## Effect of Base Nature on the Oxidation of Dimethyl Sulfoxide with Hydrogen Peroxide in Superbasic Media

A. F. Choban, I. R. Yurchuk, and A. S. Lyavinets

Fedkovych Chernovitskii National University, ul. Kotsubinskogo 2, Chernovtsy, 58012 Ukraine e-mail: o.liavinets.@chnu.edu.cv.ua

Received November 8, 2010

**Abstract**—Kinetic relationships of the dimethyl sulfoxide oxidation to dimethyl sulfone with hydrogen peroxide in the presence of an alkali (MOH) or sodium *tert*-butoxide were investigated. Kinetic parameters of the process were calculated. The process was found to proceed through the intermediate formation of the alkaline salts MeOOH. The effect of the base nature on the stage of salt formation and oxidation was revealed.

DOI: 10.1134/S1070363212020144

Dimethyl sulfoxide (DMSO) is well known as a compound possessing reducing properties. In particular, it is oxidized in benzene, chloroform, acetic acid, dichloroethane, and ether solutions by peracids, ozone, and hydrogen peroxide. Reducing properties of DMSO form a ground for the industrial methods of dimethylsulfone production. In the industry, dimethylsulfone is produced by oxidation of DMSO in two ways: with ozone in chloroform or with hydrogen peroxide at boiling. However, both methods have drawbacks. Thus, at the treatment with ozone it should be taken into account the negative impact of unreacted oxidant on the environment and the toxicity of chloroform. At the oxidation with hydrogen peroxide at boiling it should be accounted for the corresponding energy consumption, as well as the ability of DMSO to inflammation.

Therefore the search for the new ways of the DMSO oxidation is continuing. In particular, recently the methods were developed of biological oxidation of DMSO [1], oxidation with hydrogen peroxide at high pressure [2], the deep degradation with ozone [3], etc. We have shown that DMSO can be oxidized in the superbasic media of the composition: a dipolar hydroxyl-free solvent–a strong ionic base. Superbasic properties of such systems are primarily due to the base ion pair separation followed by the formation of the cation bound to the complex with the solvent molecules, while the anion is almost not solvated, therefore its reactivity grows sharply [4].

We have previously shown that superbasic environment with such a composition can be used for the intensification of the nucleophilic reactions of peroxide compounds. So, using the superbasic medium of the composition hexamethylphosphoramide-alkali could significantly optimize the well-known alkylation reaction of hydroperoxides with haloalkanes: The rate of the process increased, the yield of the products increased, in the reaction less reactive, but more accessible chloroalkanes were used, the apparatuses for performing the synthesis were simplified [5, 6]. Similar results were obtained in the acylation of hydroperoxides [7]. In this connection it was interesting to expand the application of superbasic media to the other reactions of peroxide compounds, in particular, to use them at the oxidation of dimethyl sulfoxide.

Previously it was shown that the introduction of peroxide compounds (hydroperoxides or acylperoxides) in a system of a dipolar nonhydroxylic solvent-strong ionic base at 293–303 K results in the oxidation of DMSO to dimethylsulfone [8–10]. In both cases, this is an ion-chain process, which occurs at a high rate at relatively low temperatures without the side processes involving peroxide compounds, and it is accompanied with the re-conversion of alkali, which makes it preferable economically. Therefore, we suggest that this process can be considered as an alternative to the above-mentioned methods for dimethylsulfone production.



Fig. 1. Dependence of initial rate of the active oxygen consumption on the amount of introduced base. T = 293 K,  $[H_2O_2]_0 = 0.38$  M,  $[DMSO]_0 = 0.38$  M, V(DMF) = 15 ml, (1) KOH, (2) NaOH, (3) t-BuONa, and (4) LiOH.

