

BRIEF  
COMMUNICATIONS

## Hydrolysis of Nitrosylsulfuric Acid

P. P. Kim, G. V. Pastukhova, and A. A. Peretrutov

Dzerzhinsk Branch, Nizhni Novgorod State Technical University, Dzerzhinsk, Russia

Received May 21, 1998; in final form, March 1999

**Abstract**—The statics and kinetics of hydrolysis of nitrosylsulfuric acid were studied at the initial sulfuric acid concentrations in the range 60–76 wt % and temperatures in the range 20–100°C or 30–130°C. The results were compared with the published data.

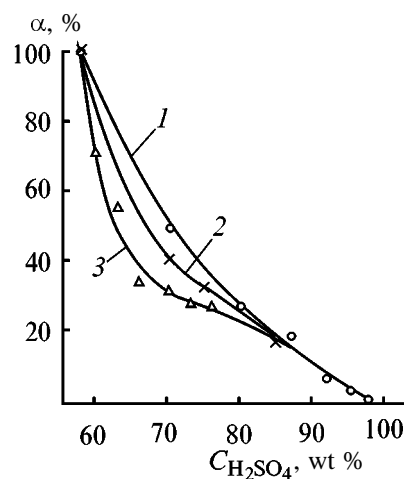
The reactivity of nitrosylsulfuric acid (NSA) depends on the degree of its hydrolysis and is determined by the concentration of nitrogen compounds formed in the solution in the free state in the course of hydrolysis. The NSA hydrolysis is an important industrial process, which has been little studied so far because of experimental difficulties. Data for diluted (60–70%) sulfuric acid are lacking.

In this work, the statics of NSA hydrolysis was studied with an SF-46 spectrophotometer. A cell with the nitrose sample and a reference cell were maintained at constant temperature using a special attachment in the form of a 1-mm-thick brass plate containing pockets for two cells and light-transmitting holes. Silicone oil delivered from a UH-8 thermostat through a heat-resistant pipe was circulated within the attachment. It was found that in the concentration range 0–5%  $N_2O_3$  and 57.5–100%  $H_2SO_4$  the Lambert–Beer law is fulfilled. The degree of NSA hydrolysis was calculated from the residual NSA concentration of the nitrose sample, as determined from comparison of its optical density with that of the nitrose sample containing 57.7 wt % of the initial sulfuric acid (assuming 100% hydrolysis of NSA).

The degrees of NSA hydrolysis are given in Table 1, and the dependences of the hydrolysis degree  $\alpha$  on the initial sulfuric acid concentration  $C_{H_2SO_4}$  at about 20°C are shown in the figure. The Shperling's data [1] for nitroses with about 0.2%  $N_2O_3$  (curve 1), the data of [2] for nitroses with 0.19%  $N_2O_3$  (curve 2), and experimental data obtained in this study (curve 3) were compared. As seen, for the  $H_2SO_4$  concentration exceeding 80% the data of [1, 2] are similar, whereas at concentrations less than 80% the hydrolysis degree is lower than that found in [1]. Our results are underestimated compared to [2]. The degree of NSA hydrolysis decreases considerably as

the sulfuric acid concentration grows from 57.5 to 75 wt % (concave curve), passes through an inflection point at 73 wt %  $H_2SO_4$ , and then decreases more slowly (convex curve). Such behavior is observed over the entire studied range of  $N_2O_3$  concentrations. The increase in the  $N_2O_3$  concentration facilitates the NSA hydrolysis. The lower the sulfuric acid concentration, the wider the  $N_2O_3$  concentration range corresponding to a drastic growth of the hydrolysis degree. For the  $H_2SO_4$  concentrations up to 66 wt %, this range is 0–0.55%. At a further increase in the  $N_2O_3$  concentration, the degree of NSA hydrolysis increases to a considerably lesser extent. At  $N_2O_3$  concentrations above 1.2–1.6% the hydrolysis degree increases virtually linearly for temperatures within 20–100°C, depending on the decrease in the sulfuric acid concentration.

The experimental data obtained confirm once again that the hot regime is efficient for operation of sulfuric



Degree  $\alpha$  of NSA hydrolysis vs. the initial sulfuric acid concentration  $C_{H_2SO_4}$ . Temperature 20°C;  $N_2O_3$  concentration 0.2%. (1–3) For comments, see text.

