A synergetic effect in nitrous acid formation by sonolysis of nitric acid in the presence of nitrous oxide

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A synergetic effect is found in the sonochemical formation of HNO_2 in HNO_3 solution in the presence of an N_2O—Ar gaseous mixture. The maximum rate of HNO_2 formation is observed at an N_2O : Ar ratio of 15 : 85 (v/v). During the sonolysis of 4 *M* HNO_3 solutions, the rate of HNO_2 formation increases multifold due to the synergetic effect. The rate of sonochemical hydrazine decomposition in nitrate solutions also increases considerably in the presence of N_2O.

Key words: ultrasound, nitric acid, nitrous acid, nitrous oxide, hydrazine.

It is known that the ultrasonic treatment (sonolysis) of aqueous solutions of nitric acid[1—3] and nitrous oxide N_2O produces[4] nitrous acid, and this process considerably accelerates many redox reactions. In this work, we studied the influence of N_2O on HNO_2 formation during sonolysis of aqueous solution of HNO_3.

Experimental

Sonolysis was carried out in a thermostatted cylindrical glass reactor by an UZDN-A ultrasound dispergator (f = 21 kHz, I = 2.6 W cm^{-2}, S_{surf} = 3.5 cm^2, P_{acoust} = 0.46 W mL^{-1}, V = 20 mL, T = 20 °C) according to a previously described procedure.[5]

An N_2O—Ar gas mixture with a specified composition was prepared using the Venturi mixer.[6] The gas mixture was bubbled with a flow rate of 100 mL min^{-1} through the sonicated liquid for 30 min before sonolysis and during sonolysis.

The concentration of HNO_2 in samples taken from the sonicated solution was determined spectrophotometrically by the Griess method[7] (ε = 42500 L cm^{-1} mol^{-1}, λ = 530 nm). The hydrazine concentration was found using the reaction with 4-(dimethylamino)benzaldehyde[7] (ε = 52600 L cm^{-1} mol^{-1}, λ = 458 nm).

The reaction rates were calculated from the initial portions of the kinetic curves of HNO_2 accumulation or hydrazine decomposition. The statistical error of determination of the reaction rate found from three parallel measurements was at most 15%.

Results and Discussion

N_2O bubbling in water or in solutions of HNO_3 did not result in the formation of HNO_2, and HNO_2 was accumulated only under the action of ultrasound. The maximum rate of HNO_2 formation is achieved at a volume ratio of Ar : N_2O equal to 85 : 15 (Fig. 1), whereas at an ultrasound frequency of 300 kHz this ratio is[4] 70 : 30. Thus, a decrease in the ultrasound frequency decreases the N_2O concentration in the gas phase corresponding to the maximum rate of HNO_2 formation.

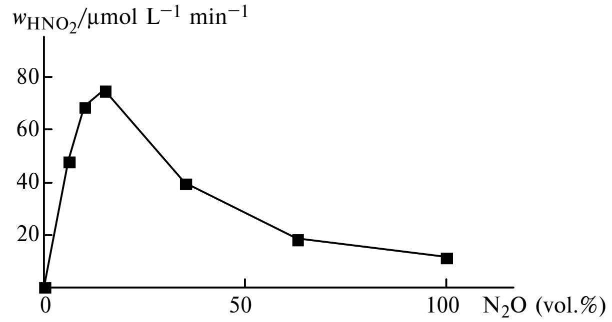

Fig. 1. The plot of the rate of HNO_2 formation *vs.* composition of an N_2O—Ar mixture during sonolysis in water.