Since hydrogen peroxide is more widely available reagent than hydroperoxides and acetylperoxides, and complies with "green" chemistry, we used it for the dimethyl sulfoxide oxidation. The kinetics of the DMSO oxidation with hydrogen peroxide in the presence of KOH depending on the nature of the dipolar nonhydroxylic solvet as one of the components of superbasic media was described in [11]. The dipolar nonhydroxylic solvents were shown to affect significantly both the salt formation stage and the oxidation stage, accelerating or inhibiting them. Another component of the superbasic media is a strong ionic base. The purpose of this study was to investigate the effect of the base on the DMSO oxidation with hydrogen peroxide in a superbasic medium. As the medium, we used a system based on dimethylformamide (DMF). This solvent was chosen due to its inertness to the components of the system at 293 K [12] and closeness of its properties to those of DMSO. As in [11], we analyzed only the initial stage of the process, and as an indicator was selected the initial rate of consumption of active oxygen  $(W_0)$ , which was determined by graphic differentiation.

With KOH as a base, the process proceeded according to the first order with respect to both alkali and  $H_2O_2$  (Figs. 1 and 2, curves *I*). As seen from the curves, they are of the type of saturation curve, and the rising parts are linear. The first orders with respect to both KOH and  $H_2O_2$  indicate that the oxidation of DMSO in DMF proceeds through intermediate formation of the peroxide salt, which then oxidizes DMSO:



Fig. 2. Dependence of initial rate of the active oxygen consumption on the initial concentration of  $H_2O_2$ . T = 293 K. The v(base) 9 mmol, V(DMF) 15 ml. (1) KOH, (2) NaOH, (3) *t*-BuONa, and (4) LiOH.

$$KOH + H_2O_2 \rightleftharpoons KOOH + H_2O_2 \qquad (1)$$

$$(CH_3)_2SO + KOOH \rightarrow (CH_3)_2SO_2 + KOH.$$
 (2)

The reaction order with respect to DMSO in DMF-KOH is zero.

Thus, when KOH is used as a base, the oxidation of dimethyl sulfoxide with hydrogen peroxide in DMF is described by the second order kinetic equation:

$$W_0 = k_1 [\text{KOH}] [\text{H}_2\text{O}_2].$$
 (3)

Under these conditions, the limiting stage is the salt formation by reaction (1).

With NaOH, the DMSO oxidation proceeds by first order with respect to the base (Fig. 1, curve 2), and by the second order with respect to hydrogen peroxide (Fig. 2, curve 2). The reaction order on DMSO in this case is also zero. The rate-limiting step now is the dissolution of the salts formed on the surface of alkali:

$$NaOOH + H_2O_2 + n(CH_3)_2SO$$
  

$$\rightarrow Na^+ \cdots nOS (CH_3)_2 + OOH^- \cdots H_2O_2, \qquad (4)$$

where n is the coordination number of the sodium ion.

Thus, the oxidation of DMSO with hydrogen peroxide in DMF–NaOH is described by a kinetic equation of the form:

$$W_0 = k_2[H_2O_2]_2[NaOH].$$
 (5)

Replacement of NaOH by the *t*-BuONa does not change the nature of the kinetic pattern (Figs. 1, 2, curves 3), but the process rate becomes higher. We believe that this is due to better solubility of *t*-BuONa than NaOH in DMF, the higher reactivity of the



**Fig. 3.** Kinetic curves of the active oxygen consumption at the oxidation of DMSO with hydrogen peroxide in the presence of alkali. T = 293 K, v(MeOH) = 2.7 mM,  $[H_2O_2]_0 = 0.38$  M,  $[DMSO]_0 = 0.38$  M, V(DMF) = 15 ml. (1) KOH, (2) NaOH, and (3) LiOH.

sodium alkoxide and, consequently, higher concentrations of the sodium salt NaOOH in the reaction medium:

$$t$$
-BuONa + H<sub>2</sub>O<sub>2</sub>  $\rightleftharpoons$  NaOOH +  $t$ -BuOH. (6)

In the case of NaOH the rate of the DMSO oxidation is lower compared with KOH, which can be attributed to weaker basic properties of NaOH not only in water but also in a dipolar nonhydroxylic solvents. Consequently, the MOOH (M = K, Na, Li) salt which is the actual DMSO oxidant is generated with difficulty. With LiOH we obtained anomalous results: This alkali provides higher rate of DMSO oxidation than NaOH, and the oxidation is deeper than with KOH (see Fig. 3 showing a typical example of comparing the activity of alkalis in the oxidation of DMSO). Therefore we further investigated kinetics of the dimethyl sulfoxide oxidation with hydrogen peroxide in the presence of LiOH at 293 K.

