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# Kinetics and mechanism of the reaction of sodium azide with hypochlorite in aqueous solution

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ABSTRACT

Production of toxic sodium azide ($NaN_3$) surged worldwide over the past two decades to meet the demand for automobile air bag inflator propellant. Industrial activity and the return of millions of inflators to automobile recycling facilities are leading to increasing release of $NaN_3$ to the environment so there is considerable interest in learning more about its environmental fate. Water soluble $NaN_3$ could conceivably be found in drinking water supplies so here we describe the kinetics and mechanism of the reaction of azide with hypochlorite, which is often used in water treatment plants. The reaction stoichiometry is: $HOCl + 2N_3^- = 3N_2 + Cl^- + OH^-$, and proceeds by a key intermediate chlorine azide, $ClN_3$, which subsequently decomposes by reaction with a second azide molecule in the rate determining step: $ClN_3 + N_3^- \rightarrow 3N_2 + Cl^-$ ($k = 0.52 \pm 0.04\ M^{-1}\ s^{-1}$, 25 °C, $\mu = 0.1$ M). We estimate that the half-life of azide would be ≈15 s at the point of chlorination in a water treatment plant and ≈24 days at some point downstream where only residual chlorine remains. Hypochlorite is not recommended for treatment of concentrated azide waste due to formation of the toxic chlorine azide intermediate under acidic conditions and the slow kinetics under basic conditions.

## 1. Introduction

The industrial production of sodium azide ($NaN_3$) has surged over the past decade to meet the demand for automobile airbag inflator propellant. However it is highly toxic—even a cursory search of the Internet reveals that sodium azide toxicity is comparable to that of sodium cyanide when ingested [1]. The United States National Highway Traffic Administration (NHTSA) mandated that new passenger vehicles sold in the United States after 1996 have both driver-side and passenger-side air bags. As a result, sodium azide demand quickly rose to exceed 5 million kg in the U.S. by 1995 and has continued to rise, although the trend is now leveling off with the advent of azide-free inflators [2,3]. An inflator module typically contains compressed disks or pellets of ≈60% (w/w) $NaN_3$, blended with other ingredients, and packed into a sealed metal canister [4,5]. Each driver-side inflator contains approximately 50–80 g $NaN_3$, while the larger passenger-side inflator contains approximately 250 g [6]. The actual amount depends on the specific inflator, but the total installed in U.S. vehicles alone is now on the order of 50 million kg [7]. The smooth, rapid thermal decomposition characteristics, the high specific nitrogen content (65 mol%), and the long shelf life make sodium azide an attractive propellant material [6,8].

$$NaN_3 \rightarrow Na + \tfrac{3}{2}N_2 \quad (1)$$

Sodium azide has other uses. In the 1970s, it was used in some registered pesticide formulations, mainly for crops, and consequently discarded commercial products, off-specification product, container residues and spill residues were listed as hazardous waste by the United States Environmental Protection Agency (EPA) [9]. Lately, interest in sodium azide pesticide formulation has been revived as a replacement for methyl bromide [10]. Accordingly, sodium azide toxicity was recently on the agenda of an EPA Human Studies Internal Review Board [11]. Sodium azide is used as a preservative in certain laboratory reagents, samples and clinical fluids, and in 1989, there was an alert from the Food and Drug and Administration and the Center for Disease Control (CDC) concerning the need to rinse out sodium azide preservative in certain water filters prior to use [12]. Azide can also combine with metals to form explosive metal–azide complexes. The accumulation of azide in laboratory apparatus and drains, where it can react with lead or copper-containing fixtures, has caused explosions when routine maintenance work has been attempted [13].

The azide ion is readily protonated in aqueous solution ($pK_a = 4.65$) to yield volatile hydrazoic acid ($HN_3$), which is itself toxic, so the atmospheric fate of azide substance is also of interest

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and has recently been described [5,14–16].

$$HN_3 \overset{pK_a=4.65}{\rightleftharpoons} H^+ + N_3^- \tag{2}$$

Sodium azide is highly soluble, which implies that releases into the environment could potentially migrate into sewers, streams, lakes and groundwater systems. And in fact, sodium azide has been found in groundwater at three manufacturing sites in three states, resulting in a multi-million dollar civil and criminal settlement [17].

