

Mechanism and Kinetics of the Reaction of Ozone with Sodium Chloride in Aqueous Solutions

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Abstract—It is shown experimentally that Cl^- appreciably accelerates ozone decomposition in water ($\tau_{1/2} = 1.5$ h versus 6 h in pure water). The decomposition of ozone in NaCl solutions includes the reversible reaction of ozone with the chloride ion ($\text{O}_3 + \text{Cl}^- \rightarrow \text{O}_3^- + \text{Cl}$) as the key step, which is followed by the development of a chain reaction in which chain propagation is performed alternately by the chlorine atom Cl and its monoxide ClO. The current concentrations of the chlorine atom are rather low ($[\text{Cl}] \sim 10^{-14}$ mol/l). The overall process is satisfactorily described by a first-order rate law with respect to ozone. The decomposition of ozone in aqueous solutions of NaCl is not accompanied by the formation of products other than oxygen. In particular, no noticeable amounts of hypochlorites and chlorates are observed. This is particularly significant for medicinal applications of ozonized isotonic solutions.

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INTRODUCTION

Solutions of ozone in the isotonic solution (0.9% NaCl in distilled water) are finding increasing use in the medical practice in Russia and abroad [1–3]. Proponents and opponents of the application of ozone are actively disputing the positive and negative results of curing people and animals with these solutions [4–7]. The main argument against these solutions is that ozone reacts with the chloride ion to form hypochlorite [5], which can exert an ill effect on the organism of a patient. Both physicians [5, 6] and chemists [4, 7] are involved in the discussions. However, the absence of direct experimental data on the reaction of ozone with the chlorine ion and on the composition and behavior of intermediate reaction products (if this reaction does take place) does not allow one to resolve this controversy in a rational way and accept or reject the new medicine. Here, we report the behavior of the ozone–aqueous NaCl system. This study provides better reason to obviate concerns that hypochlorite or chlorates (products of deeper oxidation) might cause harm to the patient treated with an ozone-containing isotonic solution.

EXPERIMENTAL

Ozone was synthesized from oxygen in electric discharge using a UOTA-60-01 medical ozone generator [8]. The initial ozone concentration was varied

between 3 and 20 mg/l. The gas mixture flow rate was 50 ml/min.

Sodium chloride (NaCl) was special-purity grade, sodium perchlorate (NaClO_4) was high-purity grade, and calcium chloride (CaCl_2) was reagent grade. Sodium hypochlorite (NaClO) was used as a 10% solution prepared by the electrolysis of an aqueous solution of sodium chloride.

The active oxygen content was measured by the iodometric method with strong acidification of the analyzed solution with H_2SO_4 (~6 M) [9].

Water to be used in experiments was prepared as follows. Distilled water was boiled with an excess of KMnO_4 for 60 min and was then distilled twice, rejecting the head fraction (5 vol %) and the bottoms (5 vol %). The tridistillate was deionized in ion-exchange columns. The quality of water was characterized by its resistivity ($>1 \text{ M}\Omega/\text{cm}$).

The ozone concentration was measured spectrophotometrically at a wavelength of 254 nm. The reactor was a quartz optical cell with an optical path length of 1 cm, 3.5 ml in volume, with a long narrow neck and a ground-in quartz stopper. The solution was saturated with ozone directly in the cell by bubbling ozonized oxygen for 15 min. The solution was poured into the cell in such a way as to leave the minimum possible free space (<0.1 ml) in the cell and thus rule out any effect on the subsequent processes. The cell was shielded from the light in the intervals between absorbance measurements.