We found that the oxidation process in the DMF– LiOH medium with hydrogen peroxide proceeds by the first order with respect to both LiOH and  $H_2O_2$ (Figs. 1, 2, curves 4) and by zero order with respect to DMSO. Considering these results, we concluded that the DMSO oxidation with hydrogen peroxide in the LiOH–DMF medium also occurs through the intermediate formation of the alkaline salts LiOOH.

Conductometric studies showed that at the use of KOH, NaOH, and *t*-BuONa the process proceeds by ionic pathway. Figure 4 shows the kinetics of the change in the specific conductivity of the MOH– $H_2O_2$ –DMSO–DMF system. We found that the electric conductivity of both the systems, MOH–DMF and



**Fig. 4.** Specific electrical conductivity of the systems MeOH–H<sub>2</sub>O<sub>2</sub>–DMSO–DMF. T = 293 K, v(MeOH) = 2.7 mmol, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.38 mol , [DMSO]<sub>0</sub> = 0.38 M, V (DMF) = 15 ml. (*1*) KOH, (*2*) NaOH, and (*3*) LiOH.

 $H_2O_2$ -DMF, is low. However, it increases substantially at the introduction of hydrogen peroxide in the KOH (NaOH)-DMSO-DMF medium, or at introducing alkali in the medium of  $H_2O_2$ -DMSO-DMF, which is due to the dissociation of the salt:

$$MOOH \rightleftharpoons M^+ OOH^-. \tag{7}$$

Just the appearance of the hydroperoxide anion in the reaction medium causes the DMSO oxidation in the presence of KOH or NaOH:

$$(CH_3)_2SO + OOH^- \rightarrow (CH_3)_2SO_2 + OH^-.$$
 (8)

In turn, the hydroxide anions react to generate new portions of the hydroperoxide anions causing the chain propagation:

$$H_2O_2 + OH^- \rightarrow OOH^- + H_2O.$$
 (9)

These ionic processes are primarily ensured by DMF having a high dipole moment  $[\mu = 3.82 D]$ , dielectric constant [ $\varepsilon = 37.6$ ] and the donor number,  $DN = 111.3 \text{ kJ mol}^{-1}$ . Due to the high dipole moment, a strong dipole interaction between the DMF and the polar solute (in this case MOOH) is provided. Moreover, the electric permittivity of the solvent is such that facilitates the dissociation of dissolved polar substances and the appearance in the reaction medium of the hydroperoxide anions. In addition, DMF has a high donor number. The latter is a quantitative characteristic of the solvent as a donor of electron pairs [13]. Being a strong donor of electron pairs, hence, being a strong specific solvating agent, DMF effectively separates the ion pairs and readily generates the solvent-separated "bare" hydroperoxide anions, which are the actual oxidants of dimethyl sulfoxide.

However, conductometric study shows that in the case of LiOH the introduction of hydrogen peroxide practically does not change electrical conductivity of the reaction medium (Fig. 4, curve 3), that is, the process proceeds by a molecular pathway.

Thus, the nature of alkali affects considerably the DMSO oxidation with hydrogen peroxide.

When KOH or LiOH are used as a base, the limiting step is the formation of the salt MOOH. Therewith, the KOOH salt formed on the alkali crystal surface easily dissociate, due to large atomic radius of the potassium cation. On the contrary, the LiOOH salt is in nondissociated state due to the small atomic radius of lithium cation. In the case of NaOH, the formed NaOOH salt dissociates, but due to the smaller atomic radius of sodium than potassium this process occurs more slowly (or partially). The process of dissolution-dissociation of the salt formed on the surface of the crystal of base becomes the limiting stage. Attention should be paid also to the higher reactivity of LiOH than NaOH in the oxidation of DMSO. We think this is due to the fact that the dissolution of the LiOOH salt proceeds easier due to occurrence of fewer molecules of DMSO in the coordination sphere of Li<sup>+</sup>:

$$LiOOH + HOOH + mS \rightarrow mS...LiOOH...OOH. (10)$$
$$| H$$

Here *m* is the coordination number of lithium ion.

