Synthesis of Hydroxyethylhydrazine by the Raschig Process and Comparison with Synthesis by the Alkylation Process

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ABSTRACT: The Raschig synthesis of hydroxyethylhydrazine (HEH) is studied, that is, the reaction of monochloramine on ethanolamine. The formation of HEH is monitored by UV spectrometry, and the influence of temperature and pH is studied. The primary reaction is an SN₂-type mechanism, whereas the main secondary reaction is the oxidation of HEH by monochloramine. This reaction is also monitored by UV spectrometry, and the oxidation product is identified by GC–MS analysis, showing the formation of hydroxyethylhydrazone. The reaction mechanisms and the rate constants were determined, and the results permit establishing the main reactions occurring during HEH synthesis. These reactions were validated in a concentrated medium, with the systematic study of the influence of the molar ratio p ([HEH]₀/[NH₂Cl]₀) and the final sodium hydroxide concentration and temperature. A comparison is made with the other synthesis process already published, that is, the alkylation of hydrazine by either chloroethanol or epoxide. © 2011 Wiley Periodicals, Inc. Int J Chem Kinet 43: 331–344, 2011

INTRODUCTION

2-Hydroxyethylhydrazine (HEH) is currently used as a precursor in the pharmaceutical industry [1]; it is also used in the cosmetics, agrochemical and photographic industries. However, the most promising application is the aerospace industry [2,3] because it will be a good

candidate for the satellite propulsion system. Indeed, its specific impulsion is of the same order as that of hydrazine (273 s for HEH and 283 s for hydrazine), but its saturated vapor pressure is much smaller (1.33 Pa for HEH and 1.89×10^3 Pa for hydrazine). This is very important because hydrazine and its derivatives are toxic molecules. In consequence, studies were carried out by different laboratories and in 2001, the U.S. Air Force took out a patent [3] for the preparation of HEH salts and their applications as ergols or explosives. The different salts are as follows:

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$$HO-CH_2-CH_2-NH-NH_2 + mHX \longrightarrow$$

[HO-CH₂-CH₂-NH₂-NH₂⁺][X⁻]or

[HO-CH₂-CH₂-NH₂-NH₃²⁺][X⁻]₂

with $HX = HNO_3$, $HClO_4$, $HN(NO_2)_2$, $HC(NO_2)_3$ m = 1, 2

Since that time, the interest in this molecule has remained relevant.

In a previous paper [4], HEH was synthesized by alkylation of N₂H₄ with 2-chloroethanol (CletOH) with or without a strong base. Another widely used method is the Raschig process. However, it has two main disadvantages: low reagent concentrations, especially chloramine, and a large number of secondary reactions. On the other hand, it has several advantages: the reaction is carried out in water, the reagents are less pollutant and expensive, and the process does not use highly toxic reagents such as carcinogenic nitrate and nitroso derivatives, thereby preserving the environment. Thus, the aim of this paper is to describe HEH synthesis by using the Raschig process and its advantages and then compare the two methods.

EXPERIMENTAL

Reagents

Ethanolamine (99% purity) was provided by Aldrich, and ammonia in aqueous solution (32%) was provided by Prolabo. The solutions of sodium hypochlorite at 48° chlorometry were provided by ELF-ATOCHEM, kept at 5°C, and systematically analyzed before use.

Monochloramine (NH₂Cl) is not commercially available so it was prepared at -10° C by reacting sodium hypochlorite (25 mL, 48° chlorometry) with a mixed ammonia solution NH₃/NH₄Cl (25 mL, 3.6 M/2.38 M) in the presence of ethyl ether (40 mL). For the kinetic studies, NH₂Cl was purified by successive extractions with water and then stored at 5°C in ethyl ether to keep it stable. The aqueous solutions were obtained just before use by reextraction from the ether phase. The residual solvent and ammonia traces were eliminated by vacuum treatment. At this stage of preparation, the NH₂Cl concentration was between 0.1 and 0.15 M.

The other reagents and salts used in this study (NaOH, NH₄Cl, Na₂HPO₄, KH₂PO₄, etc.) were products for analysis at +99% (reagents from Prolabo RP, Merck, Aldrich, etc.).

Water was purified by using an ion exchange resin.

The Apparatus and Experimental Protocol

The apparatus was composed of two parts: The upper part consisted of a double-walled cylindrical bulb with a capacity of 200 mL in which a temperature sensor was introduced. A wide diameter needle valve at the base of the bulb ensured that the liquid flowed rapidly. The bulb was connected to the lower part which was a thermostatic reactor with a capacity of 500 mL. Several inlets allowed the introduction of nitrogen into the reactor, taking samples and measuring temperature. Agitation was ensured by using a magnetic stirring bar. The bulb and the reactor were kept at constant temperature by using a Julabo cryo-thermostat.

The ethanolamine (EA) or HEH solution (50 mL) was introduced under nitrogen into the reactor, whereas the NH₂Cl solution (50 mL) was introduced into the upper part. When the temperature was homogeneous, the reagents were mixed together and samples were taken under nitrogen.

Analyses

The different reactions involved in the system EA/NH₂Cl were studied by ultraviolet (UV) either directly or by HPLC (high performance liquid chromatography). The reaction products were characterized by coupled GC-MS (gas chromatography-mass spectrometry).

The different tests were carried out at pH 12.89 and $T = 25^{\circ}$ C, in a reductive medium for HEH concentrations between 8 and 40×10^{-3} M.

UV Spectrometry. A CARY 100 dual beam spectrometer from VARIAN was used (quartz cells from 1 to 10 mm light pathway), linked to a data acquisition system. This device can perform repetitive spectrum scans between 900 and 180 nm, programmable as a function of time, measure absorbance at each wavelength, and superpose and add curves.

HPLC Analysis. Five milliliters of the synthesis solution was taken and added to the same volume of ethyl ether. After mixing, the solution separated itself into two phases and the upper phase was extracted and conditioned at a temperature of 0°C. The two reagents

were isolated in each phase after which the sample was analyzed. An Agilent 1100 chromatograph with a bar iodine detector was used with an Eclipse ODS XDB-C8 column (grafted phase octadecylsilane) of 150 mm length and 3 mm diameter (dp = 5 μ m). A precolumn was used for basic injections. The mobile phase was a mixture of 95% water/5% acetonitrile. The volume of the manual injection loop was 20 μ L, and the flow rate was 0.5 mL/min. The wavelengths measured by the bar iodine detector were established at $\lambda = 200$, 243, 254 nm.