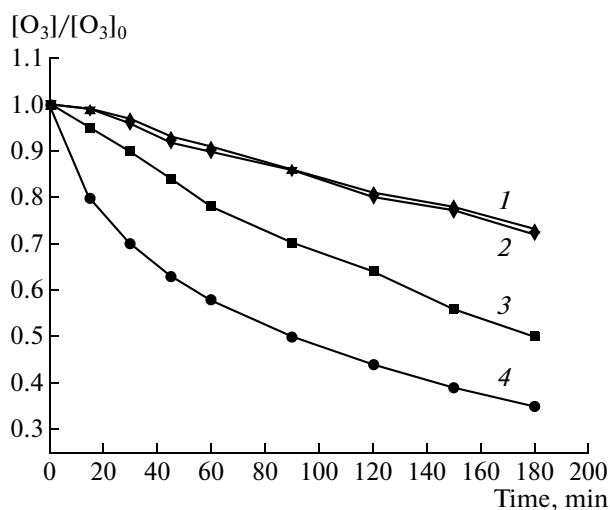
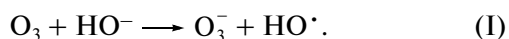


Fig. 1. Time dependences of the relative current concentration of ozone dissolved in (1) pure water and (2–4) aqueous solutions of (2) $NaClO_4$, (3) $NaCl$, and (4) $CaCl_2$. The salt concentration is 0.9 g/100 ml H_2O ; pH 6.3.

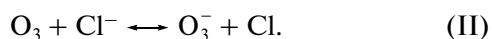
UV–vis spectra were recorded on a Specord-M40 spectrophotometer at $T = 20^\circ C$.

RESULTS AND DISCUSSION

The solutions of ozone in water are unstable: even in highest purity water, ozone decomposes to approximately 50% of the initial concentration within 6–17 h [10, 11]. Ozone dissolved in an isotonic solution (0.9% $NaCl$ in distilled water) decomposes still more intensively. Since the system contains only ozone, water, and chloride and sodium ions, it is easy to find the cause of the acceleration of ozone decomposition. A comparison of the kinetics of ozone decomposition in pure water and in water containing $NaCl$, $CaCl_2$, and $NaClO_4$ (Fig. 1) shows that the Na^+ and Ca^{2+} cations and the ClO_4^- anion exert a weak, if any, effect on the rate of ozone decomposition in water (the inertness of ClO_4^- toward ozone was also noted by other authors [12]). The observed speedup of ozone decomposition in the $NaCl$ solution is solely due to the presence of chloride ions. The reaction mechanism in this case is similar to the mechanism of ozone decomposition in aqueous solutions of an alkali [13], in which the first step is electron transfer from the hydroxide ion HO^- to ozone:



Correspondingly, the reaction of ozone with the chloride ion can be written as



Another scheme, namely, $S^- + O_3 \longrightarrow SO^- + O_2$, is usually suggested as a more likely one for the reactions

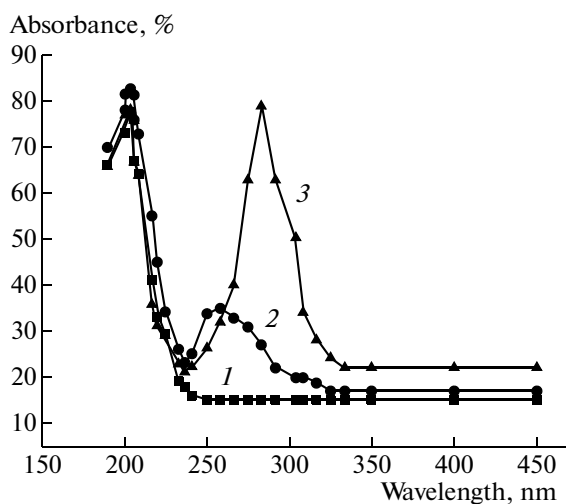
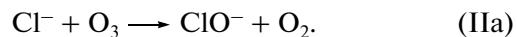


Fig. 2. UV spectra of solutions of (1) $NaCl$ (0.9 g/100 ml), (2) ozone with $NaCl$ (0.9 g/100 ml) stored until the half-decay of the dissolved ozone, and (3) $NaClO$ in water.

