*ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 11, pp. 2071–2074. © Pleiades Publishing, Ltd., 2008.*
*Original Russian Text © A.F. Choban, I.R. Yurchuk, A.S. Lyavinets, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 11, pp. 1838–1841.*

# Oxidation of Dimethyl Sulfoxide with Hydrogen Peroxide in the Presence of Potassium Hydroxide

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

*Fed'kovich Chernovtsy National University,*
*ul. Kotsyubinskogo 2, Chernovtsy, 58012 Ukraine*
*e-mail: liavinetz@chnu.cv.ua*

Received April 17, 2008

**Abstract**—Kinetic relationships in oxidation of DMSO to dimethyl sulfone with hydrogen peroxide in the presence of potassium hydroxide were studied. Kinetic parameters of the process were calculated. It was established that the reaction proceeded through the intermediate formation of potassium hydroperoxide.

**DOI:** 10.1134/S1070363208110157

The superbasic media already long ago became an effective instrument for intensifying the nucleophilic reactions [1]. With their aid many of the traditional reactions were improved and new transformations were carried out [2–4]. We showed [5–8] that superbasic media may be used for performing the reactions of hydroperoxides proceeding with the preservation of peroxy group as well as with its decomposition. In particular, it was shown by an example of alkylation that such media may be used for intensifying the nucleophilic reactions of hydroperoxides [8].

Besides, it proved that superbasic media may be used for performing the oxidative processes [9–11]. Under such conditions high reactivity is exhibited by the peroxide oxidants because the oxidation proceeds here according to the heterolytic mechanism.

Results of the investigation presented in this work show that oxidation of DMSO with hydrogen peroxide in the presence of KOH belongs to such processes. Accumulation of dimethyl sulfone at the introduction of hydrogen peroxide in the superbasic DMSO–KOH medium was established by GLC. Note that the KOH–DMSO system is the simplest and most available superbasic medium [12] where the dipolar hydroxy-free solvent solvates specifically only cations while the anions remain bare [1] resulting in significant growth of reactivity of nucleophilic agents. The aim of this work was the investigation of kinetic relations of the oxidation of DMSO with hydrogen peroxide in the presence of KOH.

Typical kinetic curves of consumption of the active oxygen and the variation in the electroconductivity of the $H_2O_2$–DMSO–KOH system at 293 K are presented in Fig. 1. Analysis of the kinetic curves of the active oxygen contsumption shows that they cannot be described by the formal kinetic equations. This feature significantly complicates analysis of the processes proceeding under these conditions. Therefore the kinetic curve was tentatively divided in two parts: initial stage and the stage of the developed process. Within the framework of this study only the initial period was analyzed basing on the initial rate of the active oxygen consumption ($W_0$). This value was obtained by graphic differentiation. Since no other processes involving

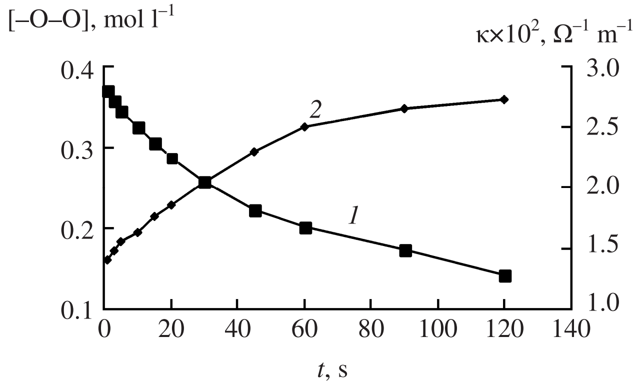


**Fig. 1.** Kinetic curves of consumption of (*1*) active oxygen and (*2*) variation in the specific electroconductivity of the $H_2O_2$–KOH–DMSO system at 293 K. ν(KOH) 2.7 mmol, $[H_2O_2]$ 0.38 mol $l^{-1}$, *V*(DMSO) 15 ml.

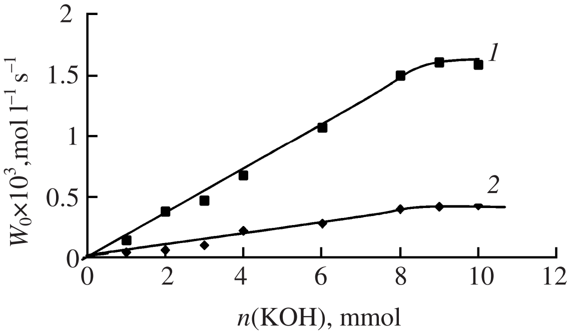


**Fig. 2.** Dependence of the initial rate of consumption of the active oxygen on the amount of KOH at 293 K. $[H_2O_2]_0$ 0.38 mol l$^{-1}$, $[DMSO]_0$ 0.35 mol l$^{-1}$, *V*(S) 15 ml, S: (*1*) DMSO and (*2*) DMF.