GC–MS. The samples were analyzed with a 5970 spectrometer from Agilent Technologies, equipped with a quadrupole analyzer, and the molecules were ionized by electronic impact (70 eV). The ionic fragments were identified according to their mass/charge (m/z) ratio. The GC–MS analyses were performed with an HP-5MS trace analysis column (30 m, 250 µm, df = 0.25 µm).

RESULTS AND DISCUSSION

Kinetics of HEH Formation by the Reaction of Monochloramine on Ethanolamine

HEH formation kinetics was initially monitored at a temperature of 25°C and a pH of 12.89 (0.1 M NaOH). Excess EA was used to limit the secondary reactions. These experimental conditions are in accordance with the constraints imposed by the Raschig synthesis:

NH₂Cl was separately prepared from sodium hypochlorite and ammonia:

$$OCl^- + NH_3 \xrightarrow{NH_4Cl} NH_2Cl + OH^-$$

Then it was used as a reagent to form HEH:

$$NH_{2}Cl + HO-(CH_{2})_{2}-NH_{2}$$

$$\xrightarrow{k_{1}} HO-(CH_{2})_{2}-NH-NH_{2} + Cl^{-} + H_{2}O$$

$$NH_{2}Cl + OH^{-} \xrightarrow{k_{2}} NH_{2}OH + Cl^{-}$$

These two reactions, formation of HEH from NH₂Cl and hydrolysis of NH₂Cl, are simultaneous.

Because of the high value of the reaction constants, the experiments were carried out in a diluted medium, using reagent concentrations between 10^{-3} and 10^{-2} M. The ionic strength of the medium was imposed by the NaOH concentration (0.1–1 M). Under these conditions, the kinetic parameters of the reaction between NH₂Cl and EA were determined by UV spectrometry,



Figure 1 Variation of the absorbance with time at $\lambda = 243$ nm, $T = 25^{\circ}$ C, p = 21.4, pH 12.89.

by monitoring the NH₂Cl concentration. The spectrum of a reaction mixture at different times is complex and involves several steps. Initially, the absorbance of NH₂Cl decreases and shifts to a higher wavelength. The absorbance does not tend toward zero, but toward a value that depends on the initial conditions. At the end of the reaction, a new absorption peak appears. It increases slowly and shifts to lower wavelengths. These results can be expressed quantitatively when monitoring the variation of the absorbance with time at $\lambda =$ 243 nm (Fig. 1). After a continuous decrease to about 37%, the curve stabilizes and then increases again. The anomaly observed at the end of the reaction is due to interference between the absorption peak of NH₂Cl, which decreases, and the increase of a peak related to a chromophore product "P" that is not due to the formation of HEH, the latter failing to provide any peak under UV spectrometry. The absence of isobestic points $(dD_{\lambda}/dt = 0)$ excludes any stoichiometric relation between NH₂Cl and P. Consequently, the formation of P is subsequent to the NH₂Cl/EA reaction. It must result from an interaction between HEH and one of the two reagents, namely NH₂Cl. This interpretation will be further confirmed by an exhaustive study of HEH oxidation by NH₂Cl. Indeed, interference is null at the beginning of the reaction, but increases with the degree of conversion. UV spectrometry then permits the

<i>T</i> (°C)	$[EA]_0 (10^{-2} \text{ M})$	[NH ₂ Cl] ₀ (10 ⁻³ M)	$p = [\text{EA}]_0 / [\text{NH}_2\text{Cl}]_0$	$k_1 (10^{-1} \text{ M}^{-1} \text{ min}^{-1})$	R^2
25	2.2	2.8	7.9	1.62	0.999
25	2.6	2.8	9.2	1.61	0.998
25	3.2	2.9	11.2	1.62	0.999
25	4.8	2.9	16.2	1.62	0.998
25	6.1	2.9	21.4	1.61	0.993

Table I Determination of the Kinetic Parameters of the Reaction between NH₂Cl and EA ($T = 25^{\circ}$ C, [NaOH] = 0.1 M)

precise determination of the rate laws from the NH₂Cl concentration–time curves, limiting the measurement to the half time of the reaction.

The Rate Laws. The rate of NH_2Cl disappearance is expressed by the relation (1) according to the two reactions described above: formation of HEH from NH_2Cl and hydrolysis of NH_2Cl .

$$-\frac{d[\mathrm{NH}_{2}\mathrm{Cl}]}{dt} = \nu_{1}k_{1} [\mathrm{NH}_{2}\mathrm{Cl}]^{\alpha} [\mathrm{EA}]^{\beta}$$
$$+ k_{2} [\mathrm{NH}_{2}\mathrm{Cl}] [\mathrm{OH}^{-}] \qquad (1)$$

where v_1 is the stoichiometry coefficient and k_1 , α , β , respectively, the rate constant of the reaction compared to NH₂Cl and the partial orders compared to the reagents. The second term is related to NH₂Cl hydrolysis, which can be neglected under the experimental conditions studied (pH < 13).

The kinetic parameters were determined by integration, by considering $\alpha = \beta = 1$. Under these conditions, the NH₂Cl concentration was determined from the absorbance at $\lambda = 243$ nm at each instant.

$$[\mathrm{NH}_{2}\mathrm{Cl}] = \frac{D_{\lambda}(t)}{\varepsilon l}$$

(\varepsilon = 4581 \text{ mol}^{-1}\text{ cm}^{-1}; l = 1 \text{ cm}) (2)

For unity stoichiometry ($\nu = 1$), the instantaneous concentration of EA was deduced by the formula

$$[EA] = [EA]_0 - [NH_2Cl]$$

where $[EA]_0$ represents the amine concentration at t = 0.

