

## THE CATALYTIC EFFECT OF CATIONS ON THE DECOMPOSITION OF ALKALINE SOLUTIONS OF HYDROXYLAMINE

S. LUŇÁK and J. VEPŘEK-ŠIŠKA

*Institute of Inorganic Chemistry,  
Czechoslovak Academy of Sciences, 160 00 Prague 6*

Received December 29th, 1972

The decomposition of hydroxylamine in an alkaline medium is a first order reaction with respect to the concentration of hydroxylamine and a third order reaction with respect to the concentration of hydroxyl ions. The decomposition is speeded up by various cations, most markedly by ferrous salts. The catalysing ions strongly affect the proportion of nitrogen and dinitrogen monoxide in the reaction product. The probable intermediates of the decomposition are nitrosohydroxylamine complexes of the catalysing cations.

The decomposition products of hydroxylamine in an alkaline medium are ammonia, nitrogen, dinitrogen monoxide and hyponitrite. The reaction was assumed<sup>1-3</sup> to proceed *via* the nitroxyl biradical (HNO) as intermediate. The presence of nitroxyl in the reaction mixture was considered proved<sup>3</sup> by the appearance of the violet tricyanonitrosnickelate(II) on the addition of tetracyanonickelate(II) to the reaction mixture. We have shown<sup>4</sup>, however, that a probable intermediate in the formation of tricyanonitrosnickelate is not nitroxyl, but a tricyanohydroxylammonickelous complex, resulting from replacement of a cyanide group in tetracyanonickelate by a molecule of hydroxylamine.

The present paper deals with the controversy of the reported data on the decomposition of hydroxylamine, including the problem of the reaction intermediates.

### EXPERIMENTAL

#### Chemicals

All the chemicals employed were of A. R. grade. Hydroxylamine hydrochloride was twice recrystallized before use. Some experiments were performed with potassium hydroxide purified by zonal refining<sup>5</sup>; by this treatment the concentrations of cations that might catalyse the decomposition ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ) were reduced to about a hundredth of those usually present in A. R. potassium hydroxide (Lachema, Brno).

#### Methods and Procedure

Hydroxylamine was determined by titration according to Bhaskara-Rao<sup>6</sup>. Decomposition of hydroxylamine in the withdrawn samples was discontinued by bringing them to pH 2 with hydrochloric acid. Nitrogen and dinitrogen monoxide were determined by gas chromatography<sup>4</sup>.

## RESULTS AND DISCUSSION

*Catalytic Effect of Cations on the Reaction Rate*

Since the decomposition rate of hydroxylamine proved to be dependent on purity of the chemicals we first investigated the effects of equal molar additions of different cations on the quantity of the hydroxylamine decomposed. According to the force of their catalytic effect the cations form the order  $\text{Fe(II)} > \text{Ni(II)} > \text{Cu(II)} > \text{Co(II)} > \text{Ag(I)} > \text{Zn(II)} > 0$ . The catalysis is especially marked in neutral or mildly alkaline solutions, where in the absence of a catalyst the decomposition practically does not occur. In the presence of the catalysing cations there were formed hydroxylamine complexes of characteristic colours. The catalytic activity of the cations decreased with the advancing decomposition and precipitates separated in the case of cations of  $\text{Fe(II)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(I,II)}$ .  $\text{Ag}^{\dagger}$  ions were immediately reduced to  $\text{Ag}$ .

*Stoichiometry of the Reaction*

The decomposition of hydroxylamine gives rise to nitrogen, ammonia, dinitrogen monoxide and hyponitrite. Proportion of the products depends not only on alkalinity of the medium and concentration of hydroxylamine, but also on concentration of the catalysing cations.

In the first place we investigated the effect of concentrations of  $\text{KOH}$  and the catalysing cations on the composition of the gaseous mixture produced by the decomposition of hydroxylamine, *i.e.* the ratio  $c_{\text{N}_2}/c_{\text{N}_2\text{O}}$ . This ratio had a least value at  $\text{pH } 7.1$ , when at  $[\text{NH}_2\text{OH}] = 2.2\text{M}$ ,  $[\text{Fe}^{2+}] = 1 \cdot 10^{-4}\text{M}$  and  $t = 95^\circ\text{C}$  dinitrogen monoxide was the predominant product ( $c_{\text{N}_2}/c_{\text{N}_2\text{O}} = 0.6$ ). The portion of nitrogen was the greater the more was the  $\text{pH}$  value remote from  $7.1$ , no matter to which side.

An addition of  $\text{Fe(II)}$ ,  $\text{Co(II)}$  and  $\text{Cu(II)}$  invariably reduced the ratio  $c_{\text{N}_2}/c_{\text{N}_2\text{O}}$ . This effect of the catalysing cations was observed even in strongly alkaline media. For if the zone-refined  $\text{KOH}$  was employed instead of a commercial A.R. chemical the ratio  $c_{\text{N}_2}/c_{\text{N}_2\text{O}}$  considerably increased. Thus at  $[\text{NH}_2\text{OH}]_0 = 2.2\text{M}$ ,  $[\text{KOH}] = 3\text{M}$  and  $t = 25^\circ\text{C}$ , the ratios for the  $\text{KOH}$  (A.R.) and for the zone hydroxide were approximately 3 and 7, respectively.