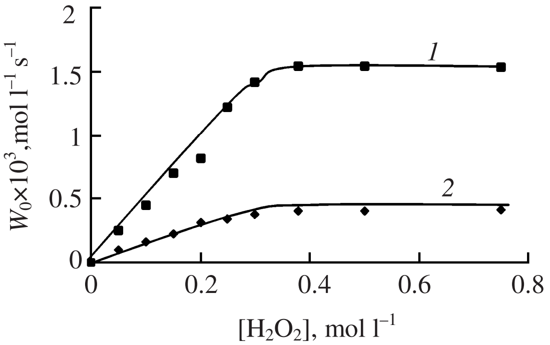


**Fig. 3.** Dependence of the initial rate of the active oxygen consumption on the concentration of $H_2O_2$ at 293 K. ν(KOH) 8.9 mmol. (*1*) *V*(DMSO) 15.4 ml and (*2*) $[DMSO]_0$ 0.35 mol l$^{-1}$, *V*(DMF) 15 ml.

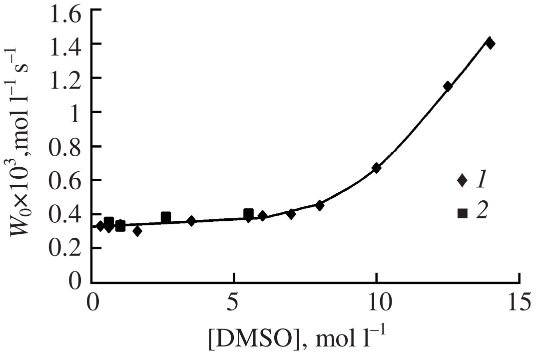


**Fig. 4.** Dependence of the initial rate of the active oxygen consumption on the concentration of DMSO, ν(KOH) 0.0025 mol, $[H_2O_2]_0$ 0.58 mol l$^{-1}$, *V*(DMF) 15 ml, 293 K, (*1*) DMSO and (*2*) DMSO–$d_6$.

$H_2O_2$ were observed under these conditions $W_0$ can be regarded as a rate of oxidation of DMSO.

Dependence of the initial rate of the active oxygen consumption on the amount of alkali is presented in Fig. 2 (curve *1*). As seen, this dependence is described by the saturation curve, and the ascending part is linear indicating the first order of the process with respect to KOH.

Dependence of $W_0$ on the initial $H_2O_2$ concentration (Fig. 3, curve *1*) also has the character of the saturation curve. The linear character of this dependence shows the first order of process on $H_2O_2$. From the slope of the straight line the effective constant was evaluated, $k' = 1.72\times10^{-3}$ s$^{-1}$.

First order by KOH and $H_2O_2$ and also the saturation character of the concentrational dependences of $W_0$ (Figs. 2, 3) shows that oxidation of DMSO proceeds through the intermediate formation of KOOH salt.

$$KOH + HOOH \rightarrow KOOH + H_2O. \quad (1)$$

Inasmuch as no accumulation of dimethyl sulfone is observed in the absence of alkali it may be concluded that just KOOH salt is the key agent of oxidation of DMSO.

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

For evaluation of the reaction order with respect to DMSO which in this case plays the role of reagent and a solvent dependence of the reaction rate on its concentration was studied. DMF was chosen as an inert solvent due to the following considerations. Firstly, DMF is also a dipolar hydroxy-free solvent. Besides, $H_2O_2$ does not decompose in KOH–DMF system and does not cause the oxidation of solvent at 293–298 K.

Dependence of the initial rate of DMSO oxidation on its initial concentration is presented in Fig. 4. As seen, at the DMSO concentration 0.1–7.0 mol l$^{-1}$ the rate of the active oxygen consumption does not materially depend on its concentration (the order on DMSO is 0.15). This conclusion is confirmed by the experiments with the deuterated analog DMSO-$d_6$. It was shown that this change does not practically affect $W_0$ in the DMSO-$d_6$ concentration range 0.2–7 mol l$^{-1}$. Hence, at the above-mentioned DMSO concentrations in DMSO–DMF–KOH system the oxidative process is described by the kinetic equation (3). The salt formation stage is evidently the limiting one [reaction (1)].

$$W_0 = k_1[H_2O_2][KOH]. \quad (3)$$

But as seen from Fig. 4 at the DMSO concentrations above 7 mol $l^{-1}$ the transformation of the order with respect to DMSO occurred from zero to the first. At the ascending part the slope gives the value of the effective constant $1.02\times10^{-4}$ $s^{-1}$.