By representing the initial NH_2Cl concentration by $[NH_2Cl]_0$, the integration of relation (1),

$$-\int_{[\rm NH_2Cl]_0}^{[\rm NH_2Cl]} \frac{\rm d[\rm NH_2\,Cl]}{[\rm NH_2Cl]([\rm EA]_0 - [\rm NH_2\,Cl])} = k_1 \int_0^t \rm dt$$

leads to the following equation:

$$\frac{1}{[\text{EA}]_0 - [\text{NH}_2\text{Cl}]_0} \ln \frac{[\text{NH}_2\text{Cl}]_0 [\text{EA}]}{[\text{EA}]_0 [\text{NH}_2\text{Cl}]} = k_1 t \quad (3)$$

The plot $\ln A/([EA]_0 - [NH_2Cl]_0) = f(t)$, with $A = [NH_2Cl]_0 [EA]/[EA]_0 [NH_2Cl]$ at 25°C, pH 12.89, and a molar ratio $p = [EA]/[NH_2Cl] = 11.2$, is linear. The straight line obtained goes through the origin with a slope equal to 1.62×10^{-1} L mol⁻¹ min⁻¹ and a correlation coefficient $R^2 = 0.999$.

A similar treatment was carried out for a series of mixtures of different reagent compositions, to verify invariability k_1 at a fixed pH and temperature. The uncertainty of measurement is about 5% for k_1 and the other kinetic parameters determined in this paper. The results are presented in Table I.

The values obtained are almost constant considering the experimental errors. Thus, at $T = 25^{\circ}$ C and pH 12.89, the average value of k_1 is 1.62×10^{-1} L mol⁻¹ min⁻¹.

Influence of pH. Concerning the Raschig process, an increase in medium alkalinity generally leads to an increase in the reaction rate. A systematic study was carried out for HEH for a concentration of NaOH between 0.1 and 1 M. The pH values were calculated by using the works of Akerlof and Kegeles [5,6] concerning the determination of activity coefficients in concentrated solutions. The tests were carried out for a constant concentration of NH₂Cl ($\sim 2.9 \times 10^{-3}$ M) and EA ($\sim 60 \times 10^{-3}$ M).

The application of the same analytical method leads to an almost twofold increase in k_1 (2.38 × 10⁻¹ M⁻¹ min⁻¹ at pH 14). However, these values require a correction because NH₂Cl hydrolysis cannot be neglected under the experimental conditions studied. This reaction was studied by Anbar and Yagil [7]. It follows a kinetic law of order 2 compared to the reagents ($k_2 = 62 \times 10^{-6}$ M⁻¹ s⁻¹ or 3.72 × 10⁻³ M⁻¹ min⁻¹ at $T = 25^{\circ}$ C).

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pН	$[EA]_0 (10^{-2} \text{ M})$	[NH ₂ Cl] ₀ (10 ⁻³ M)	$p = [\text{EA}]_0 / [\text{NH}_2\text{Cl}]_0$	$k_1 (10^{-1} \text{ M}^{-1} \text{ min}^{-1})$	$\varphi_0 \ (10^{-1} \ \mathrm{M}^{-1} \ \mathrm{min}^{-1})$
12.9	6.1	2.9	21.4	1.61	1.55
13.2	6.0	2.9	21.0	1.71	1.59
13.6	6.1	2.9	21.5	2.04	1.65
13.8	6.0	2.8	21.4	2.38	1.76

Table II Influence of pH on the Hydrazine Formation Constant k_1 and Its Corrected Value φ_0 (T = 25°C)

Under these conditions, we can write

$$-\frac{\mathrm{d}[\mathrm{NH}_2\mathrm{Cl}]}{\mathrm{d}t} = [\mathrm{NH}_2\mathrm{Cl}](k_1[\mathrm{EA}]_0 + k_2[\mathrm{OH}^-]_0)$$
$$= \varphi_0[\mathrm{NH}_2\mathrm{Cl}]$$

To ensure sufficient excess EA and during the first moments of the reaction (isolation method), the term between brackets can be considered as constant.

The bimolecular constant k_1 can be written as

$$k_1 = \frac{\varphi_0 - k_2 [OH^-]_0}{[EA]_0} \tag{4}$$

The results for both treatments are reported in Table II. After correction, we noted a moderate increase in the reaction rate. Therefore, it is not useful to carry out the synthesis in a very alkaline medium.

Influence of Temperature. The influence of temperature was studied between 15 and 45°C for NH₂Cl and EA concentrations equal to 2.8×10^{-3} and 60×10^{-3} M, respectively. The variation of k_1 versus temperature obeys Arrhenius' law (Fig. 2).



Figure 2 Determination of activation energy E_{a1} . [NH₂Cl]₀ = 2.8 × 10⁻³ M, [EA]₀ = 60 × 10⁻³ M, [NaOH]₀ = 0.1 M.

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The plot $\ln k_1 = f(1/T)$ gives a straight line with a slope $-E_a/R$ and a y-intercept $\ln A_1$. This corresponds to the activation energy and to the Arrhenius factor:

$$k_1 = 3.06 \times 10^7 \exp(-57.5/\text{RT})$$

 $(k^{-1} \text{ in } \text{M}^{-1} \text{ s}^{-1}, \text{E}_{a1} \text{ in } \text{kJ } \text{mol}^{-1})$

from which the enthalpy and the entropy can be deduced:

$$\Delta H_1^{0\#} = E_{a1} - RT; \Delta S_1^{0\#} = R \ln(A_1 h / ek_B T) \quad (5)$$

where $k_{\rm B}$ and *h* represent the Boltzmann constant and the Planck universal constant, respectively ($k_{\rm B} =$ 1.380×10^{-23} J K⁻¹: $h = 6.623 \times 10^{-34}$ J s).

1.380 × 10⁻²³ J K⁻¹; $h = 6.623 \times 10^{-34}$ J s). This gives $\Delta H_1^{0\#} = 55.0$ kJ mol⁻¹ and $\Delta S_1^{0\#} = -110$ J K^{-1} mol⁻¹. The uncertainty of measurement is about 6% for these thermodynamic values.

Mechanistic Aspect. The HEH formation mechanism is of the SN_2 -type. The limiting step corresponds to a nucleophilic attack of the electron doublet of the nitrogen from the amine on the weakly electropositive site of the nitrogen of the chlorinated derivative. Proton elimination is instantaneous.

$$HO-(CH_2)_2-NH_2 + NH_2-CI \longrightarrow [H_2N-NH_2-(CH_2)_2-OH] CI$$

$$H_2N-NH-(CH_2)_2-OH + HCI$$

The rate of HEH formation, controlled by the limiting step, is bimolecular and thus agrees with the kinetic results. Its value is linked to the nucleophilicity of the amine, its degree of substitution, and its electronic environment. Table III gives the rate constants of the different hydrazines evaluated in the laboratory. This table shows that the ratio of the rate constants k_f of the primary, secondary, and tertiary amines compared to N₂H₄ are equal to 65, 800, and 2000, respectively, thus equivalent to those observed in the case of the Hofmann reactions (reaction of NH₃ and amines on the halogenated carbonated derivatives).

