Kinetics of the Oxidation of Hydrazine by Hydrogen Peroxide, Catalyzed by Hydrated Copper(II)

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Abstract: Hydrazine is oxidized by hydrogen peroxide in the presence of copper(II) to form nitrogen and water. The rate of reaction between stoichiometric amounts of hydrazine and hydrogen peroxide in the presence of copper(II) was followed by monitoring the rate of evolved nitrogen. The rate was first order with respect to concentrations of hydrogen peroxide and copper(II), but was independent of the concentration of hydrazine. The most likely mechanism involves formation of a copper(II)-hydrazine complex that reacts with the hydrogen peroxide. The enthalpy of activation and the entropy of activation determined from experiments between 288 and 308 K were 5.8 ± 0.2 kcal/mol and −28 ± 1 cal/(mol K).

Hydrazine, a common ingredient in liquid propellants, has been extensively investigated over the past 70 years.[1] The kinetics and mechanism of reactions involving hydrazine are of interest in understanding the ignition and combustion of such propellants and also in understanding reactions that might lead to reduced shelf life.

In 1949 Gordon[2] measured the kinetics of the reaction between hydrogen peroxide and hydrazine in aqueous solution. The reaction rate was first order in both hydrazine and hydrogen peroxide, and the rate of the reaction at 25 °C was relatively slow. For nearly equal molar solutions of hydrazine and hydrogen peroxide the rate coefficient was reported as $4.1 \times 10^{-5}\ M^{-1}\ s^{-1}$.

In 1961 Corey[3] reported that the cis hydrogenation of olefins was possible in the presence of hydrazine, hydrogen peroxide, and trace amounts of copper(II). Interestingly, he reported that the reaction occurred "instantaneously". Thus, the rate of reaction in the presence of copper(II) would have to be much faster than the one studied by Gordon in 1949. In addition, Corey argued that the reactive species involved in the olefin hydrogenation was diimide, N_2H_2. This was confirmed and further studies on N_2H_2 ensued.[4-9]

Despite this attention to N_2H_2 as a hydrogenating agent, the kinetics and mechanism of the copper(II)–hydrazine–hydrogen peroxide reaction have not been elucidated. Sigel and co-workers[10,11] examined the kinetics of the oxidation of hydrazine by hydrogen peroxide in the presence of copper(II)-2,2′-dipyridyl complex, but were not able to measure the kinetics in the presence of hydrated copper(II) because copper oxide precipitated. In this article the kinetics have been successfully measured by using sufficiently small quantities of copper(II) to avoid precipitation of oxide.

Experimental Section

Reagents. Anhydrous hydrazine, 97% solution, was obtained from Matheson Coleman and Bell, Norwood, Ohio. Hydrogen peroxide, 90% solution, was obtained from the Becco Chemical Division, FMC Corp., Buffalo, N.Y. A 4 M stock solution of each reagent was prepared with cold double distilled water. The stock solutions were stored in a refrigerator when not in use. All metal salts used in these experiments were reagent grade.

Kinetic Measurements. The experiments were initially conducted in a 125-ml Erlenmeyer flask equipped with a side arm that led to a gas bubbler and gas buret for measuring and collecting the evolved gas over mercury. The neck of the 125-ml reaction flask was firmly fitted with a silicone rubber stopper that contained a 15-ml buret for the addition of hydrazine and an inlet tube for the introduction of helium or argon to deaerate the reaction mixture. The reaction flask temperature was controlled by immersing in a thermostated water bath at the desired reaction temperature. Vigorous stirring was maintained with a Teflon-coated magnetic stirring bar. After adding the desired amount of copper(II), hydrogen peroxide, and double distilled water, the reaction flask was placed in the constant temperature water bath. The reaction flask's contents were deaerated for at least 15 min by bubbling helium or argon through the solution while stirring vigorously. The flow of inert gas was stopped and the desired amount of 4 M hydrazine introduced through the altered buret tip. The timer was started and the reaction product gas was collected in the 100-ml gas buret. The gas was maintained at atmospheric pressure with the leveling bulb of the gas buret. The time elapsed for the collection of every 10 ml of gas was recorded.

