Spectrophotometric Study of the Reaction between Hydrazine and p.dimethylaminobenzaldehyde

Christine GOJON\textsuperscript{t} and Bernard DUREAULT

Centre Etudes Nucléaires de Valrô\textsuperscript{a}, DRDD/SPHA/SPRA/GSIA*

(Received October 23, 1995), (Revised April 12, 1996)

In order to realize an optical fibre chemical sensor for hydrazine in the Purex process, the reaction between hydrazine and p.dimethylaminobenzaldehyde (p.DMAB) in nitric acid medium was studied by spectrophotometry and \textsuperscript{1}H.NMR. The effect of temperature and acidity were determined. The equilibrium constant is of 7,800 l/mol at 15°C and decreases to 600 at 55°C. The reaction is fully reversible. In order to keep p.DMAB out of damage, the acidity working range has to be within 0.1 to 1.0 M in nitric acid medium. This reaction is suitable for the application of optical fibre chemical sensors because direct reversibility or regeneration by temperature or acidity may be possible.

KEYWORDS: hydrazine, p.dimethylaminobenzaldehyde, Purex process, spectrophotometric analysis, nitric acid, equilibrium constant

I. INTRODUCTION

Hydrazine is important in the nuclear industry. It is used as an anticorrosion protective agent in the water of both the primary and secondary circuits of nuclear power plants with VVER 440 reactor\textsuperscript{1} and as a scavenger for nitrous acid in the Purex process for the separation of uranium and plutonium\textsuperscript{2}. In the Purex process, a strong consumption of hydrazine leads its excess addition. In the aim of optimizing hydrazine concentration in the process, an on-line measurement is required, but there is not yet available.

Optical fibre chemical sensors are chosen because they represent a new technology for on-line measurements. In the Purex process they would be adapted because of their advantages compared with conventional techniques: no electric and electromagnetic interferences, intrinsically safe and suitable for operations in hostile and harsh environments, remote sensing applications, corrosion resistant, real-time-monitor\textsuperscript{3,4} and lack of waste. The reversibility or regeneration of such sensor depends on the reaction involved between the analyte and the immobilized reactive agent.

Among the conventional ways of determining hydrazine by absorption or fluorescence, p.dimethylaminobenzaldehyde (p.DMAB) is chosen because the method is the only one fitting with the nuclear conditions (Table 1). There must be a good way for regenerating it. It has to be fully recovered to the initial conditions without damage. For this purpose, the reaction of hydrazine with p.DMAB has to be reversible enough and if it is so, change of temperature or environment conditions will be a good way for shifting the reaction backward.

* Bât G1, BP 171, 30 207 Bagnols sur Cèze FRANCE.
\textsuperscript{t} Corresponding author, Tel. +33-66-79-16-36, Fax +33-66-79-16-22, E-mail: gojon@genoise.cea.fr

Therefore, in this article, the equilibrium constant of this reaction is carefully investigated as a function of temperature in order to check its reversibility. Because there is another possibility in utilizing acidity for the regeneration, its effect is also investigated.

II. EXPERIMENTAL

1. Apparatus

Shimadzu UV 160A spectrophotometer, using a 1 cm quartz cell, is used for measuring optical density. Temperature of the solution is controlled with a CPS 240, a cell positionner with a temperature controller based on the Peltier effect with 0.1 degree in sensitivity. Briüer NMR device is used to perform the study on acidity.

2. Reagents

Analytical-reagent grade chemicals and demineralized water were used. Solutions of hydrazine sulfate 0.1 M (Aldrich) and p.DMAB 0.3 M (Prolabo, purity=98%) were prepared in 1 M nitric acid, from which the standard solutions were prepared. The hydrazine solutions were standardized by titration with standard potassium iodate solutions\textsuperscript{6}. For \textsuperscript{1}H.NMR study, p.DMAB was dissolved in deuterium nitric acid medium (Eurisop, isotopic enrichment=99%) with heavy water (purity=99.9%) in the range of 0.01 to 5.00 M and in deuterium dimethylsulfoxide (purity=99.8%).

