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LIQUID-PHASE OXIDATION OF HYDROXYLAMINE WITH ULTRASONIC IRRADIATION

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The sonochemical oxidation of hydroxylamine in alkaline aqueous, aqueous-methanol and methanol solutions yielded peroxonitrite ion as a main product. A little nitrite and nitrate were also formed. The oxidation yield increased with methanol concentration in the solution. The mechanism of oxidation both in aqueous solution and in the presence of alcohol is discussed.

Badano sonochemiczne utlenianie hydroksylaminy w alkalicznym roztworze wodnym oraz w roztworach wodno-metanolowych. Głównym produktem utleniania był jon ONO_2^- oraz niewielkie ilości azotynów i azotanów. Stwierdzono, że wydajność utleniania wzrasta ze wzrostem stężenia metanolu w roztworze. Przedyskutowano mechanizm utleniania w roztworze wodnym oraz w obecności metanolu.

1. Introduction

The raction of hydroxylamine with various oxidizing agents has been a subject of many papers. HUGHES and NICKLIN [1] studied oxidation of hydroxylamine in alkaline solutions by saturations with gaseous oxygen. The oxidation products were peroxonitrite, nitrite and nitrate. The reaction was catalyzed by traces of Cu (II), Co (II) and Fe (II) unavoidably introduced with the reagents. On the other hand, BUTLER and GORDON [2] found that the oxidation of hydroxylamine by iron (III) yielded nitrous oxide.

The aim of this paper is investigation of the sonochemical oxidation of hydroxylamine in both aquoeus and aqueous-methanol solutions.

2. Experimental

Instruments

Sonochemical investigations were carried out by using a „Techpan" UDM-10 ultrasonic desintegrator of the following parameters: working frequency 22 ± 1.65 kHz, maximum output power 180 W. The spectrophotometrical measurements were performed on a C. Zeiss Jena „Specord UV-VIS" spectrometer.

Reagents

All chemicals (analytical grade purity hydroxylamine, hydrochloride, NaOH, $CuSO_4 \cdot 5H_2O$) were used without further purification. The solutions were prepared using twice distilled water or methanol pure for spectroscopy. EDTA solutions were prepared by dissolving a weighted amount of disodium salt of ethylenediaminetetraacetic acid.

Procedures

The $NH_2OH.HCL$ solutions of the concentration of 0.01 mole/dm^3 (40 ml) containing 0–1 mole/dm^3 of NaOH were irradiated with ultrasound by using a Ti tip immersed into the solution. Samples were taken at intervals and analyzed for the different products. The concentration of peroxonitrite was estimated from the absorbance at 302 nm, molar absorptivity being 1670 cm^{-1} mole^{-1} dm^3 [3]. Other oxidation products, nitrate and H_2O_2 also absorb in this range but with negligible intensity (molar absorptivities = 7 and 40, respectively).

Nitrate was determined by the UV spectrometric method [4]. Nitrite was determined by the standard colorimetric method involving diazotization of sulfanilic acid and coupling with α-naphthylamine.

3. Results and discussion

In both aqueous and methanol solutions sonochemical oxidation produces peroxonitrite as a main initial product, similary as in the case of O_2 oxidation (Fig. 1 and 2). Also, small amounts of NO_2^- and NO_3^- are formed (Table 1). The concentration of peroxonitrite increases almost linearly with time. The peroxonitrite yield increases

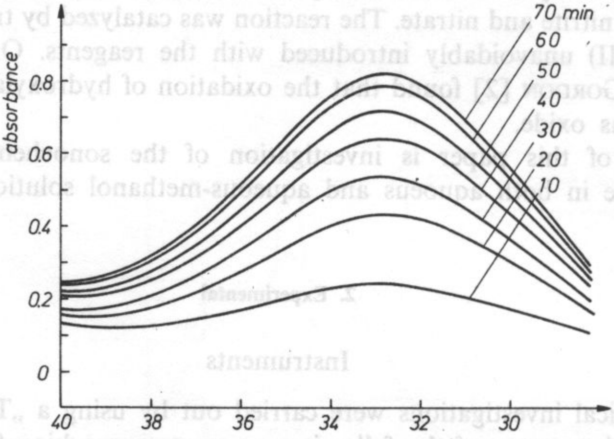

Fig. 1. Electronic spectra of 0.01 mole/dm^3 aqueous hydroxylamine solutions containing 0.5 mole/dm^3 NaOH after sonification for different time. The optical path 1 cm