For establishing the reason of variation in the order with respect to DMSO at the change in its volume fraction in the solution and elucidating the role of the dipolar hydroxy-free solvent in the mechanism of the process under consideration kinetic rules of this reaction in presence of DMF as the constituent of the superbasic medium were studied.

Dependence of $W_0$ on the amount of alkali in the KOH–DMF medium is presented by the curve *2* in Fig. 2. As seen, this dependence also has a character of the saturation curve, and its ascending branch is linear indicating the first reaction order on KOH also in the case of using DMF as a solvent.

Dependence of $W_0$ on the initial $H_2O_2$ concentration is presented in Fig. 3 (curve *2*). It is also the saturation curve, and its ascending part is linear. Hence, in the DMF–KOH medium DMSO oxidation is of the first order on hydrogen peroxide, the effective constant value being $k''$ 4.57 $10^{-4}$ $s^{-1}$.

First orders on $H_2O_2$ and KOH (and therefore on KOOH) and also on dimethyl sulfoxide show that in the superbasic DMF–DMSO–KOH medium oxidation of DMSO is described by the kinetic equation (4). Oxidation of DMSO [reaction (2)] becomes the rate-limiting stage.

$$W_0 = k_2[\mathrm{KOOH}][\mathrm{DMSO}]. \quad (4)$$

Hence, at the transition from DMSO to DMF the rate-limiting stage of oxidation of DMSO with hydrogen peroxide in presence of KOH changes. It was established conductometrically that in both cases the oxidation proceeds by the ionic pathway. Specific conductivity of KOH–DMSO (DMF) system is not high because the solubility of KOH in both systems is insignificant. It is connected with the ability of the dipolar hydroxy-free solvent to the specific salvation only of cations. Besides, the electroconductivity of $H_2O_2$–DMSO (DMF) system is not high showing the sufficiently low degree of dissociation of hydrogen peroxide in the above-mentioned solvents. Under these conditions hydrogen peroxide exists as the solvate $(CH_3)_2S{=}O{\cdots}H{-}O{-}O{-}H{\cdots}O{=}S(CH_3)_2$. At the same time introduction of $H_2O_2$ in the superbasic KOH–DMSO (DMF) system causes the increase in the specific electroconductivity (Fig. 1, curve *2*). It is connected with the formation of KOOH on the surface of KOH crystals that dissolves with the subsequent dissociation.

$$(CH_3)_2S{=}O{\cdots}H{-}O{-}O{-}K{\cdots}O{=}S(CH_3)_2$$
$$\rightleftarrows (CH_3)_2S{=}O{\cdots}H{-}O{-}O^- + K^+{\cdots}O{=}S(CH_3)_2. \quad (5)$$

Formation of salt and its dissociation proceeds considerably easier in DMSO than in DMF (see table).

We believe that it is directly related to the nature of the solvents used. [1] Both solvents are known to possess high permittivity ($\varepsilon > 30$) and dipole moments [$\mu$(DMF) 3.82 D, $\mu$(DMSO) 4.30 D]. Due to high dipole moments these solvents are easily polarized, and strong dipolar interaction exists between them and the dissolved polar substance (KOOH in our case). Besides, the permittivity of both solvents favors the dissociation of the dissolved polar substance and the appearance of hydroperoxy anions in the reaction medium. At the same time, according to the kinetic studies, these reactions proceed faster in DMSO that possesses higher $\varepsilon$ and $\mu$ values as compared to DMF. Besides, DMSO has the higher donor number. The latter according to [13] is the quantitative characteristic of solvent as the electron pair donor. The value of this parameter for DMSO $DN_{DMSO}$ = 124.7 kJ $mol^{-1}$, and for DMF $DN_{DMF}$ = 111.3 kJ $mol^{-1}$ [13]. Being the stronger electron pair donor, and hence the stronger specific solvating agent DMSO effectively separates the ion pairs and easily generates “bare” hydroperoxy anions, the direct DMSO oxidants.

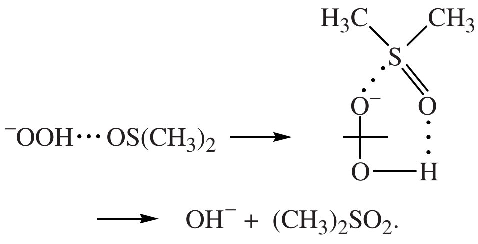
Hence, dipolar hydroxy-free solvents significantly affect the stage of salt formation during the oxidation of DMSO.