The rate constant of HEH formation is about two times lower than its monosubstituted homologue

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Amine	Substitution Degree	Hydrazine Formed	$k_{\rm f} ({\rm M}^{-1}~{\rm s}^{-1})$	<i>T</i> (°C)	Reference
NH ₃	0	N_2H_4	0.09×10^{-3}	27.5	[12]
CH ₃ NH ₂	1	CH ₃ NHNH ₂	5.09×10^{-3}	25	[13]
HO(CH ₂) ₂ NH ₂	1	HO(CH ₂) ₂ NHNH ₂	2.7×10^{-3}	25	
(CH ₃) ₂ NH	2	$(CH_3)_2NNH_2$	72×10^{-3}	25	[14]
C7H12NH	2 (cyclic)	C ₇ H ₁₂ NNH ₂	45.5×10^{-3}	25	[15]
C ₅ H ₁₀ NH	2 (cyclic)	C ₅ H ₁₀ NNH ₂	56×10^{-3}	25	[16]
(CH ₃) ₃ N	3	(CH ₃) ₃ NNH ₂	205×10^{-3}	27.5	[12]

Table III Influence of Amine Nucleophilicity on the Hydrazine Formation Constant k_f (pH 13 and T = 25°C)

(monomethylhydrazine CH_3NHNH_2). This result is due to the electroattractive effect of the terminal hydroxyl.

At pH \leq 12.89, k_1 is practically constant, whereas it increases progressively at pH \geq 12.89. Anbar and Yagil [8] first established that the catalytic effect of OH⁻ ions could be explained considering the partial dissociation of NH₂Cl into chloramide NHCl⁻ ion ($pK_a^{NH_2Cl} =$ 18). They compared the relative rates of the reaction of ammonia, mono-, di-, and triamine in alkaline medium with NH₂Cl. These rates increase sharply with the degree of amine substitution. On the contrary, they noted the absence of any diminution of the rate when NH₂Cl was substituted. Previous works of our laboratory [9,10] confirmed these results and permitted establishing the following reaction scheme:

$$\begin{split} \mathrm{NH}_2\mathrm{Cl} &+ \mathrm{HO}\text{-}(\mathrm{CH}_2)_2\text{-}\mathrm{NH}_2 \\ &\rightarrow \mathrm{HO}\text{-}(\mathrm{CH}_2)_2\text{-}\mathrm{NH}\text{-}\mathrm{NH}_2 + \mathrm{HCl} \\ \mathrm{NH}_2\mathrm{Cl} &\rightleftharpoons \mathrm{NH}\mathrm{Cl}^- + \mathrm{H}^+ \\ \mathrm{HO}\text{-}(\mathrm{CH}_2)_2\text{-}\mathrm{NH}_2 + \mathrm{NH}\mathrm{Cl}^- \\ &\rightarrow \mathrm{HO}\text{-}(\mathrm{CH}_2)_2\text{-}\mathrm{NH}\text{-}\mathrm{NH}_2 + \mathrm{Cl}^- \end{split} \tag{6}$$

This reaction scheme is in accordance with the fact that NH_2Cl reacts with trimethylamine to give a salt and, as this reaction is also catalyzed by the OH^- ions [8–11], we obtain

$$(CH_3)_3N + NH_2Cl \rightarrow (CH_3)_3NNH_2^+Cl^-$$

(basic catalysis)

Kinetics of HEH Oxidation by NH₂Cl

Characterization of the Products. The reaction system HEH/NH₂Cl was studied either by UV or by HPLC, and the reaction products were characterized by GC–MS. In addition, the experiments were carried out at pH 12.89 and $T = 25^{\circ}$ C and for HEH concentrations between 8 and 40 × 10⁻³ M.

The UV analysis (Fig. 3) shows two consecutive reaction processes: First, the decrease in the NH₂Cl peak at $\lambda = 243$ nm is limited by the increase of a chromogen peak "D" that gives an isobestic point at $\lambda_1 = 290$ nm and a pseudoisobestic point at $\lambda_2 = 234$ nm. These two points mean that the disappearance of NH₂Cl and the formation of D are simultaneous.

$$\nu_1 \text{NH}_2 \text{Cl} + \nu_2 \text{HEH} \xrightarrow{k_3} \nu_3 \text{D}$$

After a longer period, UV analysis showed that the absorption bands do not pass through the isobestic points and that, finally, a new isobestic point appears at $\lambda_3 =$ 247 nm. At this point, only two products were present in the medium, D, and a new peak F at $\lambda = 224$ nm. The NH₂Cl was totally consumed. The chromogen products D and F are linked together by the relation

$$\nu_3 D \xrightarrow{k_4} \nu_4 F$$

To characterize the two processes, GC–MS analyses were carried out. The initial concentrations for NH₂Cl, HEH, and NaOH were equal to 0.1, 0.11, and 0.5 M, respectively, which corresponds to HEH/NH₂Cl, and NaOH/NH₂Cl ratios almost equal to 1.1 and 5.

The concentrations were a little higher than the reaction medium, to obtain sufficient sensitivity for the analyses.

After 10 min reaction, the GC–MS spectrum shows that residual HEH was observed at $t_2 = 4.8$ min and a bulky peak located at $t_1 = 3$ min corresponds to the reaction product. GC–MS analysis gives a mass of m/z= 74 for this product. Also, the fragmentation analysis gives the formula

$$HO-CH_2-CH = N-NH_2$$

that is, the hydroxyethylhydrazone. Its functional group corresponds to the UV peak of product F at $\lambda = 224$ nm.

