Indian Journal of Chemistry
Vol. 31A, July 1992, pp. 423-426

Kinetics of the reaction of hydrazine with 2-hydroxy-1-naphthaldehyde

R Garcia Domenech*, J Mañes Vinuesa, M Pascual Pastor & J Mari Buigues
Department of Chemical Physics, Faculty of Pharmacy, University of Valencia, Avda Blasco Ibañez, 13. 46010-Valencia, Spain

Received 22 October 1991; revised and accepted 29 January 1992

Hydrazine in aqueous solution reacts with 2-hydroxy-1-naphthaldehyde in ethanol leading slowly to highly insoluble yellow reaction product. Based on UV-Vis, IR and mass spectrophotometric studies, the **compound is characterized as an aldazine, 2,2′-dihydroxy-1-naphthaldazine. Kinetics of the reaction has been followed by spectrophotometric measurements of the absorbance of the reaction product as a function of time. Under excess [2-hydroxy-1-naphthaldehyde] the reaction follows a pseudo-first order kinet**ics. Under excess [hydrazine], also the reaction follows a pseudo-first order kinetics. Yet important kinetic **differences have been found between both the processes. Under excess of 2-hydroxy-1-naphthaldehyde, the reaction is controlled thermally, under excess of hydrazine, the rate constant is temperature independent. According to these results the process takes place in two steps with the formation of an intermediate product. The mathematical treatment of the kinetic results is consistent with the proposed mechanism.**

Hydrazine (NH_2-NH_2) is widely used as a strong reducing agent for corrosion control in boilers and hot-water heating systems; also for metal plating, and for reducing noble-metal catalysts and unsaturated bonds in organic compounds[1]. It is the starting material for many derivatives like antioxidants, polymers, plant-growth regulators and pesticides[2]. Besides this, hydrazine is used in the synthesis of pharmaceuticals, such as hydralazine, hydrocarbazine, mebanazine, isoniazide, etc. Since hydrazine is a highly toxic compound[3,4] (at high doses it may cause hepatic damage and depression of the nervous system[5] as well as mutagenic[6,7] and carcinogenic effects) it becomes necessary to determine its existing levels in drugs[8-10].

The aim of this work is to complete recent studies dealing with the determination of hydrazine based on its reaction with 2-hydroxy-1-naphthaldehyde and subsequent extraction of the reaction product with chloroform[11]. The present study deals with two basic aspects, the structural characterization of the reaction product and the evaluation of the stoichiometry of the process: hydrazine + 2-hydroxy-1-naphthaldehyde → product and the study of the reaction mechanism. Thin layer chromatography (TLC) and spectroscopic techniques, such as UV, IR and mass spectrophotometric are used in this study.

Materials and Methods

Hydrazine stock solution was prepared weekly from hydrazine sulphate (Panreac) in distilled water and standardized by bromate titration[11]. 2-Hydroxy-1-naphthaldehyde (Ega-Chemie), was prepared in ethanol. Both solutions were maintained with refrigeration while not in active use. All other chemicals used like acetic acid, sodium acetate, Na_2-EDTA and $CHCl_3$ were provided by Panreac.

Isolation of product

Hydrazine sulphate 0.01*M* and 2-hydroxy-1-naphthaldehyde in ethanol 0.01*M*, were added to distilled water (25 ml) in approximately stoichiometric proportions. The contents were mixed by gentle shaking, and kept at 100°C for 5 min. A yellow precipitate appeared, which was filtered off and washed with three portions of ethanol and dried at 80°C to constant weight.

Influence of pH

The effect of *p*H on the reaction has been studied within the *p*H range of 1.8-8.4. With a *p*H of less than 7.0, hydrazine condenses with 2-hydroxy-1-naphthaldehyde, and the corresponding yellow aldazine is formed. The absorbances are proportional to the concentration of the problem substance. The sensitivity of the reaction increases with *p*H and the optimum values in order to determine hydrazine in the area between 3.6 and 6.6 are to be found.