of inorganic ions (S^-) with ozone [14]. In our case, this scheme will appear as



We used our and literature data on the composition of the reaction products of ozone with ClO^- to choose between (II) and (IIa). The UV spectrum of ClO^- (product of reaction (IIa)) exhibits an intense absorption band ($\lambda_{max} = 292$ nm) occurring at longer wavelengths than the ozone band ($\lambda_{max} = 255$ – 260 nm). This would allow one to observe the appearance of ClO^- in the solution if this ion actually formed. Figure 2 shows the UV spectra of a $NaCl$ solution in water (curve 1), a solution of ozone in water + $NaCl$ (0.9 g) stored until the half-decay of dissolved ozone followed by purging the reactor from unreacted ozone (curve 2), and a solution of $NaClO$ (curve 3). The data in Fig. 2 indicate that neither ClO^- nor deeper oxidation products accumulate in the system ($\lambda_{max}(ClO_2^-) = 260$ nm with gradual absorption decay to 320 nm). This observation is not sufficient to exclude reaction (IIa) from the scheme, because ClO^- reacts rather readily with ozone ($k_{IIa} = 120$ l mol $^{-1}$ s $^{-1}$) [15] and, as a consequence, its disappearance rate is higher than its formation rate. The major products of the $ClO^- + O_3$ reaction are Cl^- (70%) and ClO_3^- (30%) [15]. Therefore, if there were an appreciable contribution of reaction (IIa) to ozone decomposition, approximately 1/3 of the decomposed ozone would be converted into ClO_3^- (which is stable under the experimental conditions) or even into perchlorate. The additional oxygen in ClO_3^- would increase the weight of the mineral component of the aqueous solution. This would allow one

to detect ClO_3^- in the products as the increase in the weight of the dry residue after the removal of water in vacuo. These experiments were carried out. A solution of NaCl (10 ml) was placed in a flask ($V = 1$ l) with a ground-in stopper, and the solute was dried and weighed. Next, water (10 ml) was added and the flask was filled with an ozone–oxygen mixture ($[\text{O}_3] = 1.5 \times 10^{-3}$ mol/l). The flask was held for 48 h in the dark with shaking, the ozone–oxygen mixture was blown off, and water was distilled out. The residue was dried and weighed. The same was made in parallel with sodium oleate. No weight gain was found for the aqueous solution of NaCl. A weight gain of 64 mg was observed for an aqueous solution of oleate, which approximately corresponded to the weight of ozone introduced into the flask. The above data led us to accept reaction (II) as being dominant. The ozonide ion O_3^- forming simultaneously with Cl turns into O_2 via a familiar mechanism [13].

The likely Cl concentration in the solution can be estimated thermodynamically. Neglecting the solvation effects in the aqueous medium and taking into account only the electron affinity of the Cl atom and ozone molecule, one can infer that the equilibrium in reversible reaction (II) is strongly shifted to the left and the concentration of chlorine atoms is very low. Such Cl concentrations are generally neglected. However, in this case Cl is the initiator of a chain of repeated ozone decomposition events, causing a quite appreciable decrease in the ozone concentration in the solution ($\tau_{1/2} \sim 90\text{--}100$ min). Assuming that reversible reaction (II) rapidly comes to equilibrium, that $(T\Delta S)_{\text{left}} = (T\Delta S)_{\text{right}}$, and that the heats of solvation and evaporation of species on the right- and left-hand sides of the equation are similar and using the known values of the electron affinity of O_3 and Cl in the gas phase (3.6 [16] and 2.1 eV [17], respectively), we can determine the chemical potential ΔF^0 of reversible process (II):

$$\Delta F^0 = 3.6 - 2.1 = 1.5 \text{ eV.}$$

The equilibrium constant K is related to the potential of the system by the equation

$$RT \ln K = -\Delta F^0.$$

The K value can be found by solving this equation for $\ln K$ after converting the potential from the energy units to thermal units (1 eV = 23 kcal/mol):

$$\ln K = \frac{-\Delta F}{RT} = \frac{-23000 \times 1.5}{1.98 \times 293} = 59.5.$$