Reaction Mechanisms. By analogy with the phenomena observed in our laboratory in the case



Figure 3 UV spectra for a reaction mixture HEH + NH₂Cl at 25°C. [HEH]₀ = 40×10^{-3} M; [NH₂Cl]₀ = 1.6×10^{-3} M; [NaOH]₀ = 0.1M. The first trace was recorded at 2 min and then at every 5 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of unsymmetrical dimethylhydrazine (UDMH), *N*-aminoaza-3-bicyclo[3,3,0]octane and *N*-aminopiperidine (NAP), the first step corresponds to the formation of diazene (aminonitrene):

HO-(CH₂)₂-NH-NH₂ + NH₂Cl

$$\xrightarrow{k_3}$$
 HO-(CH₂)₂-NH = $\stackrel{-}{N}$ +NH₄Cl

This is the result of the two following oxidation–reduction reactions:

HO-(CH₂)₂-NH-NH₂

$$\rightarrow$$
 HO-(CH₂)₂-NH = \overline{N} +2H⁺+2e⁻
NH₂Cl + 2H⁺+2e⁻ \rightarrow NH₄Cl

In aqueous medium, the diazene can be considered as an alkaline compound capable of trapping protons according to the following acid–base balance:

$$HO-(CH_2)_2 - \overset{+}{NH} = \overset{-}{N} + H_2O \rightleftharpoons HO-(CH_2)_2 - \overset{+}{NH}$$
$$= N-H + OH^-$$

In alkaline medium, the equilibrium shifts toward the neutral entity. In this configuration, since the hydrogen atom linked to the quaternary nitrogen is "acid," it is easily extracted in alkaline medium, leading to an azo compound that rearranges itself immediately by dynamic isomerism to give a hydrazone with a molecular weight of 74:

$$HO-(CH_2)_2-N = NH \leftrightarrow HO-CH_2-CH = N-NH_2$$

Rate Laws. The previous results show that the oxidation mechanism of HEH by NH_2Cl can be described by the following two reactions:

$$NH_{2}Cl + HO-(CH_{2})_{2}-NH-NH_{2}$$

$$\xrightarrow{k_{3}} HO-(CH_{2})_{2}-\overset{+}{N}H = \overset{-}{N}+NH_{3}+Cl^{-}+H_{2}O$$

$$HO-(CH_{2})_{2}-\overset{+}{N}H = \overset{-}{N}$$

$$\xrightarrow{k_{4}} HO-CH_{2}-CH = NH-NH_{2}$$

The second process, that is, the rearrangement of diazene/hydrazone does not control the HEH yield as it is consecutive. Therefore, only the kinetic parameters of the aminonitrene formation were determined. The rate laws were established at pH 12.89 and $T = 25^{\circ}$ C.

A specific method was developed to monitor the chlorinated compound analytically. It consists of extracting NH_2Cl by demixion with a solvent, namely diethylether. The chlorinated compound is then separated and analyzed by HPLC equipped with a UV detector. By using this method, the hydroxylated derivatives that have good affinity with water can be isolated in the aqueous phase. At the same time, the interaction is blocked in the solvent as no organic reagent is present.

The initial concentrations were between 1.7×10^{-3} and 2×10^{-3} M for NH₂Cl and between 8×10^{-3} and 40×10^{-3} M for HEH ($4.5 \le [\text{HEH}]_0/[\text{NH}_2\text{Cl}]_0 \le 24$).

Table IV and Fig. 4 show the variation of the NH₂Cl concentration as a function of time for initial concentrations of 1.7×10^{-3} M for NH₂Cl and 40×10^{-3} M for HEH.



Figure 4 Evolution yield of HEH in a concentrated medium with reagent ratio p ([NAOH]_f = 0, 3 M; $T = 25^{\circ}$ C; $k_{1 \exp} = 1.62 \times 10^{-1} \text{ M}^{-1} \text{ min}^{-1}$; $k_{2 \exp} = 2.62 \text{ M}^{-1} \text{ min}^{-1}$; $k_{3} = 3.72 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$).

The kinetic parameters were determined by integration using the same methods as described previously:

$$r_3 = -\frac{\mathrm{d}[\mathrm{NH}_2\mathrm{Cl}]}{\mathrm{d}t} = \nu_3 \, k_3 [\mathrm{NH}_2\mathrm{Cl}]^{\alpha} [\mathrm{HEH}]^{\beta}$$

The plot

$$\frac{1}{[\text{HEH}]_0 - [\text{NH}_2\text{Cl}]_0} \ln\left(\frac{[\text{NH}_2\text{Cl}]_0[\text{HEH}]}{[\text{HEH}]_0[\text{NH}_2\text{Cl}]}\right) = f(t)$$

is linear up to the end of the reaction with a correlation coefficient of 0.996. Consequently, NH₂Cl does not participate in a secondary reaction process; in fact the

Table IVEvolution of Rate Constant k_3 with Time

Time (min)	[NH ₂ Cl] (10 ⁻³ M)	ln A	$\ln A/([\text{HEH}]_0 - [\text{NH}_2\text{Cl}]_0)$	$k_3 (\mathrm{M}^{-1} \mathrm{min}^{-1})$	
1	1.54	0.08	2.14	2.14	
1	1.56	0.07	1.72	1.72	
6	0.99	0.51	13.21	2.40	
6	1.00	0.49	12.89	2.34	
16	0.33	1.6	41.82	2.70	
16	0.31	1.66	43.27	2.79	
31	0.08	2.99	78.06	2.52	
31	0.08	3.03	79.00	2.55	
47	0.02	4.29	111.97	2.38	
47	0.02	4.25	110.86	2.36	

 $T = 25^{\circ}\text{C}, [\text{NH}_2\text{Cl}]_0 = 1.7 \times 10^{-3} \text{ M}, [\text{HEH}]_0 = 40 \times 10^{-3} \text{ M}, [\text{NaOH}] = 0.1 \text{ M with } A = ([\text{NH}_2\text{Cl}]_0 \times [\text{HEH}])/([\text{HEH}]_0 \times [\text{NH}_2\text{Cl}]).$