Spectroscopic studies

Absorbance measurements and spectra of 2-hydroxy-1-naphthaldehyde and of reaction product were recorded using a Shimadzu UV-240 spectrophotometer equipped with 1 cm quartz cells. A Riber 10C spectrometer was used for the mass spectrum of reaction product. Accelerating voltage was 1800V. Ionization energy was 70 eV. Solid injector temperature was set at 180°C.

The infrared spectra were obtained using a Perkin-Elmer 843 infrared spectrophotometer, on solid samples prepared as potassium bromide discs.

Chromatographic determinations

TLC aluminium sheet silicagel 60, layer thickness 0.2 mm (Merck) was used as adsorbent for the separation of reaction product. Chloroform-ethanol-toluene-ammonia (14:11:80:0.5) was chosen as the developing solution. Reaction product spots on the chromatogram were detected by exposure to UV radiation and later evaporated off to allow the formation of crystals.

Linearity study

Stock solution of reaction product in $CHCl_3$ were prepared to contain 100 mg/ml. Aliquots of this solution, representing amounts of reaction product ranging from 20 to 0.3 mg was pipetted into individual volumetric flask (10 ml) and the absorbance of each solution was recorded at 412 nm.

Kinetics studies

Reactions of the hydrazine with 2-hydroxy-1-naphthaldehyde were studied at *p*H 4.5 and at temperatures of 20, 30, 40, 50 and 60°C. Two series were made, one under excess of 2-hydroxy-1-naphthaldehyde and another with excess hydrazine. Experimental conditions for each study were as follows:

Under excess of 2-hydroxy-1-naphthaldehyde, hydrazine solution (1 ml, 2×10^{-4} *M*) was pipetted into a series of glass-stoppered tubes and diluted to 5 ml with distilled water; added acetate buffer (1 ml), Na_2-EDTA (1 ml, 0.02 *M*) and 2-hydroxy-1-naphthaldehyde (1 ml, 0.01 *M*) were added all under thermal equilibrium and absorbance was recorded at 412 nm as a function of time. For pseudo-first order kinetic studies, the rate constants were calculated from the appropriate logarithmic relationship by linear least-square analysis. The rate constant was calculated using Eq. (1).

$$\ln\{(A_f - A_t)/(A_f - A_0)\} = -k_{obs}.t \qquad \ldots (1)$$

where A_0 = initial absorbance of the reaction product, A_f = final absorbance and k_{obs} = apparent rate constant.

Under excess of hydrazine, the same experimental conditions were used except that [hydrazine] was 0.01 *M*, and [2-hydroxy-1-naphthaldehyde solution] was 2×10^{-4} *M*.

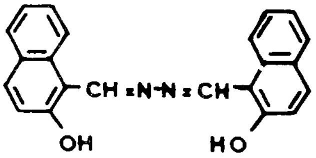
Results and Discussion

Characterization of the reaction product

Hydrazine reacts in aqueous-ethanolic phase with 2-hydroxy-1-naphthaldehyde to form a water and alcohol insoluble yellow product. Purification of the reaction product was accomplished by TLC and the compound showed an R_f value of 0.90 while 2-hydroxy-1-naphthaldehyde had an R_f value less than 0.62.

The UV-visible spectrum of the product in chloroform, and of 2-hydroxy-1-naphthaldehyde in ethanol showed different absorption bands. It has a maximum at 412 nm, whereas 2-hydroxy-1-naphthaldehyde has no absorption around this wavelength hence studies were carried out at 412 nm.

The IR spectrum for the product shows bands at 3444, 2920, 1618, 1602 and 1576 cm^{-1} and is consistent with the absence of C=O stretching vibrations. The new band at 1618 cm^{-1} is assigned to $-CH=N-N=CH-$ stretching vibrations. The mass spectrum contains a molecular ion peak at m/z 340 and 40.92% relative abundance a value which coincides with molecular weight of the expected product. Based on these results, it was concluded that the reaction product is an aldazine, the 2,2′-dihydroxy-1-naphthaldazine (I), with a molecular weight of 340, in agreement with the studies reported by Manes *et al.*[12].