According to the physical meaning of the equilibrium constant K ,

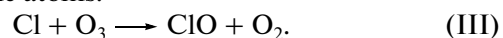
$$K = \frac{[\text{O}_3^-][\text{Cl}]}{[\text{O}_3][\text{Cl}^-]} = e^{-59.5} = 6.9 \times 10^{-25}. \quad (1)$$

In our experiments, the working concentrations were $[\text{O}_3] \sim 1 \times 10^{-3}$ and $[\text{Cl}^-] \sim 150 \times 10^{-3}$ mol/l, O_3^- and Cl appeared pairwise, and their concentrations

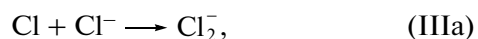
were equal. This made it possible to solve Eq. (1) and to estimate the upper limit of $[\text{Cl}]$:

$$[\text{Cl}] = ([\text{O}_3][\text{Cl}^-]K)^{1/2} = \sim 10^{-14} \text{ mol/l.}$$

This $[\text{Cl}]$ value seems rather idealized. Possibly, the actual $[\text{Cl}]$ values are even lower because ozone reacts with chlorine atoms:



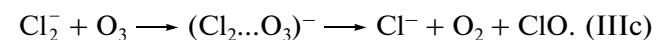
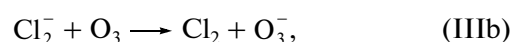
The resulting chlorine atom can either add rapidly to Cl^- [18],



or attack another ozone molecule [19] (reaction (III)).

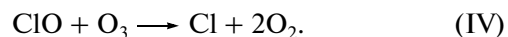
The complex radical ion Cl_2^- can be considered a chlorine atom reservoir capable of both binding chlorine atoms and donating them to the solution.

It would be expected that Cl_2^- can react with ozone as well as Cl:

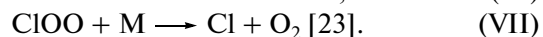
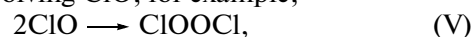


The final products of reaction (IIIb) and subsequent transformations of intermediate species would be ClO^- and O_2 . The absence of ClO^- in the reaction mixture allows reaction (IIIb) to be excluded from further consideration. Reaction (IIIc) seems quite plausible, even though there is no experimental evidence in favor of or against it.

The product of reactions (III) and (IIIc) (chlorine monoxide ClO) is an active molecule or, more precisely, a radical. It can participate in many reactions, including multiple recombination routes and reactions with ClO_2 , H_2 , and nitrogen oxides [20]. For this reason, jet methods [20] or matrix isolation techniques [21] have to be used in the study of the properties of ClO. Chlorine monoxide can also react with ozone [20, 22]:



The study of the kinetics of this reaction in jet devices at short residence times made it possible to estimate the upper limit of its rate ($k_4 < 10^{6.2}$ l mol⁻¹ s⁻¹). This allowed us to neglect reaction (IV) in calculations on the chemical dynamics of the atmosphere, where most basic reactions occur rapidly. In our case, when the overall ozone decomposition process occurs slowly and the ozone concentration is comparatively high, reaction (IV) can become rate-determining in the regeneration of the Cl atom. The participation of ClO in ozone decomposition accounts well for the absence of products of the deep oxidation of chlorine ions in the system. There are other chlorine atom regeneration routes involving ClO; for example,



However, the occurrence of these reactions under experimental conditions seems doubtful for thermodynamic reasons. The reference literature offers $\Delta_f G^0$

data for the participants of reactions (IV)–(VII). These data allow one to estimate the change in the Gibbs energy of the system due to these reactions. For instance, $\Delta_f G^0$ for $O_3(g)$, $Cl(g)$, and $ClO(g)$ is 39, 106, and 98 kJ/mol, respectively [24]. The change in the Gibbs energy for the overall reaction $2ClO(g) \rightarrow 2Cl(g) + O_2(g)$ is +16 kJ/mol, and, hence, the reaction will not occur spontaneously. At the same time, the change in the Gibbs energy for reaction (IV) is -130 kJ/mol, and the probability of this reaction occurring spontaneously is high. For this reason, we will dwell on reaction (IV), which seems the most effective and simplest among the reactions considered above.