3. Procedure

An aliquot of a solution of hydrazine was placed in a 10 ml flask and an aliquot of a p.DMAB solution was added. Solution of 1 M nitric acid was added to complete the volume. The solution was stirred for 15 min to obtain full colour development. The absorbance of the p.DMAB and the yellow coloured dye were measured respectively at 352 and 454 nm. A reagent blank was prepared in the
C. GOJON and B. DUREAULT

Temperature was adjusted by the temperature controller and the absorbance was measured after 20 min of heating.

For the NMR measurements, 10⁻³ g of p.DMAB was added to a 0.5 ml solution of deuterium nitric acid (0.01 to 5.00 M) in capillary tubes. They were stirred and then placed in the device. The standard was TMS (tetramethylsilane).

II. RESULTS AND DISCUSSION

1. Reaction and Definition of the Coefficients

The reaction involves a condensation of hydrazine with p.DMAB to form p.dimethylaminobenzalazine(n, called D₂N. This reaction is well known in organic chemistry to protect carbonyl group(8). It is an equilibrium and is shifted by a change of acidity to recover carbonyl group.

\[2p\text{-DMAB} + N_2H_5^+ \rightleftharpoons D_2N + H^+\].

The expression of the equilibrium constant is:

\[K = \frac{[D_2N][H^+]}{[p\text{-DMAB}]^2[N_2H_5^+]^1}\] (2)

where \([\cdot]\) defines the concentration of the reagents in mol/l.

The concentration are determined by the Lambert Berr's law:

\[A_\lambda = [\cdot] \times \varepsilon_\lambda \times L,\] (3)

where \(A_\lambda\) is the absorbance at \(\lambda\) nm, \(\varepsilon\) is the molar extinction coefficient (l/mol·cm⁻¹) and \(L\) is the length of the cell (\(L=1\) cm).

\[[D_2N] = A_{454}/\varepsilon_{454}\] (4)

\[[p\text{-DMAB}] = A_{352}/\varepsilon_{352}.\] (5)

Hydrazine has no absorbance band in the U.V.-visible range. Its concentration is either calculated from the concentration of p.DMAB or from the concentration of \(D_2N\):

\[[N_2H_5^+] = [N_2H_5^+]_0 - 0.5([p\text{-DMAB}]_0 - [p\text{-DMAB}])\] (6)
or

\[[N_2H_5^+] = [N_2H_5^+]_0 - [D_2N]\] (7)

with \([N_2H_5^+]_0\) as the initial hydrazine concentration.

In order to determine the concentrations of both p.DMAB and \(D_2N\), the respective molar extinction coefficients are determined by a spectrophotometric method.

2. Spectral Characteristics

The spectral characteristics of p.DMAB and \(D_2N\) in 1 M nitric acid medium are presented in Fig. 1. p.DMAB has an absorbance peak at 352 nm whereas \(D_2N\) has its maximum absorption at 454 nm. Hydrazine has no spectral characteristics in the ultra-violet and visible range. Nitrate ions absorb at 300 nm.

3. Determination of Molar Extinction Coefficient

(1) Molar Extinction Coefficient of p.DMAB

Different concentrations of p.DMAB in 1 M nitric acid are measured. The molar extinction coefficient is determined by the slope of the straight line (Fig. 2):

\[A_{352} = [p\text{-DMAB}] \times \varepsilon_{352}\]

At 20°C, \(\varepsilon_{352}\) is equal to 330 l/mol·cm.

The molar extinction coefficient of p.DMAB is weak compared to those of pH indicators or complexing agents. This weak value does not allow a good sensitivity
Spectrophotometric Study of the Reaction between Hydrazine and p.dimethylaminobenzaldehyde

For this purpose, the concentration of p.DMAB can be expressed with the two following relationships:

\[ [\text{p.DMAB}] = A_{352} / \varepsilon_{352} \]  
\[ [\text{p.DMAB}] = [\text{p.DMAB}]_0 - 2 \times A_{454} / \varepsilon_{454}. \]  

\( \varepsilon_{352} \) is determined at different temperatures in order to calculate the equilibrium constant. \( \varepsilon_{352} \) increases with temperature but its variation is non significative (Fig. 3).