**Table 1.** Hydrolysis of nitrosylsulfuric acid

| N <sub>2</sub> O <sub>3</sub> concentration, % | Hydrolysis degree, %, at indicated temperature <i>T</i> , °C |      |      |      | N <sub>2</sub> O <sub>3</sub> concentration, % | Hydrolysis degree, %, at indicated temperature <i>T</i> , °C |      |      |      |
|--|--|------|------|------|--|--|------|------|------|
|  | 20   | 50   | 80   | 100  |  | 20   | 50   | 80   | 100  |
| 76 wt % H <sub>2</sub> SO <sub>4</sub>         |  |      |      |      | 66 wt % H <sub>2</sub> SO <sub>4</sub>         |  |      |      |      |
| 4.19   | 73.5   | 75.0 | 76.1 | 77.1 | 4.28   | 82.2   | 85.2 | 85.9 | 91.2 |
| 2.67   | 69.2   | 69.9 | 70.6 | 72.1 | 2.80   | 77.7   | 82.8 | 83.9 | 88.0 |
| 0.55   | 54.4   | 57.9 | 59.8 | 61.7 | 1.60   | 73.2   | 78.9 | 79.1 | 84.2 |
| 0.16   | 19.7   | 25.2 | 28.3 | 30.0 | 0.94   | 72.1   | 75.5 | 77.3 | 82.4 |
|  |  |      |      |      | 0.47   | 48.6   | 51.2 | 54.2 | 56.6 |
| 73 wt % H <sub>2</sub> SO <sub>4</sub>         |  |      |      |      | 63 wt % H <sub>2</sub> SO <sub>4</sub>         |  |      |      |      |
| 4.22   | 74.3   | 75.1 | 77.8 | 77.9 | 5.26   | 88.1   | 89.5 | 90.5 | 91.6 |
| 1.05   | 71.6   | 74.9 | 76.0 | 77.0 | 2.62   | 81.9   | 83.2 | 87.3 | 88.6 |
| 0.80   | 68.6   | 69.9 | 74.8 | 75.0 | 1.73   | 77.2   | 83.0 | 84.5 | 85.7 |
| 0.54   | 60.0   | 62.0 | 62.7 | 65.4 | 1.12   | 75.4   | 82.3 | 83.8 | 84.9 |
| 0.37   | 37.6   | 41.1 | 43.6 | 44.8 | 0.15   | 53.2   | 54.0 | 57.9 | 59.9 |
| 70 wt % H <sub>2</sub> SO <sub>4</sub>         |  |      |      |      | 60 wt % H <sub>2</sub> SO <sub>4</sub>         |  |      |      |      |
| 4.22   | 76.1   | 78.5 | 79.7 | 80.2 | 4.54   | 92.8   | 92.9 | 97.3 | 98.0 |
| 1.57   | 71.3   | 77.6 | 77.8 | 79.2 | 2.67   | 88.0   | 90.6 | 96.0 | 97.0 |
| 1.29   | 70.9   | 76.5 | 77.7 | 79.2 | 1.15   | 81.6   | 90.3 | 91.4 | 93.0 |
| 0.62   | 66.2   | 68.6 | 69.2 | 70.8 | 0.69   | 78.6   | 86.5 | 88.1 | 89.2 |
| 0.40   | 46.2   | 49.7 | 50.9 | 52.4 | 0.28   | 76.7   | 85.8 | 87.0 | 88.1 |

acid system and NSA denitration. The high efficiency of utilization of high-nitrose solution was also confirmed. In the process, the nitrose activity increases not only owing to the increase in the N<sub>2</sub>O<sub>3</sub> concentration, but also owing to the fact that the equilibrium in the nitrose is shifted toward the products of NSA hydrolysis.

The kinetics of NSA hydrolysis was studied on an Impul's KL-2 conductometer. The nitrose studied

was charged into two cells of the conductometer and cooled to 0°C. Then, the cells were rapidly transported into a thermostat preheated to a specified temperature. After that, the time and the conductometer readings were recorded. In the course of the NSA hydrolysis the nitrose conductivity increased and then remained constant after the lapse of some time. This time was assumed as the time of complete hydrolysis. The second cell served for measuring temperature.