Thus, the nature of the base significantly affects the dimethyl sulfoxide oxidation with hydrogen peroxide in DMF accelerating or decelerating the phase of the salt formation. The alkali used in the oxidation of DMSO with hydrogen peroxide can be arranged by activity: KOH > LiOH > NaOH. Sodium hydroxide is less active in the investigated reaction than sodium *tert*-butoxide. In the case of NaOH or *t*-BuONa the limiting step of the process is the formation of the hydrogen peroxide sodium salt, while with KOH or LiOH the process of DMSO oxidation with the corresponding salt becomes the limiting one. In the presence of KOH, NaOH or *t*-BuONa, the DMSO oxidation proceeds by ionic mechanism, while with LiOH a molecular mechanism is realized.

## **EXPERIMENTAL**

The experiments on the DMSO oxidation with hydrogen peroxide in the presence of bases was carried out in a temperature-controlled cell with a magnetic stirrer at 298 K. The reactor was charged with the required amount of a base crushed under argon, DMF and DMSO (if necessary). The mixture was maintained at the required temperature while stirring for 20 min, and then the reactor was charged with hydrogen peroxide. This time was registered as the reaction beginning. The reaction was carried out while monitoring its kinetics by determining the amount of active oxygen in the samples by iodometric technique. The dimethyl sulfone accumulation was monitored by gasliquid chromatography with a Chrom-5 chromatograph with a flame ionization detector. The glass column of the chromatograph was of 3 m length and of  $3 \times 10^{-3}$  m inner diameter, filled with the phase Cromaton-N Super (0.16–0.22 mm) treated with 5% alcohol solution of SE-30. Evaporator temperature 473 K, programmed rate of heating 12 K min<sup>-1</sup>. Carrier gas argon, the inlet flow rate 40 ml min<sup>-1</sup>. Volume of the sample 1 µl. Measuring the electrical conductivity was carried out using a P 577 circuit and a F 582 null indicator.

Used solvents were preliminarily purified according to [14].

## REFERENCES

- Lee, Y., Lee, C., and Yoon, J., *Water Res.*, 2004, vol. 10, p. 2579.
- 2. Jones, C., USA Patent no. 6552231, 2003.
- Wu, J.J., Muruganandham, M., and Chen, S.H., *J. Hazard. Mater.*, 2007, vol. 149, p. 218.
- 4. Trofimov, B.A., Usp. Khim., 1981, vol. 4, no. 2, p. 248.
- 5. Lyavinets, A.S., Abramyuk, I.S., and Choban, A.F., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 7, p. 1157.
- 6. Choban, A.F., Abramyuk, I.S., and Lyavinets, A.S., *Zh. Obshch. Khim.*, 2007, vol. 77, no. 12, p.1950.
- Rindich, N.O. and Lyavinets, O.S., Ukr. Khim. Zh., 2009, vol. 75, no. 8, p. 123.
- Lyavinets, A.S., Choban, A.F., and Chervinskii, K.A., *Zh. Fiz. Khim.*, 1993, vol. 67, no. 7, p. 1364.
- Choban, A.F. and Lyavinets, O.S., Ukr. Khim. Zh., 1997, vol. 63, no. 2, p. 117.
- 10. Lyavinets, A.S. and Marushchak, N.T., Zh. Obshch. Khim., 2004, vol. 74, no. 6, p. 959.
- 11. Choban, A.F., Yurchuk, I.R., and Lyavinets, A.S., *Zh. Obshch. Khim.*,2008, vol. 78, no. 11, p. 1838.
- 12. Lyavinets, A.S., Yurchuk, I.R., and Chervinskii, K.A., *Zh. Fiz. Khim.*, 1998, vol. 72, no. 11, p. 1971.
- 13. Gutmann, V., Coordination Chemistry in Non-Aqueous Solutions, Moscow: Mir, 1971.
- 14. Gordon, A.J. and Ford, R.A., *The Chemist's Com*panion. A Handbook of Practical Data, Techniques and *References*, New York: Wiley, 1972.