	· *			
Substitution Degree	Product Formed	$k_{\rm f} ({\rm M}^{-1}~{\rm s}^{-1})$	<i>T</i> (°C)	Reference
1 1	CH ₃ NHNH ₂ HO-(CH ₂) ₂ -NH-NH ₂	5.09×10^{-3} 2.66×10^{-3}	25 25	[13] This work
Substitution Degree	Intermediary Product	$k_{\rm d} ({\rm M}^{-1} {\rm s}^{-1})$	<i>T</i> (°C)	Reference
1	$CH_3N^+H=N^-$ $HO-(CH_2)_2-N^+H=N^-$	$\begin{array}{c} 2.27 \times 10^{-2} \\ 4.37 \times 10^{-2} \end{array}$	25 25	[13] This work
	Substitution Degree 1 1 Substitution Degree 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Substitution DegreeProduct Formed1 CH_3NHNH_2 1 $HO-(CH_2)_2-NH-NH_2$ Substitution DegreeIntermediary Product1 $CH_3N^+H=N^-$ 1 $HO-(CH_2)_2-N^+H=N^-$	Substitution Degree Product Formed $k_{\rm f}$ (M ⁻¹ s ⁻¹) 1 CH ₃ NHNH ₂ 5.09×10^{-3} 1 HO-(CH ₂) ₂ -NH-NH ₂ 2.66×10^{-3} Substitution Degree Intermediary Product $k_{\rm d}$ (M ⁻¹ s ⁻¹) 1 CH ₃ N ⁺ H=N ⁻ 2.27×10^{-2} 1 HO-(CH ₂) ₂ -N ⁺ H=N ⁻ 4.37×10^{-2}	Substitution Degree Product Formed $k_{\rm f}$ (M ⁻¹ s ⁻¹) T (°C) 1 CH ₃ NHNH ₂ 5.09×10^{-3} 25 1 HO-(CH ₂) ₂ -NH-NH ₂ 2.66×10^{-3} 25 Substitution Degree Intermediary Product $k_{\rm d}$ (M ⁻¹ s ⁻¹) T (°C) 1 CH ₃ N ⁺ H=N ⁻ 2.27×10^{-2} 25 1 CH ₃ N ⁺ H=N ⁻ 4.37×10^{-2} 25

Table V Formation and Oxidation Constants of MMH and HEH, pH 12.89

reaction is composed of two consecutive reactions that explain the isobestic points.

The linear plots obtained at 25° C for a NaOH concentration of 0.1 M (pH 12.89) and different initial concentrations of HEH and NH₂Cl, permit establishing the kinetic parameters of the reaction between HEH and NH₂Cl:

$$\nu_3 = \alpha = \beta = 1$$
 and $k_3 = 2.62$ L mol⁻¹ min⁻¹

Table V compares the bimolecular kinetic constants of formation and degradation for two hydrazines with a substitution degree equal to unity: monomethylhydrazine (MMH) and HEH.

At 25°C and pH 12.89, ratio k_d/k_f is less favorable for HEH. It is necessary to operate under nonstoichiometric conditions, that is, with a large amount of excess EA to limit the contact time between NH₂Cl and HEH.

Influence of the Temperature. The influence of the temperature was studied at pH 12.89, between 15 and 35°C for constant concentrations of NH₂Cl and HEH equal to 2×10^{-3} and 40×10^{-3} M, respectively $(p = [\text{HEH}]_0/[\text{NH}_2\text{Cl}]_0 \approx 20)$ (Table VI). A plot ln $k_3 = f(1/\text{T})$ leads to the Arrhenius relation (E_{a3} in kJ mol⁻¹):

$$k_3 = 7.95 \times 10^6 \exp(-47.7/RT)$$

($k_3 \text{ in } \text{M}^{-1} \text{ s}^{-1}, E_{a3} \text{ in } \text{kJ } \text{mol}^{-1}$)

The enthalpy and the entropy are as follows:

$$\Delta H_3^{0\#} = 45.2 \,\mathrm{kJ}\,\mathrm{mol}^{-1}; \Delta S_3^{0\#} = -121 \,\mathrm{J}\,\mathrm{K}^{-1}\,\mathrm{mol}^{-1}$$

Formulation of a Kinetic Model

In view of the previous results, the main reactions determining the rate of HEH synthesis by the Raschig process are

$$NH_2Cl + HO-(CH_2)_2 - NH_2$$

$$\xrightarrow{k_1} HO-(CH_2)_2 - NH - NH_2 + H_2O + Cl^-$$
(7)

$$NH_2Cl + OH^- \xrightarrow{k_2} NH_2OH + Cl^-$$
 (8)

 $HO-(CH_2)_2-NH-NH_2 + NH_2Cl$

$$\stackrel{k_3}{\longrightarrow} \text{HO-(CH}_2)_2 \cdot \overset{+}{\text{NH}} = \overset{-}{\text{N}} + \text{NH}_4^+ + \text{Cl}^- \qquad (9)$$

$$HO-(CH_2)_2 - \overset{+}{NH} = \overset{-}{N}$$
$$\overset{k_4}{\longrightarrow} HO-CH_2 - CH = N-NH_2$$
(10)

Reaction (7) is the useful step of the synthesis. It is a bimolecular reaction, and its order is equal to one compared to each reagent. The second reaction (8) is the hydrolysis of the chlorinated derivative. As soon as HEH is formed, it is partially oxidized by NH_2Cl to give an aminonitrene (9) that rearranges itself into hydroxyethylhydrazone (10).

The determination of the residence times in the reactor and of the rate of synthesis as a function of initial reagent concentrations and temperature is linked to the

T (°C)	[HEH] ₀ (10 ⁻² M)	$[NH_2Cl]_0 (10^{-3} M)$	$p = [\text{HEH}]_0 / [\text{NH}_2 \text{Cl}]_0$	$k_3 (\mathrm{M}^{-1} \mathrm{min}^{-1})$	R^2
15	4.0	2.0	20.0	1.09	0.998
20	4.1	2.1	19.1	1.37	0.983
20	4.2	2.1	20	1.36	0.989
25	4.0	1.7	24.0	2.48	0.996
25	4.0	2.0	20	2.50	0.991
35	4.0	2.0	20.0	3.76	0.982

 Table VI
 Influence of Temperature on Oxidation Constant k3

[NaOH] = 0.1 M.

resolution of the following differential equations:

$$\frac{dx}{dt} = -k_1 a x - k_3 u x - k_2 x b_0$$
$$\frac{da}{dt} = -k_1 a x$$
$$\frac{du}{dt} = k_1 a x - k_3 u x$$
$$\frac{df}{dt} = k_3 u x$$

where x, a, u, and f are the concentrations of NH₂Cl, EA, HEH, and hydrazone, respectively, at instant t. The initial concentrations are $x = x_0$, $a = a_0$, u = f = 0, and b_0 stands for the initial NaOH concentration. The fourth-order Runge–Kutta method was used to resolve this differential equations system.