(I)

Structure (I) implies a stoichiometry 1:2 (hydrazine:aldehyde) for the process,

$$\text{hydrazine} + 2\ \text{aldehyde} \rightarrow \text{aldazine} \qquad \ldots (2)$$

where aldehyde = 2-hydroxy-1-naphthaldehyde and aldazine = 2,2′-dihydroxy-1-naphthaldazine.

Linearity and reversibility studies

Linearity between aldazine absorbance, A_t (at 412 nm) and [aldazine] was observed. For [aldazine] lower than 6×10^{-5} mol/dm^3, ($A_t = 0.0039 + 28590$ [aldazine]; $r = 0.9997$, $n = 7$). Absorptivity coefficient at this wavelength was of 28590 dm^3.mol^{-1}.cm^{-1}. For the reversibility study of the process, the reaction was carried out under excess of aldehyde, in a water-bath at around boiling temperature during the time needed to reach the maximum absorbance.

From the stoichiometry of the process and the relationship between [aldazine] obtained at equilibrium and the initially used [hydrazine], it can be concluded that the process should be taken as irreversible.

Kinetic study

Using the method of the integrated-rate equations, the best least-square values were obtained considering a pseudo-first order with respect to hydrazine (with [2-hydroxy-1-naphthaldehyde] excess) (at temps = 20, 30, 40, 50 and 60°C, n = 3 and r = 0.9959, 0.9966, 0.9944, 0.9922 and 0.9912 respectively). Under excess [hydrazine], the kinetic results obtained, showed a linear relationship between $\ln\{(A_f - A_t)/(A_f - A_0)\}$ and time, implying a pseudo-first order with respect to 2-hydroxy-1-naphthaldehyde (at temps = 20, 30, 40, 50 and 60°C, n = 3 and r = 0.9901, 0.9946, 0.9936, 0.9904 and 0.9913 respectively). Nevertheless, important kinetic differences were found between both processes. When the reaction was carried out under excess [aldehyde], it became thermally controlled (see Table 1). The rate constant k_{obs} increases with temperature. When the reaction was carried out under excess [hydrazine], the reaction seems to be temperature independent ($k'_{obs.}$ does not depend on temperature).

These observations lead us to assume that the process did not occur in a single step and that a probable mechanism for the reaction would be, as in Scheme 1.

$$\text{hydrazine} + \text{aldehyde} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_1 \quad \ldots (3)$$

$$C_1 + \text{aldehyde} \xrightarrow{k_2} \text{aldazine} \quad \ldots (4)$$

Scheme 1

where $k_1 \gg k_{-1}$

The reaction could take place in two steps with formation of an intermediate product C_1. The first step would be the rate-determining step of the reaction under excess [aldehyde], while the second step would be the rate-determining step under excess [hydrazine]. This is quite reasonable if we take into account the considerable size difference between hydrazine and the aldehyde and, hydrazine and C_1.

In order to verify our hypothesis the kinetic results must be consistent with our proposed mechanism,

$$v = d[\text{aldazine}]/dt = k_2[C_1][\text{aldehyde}] \quad \ldots (5)$$

Table 1—Values of the rate constant $k_{obs.}$ for the hydrazine-2-hydroxy-1-naphthaldehyde reaction at different temperatures

T(K)	$10^5\ k_{obs.}\ (s^{-1})$ under excess of [2-hydroxy-1-naphthaldehyde]	$10^5\ k'_{obs}\ (s^{-1})$ under excess of [hydrazine]
293	2.23	1.64
303	3.76	1.57
313	7.57	1.54
323	17.09	1.95
333	37.55	1.40

Equation (6) must be satisfied at all times:

$$[\text{aldehyde}]_0 = [\text{aldehyde}] + [C_1] + 2[\text{aldazine}] \quad \ldots (6)$$

where $[\text{aldehyde}]_0$ = initial [2-hydroxy-1-naphthaldehyde]

$$v = k_2[C_1]\{[\text{aldehyde}]_0 - [C_1] - 2(\text{aldazine}]\} \quad \ldots (7)$$

$$v = k_2[C_1]\{[\text{aldehyde}]_0 - [C_1]\} - 2k_2[C_1][\text{aldazine}] \quad \ldots (8)$$

Under excess [aldehyde], if the first step is the rate-determining step, i.e. $k_1 \ll k_2$, $[C_1]$ may be assumed as approximately constant and very small.