The presence of free chlorine in the system was proved by a direct experiment in which chlorine was removed with an air flow and was then quantified [25]. The amounts of free chlorine thus determined corroborate the above estimate of the free chlorine concentration in the solution. Our attempts to detect free chlorine by standard spectrophotometric methods failed. The free chlorine concentration is likely very low and is far below the sensitivity limit of our spectrophotometric procedure.

As follows from the data presented above, the decomposition of chlorine in an aqueous solution of NaCl is described by a large array of reactions. It is, therefore, incorrect to discuss the issue of the true order of the reaction. At the same time, practice shows that the overall decomposition kinetics is well describable in terms of a first-order reaction with respect to ozone up to high conversion values. To confirm this, we represent the experimental data for the decomposition of ozone in the NaCl solution (taken from Fig. 1, curve 3) as the $[O_3] = f(t)$ plot and its semilogarithmic anamorphosis (Fig. 3). Clearly, the experimental data are satisfactorily rectified in the $\log([O_3]_t/[O_3]_0) = f(t)$ coordinates.

Thus, this experimental study and data available from the literature demonstrated that Cl^- appreciably accelerates ozone decomposition in water (half-decay time of 1.5 h versus 6 h in pure water). The mechanism of ozone decomposition in NaCl solutions was suggested. It includes the reversible reaction of ozone with the chloride ion, $O_3 + Cl^- \rightleftharpoons O_3^- + Cl$, as the key step. This is followed by the development of a chain reaction in which chain propagation is executed alternately by the Cl atom and chlorine monoxide ClO. The current concentration of chlorine atoms was estimated. This concentration turned out to be very low ($[Cl] \sim 10^{-14}$ mol/l). The dynamics of ozone decomposition in an aqueous solution of sodium chloride was studied. The overall process is satisfactorily described in terms of a first-order reaction with respect to ozone. Spectrophotometric and gravimetric methods showed that the decomposition of ozone in aqueous solutions of NaCl is not accompanied by the formation of prod-

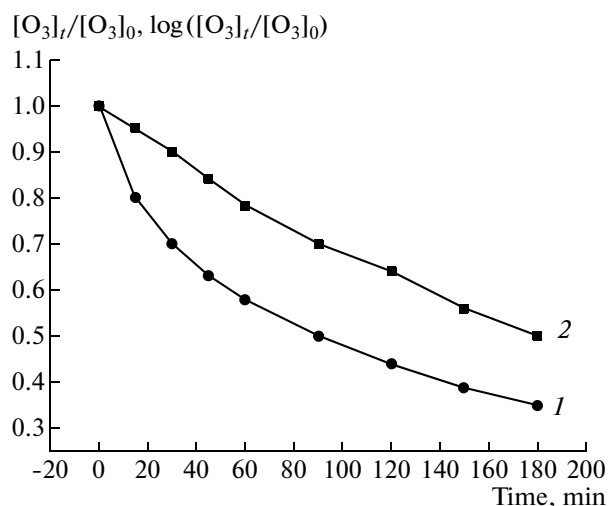


Fig. 3. (1) Dependence of the residual ozone concentration in a NaCl solution (9 g/l, pH 6.3) on time (t) and (2) its semilogarithmic anamorphosis.

ucts other than oxygen. In particular, there are no appreciable amounts of hypochlorites or chlorates. This is especially important for the medicinal applications of ozonized isotonic solutions.

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