Transfer in a Concentrated Medium and Optimiza*tion.* The results obtained during the theoretical study were validated directly in a concentrated medium by using hypochlorite solutions at a high chlorometric degree. It is necessary to know the composition of synthesis solutions at t = 0 to predict the rate of the reaction when using the kinetic model. It is also necessary to take into account the different volumes of reagents to be introduced, the resulting dilution and the reaction balance. In particular, the quantities of NaOH to be introduced at the exit of the NH₂Cl reactor (R_1) take into account the need to neutralize the residual buffer NH⁴₄/NH₃ and the H⁺ ions provided by the reaction

$$NH_2Cl + HO-(CH_2)_2-NH_2$$

$$\xrightarrow{k_1} HO-(CH_2)_2-NH-NH_2 + HCl \qquad (11)$$

At the end of the reaction, the pH of the solution is increased to 13 to avoid a chlorine transfer reaction and profit from the pseudocatalytic effect caused by the OH^- ions during the reaction (11).

The calculation was carried out by reacting a concentrated solution of sodium hypochlorite at 48° chlorometric degrees (2.14 M) at -15° C, with a mixed ammonia solution NH₃/NH₄Cl (3.64 M/2.38 M). Under these conditions, the NH₂Cl rate is almost quantitative and the resulting solution concentration is equal to 1.04 M (*B*₁) for NH₂Cl and 0.1 M (*B*₂) for NH₄Cl.

The following compounds: NH_2Cl , NH_4Cl , $HO-(CH_2)_2-NH_2$, NaOH, and $HO-(CH_2)_2-NH-NH_2$ are, respectively, represented by indices from 1 to 5. Consequently, the molecular weights and densities of the reagents and resulting solutions are, respectively, represented by the symbols M_i and d_i . We wanted to cal-

culate the global composition of the reaction mixture at t = 0, noted C_i (i = 1-5), after the injection of the reagents, and at $t = \infty$, noted D_i (i = 2-5).

To achieve this, the volumes of NH₂Cl and EA to be injected are designated by V_N and V_A , respectively:

$$V_{\rm N} = 1000 \text{ mL}, \quad V_{\rm A} = 10^3 \times p \times \frac{B_1}{C_{\rm A}}$$

where subscript A represents an EA solution with mass composition W_A :

$$C_{\rm A} = \frac{W_{\rm A} \times 10^3 \times d_3}{100} \cdot \frac{1}{M_3}$$

Under these conditions, the NaOH solution ([NaOH] = *S* M) to be introduced into the reactor is composed of two terms: $V_S = V_S^1 + V_S^2$. The first term V_S^1 corresponds to the neutralization of the residual NH₄Cl (*B*₂) and the H⁺ ions formed during hydrazine formation:

$$V_{\rm S}^1 = 10^3 \frac{(B_2 + B_1)}{S}$$

The second term corresponds to the amount of NaOH necessary to obtain the optimized value noted $[OH^-]_f$:

$$V_{\rm S}^2 = \frac{[\rm OH^-]_f (V_{\rm N} + V_{\rm A} + V_{\rm S}^1 + V_{\rm S}^2)}{S}$$

The instantaneous concentrations C_i and D_i are deduced from those equations presented in Table VII.

The results were confirmed in a concentrated medium, by systematically studying the influence of the molar ratio p, that of the final sodium hydroxide concentration $[OH^-]_f$ and that of the temperature.

The experiments were carried out using the following protocol: a freshly prepared and concentrated NH₂Cl solution (volume V_N) is alkalized with a volume V_S of a 10 M NaOH solution. The NaOH/NH₂Cl mixture is then introduced under stirring into V_A mL of an EA solution at a determined temperature.

Influence of the p Ratio. The experiments were carried out at a constant temperature of 25°C, at a constant final NaOH concentration and a constant volume of NH₂Cl ($V_N = 40$ mL), by varying the excess amine. Passing from p = 5 to p = 20 involves increasing the yield by 33%, as shown in Fig. 4. The theoretical curve, in agreement with the experimental results, was formulated by taking into account the variation of rate constant k_1 with pH. Therefore, yield ρ_N is 62% for p = 20.

Compound	NH ₂ Cl	NH₄Cl	EA	NaOH	HEH
Indices	1	2	3	4	5
$C_i(t=0)$	$B_1 \frac{10^3}{V_{\rm N} + V_{\rm A} + V_{\rm S}}$	$B_2 \frac{10^3}{V_N + V_A + V_S}$	$\frac{B_1 \times p \times 10^3}{V_N + V_A + V_S}$	$\frac{S \times V_{\rm S}}{V_{\rm N} + V_{\rm A} + V_{\rm S}}$	0
$D_i(t=\infty)$	0	0	$C_3 - C_1$	$C_4 - (C_1 + C_2)$	C_1

Table VII Instantaneous Concentrations of the Different Compounds at t = 0 and $t = \infty$



Figure 5 Calculated evolution of the HEH yield with temperature for molar ratio p = 30 (a) or p = 20 (b).

Theoretical Influence of Temperature. The influence of temperature was studied between 10 and 90°C for a final NaOH concentration of 0.3 M and for a ratio p = 20 and 30 (Fig. 5). Increasing temperature leads to better yields due to the enthalpy values.

Kinetic Profile/Residence Time. The plug-flow reactor is the most suitable reactor for limiting contact between the HEH and NH₂Cl formed. Figure 6 shows the theoretical kinetic profiles in the reactor for two mixtures (NH₂Cl/EA/NaOH) continuously injected at 20 and 80°C for molar ratio p = 20.

Comparison between the Different Processes Studied to Synthesize HEH

In another paper [4], HEH was synthesized by the alkylation of N_2H_4 with 2-chloroethanol (CletOH) in the presence or not of NaOH. In this first case, N_2H_4 is alkylated by ethylene oxide (CH₂OCH₂) formed in situ in the presence of NaOH, which is a strong base. These three processes (Raschig, alkylation by CletOH, and alkylation by CH₂OCH₂) can be compared.

The first reaction, bimolecular (k_f), involves a nucleophilic reagent (amine or hydrazine) and a molecule with an electron-deficient site (NH₂Cl, CletOH, and CH₂OCH₂).

$$N + M^{\delta +} \xrightarrow{k_{f}} HEH$$

In the second step, HEH is involved in a secondary process of consecutive parallel type (k_d) .

$$\text{HEH} + \text{M}^{\delta +} \stackrel{k_{\text{d}}}{\longrightarrow} \sum_{i} P_{i}$$

This implies that the operating conditions depend on the rate ratio between these two reactions (V_f/V_d) . k_f and k_d , measured during this study, are summarized in Table VIII, which also indicates ratio k_d/k_f and the corresponding activation enthalpy and entropy.