Analysis of the rates of HNO_2 formation during sonolysis of solutions of HNO_3 and $NaNO_3$ in the

Table 1. The influence of the composition of the solution and gas phase on the rate of sonochemical formation of HNO_2 in Ar (w_{Ar}) and in an N_2O (15%)—Ar mixture (w_{N_2O}) and the value of synergetic effect (S)

Solution	C /mol L^{-1}	w_{N_2O}	w_{Ar}	S
		μmol L^{-1} min^{-1}		
H_2O	—	78.3	—	—
HNO_3	1	79.1	5.4	0.95
HNO_3	4	360	26.7	3.4
$NaNO_3$	1	77.4	2.5	0.96
$NaNO_3$	4	79.5	9.2	0.91
HNO_3*	4	334	31.0	3.0

* The rate of hydrazine sonolysis; the calculation of the overall rate of HNO_2 formation Σw = (w_{Ar} + w_{N_2O}) gave 113 μmol L^{-1} min^{-1}.

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presence of Ar or an N_2O (15%)—Ar gaseous mixture (Table 1) allows us to conclude the following.

a. In an Ar atmosphere the rate of HNO_2 formation increases when the concentration of HNO_3 or $NaNO_3$ increases. When the concentrations of HNO_3 and $NaNO_3$ are the same, the reaction rate is higher in solutions of nitric acid.

b. In the presence of N_2O in 4 *M* HNO_3, the overall reaction rate (Σw) considerably exceeds the sum of the rates of HNO_2 formation during sonolysis of HNO_3 in Ar (w_{Ar}) or in an N_2O (15%)—Ar mixture in water (w_{N2O}). The value of synergetic effect (S) can be found using the following equation:

$$S = \Sigma w/(w_{Ar} + w_{N_2O}). \qquad (1)$$

It follows from Table 1 that the synergetic effect appears only at a sufficiently high concentration of HNO_3 and is absent from solutions of $NaNO_3$.

The synergetic effect also appears in the sonochemical decomposition of hydrazine in 4 *M* HNO_3. It is known[8] that the sonolysis of N_2H_4 in a nitrate medium in an Ar atmosphere is determined by the sonochemical formation of HNO_2 in an HNO_3 solution. The reaction rate has the zero order with respect to hydrazine and is approximately equal to the rate of sonochemical formation of HNO_2, which corresponds to the following scheme of the process:

$$HNO_3 \text{—)))}\ HNO_2 \text{ (rate-determining step)}, \qquad (2)$$

$$HNO_2 + N_2H_5^+ \longrightarrow \text{Products (fast process)}, \qquad (3)$$

where symbol "—)))" designates the sonochemical step.

The study of the kinetics of N_2H_4 sonolysis in an Ar atmosphere and in an N_2O (15%)—Ar mixture (Fig. 2, Table 1) showed that the reaction rate in the presence of both an N_2O (15%)—Ar mixture and pure Ar had the zero order with respect to hydrazine, and the rate of N_2H_4 sonolysis was close to the rate of HNO_2 formation under similar experimental conditions. In the presence of an N_2O (15%)—Ar mixture, N_2H_4 sonolysis is considerably accelerated as compared to that in pure Ar. The value of synergetic effect for N_2H_4 in 4 *M* HNO_3 is close to that for HNO_2. Thus, the observed specific features of the sonochemical oxidation of hydrazine are determined by the synergetic effect of the sonochemical formation of HNO_2.

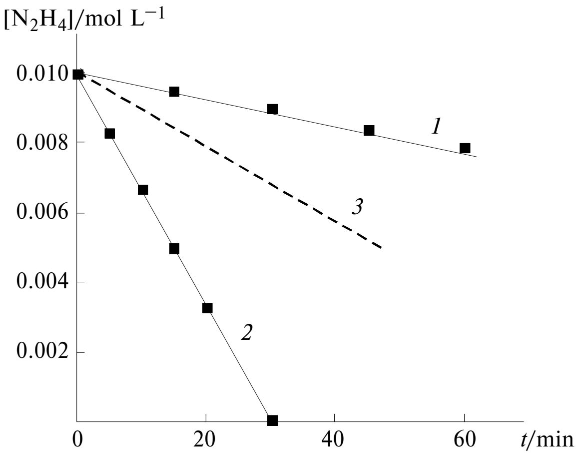

Fig. 2. Kinetic curves of hydrazine sonolysis in 4 *M* HNO_3: *1*, Ar; *2*, N_2O (15%)—Ar; and *3*, calculated curve obtained using the equation $\Sigma w = (w_{Ar} + w_{N_2O})$.

