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Temperature-dependent Kinetics on Laser Induced Photolysis of Aqueous CS_2-HONO Solutions

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Abstract: A laser photolysis/transient absorption technique has been employed to investigate the photolysis kinetics of aqueous CS_2-HONO solutions at 355 nm. Spectral analysis shows that CS_2OH will react with HONO to form CS_2OH-HONO. Temperature dependent rate coefficients for the reaction are reported for the first time. The following Arrhenius expressions adequately summarize the kinetic data obtained over the temperature range 273-313 K (units are $L\cdot mol^{-1}\cdot s^{-1}$): $\ln k = (31.6 \pm 0.6) - \{(4.1 \pm 0.2) \times 10^3/T\}$, and the activation energy in unit of $kJ\cdot mol^{-1}$ is 32.47 with the temperature accuracy 0.2 K.

Keywords: CS_2OH, CS_2OH-HONO, activation energy, laser photolysis/transient absorption.

Considerable quantities of wastewater effluents containing CS_2 are produced by industries engaged in the manufacture of artificial leather, viscose, and other synthetic fibers. In addition, CS_2 also naturally occurs in the condensation of water vapor and its precipitation from the atmosphere in the form of rain, snow or hail. The oxidation of CS_2 is the subject of a number of studies[1-4]. Nitrous acid is another pollutant which has been the subject of intensive investigation in recent years. The review of Lammel and Cape[5] suggests that NO_2^- concentrations range from 0.5 to 50 $\mu mol\cdot L^{-1}$, whereas in fogs they are 10 times higher. Therefore, the reaction of aqueous CS_2 and HONO solutions under sunlight is very important because these processes may lead to new reactions and products that can have a significant influence on the global nitrogen and sulfur cycle.

Experimental

The laser photolysis/transient absorption apparatus used in this work and the preparation of the gas saturated sample solutions have been described in a recent paper[6].

Results and Discussion

The spectrum of transient absorptions from 355 nm laser photolysis of N_2 saturated CS_2 (5.2 $mmol\cdot L^{-1}$)-HONO (2.5 $mmol\cdot L^{-1}$) solutions is shown in **Figure 1**. Four main transient absorption bands (220-250 nm, 250-400 nm, 400-600 nm and 800-1000 nm) have been observed. The 250-400 nm, 400-600 nm and 800-1000 nm zones are

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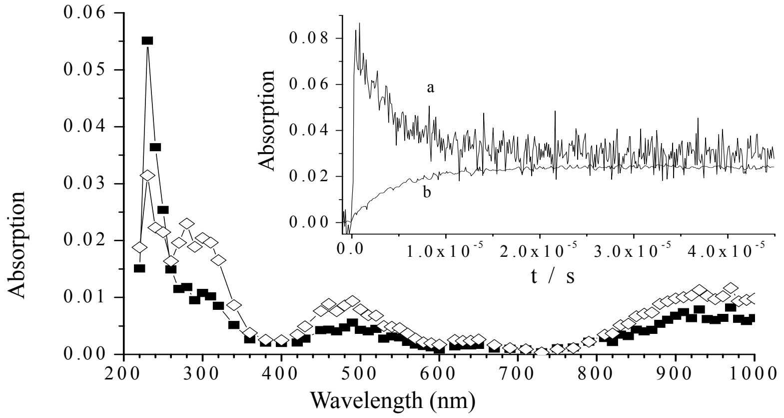
attributed to CS_2OH-HONO as in ref. 6 and further studies show that its formation is sensitive to temperature, which will be discussed below. The absorption peaking at 230 nm is attributed to CS_2OH instead of CS_2NO^+ as in ref. 6. Evidence for the suggested mechanism is provided by the following observations. First, the 230 nm signal did not reduce after appropriate amount of N, N, N', N'-tetramethyl-*p*-phenylenediamine was added into the solutions, which means that the transient species are not a cation. Furthermore, the observed absorption decay at 230 nm as shown in **Figure 1-a** is in excellent agreement with the growing absorption at 280 nm in **Figure 1-b**, and as shown in **Figure 2**, both of the two apparent first order rate constants (k_{obs}) have the same linear relationship with the HONO concentration, whereas the slope represent the rate constant of the reaction CS_2OH + HONO → CS_2OH-HONO. Therefore, it is more reasonable to attribute this absorption to CS_2OH, and the bimolecular rate constant for the CS_2 + OH → CS_2OH reaction is $(9.0 \pm 0.35) \times 10^9$ $L\cdot mol^{-1}\cdot s^{-1}$ at 298K, confirming the observations reported in previous studies[7,8].

