from the Photolysis of NDMA*

NDMA/mM[a])	Time/min[b])	k_0/mM min^{-1}	k_1/min^{-1}	E_{EO}/kWh/order/m^3	% F_{abs}[c])
		pH 3			
1	1–5	0.164	–	–	90
	7–11	–	1.31	1.04	
0.1	1–2	0.074	–	–	70
	2–4	–	2.6	0.53	
0.01	1–2	–	4	0.34	30
0.001	1–2	–	4	0.34	4
		pH 7			
1	10–60	0.017	–	–	90
	60–70	–	0.32	4.3	
	70–90	–	0.05	29.6	
0.1	1–12	0.008	–	–	70
	14–20	–	0.84	1.63	
0.01	1–4	–	1.063	1.29	30
0.001	1–2	–	2.6	0.53	4

[a]) Initial concentration of NDMA. [b]) Time interval during the irradiation of NDMA, when a specific kinetics is obeyed. [c]) Fraction of light absorbed in the UV reactor (pathlength 8 cm).

At large initial concentrations (1 and 0.1 mM), NDMA degrades according to zero-order kinetics, followed by first-order kinetic behavior after a significant depletion in concentration. The formation of NO_2^- and NO_3^- ions, to a large extent, leads to a decrease of the NDMA photolysis rate given the increased competition for light (see spectra in *Fig. 1*). The two first-order decay regimes at pH 7 and the significant differences between the first-order rate constants, characterizing the decay of NDMA in the same ranges of concentration, may also be explained by an inner-filter effect of the NO_2^- and NO_3^- ions. From the known spectral emission of the UV lamp, one can calculate that 38.2% of the total UV output of the lamp in the 200–300 nm range is emitted below 250 nm, where both NDMA and the NO_2^- and NO_3^- ions absorb significantly. Therefore, when a significant fraction of NDMA is depleted, the built-up products can compete for the light, decreasing the rate of further degradation of NDMA. For example, when starting with a 1 mM NDMA solution, pH 7, after 66 min irradiation, the NDMA, NO_2^- and NO_3^- ion concentrations were 0.011, 0.71, and 0.0436 mM, respectively. The corresponding fractions of light absorbed within 200–300 nm are 12.5, 25.5, and 3%. When starting the irradiation with a 0.01 mM NDMA, pH 7, the fraction of light absorbed by NDMA at $t = 0$ min is 30%.

Similar correlations can be made with respect to the E_{EO} values. Considering the low levels of NDMA encountered in either ground or drinking waters (ppb–ppt), it appears that UV direct photolysis is a very good treatment option.

Experimental Part

Supplies and Reagents. N-Nitrosodimethylamine (NDMA), anal.-reagent grade, was purchased from *Aldrich*. All chemicals used for the standard solns. in the instrumental analysis were anal.-reagent grade and used as received from various chemical suppliers.

UV Reactor. The UV irradiations were carried out in a semi-batch 1-kW *UV Rayox*® reactor provided by *Calgon Carbon Corporation*, Pittsburgh, VA, described in detail in [36]. A 1-kW medium-pressure Hg lamp was used in all experiments. The total incident photon flow within 200–300 nm wavelength range was $(3.03 \pm 0.08) \times 10^{-4}$ einstein s^{-1}, as determined by persulfate actinometry [37]. The 1-kW medium pressure Hg lamp requires a 50-s warm-up period to reach full power.

All experiments were conducted in aerated aq. solns. (distilled water); the pH was adjusted with $NaHCO_3$ or H_2SO_4 to the desired value.

Analytical Determinations. N*-Nitrosodimethylamine (NDMA) Analysis.* NDMA was measured by either a GC or HPLC, depending on the investigated concentration range.

A GC method was used for all the experiments starting at an initial concentration of NDMA of *ca.* 1 mM. A *HP 6890* gas chromatograph equipped with an autosampler was employed with a *HP Wax* (cross-linked polyethylene glycol) column (30 m × 0.53 mm, 1-μm film thickness) with a temp. program, as follows: 35° for 5 min, then raised to 150° at 25°/min and held for 2 min at 150°. The injector temp. was 210°, with a split injection ratio of 10:1; the detector temp. (FID) was 250°. He was used as a carrier gas at a flow rate of 16.1 ml/min. The corresponding retention time of NDMA was 8.61 min.

Concentrations as low as 0.005 mM NDMA could be accurately measured under the GC conditions stated above, by means of a multiple point calibration curve.

An HPLC method was used for the low range of the NDMA concentrations. A *Waters 510* HPLC system with a *Waters 486* tunable UV detector was used in connection with a *Supelcosil LC-18* column (25 cm × 4.6 cm, *Supelco*). The mobile phase was MeCN/H_2O 60:40 (*v*/*v*) for the experiments at pH 3, and 45:55 (*v*/*v*) for those at pH 7, acidified at pH 3 with H_3PO_4; at the flow rate of 1.2 ml/min, the retention time of NDMA was 2.7 min. The detection wavelength was set at 240 nm for most of the measurements, but shifted to 228 nm when concentrations in μM and sub-μM range were analyzed.

Concentrations of NDMA as low as 0.015 μM could be measured accurately by the HPLC method described above, based on a multiple point calibration curve.

Dimethylamine (DMA) Analysis. The reaction of DMA with CS_2 in the presence of $CuCl_2$ leads quantitatively to the yellowed-colored cupric salt of dithiocarbamic acid, which can be measured spectrophotometrically at $\lambda = 434$ nm [38]. Under the reaction conditions, the primary and tertiary amines do not interfere. This analysis is known as the *Umbreit* method. An *HP 8450A* diode-array spectrophotometer and a 1-cm path quartz cell were employed for the absorbance measurements.

NO_2^-, NO_3^-, and *$HCOO^-$ ions* were analyzed by ion chromatography. A *Dionex DX-100* ion chromatograph equipped with an anion self-regenerating suppressor (*ASRS-I*) and the *AI-450* software program was employed with an *Ion Pac AS 14* (*Dionex*; 250 nm × 4 mm) ion-exchange column preceded by an *AG 14* guard column (*Dionex*). A 9 mM sodium tetraborate soln. was used as an eluent at an isocratic flow of 1.47 ml/min. Under these conditions, the retention times of the above ions were: 2.82 min ($HCOO^-$), 3.65 min (NO_2^-), and 4.90 min (NO_3^-).

HCHO was analyzed by spectrophotometry at $\lambda = 412$ nm, based on the *Hantzsch* reaction [39].

Total Organic Carbon (TOC) Analysis. A *Shimadzu TOC-5050* analyzer was employed for organic carbon determinations, with potassium hydrogen phthalate solns. as TOC standards.

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