It can be assumed that the nature of the considered effect is related to the interaction of the sonolysis products N_2O and HNO_3, which increase the yield of HNO_2. It is known[2] that the sonolysis of nitric acid occurs mainly *via* a mechanism including the decomposition of the HNO_3 molecules inside the cavitation bubble and the NO_3^- ions in the liquid around the bubble. The formation of HNO_2 is accompanied by the evolution of NO and NO_2 into the gas phase, and the yield of NO is higher than those of HNO_2 and NO_2.[2] Thus, a considerable portion of the sonolysis products of HNO_3 leaves the reaction sphere and does not participate in the formation of HNO_2. Nitrous acid can also be formed *via* the mechanism of indirect ultrasonic action, which includes the interaction of the $OH^{\bullet}$ radicals with the NO_3^- ions followed by the hydrolysis of the $NO_3^{\bullet}$ radicals

$$H_2O \text{—)))}\ H^{\bullet} + OH^{\bullet}, \qquad (4)$$

$$OH^{\bullet} + HNO_3 \longrightarrow NO_3^{\bullet} + H_2O, \qquad (5)$$

$$NO_3^{\bullet} + H_2O \longrightarrow NO_2 + H_2O_2, \qquad (6)$$

$$2\ NO_2 + H_2O \longrightarrow HNO_2 + HNO_3. \qquad (7)$$

However, the contribution of this mechanism to the overall process is negligible. The formation rate of the $OH^{\bullet}$ radicals and, hence, the reaction rate (5) can be estimated using the data on the kinetics of sonochemical formation of H_2O_2. According to the previous results,[5] the rate of H_2O_2 formation during water sonolysis in an argon atmosphere, under experimental conditions similar to our experimental conditions, amounts to 3 μmol L^{-1} min^{-1}, which is ~10-fold lower than the rate of HNO_2 formation by sonolysis of 4 *M* HNO_3 (see Table 1).

It is known[4] that HNO_2 is not the main product of N_2O sonolysis:

$$N_2O \text{—)))}\ N_2 + O^{\bullet\bullet}, \qquad (8)$$

$$2\ O^{\bullet\bullet} \longrightarrow O_2, \qquad (9)$$

$$O^{\bullet\bullet} + N_2O \longrightarrow N_2 + O_2, \qquad (10)$$

$$O^{\bullet\bullet} + N_2O \longrightarrow 2\ NO, \qquad (11)$$

$$NO \longrightarrow HNO_2 \text{ (secondary processes in solution)}. \qquad (12)$$

The main portion of N_2O decomposes inside the cavitation bubble to form N_2 and O_2 because the reaction rates (9) and (10) exceed considerably the rates of processes (11) and (12).

The fast reaction between NO and $O^{\cdot\cdot}$ becomes possible under the combined sonolysis of HNO_3 and N_2O:

$$NO + O^{\cdot\cdot} \longrightarrow NO_2. \quad (13)$$

The hydrolysis of NO_2 results in the formation of HNO_2 (reaction (7)). Thus, the combined sonolysis provides an additional efficient channel of HNO_2 synthesis, which results in the synergetic effect. In dilute solutions of HNO_3 and in solutions of $NaNO_3$, the synergetic effect is not observed because the volatile molecular form of HNO_3 is virtually absent from these solutions. Therefore, the formation of HNO_2 proceeds only due to the decomposition of the NO_3^- ions in the solution layer surrounding the cavitation bubble:

$$NO_3^- \text{—)))}\ NO_2^- + 0.5\ O_2. \quad (14)$$

In this case, NO and NO_2 are virtually not formed, and reaction (13) becomes improbable. For the same reason, the rate of sonochemical formation of HNO_2 in solutions of 4 *M* HNO_3 is much higher than the reaction rate in solutions of 4 *M* $NaNO_3$.

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