Because of its ready availability and high toxicity, sodium azide has become a chemical of interest for the Department of Homeland Security [18], the CDC [19], and the EPA Water Supply Security Division [20]. Since it is possible that azide could be found in drinking water supplies it is of interest to know how it would behave in the presence of hypochlorite, which is commonly used in potable water treatment systems in the United States.

Oxidation by hypochlorite could also potentially be used as a treatment for much more concentrated azide-containing waste, but the results of this work lead us to recommend against such practice.

In a definitive series of mechanistic studies Margerum's group has shown that the reaction of hypochlorite with a range of nucleophiles, including $CN^-$, $I^-$, $Br^-$, $Cl^-$ and $SO_3{}^{2-}$, appears to proceed by way of $Cl^+$ transfer, and not via oxygen atom transfer, as had long been thought [21–27]. Ignoring the existence of acid catalysis, the common rate law for reaction of hypochlorite with any of these nucleophiles, $X^-$, can be represented by:

$$\frac{-d[OCl^-]}{dt} = (k_{HOCl}[HOCl] + k_{OCl}[OCl^-])[X^-] \tag{3}$$

Thus, oxidation can proceed via HOCl and $OCl^-$, and the reaction is first-order in both hypochlorite and $X^-$. For all $X^-$, except $SO_3{}^{2-}$, the ratio $k_{HOCl}/k_{OCl^-}$ is greater than $10^6$. Therefore, the HOCl route will dominate in all natural waters ($pK_a$ HOCl = 7.31). In the case of $SO_3{}^{2-}$, the $k_{HOCl}/k_{OCl^-}$ ratio falls to $10^4$ and so the $OCl^-$ route could become significant at pH $\geq \approx 11.3$. The value of $k_{HOCl}$ ($M^{-1}\,s^{-1}$) decreases with the nucleophilicity of $X^-$: $CN^-$ ($1.22 \times 10^9$) > $SO_3{}^{2-}$ ($7.6 \times 10^8$) > $I^-$ ($1.4 \times 10^8$) > $Br^-$ ($1.55 \times 10^3$) > $Cl^-$ ($\leq 0.16$) [28]. Since azide, the subject of this paper, is a pseudohalide with a nucleophilicity similar to that of bromide, it is of interest to compare the behavior of these two species in particular [29].

The first step of the HOCl route involves $Cl^+$ transfer to an anion.

$$HOCl + X^- \xrightarrow{k_{HOCl}} XCl + OH^- \tag{4}$$

whereas the first step of the much slower $OCl^-$ pathway formally involves an encounter between two anions, and so may be acid assisted.

$$OCl^- + X^- + H_2O \xrightarrow{k_{OCl}} XCl + 2OH^- \tag{5}$$

Nevertheless, both pathways lead to a common intermediate, XCl, which may be quite stable, e.g., cyanogen chloride (CNCl) or bromochloride (BrCl) [28,30]. XCl is subsequently lost through either alkaline hydrolysis:

$$XCl + 2OH^- \overset{fast}{\rightleftharpoons} XO^- + Cl^- + H_2O \tag{6}$$

or by reaction with a second $X^-$ [30].

$$XCl + X^- \overset{fast}{\rightleftharpoons} X_2 + Cl^- \tag{7}$$

In the case of $X^- = N_3{}^-$, this would lead to $(N_3)_2$, which would rearrange to $3N_2$. In fact, we will show later that this path is the dominant route for azide, unlike the halides, presumably because the production of $N_2$ is thermodynamically so favorable.

Here we describe the kinetics and mechanism of the hypochlorite/azide reaction in aqueous solution and propose a mechanism to explain the observed rate laws. We use this information to estimate the lifetime of azide in chlorinated drinking water and to comment on the possible treatment of concentrated aqueous azide-containing waste with hypochlorite.