A number of experiments were conducted in the 125-ml reaction flask using a total constant volume of 50 ml. From these runs the order of reaction with respect to the total concentration of copper(II) increased as the concentration of copper(II) increased. This was found to be caused by the high enthalpy of reaction (196 kcal/mol) which raised the temperature of the reaction during the course of a run. In all subsequent experiments the reaction flask contents were monitored with a 10-mil copper-constantan thermocouple enclosed in a thin-wall Pyrex tube inserted through the silicone rubber stopper and immersed in the reaction solution. The analogue signal received was displayed on a strip-chart potentiometric recorder. In this manner, it was possible to determine the experimental conditions required to minimize the effect of the heat of reaction on the rate. In order to keep the temperature constant throughout the kinetic run, the reaction solution was increased to 300 ml and the concentrations of hydrogen peroxide and of hydrazine were halved.

The stock solutions of hydrazine, hydrogen peroxide, and copper(II) were analyzed by standard iodimetric procedures.[12,13]

Results and Discussion

The stoichiometry of the reaction was reported by Graham[14] as

$$N_2H_4 + 2H_2O_2 \xrightarrow{Cu^{2+}} N_2 + 4H_2O \qquad (1)$$

The stoichiometry was confirmed by measuring the total amount of nitrogen produced.

The rate law was determined by measuring the initial rate of reaction.[15] The pH of the reaction solution was estimated from eq 2,

$$[H^+] = (K_1K_2[H_2O_2]/(K_2 + [N_2H_4]))^{1/2} \qquad (2)$$

where K_1 and K_2 are the acid dissociation constants for H_2O_2 and $N_2H_5^+$, respectively. The pK_a's for K_1 and K_2 are 11.6[16] and 8.07.[10]

The results for the runs in which the concentration of copper(II) was kept the same are shown in Table I. In Table II the results with varying copper(II) concentrations are presented. From these results it is clear that the rate law may be represented as

$$d(N_2)/dt = k_{obsd}[H_2O_2]_T[Cu(II)]_T \qquad (3)$$

Table I. Determination of the Reaction Order of Hydrazine and Hydrogen Peroxide[a,b]

N_2H_4, M × 10^2	H_2O_2, M × 10^2	Rate, ml of N_2/min	pH[c]
1.64	6.54	7.3	9.5
3.27	6.54	7.4	9.7
6.54	6.54	7.4	9.8
13.1	6.54	7.4	10.
3.27	3.27	3.6	9.8
3.27	6.54	7.4	9.7
3.27	13.1	15	9.
1.64	3.27	3.6	9.7
3.27	6.54	7.4	9.7
6.54	13.1	15	9.7

[a] Total volume equal to 300 ml, T = 298 K. [b] Copper(II) sulfate concentration 1.23 × 10^{-6} M. [c] Calculated from eq 2.

Table II. Determination of Reaction Order of Copper(II) Sulfate[a,b]

Copper(II), M × 10^7	Rate, ml of N_2/min	Copper(II), M × 10^7	Rate, ml of N_2/min
3.29	1.95	13.2	8.3
6.57	4.1	16.4	10.4
9.86	6.2	24.6	16.2

[a] Total volume of solution is 300 ml, T = 298 K. [b] $[N_2H_4]$ = 0.033 M, $[H_2O_2]$ = 0.0654 M, pH 9.7.

where $[H_2O_2]_T$ and $[Cu(II)]_T$ stand for the total concentrations of hydrogen peroxide and copper(II). In addition the rate is independent of pH within the limited range examined here. Some additional runs were made with copper(II) acetate and copper(II) perchlorate which demonstrated the reaction rate to be independent of the anion of the copper(II) salt.