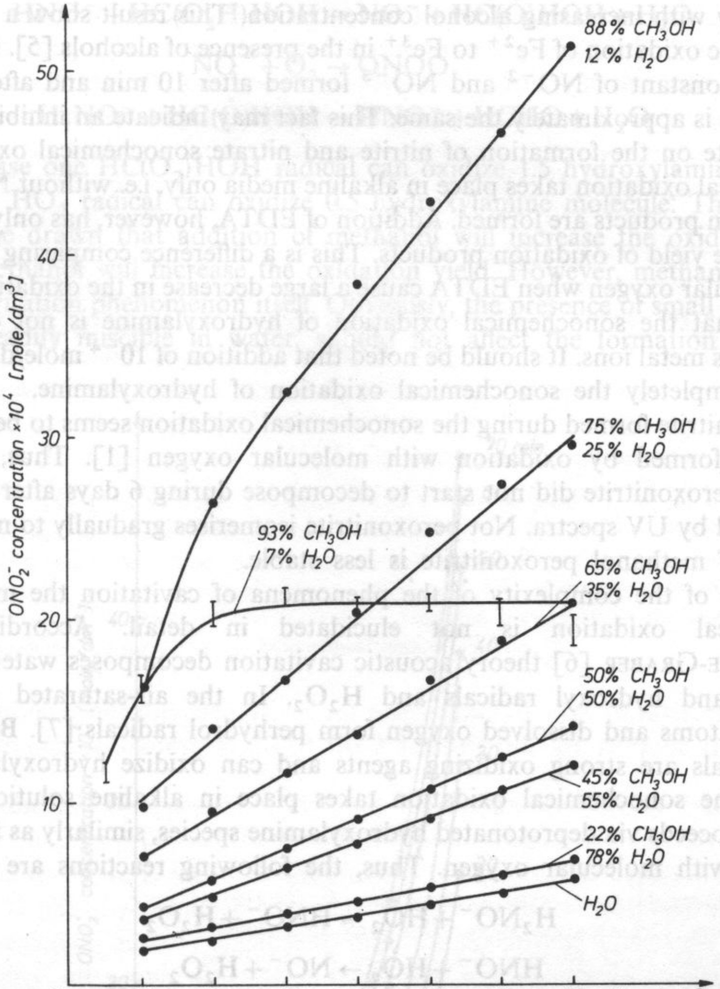

Fig. 2. The sonochemical oxidation of 0.01 mole/dm³ hydroxylamine containing 0.5 mole/dm³ NaOH in aqueous and aqueous-methanol solutions (in vol. %).

Table 1. Products of sonochemical oxidation of 40 ml of 0.01 mole/dm³ aqueous, aqueous-methanol and methanol hydroxylamine solution with 0.5 mole/dm³ NaOH added after 70 min. of sonification

vol. % H_2O / vol. % CH_3OH	100 / —	78 / 22	55 / 45	35 / 65	12 / 88	7 / 93
$ONO_2^- \times 10^4$ mol/dm³	5.9	6.7	12.0	20.4	49.0	20.0
$NO_3^- \times 10^4$ mol/dm³	1.5	1.2	1.8	2.0	5.5	0.6
$NO_2^- \times 10^5$ mol/dm³	2.0	2.0	3.0	3.5	5.0	7.0