In further experiments we investigated how the ratio  $c_{\text{N}_2}/c_{\text{N}_2\text{O}}$  was related to the concentration of hydroxylamine. In strongly alkaline media ( $[\text{KOH}] > 1\text{M}$ ) the ratio  $c_{\text{N}_2}/c_{\text{N}_2\text{O}}$  decreased with the advancing decomposition. In neutral or mildly alkaline solutions the ratio first increased, then, towards the end of the reaction, it decreased. This decrease was probably due to decomposition of hyponitrite, accumulated in the course of the reaction.

## Kinetics

We investigated the change of hydroxylamine concentration with time for  $[\text{OH}^-] = 1$  to  $3\text{M}$  (Fig. 1). The rate of the decomposition was found directly proportional ( $k'$ ) to the instant concentration of hydroxylamine,  $-\text{d}[\text{NH}_2\text{OH}]/\text{dt} = k'[\text{NH}_2\text{OH}]$ , so that the decomposition of hydroxylamine is a first-order reaction.

Fig. 1 shows that the slopes of the straight lines ( $k'$ ) increase with increasing concentration of KOH, and in strongly alkaline media (Fig. 2) it applies that  $k' = k[\text{OH}^-]^3$ . Consequently, the decomposition rate of hydroxylamine in an alkaline solution can be described by the equation

$$-\text{d}[\text{NH}_2\text{OH}]/\text{dt} = k \cdot [\text{OH}^-]^3 \cdot [\text{NH}_2\text{OH}], \quad (1)$$

where  $k$  (for the given purity of hydroxylamine and for the KOH (A.R.) from Lachema, Brno) at  $20^\circ\text{C}$  was  $7 \cdot 10^{-6} \text{ mol}^{-3}\text{s}^{-1}$ .

## Reaction Mechanism

The decomposition of hydroxylamine has been described by a number of mechanisms. Most of them are based on the postulated intermediary formation of nitroxyl.

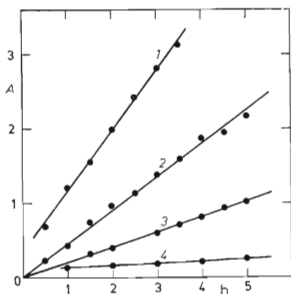


FIG. 1

## The Kinetics of the Reaction

The plot of  $A = 2.303 \log [\text{NH}_2\text{OH}]_0 / [\text{NH}_2\text{OH}]$  vs time.  $[\text{NH}_2\text{OH}]_0 = 2.79\text{M}$ ;  $20^\circ\text{C}$ ; 1  $[\text{OH}^-] = 3.21\text{M}$  2  $[\text{OH}^-] = 2.61\text{M}$  3  $[\text{OH}^-] = 2.01\text{M}$  4  $[\text{OH}^-] = 0.81\text{M}$ .

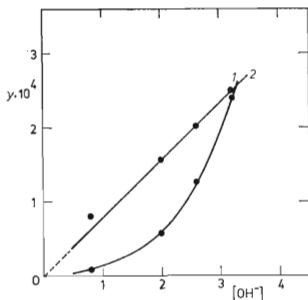


FIG. 2

The Rate Constant,  $k'$  ( $\text{s}^{-1}$ ), as Function of  $[\text{OH}^-]$ 

The values of  $k'$  were calculated from the slopes of the straight lines 1 to 4 in Fig. 1. 1  $y = k'$ ; 2  $y = 2.5 \cdot 10^{-2} \cdot \sqrt[3]{k'}$ .