In the case of DMF as a solvent this stage is the rate-limiting one, while in the case of oxidation in

Specific electroconductivity of the compounds under investigation and the rate of oxidation of DMSO with hydrogen peroxide

| System composition | | | $\kappa_{max}\times10^2$, $\Omega^{-1}$ $m^{-1}$ | $W_0\times10^3$, mol $l^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| solvent | $\mu$(KOH), g | $[H_2O_2]$, mol $l^{-1}$ | | |
| DMF | – | – | 0.80 | – |
| DMF | 1.4 | – | 0.96 | – |
| DMF | 1.4 | 0.33 | 1.62 | 0.68 |
| DMSO | – | – | 0.84 | – |
| DMSO | 1.4 | – | 1.17 | – |
| DMSO | 1.4 | 0.33 | 2.63 | 1.42 |

DMSO the limiting stage is the direct oxidation with hydroperoxy anion. At the same time it must be mentioned that the mechanism of oxidation may be differently interpreted. Considering the electronic density distribution in the DMSO molecule it may be suggested that its oxidation proceeds through the following transition complex.



(6)

It is quite possible that due to the fast oxidation of DMSO (as show the high $W_0$ values) the $OOH^-$ ions transform to hydroxy ions having higher mobility under the conditions described. That is why the decrease in the active oxygen concentration in the reaction mixture is accompanied by the increase in the specific electroconductivity (Fig.1, curve *2*). Finally, the growth of specific electroconductivity stops and it becomes contstant. Its value is determined by the amount of $K^+$ ions transported to the solution and of the generated $OH^-$ ions.

## EXPERIMENTAL

Accumulation of dimethyl sulfone was controlled by GLC on a Chrom-5 chromatograph with the flame ionization detector and a 3×3000 mm glass column filled with Cromaton-N Super (0.16–0.22 mm) saturated with 5% SE-30, evaporator temperature 473 K, programming rate 40 ml $min^{-1}$, carrier gas argon, 40 ml $min^{-1}$, sample volume 1 μl. Electroconductivity measurements were carried out on a R 577 bridge and a F-582 zero indicator.

Oxidation of DMSO with hydrogen peroxide in the presence of KOH was carried out in the temperature-controlled cell with the magnetic stirrer at 298 K. The desired amount of KOH ground under argon, DMSO, and solvent (if necessary) were placed in the reactor, and the mixture obtained was kept at the required temperature for 20 min. After that hydrogen peroxide was added, and the moment of its introduction was taken as the beginning of the reaction. Reaction progress was monitored by the iodometric evaluation of active oxygen in the samples.

All the solvents used were purified according to the typical procedures [14].

## REFERENCES

1. Raihardt, K., *Rastvoriteli i effecty sredy v organicheskoi khimii* (Solvents and the Effects of Medium in Organic Chemistry), Moscow: Mir, 1991.
2. Trofimov, B.A., *Zh. Org. Khim.*, 1986, vol. 22, no. 9, p. 1991.
3. Trofimov, B.A., *Usp. Khim.*, 1981, vol. 4, no. 2, p. 248.
4. Trofimov, B.A. and Mikhaleva, A.I., *N-Vinilpirroly* (*N*-Vinylpyrroles), Novosibirsk: Nauka, 1984.
5. Lyavinets, A.S., Choban, A.F., Slipchenko, E.K., and Chervinskii, K.A., *Neftekhimiya*, 1993, vol. 33, no. 5, p. 445.
6. Lyavinets, A.S., Choban, A.F., and Chervinskii, K.A., *Neftekhimiya*, 1995, vol. 35, no. 5, p. 448.
7. Lyavinets, A.S., Choban, A.F., and Chervinskii, K.A., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 7, p. 1169.
8. Lyavinets, A.S., Abramyuk, I.S., and Choban, A.F., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 7, p. 1157.
9. Opeida, I.A. and Kasyanchuk, M.G., *Zh. Org. Khim.*, 2002, vol. 38, no. 6, p. 946.
10. Lyavinets, A.S., Choban, A.F., and Chervinskii, K.A., *Zh. Fiz. Khim.*, 1993, vol. 67, no. 7, p. 1364.
11. Lyavinets, A.S. and Marushchak, N.T., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 6, p. 959.
12. Trofimov, B.A., Vasil'tsov, A.M., and Amosova, S.V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, no. 4, p. 751.
13. Gutman, V., *Khimiya koordinatsionnykh soedinenii v nevodhykh rastvorakh* (Chemistry of Coordination Compounds in Nonaqueous Solvents), Moscow: Mir, 1971, p. 202.
14. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.