significantly with increasing alcohol concentration. This result show a resemblance to ultrasonic oxidation of Fe^{2+} to Fe^{3+} in the presence of alcohols [5]. On the other hand, the constant of NO^{-2} and NO^{-3} formed after 10 min and after 70 min of sonification is approximately the same. This fact may indicate an inhibiting affect of peroxonitrite on the formation of nitrite and nitrate sonochemical oxidation. The sonochemical oxidation takes place in alkaline media only, i.e. without NaOH added no oxidation products are formed. Addition of EDTA, however, has only a negligible effect on the yield of oxidation products. This is a difference comparing to oxidation with molecular oxygen when EDTA cause a large decrease in the oxidation rate. This indicates that the sonochemical oxidation of hydroxylamine is not catalysed by adventitious metal ions. It should be noted that addition of 10^{-4} mole/dm^3 of Cu (II) inhibits completely the sonochemical oxidation of hydroxylamine.

Peroxonitrite formed during the sonochemical oxidation seems to be more stable than that formed by oxidation with molecular oxygen [1]. Thus, in aquaeus solutions peroxonitrite did not start to decompose during 6 days after sonification, as indicated by UV spectra. Not peroxonitrite isomerises gradually to nitrate. In the presence of methanol peroxonitrite is less stable.

In view of the complexity of the phenomena of cavitation the mechanism of sonochemical oxidation is not elucidated in detail. According to the PRUDHOMME-GRABER [6] theory acoustic cavitation decomposes water to produce hydrogen and hydroxyl radicals and H_2O_2. In the air-saturated solution the hydrogen atoms and dissolved oxygen form perhydrol radicals [7]. Both $\cdot OH$ and $H\dot{O}_2$ radicals are strong oxidizing agents and can oxidize hydroxylamine.

Since the sonochemical oxidation takes place in alkaline solutions only the reaction proceeds via deprotonated hydroxylamine species, similarly as in the case of oxidation with molecular oxygen. Thus, the following reactions are suggested:

$$H_2NO^- + H\dot{O}_2 \rightarrow HNO^- + H_2O_2$$

$$HNO^- + H\dot{O}_2 \rightarrow NO^- + H_2O_2$$

$$NO^- + \dot{O}_2 \rightarrow ONOO^-$$

A large increase of the oxidation yield in the presence of methanol is not unexpected because the alcohol scavanges the radicals $H\dot{O}_2$ and $\cdot OH$ to produce $R\dot{C}HOH$ [5, 8] which further reacts with O_2 to give $Rc(\dot{O}_2)HOH$. These organic peroxide radicals of strong oxidizing properties are formed during both γ-rays and sonochemical irradiation. The mechanism proposed for both radiation and ultrasonic studies [5] can be applied to sonochemical oxidation of hydroxylamine and is represented by the following reactions:

$$2HCH_2OH \xrightarrow{\cdot OH,\ H\dot{O}_2} 2H\dot{C}HOH + H_2O + H_2O_2$$

$$H\dot{C}HOH \xrightarrow{O_2} HC(\dot{O}_2)HOH$$

$$H_2NO^- + HC(\dot{O}_2)HOH \rightarrow HNO^- + HC(O_2H)HOH$$

$$HNO^- + HC(O_2H)HOH \rightarrow NO^- + HC(\dot{O})HOH + H_2O$$

$$NO^- + O_2 \rightarrow ONOO^-$$

$$H_2NO^- + HC(\dot{O})HOH \rightarrow HNO^- + HCHO + H_2O$$

In this case one $HC(O_2)HOH$ radical can oxidize 1.5 hydroxylamine molecule whereas one HO_2 radical can oxidize 0.5 hydroxylamine molecule. Thus, a conclusion can be drawn that addition of methanol will increase the oxidation yield. However, methanol will increase the oxidation yield. However, methanol can also affect the cavitation phenomenon itself. Obviously, the presence of small amounts of methanol, readily miscible in water, should not affect the formation of cavities