Under this assumption Nast<sup>3,7</sup> advanced a reaction scheme according to which the decomposition of hydroxylamine is controlled by disproportionation of hydroxylamine to ammonia and nitroxyl. Nitrogen is supposed to arise from the reaction of nitroxyl with hydroxylamine, hyponitrite from dimerization of nitroxyl, and dinitrogen monoxide from decomposition of the hyponitrite. This mechanism can be objected to on the basis of the following facts, ascertained by ourselves: 1) Dinitrogen monoxide was formed even in the decomposition of hydroxylamine in strongly alkaline media, where hyponitrite is known to be rather stable<sup>8,9</sup>, and the decomposition rate of the hyponitrite was much lower than the formation rate of dinitrogen monoxide. Consequently, the development of N<sub>2</sub>O cannot be ascribed to decomposition of potassium hyponitrite. This fact has already been pointed out by Hughes and Nicklin<sup>10</sup>, who studied oxidation of hydroxylamine by oxygen and also supposed the formation of nitroxyl as an intermediate. To solve the discrepancy they have introduced the assumption that dimerization of nitroxyl produces not only the normal hyponitrite, which they refer to as "trans-hyponitrite", but also "cis-hyponitrite", decomposing immediately even in strongly alkaline media. As "cis-hyponitrite" they denoted<sup>10,11</sup> the reaction product of NO with a solution of sodium in liquid ammonia. This product decomposes immediately on dissolution, even in strongly alkaline media, with the formation of dinitrogen monoxide. 2) With increasing alkalinity the decomposition rate increases ( $v = k[\text{OH}^-]^3 [\text{NH}_2\text{OH}]$ ), and so does the portion of nitrogen in the reaction product. According to the mechanism postulating the intermediary nitroxyl the very opposite should be the case: with the increasing decomposition rate the concentration of nitroxyl should also increase, and so should the quantity of its dimer, with the consequential increase in the portion of N<sub>2</sub>O in the reaction product. Nast's interpretation of this variance (by the higher stability of hyponitrite with increasing alkalinity) cannot be accepted since it has been shown (point 1) that if the nitroxyl mechanism were correct the major portion of N<sub>2</sub>O should be formed, in alkaline solutions, by decomposition of "cis-hyponitrite", which, however, is rapid and complete and could not be retarded by an increase in alkalinity. 3) The nitroxyl mechanism does not involve, and consequently does not explain, the catalytic effect of cations on the decomposition of hydroxylamine. However, the presence of the catalysing cations seems to be a prerequisite for the decomposition to occur. We have demonstrated<sup>4</sup> that even the addition of a small amount of tetracyanonickelate (complexing the catalysing cations) reduces the decomposition rate to less than a thousandth. Hence it can be concluded that in the absolute absence of catalysing cations the decomposition would, most probably, not occur at all. 4) The formation of the violet tricyanonitrososnickelate on the addition of tetracyanonickelate to the reaction mixture cannot be regarded as proving the intermediary formation of nitroxyl<sup>4</sup>, in contrast to what was believed.

Holzapfel<sup>12</sup> considered that decomposition of hydroxylamine might proceed *via* the hypothetical intermediates HO—NH—OH and HO—NH—NH—OH, but there

is no evidence substantiating this view. Like the nitroxyl mechanism, Holzapfel's reaction scheme fails to explain the catalytic effects of cations in the decomposition of hydroxylamine, or the inhibitory effect of tetracyanonickelate. Besides, Holzapfel assumes that dinitrogen monoxide is generated by decomposition of hyponitrous acid (hyponitrite), which possibility has been discussed above (point 1).

The ascertained catalytic activity of some cations and the fact that hydroxylamine forms strong complexes with the catalysing cations<sup>13-15</sup>, decomposing in water<sup>16</sup>, suggest the idea that the decomposition intermediates are hydroxylamine complexes with the catalysing cations. These would decompose to a nitrosyl complex, whose subsequent reaction depends on the alkalinity of the medium: either it reacts with hydroxylamine and nitrogen evolves, or two nitrosyl ligands (on one central atom or on two central atoms) produce hyponitrite and dinitrogen monoxide. A more detailed description of the mechanism would require kinetic data on the decomposition of hydroxylamine complexes in alkaline solutions and on the reactions of the nitrosyl complexes with hydroxylamine. These reactions have been given little attention and their kinetics have not yet been studied.

## REFERENCES

1. Kurtenacker A., Werner F.: *Z. Anorg. Chem.* **160**, 389 (1927).
2. Oesterheld G.: *Z. Anorg. Allgem. Chem.* **131**, 86 (1944).
3. Nast R., Föppel J.: *Z. Anorg. Allgem. Chem.* **263**, 310 (1950).
4. Vepřek-Šiška J., Luňák S.: *This Journal*, in press.
5. Eckschlager K., Vepřek-Šiška J.: *This Journal* **36**, 2436 (1969).
6. Bhaskara-Rao K.: *Chemist Analyst* **49**, 40 (1960).
7. Nast R., Proeschel E.: *Z. Anorg. Chem.* **256**, 159 (1948).
8. Hughes M. N., Stedman G.: *J. Chem. Soc.* **1963**, 2824.
9. Hughes M. N.: *Quart. Rev.* **22**, 1 (1968).
10. Hughes M. N., Nicklin H. G.: *J. Chem. Soc. A* **1970**, 925.
11. Gee N., Nichols D., Vincent V.: *J. Chem. Soc.* **1964**, 5897.
12. Holzapfel H.: *Wiss. Z. Karl Marx Univ., Leipzig, Math. Naturwiss. Reihe* **9**, 17 (1960).
13. Szilard J.: *Acta Chem. Scand.* **17**, 2674 (1961).
14. Bhat T. R., Radhama D., Shankar J.: *J. Inorg. Nucl. Chem.* **27**, 2641 (1965).
15. Falgui M. T., Ponticelli G., Sotgin F.: *Ann. Chim. (Roma)* **56**, 464 (1966).
16. Yoneda H.: *Bull. Chem. Soc. Japan* **30**, 132 (1957).

Translated by J. Salák.