Then

$$k_2[C_1]\{[\text{aldehyde}]_0\text{-}[C_1]\} \approx \text{constant} = A \quad \ldots (9)$$

$$2k_2[C_1] \approx \text{constant} = B \quad \ldots (10)$$

and

$$v \approx A - B[\text{aldazine}] \quad \ldots (11)$$

Plotting the rate of reaction versus [aldazine] for the runs carried out at different temperatures a linear dependence between them (Fig. 1) is obtained.

Quite different conclusions are reached under excess of [hydrazine]. If the rate determining step is the second one, $[C_1]$ will not be constant and consequently there will be no linear dependence between the rate of reaction and [aldazine]. (Fig. 2).

In fact, since

$[\text{aldehyde}]_0 = [\text{aldehyde}] + [C_1] + 2[\text{aldazine}]$ and

$[\text{hydrazine}]_0 = [\text{hydrazine}] + [C_1] + [\text{aldazine}]$, then

$$[\text{aldehyde}] = [\text{aldehyde}]_0 - [\text{hydrazine}]_0 + [\text{hydrazine}] - [\text{aldazine}]$$ and

$$[C_1] = [\text{hydrazine}]_0 - [\text{hydrazine}] - [\text{aldazine}]$$

and Eq. (7) becomes:

$$v = k_2\{[\text{hydrazine}]_0 - [\text{hydrazine}] - [\text{aldazine}]\}\{[\text{aldehyde}]_0 - [\text{hydrazine}]_0 + [\text{hydrazine}] - [\text{aldazine}]\} \quad \ldots (12)$$

Under these conditions $[\text{hydrazine}] \approx [\text{hydrazine}]_0$, and

$$v = -k_2[\text{aldehyde}]_0[\text{aldazine}] + k_2[\text{aldazine}]^2 \quad \ldots (13)$$

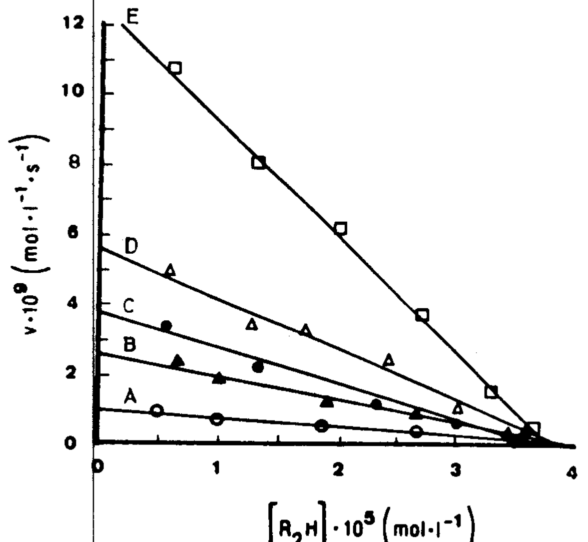


Fig. 1—Plots of the reaction rate versus [aldazine] under excess [2-hydroxy-1-naphthaldehyde], at different temperatures. (A – 20°; B – 30°, C – 40°, D – 50°, E – 60°C)

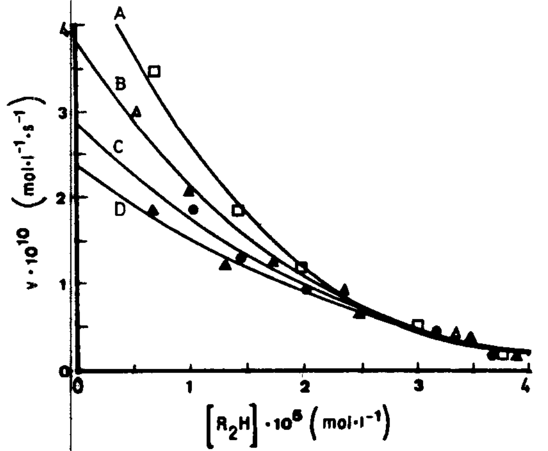


Fig. 2—Plots of the reaction rate (v) versus [aldazine] under excess [hydrazine], at different temperatures. (A – 20°, B – 30°, C – 40°, D – 60°C)