Figure 1 Transient absorption spectra observed after pulse irradiation of 5.2 $mmol\cdot L^{-1}$ CS_2 and 2.5 $mmol\cdot L^{-1}$ HONO solution in H_2O saturated with N_2 at pH 1.5.



—■— 2.94 μs, —◇— 14.9 μs; Inset: Absorption *vs.* time profiles of the decay of a (230 nm) and the formation of b (280 nm).

Figure 2 Plots of k_{obs} vs HONO concentration

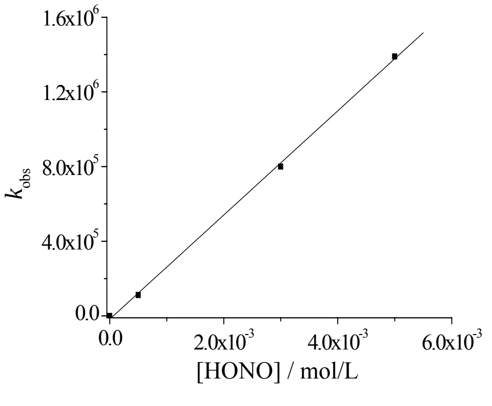
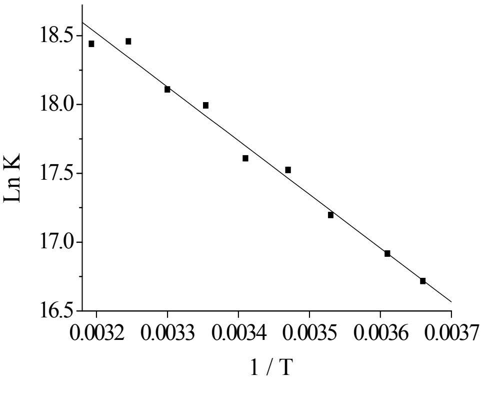


Figure 3 Arrhenius plots for CS_2OH reaction with HONO



As mentioned above, the reaction $CS_2OH + HONO \rightarrow CS_2OH\text{-}HONO$ is sensitive to temperature change. **Table 1** summarizes various rate constants over the temperature range of 273-313 K, and Arrhenius plot for this reaction is shown in **Figure 3**. Linear analysis of the ln K *versus* 1/T data give the following Arrhenius expressions (units are $L \cdot mol^{-1} \cdot s^{-1}$):

$$\ln K = (31.6 \pm 0.6) - \frac{(4.1 \pm 0.2) \times 10^3}{T} \qquad (A = 2.95 \times 10^{13})$$

where the activation energies (E_a) for this reaction is 32.47 $kJ \cdot mol^{-1}$ with the temperature accuracy of 0.2 K, which is relatively low and means that this reaction will process under low temperature.

Table 1 Kinetic data for the CS_2OH + HONO reaction

T/K	273	277	283	288	293	298	303	308	313
$K/10^8\ L \cdot mol^{-1} \cdot s^{-1}$	0.38	0.44	0.61	0.83	0.88	1.38	1.53	2.25	2.33

In conclusion, HONO is very important in the aqueous phase photochemistry as it can absorb the UV-A band of sunlight (320-400 nm) and produce OH radical, which will lead to the oxidation of CS_2 and further formation of CS_2OH-HONO. The complicated reactions between CS_2 and HONO under sunlight and the temperature-dependence phenomenon implicate that these processes will probably influence the global lifetime of CS_2 and HONO.

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