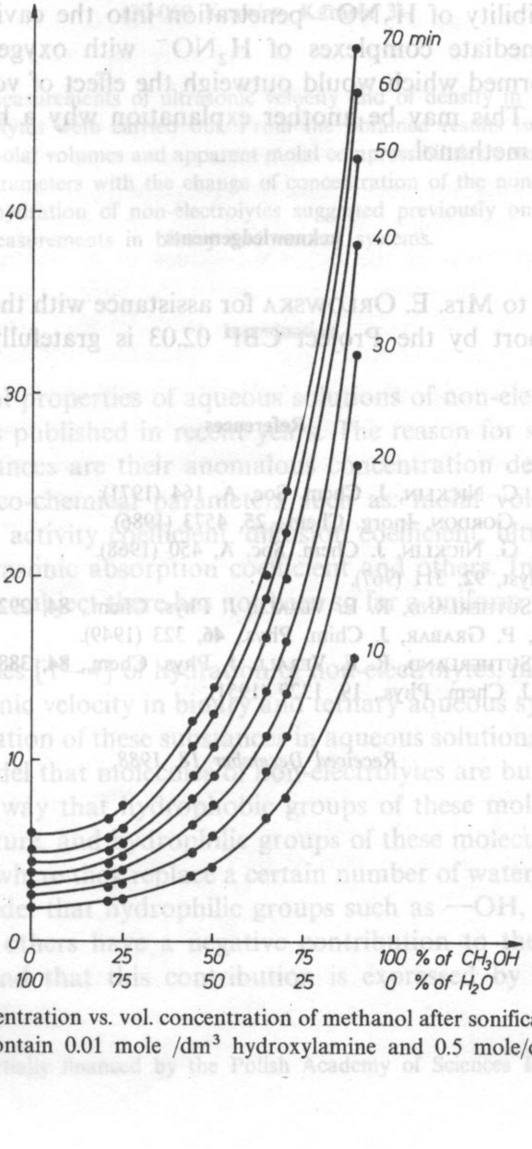

Fig. 3. Plot of ONO_2^- concentration vs. vol. concentration of methanol after sonification for different time. The solutions contain 0.01 mole /dm^3 hydroxylamine and 0.5 mole/dm^3 NaOH

significantly. However, as Seghal et al [5] pointed out, at higher concentrations because of its high vapor pressure alcohol can preferentially penetrate into the cavities and suppress cavitation. The authors anticipated, therefore, that in the case of Fe^{2+} sonochemical oxidation at higher alcohol concentrations the cavitational effect would overpower the chemical effects and thereby reduce the oxidation of Fe^{2+} (their experimental studies finished at concentration of 20% of alcohol in water). In the case of hydroxylamine oxidation, however, no levelling of the $ONOO^-$ concentration vs. alcohol concentration is observed (Fig. 3) even in 88% CH_3OH. The sonochemical oxidation rate increases throughout the whole concentration range of methanol. This may be explained probably by the fact that the reaction occurs in three different phases, i.e. in the gaseous phase (the cavities), the interphase that separates the cavity from the surrounding medium and the liquid medium. The possibility of H_2NO^- penetration into the cavities is not excluded. Thus, some intermediate complexes of H_2NO^- with oxygen of relatively high pressure may be formed which would outweigh the effect of volatile alcohol on the cavitation process. This may be another explanation why a high reaction yield is preserved even in methanol.

Acknowledgements

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References

[1] M. N. Hughes, H. C. Nicklin, J. Chem. Soc. A, 164 (1971).
[2] J. H. Butler, L. I. Gordon, Inorg. Chem., **25**, 4573 (1986).
[3] M. N. Hughes, H. G. Nicklin, J. Chem. Soc. A, 450 (1968).
[4] P. A. Cawse, Analyst, **92**, 311 (967).
[5] C. Seghal, R. G. Sutherland, R. E. Verall, J. Phys. Chem., **84**, 2920 (1980).
[6] R. O. Prudhomme, P. Grabar, J. Chim. Phys., **46**, 323 (1949).
[7] C. Seghal, R. G. Sutherland, R. E. Verall, J. Phys. Chem., **84**, 388 (1980).
[8] A. H. Dewhurst, J. Chem. Phys., 19, 1329 (1951).

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