(2) Molar Extinction Coefficient of D2N

To determine the molar extinction coefficient of p.dimethylaminobenzalazine, the equilibrium is fully right shifted by a strong excess of p.DMAB. Also, the concentration of D2N is supposed to be equal to the initial concentration of hydrazine. The molar extinction coefficient is determined by the slope of the straight line (Fig. 4):

\[ A_{454} = [\text{D2N}] \times \varepsilon_{454} \]

At 20°C, \( \varepsilon_{454} \) is equal to 59,625 l/mol.cm.

The high value of \( \varepsilon_{454} \) allows a better sensitivity and a low limit of detection. The variation of \( \varepsilon_{454} \) with temperature is relatively important compared to that of p.DMAB. \( \varepsilon_{454} \) decreases when temperature arises (Fig. 3). This phenomenon is not explained.

\[ K_1 = \frac{A_{454} / \varepsilon_{454}}{(A_{352} / \varepsilon_{352})^2 ([N_2H_4^+]_0 - A_{454} / \varepsilon_{454})} \]  

\[ K_2 = \frac{A_{454} / \varepsilon_{454}}{(A_{352} / \varepsilon_{352})^2 \left\{ [N_2H_4^+]_0 - 0.5 \times ([\text{p.DMAB}]_0 - A_{352} / \varepsilon_{352}) \right\}} \]  

\[ K_3 = \frac{A_{454} / \varepsilon_{454}}{([\text{p.DMAB}]_0 - 2 \times A_{454} / \varepsilon_{454})^2 \left\{ [N_2H_4^+]_0 - 0.5 \times ([\text{p.DMAB}]_0 - A_{352} / \varepsilon_{352}) \right\}}. \]  

4. Determination of Equilibrium Constant and Temperature Effect

(1) Equilibrium Constant

The equilibrium constant is determined in stoichiometric conditions. Since the concentration of hydrazine can be calculated by two manners, and since \( \varepsilon_{352} \) is not very high, the equilibrium constant can be expressed by four equations in order to compensate the different ways to determine the concentration of hydrazine and p.DMAB.
The equilibrium constant is calculated by Eq. (11) because it reduces the errors on the concentrations of p.DMAB and hydrazine to the minimum. The equilibrium constant at 20°C is the average of the constants obtained with each solutions (Table 2). At 20°C, it is equal to 5,642 l/mol.

The low value of the equilibrium constant at 20°C suggests that the equilibrium is weak in these conditions. A little D2N is produced and the most of p.DMAB is left, that can react again if the concentration of hydrazine increases. The equilibrium can be easily shifted by a variation of the concentration of hydrazine. This implies a direct reversibility for a sensor that is the best way of regeneration because the sensor can measure the concentration in real-time and no regeneration step is needed.

(2) Effect of Temperature

As the Van’t Hoff relationship demonstrated,

\[ K = K_0 \exp(-\Delta H/RT) \]  

(13)
temperature has a direct effect on the equilibrium constant. Temperature can be an eventual regenerating factor for a sensor. In addition, Watt and Chrisp(6) showed that temperature had an effect on the reaction: over the range 20 to 40°C, it was found to increase of 14%/°C (absolute transmittance). This effect is completely reversible. The spectral characteristics of D2N do not change when temperature arises. The variation of the absorbance with temperature is fully reversible (Fig. 5). The relative standard deviation is 0.30% at 15°C and 0.28% at 30°C. Temperature only affects the equilibrium and not the structure of the species. The evolution of the equilibrium constant with temperature answers to an exponential type. There are two fields of temperature: between 15 and 30°C, the equilibrium constant decreases from 7,900 to 2,885 l/mol (Fig. 6), much faster than above 40°C. The regeneration step has to be done above 40°C because the variation of the equilibrium constant is smaller. Although an error on temperature does not induce a great error on the equilibrium constant, temperature has to be controlled to have a good accuracy. But it cannot allow a perfect regeneration of the sensor because even at high temperature, the equilibrium cannot be fully displaced. So in the case of a sensor, the measurement is not an absolute one but a relative one. This implies to control both the temperature of the measurement and the temperature of the regeneration. Moreover, the working range will be restricted.