The rate law indicates that the rate-determining step for the reaction involves copper ion and hydrogen peroxide. Since copper(II) has been shown to react slowly with hydrogen peroxide,[16,17] the more likely mechanism consists of the formation of a copper(II)-hydrazine complex followed by reaction with hydrogen peroxide. Such a scheme is shown below:

$$Cu^{II} + N_2H_4 \overset{K}{\rightleftharpoons} Cu^{II}N_2H_4 \text{ (rapid preequilibrium)} \quad (4)$$

$$Cu^{II}N_2H_4 + H_2O_2 \xrightarrow[\text{slow}]{k_1} \text{intermediate products} + 2H_2O \quad (5)$$

One or more rapid reactions between the intermediate products and hydrogen peroxide follow to give the final products. The intermediate products in eq 5 are not required by the rate law, but are entered into the mechanism, since at least one intermediate, N_2H_2, has been inferred to be present.[3]

The rate law for this mechanism is then

$$\frac{d[N_2]}{dt} = \frac{k_1K[N_2H_4][H_2O_2][Cu^{II}]_T}{1 + K[N_2H_4]} \quad (6)$$

where $[Cu^{II}]_T$ represents the total concentration of copper(II) in solution. If $K[N_2H_4]$ is greater than unity, then (6) reduces to the experimentally observed rate law, eq 3. For Cu^{2+} and N_2H_4, log K was reported as 4.2.[10] Even if the reactive copper(II) complex is $Cu^{II}(OH)(N_2H_4)$ which should have a somewhat smaller value of K, the product $K[N_2H_4]$ is most certainly greater than unity.

Table III. Rate Coefficients Used to Compute Activation Parameters[a]

Cu(II), M × 10^7	H_2O_2, M	Rate, ml of N_2/min	k_1, M^{-1} s^{-1} × 10^{-2}	T, K
8.22	0.067	3.2	1.4	288
12.3	0.067	4.7	1.3	288
16.4	0.067	6.8	1.5	288
8.22	0.065	4.9	2.1	298
12.3	0.065	7.3	2.1	298
16.4	0.065	10.2	2.2	298
8.22	0.065	7.3	3.0	308
12.3	0.065	10.4	2.8	308
16.4	0.065	14.3	2.9	308

[a] $[N_2H_4]$ = 0.033 M in all runs.

Table IV. Rate Coefficients for the Catalyzed and Uncatalyzed Oxidation of Hydrazine by Hydrogen Peroxide

Catalyst	k_1, M^{-1} s^{-1} (298 K)	Ref
None	1.8 × 10^{-5}	2
Cu^{2+}-2,2,'-dipyridyl	127	11
Hydrated Cu(II)	210	This work

To obtain enthalpy and entropy of activation for this reaction, additional runs were made at 288 and 308 K. The rate of reaction was recast into M^{-1} s^{-1} by converting the volume of nitrogen evolved into moles of nitrogen evolved. The results of these runs are shown in Table III. The activation parameters were computed from a nonlinear least-squares fit[18] of the transition state equation.

The enthalpy of activation and entropy of activation along with the standard deviation are 5.8 ± 0.2 kcal/mol and −28 ± 1 cal/(mol K). The rate coefficients at 288, 298, and 308 K computed from these values of $\Delta H^{\circ\ddagger}$ and $\Delta S^{\circ\ddagger}$ are 142, 206, and 293 M^{-1} s^{-1}, respectively.

In Table IV the rate coefficients for the reaction catalyzed by hydrated copper(II) and copper(II)-2,2′-dipyridyl are compared with the rate coefficient for the uncatalyzed reaction which demonstrates the efficacy of the copper(II) catalysts. This also shows why Corey and co-workers required a trace of copper(II) salt in order to hydrogenate olefins with hydrogen peroxide and hydrazine at room temperature.

References and Notes

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