The reaction of NSA hydrolysis is of the overall second order and of the first order with respect to each component. The rate constant was calculated by the formula [3]

$$k = \frac{1}{\tau(C_{10} - C_{20})} \ln \frac{C_{20}(C_{10} - X_1)}{C_{10}(C_{20} - X_2)},$$

where  $C_{10}$  and  $C_{20}$  are the initial concentrations of HNSO<sub>5</sub> and H<sub>2</sub>O (M), respectively, and  $X_1$  and  $X_2$ , the concentrations of unchanged components (M).

The experimental data treated in the  $\tau$ -ln [ $C_{20}(C_{10} - X_1)/C_{10}(C_{20} - X_2)$ ] coordinates fall on a straight line, which confirms the value of 2 for the overall reaction order.

**Table 2.** Rate constants *k* of NSA hydrolysis

| <i>T</i> , °C | <i>k</i> , l mol <sup>-1</sup> min <sup>-1</sup> , at indicated HNSO <sub>5</sub> concentration, wt % |  |  |
|---------------|---|--|--|
|               | 4 (1.2% N <sub>2</sub> O <sub>3</sub> )   | 10 (3.0% N <sub>2</sub> O <sub>3</sub> ) | 15.2 (4.5% N <sub>2</sub> O <sub>3</sub> ) |
| 30            | 9.61 × 10 <sup>-4</sup>   | 5.52 × 10 <sup>-3</sup>                  | 0.095                                      |
| 50            | 3.36 × 10 <sup>-3</sup>   | 1.43 × 10 <sup>-2</sup>                  | 0.184                                      |
| 60            | 4.56 × 10 <sup>-3</sup>   | 1.69 × 10 <sup>-2</sup>                  | 0.238                                      |
| 80            | 7.68 × 10 <sup>-3</sup>   | 3.24 × 10 <sup>-2</sup>                  | 0.314                                      |
| 100           | 1.18 × 10 <sup>-2</sup>   | 5.90 × 10 <sup>-2</sup>                  | 0.455                                      |
| 120           | 1.66 × 10 <sup>-2</sup>   | 7.58 × 10 <sup>-2</sup>                  | 0.520                                      |
| 130           | 2.19 × 10 <sup>-2</sup>   | 9.72 × 10 <sup>-2</sup>                  | 0.780                                      |

Table 2 shows how the kinetic parameters of NSA hydrolysis at the initial sulfuric acid concentration of 72.3 wt % change with temperature. As seen, the rate constant of the hydrolysis increases with  $N_2O_3$  concentration and temperature. Depending on temperature, the increase in the  $N_2O_3$  concentration from 1.2 to 3.0 and 4.5% increases the rate constant by a factor of 5.7–4.4 and 99–36, and the increase from 3.0 to 4.5%, by a factor of 17–8. At the temperature increased from 30 to 50 and 130°C at the  $N_2O_3$  concentration of 1.2, 3.0, and 4.5% the rate constant of NSA hydrolysis increases by a factor of 3.5 and 22.8, 2.6 and 17.6, and 1.9 and 8.2, respectively, and the temperature coefficient increases from 0.57 to 1.75.

The obtained data on the statics and kinetics of NSA hydrolysis will be useful for intensifying the nitrose process.

## CONCLUSIONS

- (1) The degree of hydrolysis increases with increasing temperature and  $N_2O_3$  concentration in solution and with decreasing sulfuric acid concentration.
- (2) The hydrolysis rate is comparable with the rates of the other stages of the nitrose process.

## REFERENCES

1. *Spravochnik sernokislotchika* (Handbook on Sulfuric Acid Manufacturer), Malina, K.M., Ed., Moscow: Khimiya, 1971.
2. Kuz'minykh, I.N. and Tantsova, N.N., *Zh. Prikl. Khim.*, 1954, vol. 27, no. 6, pp. 594–599.
3. Stromberg, A.G. and Semchenko, D.P., *Fizicheskaya khimiya* (Physical Chemistry), Moscow: Vysshaya Shkola, 1988.