## 27th International Chugaev Conference on Coordination Chemistry 4th Conference-School for Young Researchers "Physicochemical Methods in Coordination Chemistry" October 2-6, 2017, N. Novgorod, Russia

## PRODUCTS OF INTERACTION OF SULFUR DIOXIDE WITH AMINES IN AQUEOUS SOLUTIONS. EFFECT OF AMINES BASICITY AND LIPOPHILICITY ON THE COMPOUNDS COMPOSITION

## R. Khoma<sup>a,b</sup>

<sup>a</sup>Odessa I.I. Mechnikov National University, Odessa, Ukraine. <sup>b</sup>Physico-Chemical Institute of Environment and Human' Protection, Odessa, Ukraine.

Reaction products have been isolated from  $SO_2 - L - H_2O - O_2$  systems (L = alkylamines, benzylamines, ethanolamines, aniline, 2,2'-bipyridine and their deravatives). The prepared compounds have been characterized by elemental analysis, X-ray diffraction analysis, X-ray powder diffraction, IR, Raman spectroscopy,  $^1H$ ,  $^{13}C$  NMR, and mass spectrometry, thermogravimetry.

The reaction of SO<sub>2</sub> with aqueous solution of aniline (p $K_a = 4.63$ ) and highly basic ethanolamines (7.76  $\leq$  p $K_a \leq$  9.85), aminoguanidine (p $K_a = 11.04$ ), benzylamines, and alkylamines (10.60  $\leq$  p $K_a \leq$  10.77) results "onium" salts of sulfur-containing oxyanions according to the equations (1) – (7).

$$SO_2 + H_2O + 2RNH_2 \rightarrow (RNH_3)_2SO_3$$
 (1)

$$SO_2 + (RNH_3)_2SO_3 + H_2O \rightarrow 2(RNH_3)HSO_3$$
 (2)

$$SO_2 + (RNH_3)_2SO_3 \rightarrow (RNH_3)_2S_2O_5$$
 (3)

$$(RNH_3)_2SO_3 + O_2 \rightarrow 2(RNH_3)_2SO_4$$
 (4)

$$4(RNH_3)HSO_3 + O_2 \rightarrow 2(RNH_3)_2SO_4 + 2SO_2 \uparrow + 2H_2O$$
 (5)

$$2(RNH_3)_2S_2O_5 + O_2 \rightarrow 2(RNH_3)_2SO_4 + 2SO_2 \uparrow$$
 (6)

$$3(RNH_3)HSO_3 + O_2 \rightarrow (RNH_3)_3SO_4(HSO_4) + SO_2 \uparrow + H_2O$$
 (7)

Van der Waals clathrates (bipy)<sub>3</sub>·(SO<sub>2</sub>)·(H<sub>2</sub>O), (bipy)<sub>2</sub>·(SO<sub>2</sub>)·(H<sub>2</sub>O)<sub>2</sub> and (Bz<sub>3</sub>N)<sub>3</sub>·(SO<sub>2</sub>) were obtained with relatively weakly basic 2,2'-bipyridine (p $K_a = 4.34$ ) and tribenzylamine (p $K_a = 3.64$ ). Thus, we can conclude salt formation to occur when p $K_a \ge 4.63$  for amine.

"Onium" hydrodisulphates were obtained for alkylmonoamines with the number of C atoms, two or more in the case of  $13.24 \le (pK_a + logP_{ow})$  in the  $SO_2 - L - H_2O - O_2$  reaction system (L - n-heptylamine, and n-octylamine);  $10.42 \le (pK_a + logP_{ow}) \le 11.63$  (L - n-butylamine, t-butylamine, n-propylamine, benzylamine,  $\alpha$ -phenylethylamine, N,N-dimethylbenzylamine, or dibenzylamine) – sulphates;  $5.81 \le (pK_a + logP_{ow}) \le 10.21$   $(L - ethanolamines except for TRIS) – sulphites and hydrosulphites, they have been isolated due to sulphooxidation inhibition. It was found dissociation thermodynamic functions to depend on bases <math>logP_{ow}$  for monoethanolammonium, diethanolammonium, and their N-methyl and N-ethyl derivatives. Acid-base dissociation of TRIS and triethanolamine "onium" cations does not correspond to said relationship because TRIS (primary amine), TEA (tertiary amine) act differently on aqueous solutions of  $SO_2$ . TRIS having in its molecule the largest number of H- donors and acceptors as compared with other ethanolamines is characterized by the lowest value  $(pK_a + logP_{ow}) = 5.76$  and promotes sulphooxidation of  $S(IV) \rightarrow S(VI)$ .

e-mail: rek@onu.edu.ua