## 2. Experimental

### 2.1. Materials

Water was first deionized (Calgon) and then distilled (Barnstead; conductivity <1 $\mu S\,cm^{-1}$). Three sources of sodium azide were used (Aldrich 99.99+%; Mallinckrodt Practical; Acros 99%); no difference was observed in their electronic spectra or their kinetic behavior. We also tested two sources of sodium hypochlorite, which was either purchased (Clorox, ≈0.44 M) or prepared by bubbling chlorine (Matheson, 99.99%) into 0.2 M sodium hydroxide until $Cl_2$ could first be seen in the headspace. The excess $Cl_2$ was immediately removed by purging with $N_2$ to yield 0.1 M hypochlorite with pH ≈7.8.

$$Cl_2 + 2OH^- = OCl^- + Cl^- + H_2O \tag{8}$$

Again, no difference was observed in the electronic spectra or kinetic behavior of these two sources, which were stored in the dark in a refrigerator. Hypochlorite was standardized iodometrically with KI (Baker) or polarographically, with phenylarsine. The concentration was conveniently checked spectrophotometrically ($\varepsilon_{292} = 3.50 \times 10^2\,M^{-1}\,cm^{-1}$) [22]. The speciation of halogens in water is governed by a complicated interplay between thermodynamics and kinetics, which has been described in detail [31]. Molecular chlorine ($Cl_2$) is insignificant under our experimental conditions (<$10^{-5}$ mole fraction total Cl).

Buffers with an ionic strength of 0.1 M were prepared from the following reagents: $CH_3COOH$, $CH_3COONa$, $Na_2HPO_4{\cdot}H_2O$, $NaH_2PO_4$, $NaHCO_3$, NaOH, from Baker; $H_3BO_3$, from Fisher [32]. The pH was measured at room temperature using a Radiometer TTT85 titrator and glass combination electrode (GK2401B) calibrated with Radiometer (pH 4.005, pH 10.012, pH 7.000, pH 12.450) or Ricca (pH 7.00, pH 10.00) buffers. We did not convert the measured pH values (proton activity) to $-\log[H^+]$ values (proton concentration) so our experimentally determined constants are "mixed". We use $K_a$ HOCl = $4.90 \times 10^{-8}$ ($pK_a = 7.31$) and $K_a$ $HN_3 = 3.72 \times 10^{-5}$ ($pK_a = 4.43$), both at 25 °C and an ionic strength, $\mu = 0.1$ M [33]. These values were calculated from the available data using the Davies equation ($\gamma = 0.8$) [34]. Where necessary, the effect of temperature on $K_w$ and $K_a$ was calculated using the appropriate enthalpies and the integrated van't Hoff equation [33].

### 2.2. Methods

#### 2.2.1. Kinetics

Kinetic studies were performed using Teflon-stoppered quartz cuvettes (1-cm) in an HP 8453 UV–visible spectrophotometer with 89090A temperature-controlled cuvette holder. (Due to the optical arrangement in this instrument the entire spectrum, rather than an absorbance at a single wavelength, is recorded each time.) The fastest reactions (low pH) were initiated by injecting the desired amount of azide into a cuvette containing the hypochlorite and rapidly mixing by inverting. In this way the entire spectrum could be recorded within 5 s of mixing and every 0.5 s thereafter. For reactions requiring several days to complete (high pH), sealed 40-mL vials containing the reactants were placed in a temperature-regulated water bath and periodically sampled to record the electronic spectrum. In most cases, the reaction was monitored for at least 5 half-lives.

The rate of reaction was studied as a function of $[N_{3T}{}^-]$ and pH (4.67–11.95). Here, $[N_{3T}{}^-] = [HN_3] + [N_3{}^-]$ and $[OCl_T{}^-] = [HOCl] + [OCl^-]$. Experiments were performed under pseudo-first-order conditions ($[N_{3T}{}^-] \gg [OCl_T{}^-]$), with $[OCl_T{}^-]$