5. Effect of Acidity

The equilibrium constant is directly proportional to the concentration of protons (2). Hence, the regeneration of the sensor could be made by a change of acidity. On the range of acidity from 0.1 and 5.0 M, the absorbance of D2N progressively decreases. Above the acidity of 2.0 M, no yellow coloured dye is formed. Two possibilities could be supposed: the equilibrium is fully shifted to the left or p.DMAB is deteriorated by high acidity. The comportment of p.DMAB with acidity is investigated by two studies: one by spectrophotometry and the other by 1H.NMR.

(1) Spectrophotometric Study

This study is performed in nitric acid medium in the range of 0.1 to 5.0 N. The shape of the absorption spectra of p.DMAB varies with the acidity (Fig. 7). In all cases, the absorbance at 352 nm decreases when acidity increases and other absorption peaks appear. From acidity of 1.5 N, a yellow coloured product appears at 420 nm. The kinetic of the formation is accelerated by higher acidity and by temperature. But this phenomenon is not reversible.

From this results, two phenomena may be explained:
Spectrophotometric Study of the Reaction between Hydrazine and p(dimethylaminobenzaldehyde)

in low acidity, from 0.1 to 2.0 N, the structure of p.DMAB is not fundamentally modified. Probably, the variation of absorbance may be due to the protonation of the amino group, that is an equilibrium. In higher acidity, the structure of the p.DMAB may be irreversibly modified.

(2) 1H.NMR Study

In deuterium nitric acid medium from 0.01 M to 1.0 M, the abscissa of the peaks are shifted but the shapes are identical than in deuterium dimethylsulfoxide (DMSO) (Fig. 8 and Table 3). No other peak appears during seven days. So p.DMAB is stable on the range of acidity from 0.01 to 1.0 M. From the concentration of nitric acid of 2.0 to 5.0 M, other peaks appear between 8.0 and 9.0 ppm. The aromatic hydrogens are disturbed. The more acidic the medium is, the faster the p.DMAB is deteriorated. It may be supposed that in highly acidic medium, p.DMAB is nitrated. Thus, the sensor could be regenerated by acidity. But the range of acidity is limited to 1.0 M because above p.DMAB is not stable and loses its structural characteristics.

IV. CONCLUSION

With the aim of realizing an optical fibre chemical sensor for hydrazine in the Purex process, the reaction between hydrazine and p.DMAB in nitric acid medium was studied. The reaction is an equilibrium. It is easily shifted by temperature and acidity. The observed equilibrium constant was revealed to be suitable enough without any regeneration step to realize reversible sensors. In addition, the possibility of the regeneration of sensor utilizing temperature effect was studied and shown. The regeneration by temperature is not perfect. It was shown that the measurements will be relative and therefore the working range will be restricted. Moreover, the acidity effect was studied. It was shown that the equilibrium reversibly shifted with change of acidity. But the acidity range was found to be restricted by the degradation of p.DMAB. For example, if the sensor is directly placed in the process, regeneration by temperature is easy. On the contrary, if the sensor is put in a bypass, both regeneration by temperature and acidity could be applied. p.DMAB has been entrapped or covalently bonded by a sol-gel technique into a glass matrix in order to realize a sensor. The study of the reaction in solid phase of hydrazine with immobilized p.DMAB is in progress to determine the direct reversibility or regeneration steps.

REFERENCES