



HYDROGEN SULPHIDE AND ETHYL MERCAPTAN OXIDATION BY OXYGEN AT THE PRESENCE OF NITROGEN OXIDES

V.S. Yemelyanova¹, A.G. Sarmurzina², A.A. Taltenov³

1 - Scientific-Research Institute of New Chemical Technologies & Materials, Administration, Almaty, Kazakhstan

2 - Kazakh National University, Department of ecology & common chemistry, Almaty, Kazakhstan

*3 - Pavlodar State University, Administration, Pavlodar, Kazakhstan
rinctm@kazsu.kz*

Methods of metals sulfides, hydrogen sulphide and mercaptans oxidation by oxygen in the water solution containing HCl and H_2SO_4 are known. Process proceeds slowly in a temperature interval 353-373K. We have discovered that hydrogen sulphide and mercaptans oxidation rate grows by 2-3 order at the presence of nitrogen(II, IV) oxides. Absence of the data concerning the mechanism of process in the literature has induced us to study the kinetic of hydrogen sulphide oxidation in details. Reaction has practical value as allows to develop scientific bases of technology of gases clearing from hydrogen sulphide.

Kinetic of process was studied on absorption of oxygen in a kinetic mode in static conditions using thermostated reactor. We judged about oxidizing condition of reacting particles in a solution on the redox-potential measured by a platinum electrode in relation to a calomel half-cell. Composition of a gas phase was established spectrophotometrical. IR-spectra was taken on spectrophotometers "Specord" JR-25 and UR-20.

The received experimental results give the basis to suppose that the mechanism of activation of oxygen varies at the presence of nitrogen(II, IV) oxides. speed-up of hydrogen sulphide and ethyl mercaptan oxidation by oxygen is concerned with changing of the oxidizer nature. Process is carried out due to two slow stages:



Oxygen does not interact directly with sulphurous compounds under such scheme. It participates in generating of stronger oxidizer NO_2 which oxidation-reduction potential achieves 1,5B against



0,77 for O_2 in the sour environment. The kinetic equation describing received experimental results and adequate to the scheme (1-2) looks like:

$$W_{O_2} = \frac{k_2 \cdot C_{NO} \cdot C_{O_2} \cdot k_1 C_{RSH} \cdot C_{NO_2}}{k_1 C_{RSH} + k_2 \cdot C_{NO} \cdot C_{O_2}}$$

values k_1 and k_2 for H_2S and C_2H_5SH at 313K and $P_{O_2}=1$ atm. are resulted below:

<i>RSH</i>	k_1 , l/mole·min	k_2 , l ² /mole ² ·min
H_2S	2·10	$4,3 \cdot 10^6$
C_2H_5HS	3,4	$3,1 \cdot 10^6$

Value k_2 in the investigated conditions at constant temperature the does not depend by nature of sulphurous compound, acidity of environment, concentration of iodide-ions in solution $NO_x - KI - H_2SO_4 - H_2O$ and is close to value of a speed constant of the third order, characteristic for the reaction (2) resulted in the literature.

Not only dependence by nature sulfide but also increasing in concentration of a iodide-ion in a solution with increasing of environment acidity are characteristic for value k_1 .

Quantum-chemical characteristics for NO_2 , NO_2HI calculated by method CNDO submitted in table 1.

Table 1 Quantum-chemical characteristics of NO_2 , NO_2HI

NO_x	Charges of atoms		Structure LVMO	E_{LVMO} , eB
	N	X		
NO_2	0,289	-0,198	-0,83P _y (N)-0,33P _y (O)	-3,27
NO_2HI	0,205	0,03	-0,80P _z (I)	-7,0

The lowest vacant molecular orbital (LVMO) of NO_2 is presented basically by p_y- orbital of nitrogen, P_z-orbital of halogen enters into structure of NO_2HI composing its basis. Energy of LVMO changes with changing of its structure and accordingly reactionary ability of an oxidizer in relation to hydrogen sulphide grows at transition from NO_2 to NO_2HI .