Table 2—Reactions under excess [hydrazine] at different temperatures. Values of the coefficients corresponding to Eq. (13). $v = -k_2[\text{aldehyde}]_0[\text{aldazine}] + k_2[\text{aldazine}]^2$

T(K)	[aldazine] coefficient $\times 10^5$ (s^{-1})	$[\text{aldazine}]^2$ coefficient ($dm^3.mol^{-1}\,s^{-1}$)	Correlation coefficient (r)
293	−7.1055	2.3045	0.993
303	−4.2277	1.4132	0.998
313	−3.4361	1.5235	0.991
333	−5.1388	1.9167	0.991

If the proposed mechanism is correct, there will be a quadratic relationship between v and [aldazine]. The coefficients for [aldazine] and $[\text{aldazine}]^2$ are shown in Table 2.

It should be noticed that the [aldazine] coefficients are always negative while the $[\text{aldazine}]^2$ coefficients are always positive as Eq. (17) shows. Also, there is no independent term, as expected from the mathematical analysis. The correlation coefficients found for a quadratic adjustment are in all the cases greater than 0.991, which again confirms the proposed mechanism.

Dependence between the rate constant and temperature using Arrhenius equation was also studied. For the process using an excess [aldehyde], $\Delta H^{\neq}$ was found to be 56.901 $kJ.mol^{-1}$ and $\Delta S^{\neq} = -22.8$ $J.mol^{-1}.K^{-1}$. Under these conditions the reaction is thermically controlled. Under excess [hydrazine], $\Delta H^{\neq} = -2.320$ $kJ.mol^{-1}$ and $\Delta S^{\neq} = -229.3$ $J.mol^{-1}.K^{-1}$. The negative $\Delta H^{\neq}$ value for the reaction using excess [hydrazine], is further evidence of a two step mechanism, i.e., that the observed rate constant is a product of the rate constant of the second step and the equilibrium constant of the initial step. Since equilibrium constants may increase or decrease with increase in temperature, the product of the rate constant and equilibrium constant may also increase or decrease with increase in temperature.

References

1 Snell F & Hilton C L, *Encyclopedia of industrial chemical analysis*, Vol. 14 (Interscience, New York), (1971) 232.
2 *Evaluation of some pesticide residues in food AGP*, 1976/M/14. Food and Agricultural organisation of the United Nations, Rome (1976) 377.
3 Smith F B & Clark D A, *Toxicol appl pharmacol*, 21 (1972) 186.
4 Frejaville J P & Bourdon R, *Toxicologie clinique et analytique. Flammarion Medecine-Sciences*, (1975) 596.
5 Lauwerys R, *Toxicologia industrielle et intoxications profesionelles* (Masson, Paris), (1982) 227.
6 Loomis T A, *Fundamentos de toxicologia*, (Ed Acribia) (1982) 247.
7 Vernot E H, MacEwen J D, Bruner R H, Haus C C & Kintread E R, *Fundam appl toxicol*, 5 (1985) 1050.
8 *Farmacopea Europea*, Vol. 1 Ed. Consejo General de Colegios de Farmacéuticos, (1969) 327.
9 *Farmacopea Internacional*, Vol. 2, Organización Mundial de la Salud, Ginebra, (1983) 175.
10 *Guia de Riesgos Químicos NIOSH/OSHA. Traduction of NIOSH/OSHA Pocket guide to chemical hazards*, Instituto Nacional de Seguridad e Higiene en el Trabajo, Barcelona (1982).
11 Mañes J, Campillos P, Font C, Martre H & Prognon P, *Analyst*, 112 (1987) 1183.
12 Mañes J, Gimeno M J, Molto J C & Font G, *J pharm biomed anal*, 6 (1988) 1023.