HEH Reaction Mechanisms and Formation Rates. The bimolecular rates are of the same order for the Raschig process and alkylation by epoxide (CH_2OCH_2) . This is due to the nucleophilic and electrophilic power of the reagents, which compensate each other. EA is much more nucleophilic and basic than N_2H_4 .

HO-(CH₂)₂-NH₂ + NH₂
$$\rightarrow$$
 Cl \rightarrow HEH ($k = 2.61 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 25^{\circ}\text{C}$)
($pK_a = 9,5$)
NH₂-NH₂ + $\delta^{+1/2}$ $\delta^{+1/2}$ \rightarrow HEH ($k = 1.71 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 25^{\circ}\text{C}$)
($pK_a = 8,1$)
HO-(CH₂)₂-NH₂ \rightarrow NH₂-NH₂ NH₂Cl $<<$ CH₂OCH₂
Nucleophilic power Electrophilic power



Figure 6 Kinetic profile at T = 20 and 80° C with $[NH_2Cl]_0 = 0.42$ M, $[EA]_0 = 8.47$ M. $T = 80^{\circ}$ C: (a) $[NH_2Cl]$; (b) [HEH]; (c) [hydrazone]. $T = 20^{\circ}$ C: (a') $[NH_2Cl]$: (b') [HEH]; (c') [hydrazone].

Thus, the situation is reversed for their electrophilic homologue.

The N-Cl linkage of NH_2Cl is not very polarized due to the very slight electronegative difference between the two atoms. This explains the polarization inversion when a hydrogen atom is replaced by an electrodonor methyl group. This substituted chloramine becomes incapable of forming N-N linkage by reacting with NH_3 in an aqueous or anhydrous medium (chlorine transfer mechanism in liquid ammonia).

$$\stackrel{\delta^{+}}{N}H_{2}-\stackrel{\delta^{-}}{Cl} \qquad CH_{3}\stackrel{\delta^{-}}{N}H-\stackrel{\delta^{+}}{Cl}$$

This is not the case of the epoxide, which is strongly electrophilic, due to its favorable spatial configuration (flat molecule, symmetry, and good site accessibility) and to greater carbon–oxygen polarization.

The very weak value of the direct alkylation constant by CletOH in comparison with CH_2OCH_2 , can be explained by the fact that the carbon–chlorine linkage is less polarized and accessible: Thus $k_{\rm f}({\rm Raschig}) \approx k_{\rm f}$ (CH₂OCH₂) $\approx 10^3 k_{\rm f}$ (CletOH)

HEH Reaction Mechanisms and Degradation and Alkylation Rates. For identical reagent ratios, the HEH yields are the same for the two alkylation methods (CletOH and CH₂OCH₂). This result is not surprising because the rate constants k_f and k_d require the same mechanisms. This is confirmed by activation enthalpies and entropies. The absolute formation rates are very different ($V_f(CH_2OCH_2) \gg V_f$ (CletOH)), but the k_f/k_d ratios are almost identical. The adjustment variable, that is, ratio $[N_2H_4]_0/$ [CH₂OCH₂]₀ or $[N_2H_4]_0/$ [CletOH]₀, will be low, close to three, to obtain rates up to 80%.

In the case of the Raschig process, the secondary reaction of dialkylation is replaced by an HEH oxidation process; the reaction mechanism of which is different

$$N_{2}H_{4} + \underbrace{\delta^{+1/2}}_{O \delta^{-}} \underbrace{\delta^{+1/2}}_{O \delta^{-}} + HEH \qquad (k = 1.71 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 25^{\circ}\text{C})$$

$$N_{2}H_{4} + CI-CH_{2}-CH_{2}-OH \longrightarrow HEH \qquad (k = 2.18 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 25^{\circ}\text{C})$$

Cl-(CH₂)₂-OH << CH₂OCH₂ Electrophilic power

|--|

Fable VIII Compar	rison of Kinetic Data Correspondin	ng to Each Process				
		Rate Law $k_i = A_i e^{(-Eai/RT)}$			Rate Constant	$k_{\text{degradation HEH}}$
Electrophilic Reagent M ⁵⁺	Nucleophilic Reagent N	$(k_{ m i} \text{ in } { m M}^{-1} { m s}^{-1} { m and} E_{ m ai} { m in } k { m J} { m mol}^{-1})$	$\Delta H_{ m i}^{0\#}$ (kJ mol ⁻¹)	$\Delta S_{\rm i}^{0\#}$ (J K ⁻¹ mol ⁻¹)	$k_{\rm i}$ at $T = 25^{\circ}$ C (L mol ⁻¹ s ⁻¹)	$k_{ m formation}$ HEH $T=25^{\circ}{ m C}$
Vanadal amina	Tthen clean in c	$2.06 \times 10^{7} c(-57.7/RT)$	66.0	110	7 61 10-3	2 01
Monochloramine	Eunanolamine	$3.00 \times 10^{\circ} e^{-100}$	0.00	-110	$_{2}$ 01 × 10.7	0.01
	2-Hydroxyethylhydrazine	$7.95 \times 10^6 e^{(-47.7/RT)}$	45.2	-121	3.53×10^{-2}	
2-Chloroethanol	Hydrazine (N ₂ H ₄)	$4.04 imes 10^8 { m e}^{(-81.4/RT)}$	79.0	-89	2.18×10^{-6}	0.7
	2-Hydroxyethylhydrazine	$8.05 \times 10^7 \mathrm{e}^{(-78.2/RT)}$	75.7	-102	1.62×10^{-6}	
Ethylene oxide	Hydrazine (N ₂ H ₄)	$3.74 \times 10^6 \mathrm{e}^{(-53.3/RT)}$	50.8	-127	1.71×10^{-3}	0.7
	2-Hydroxyethylhydrazine	$3.46 \times 10^{6} \mathrm{e}^{(-54.1/RT)}$	51.6	-128	1.16×10^{-3}	

from the formation mechanism (SN_2) . Since the bimolecular rate constants in favor of degradation are equal to 14, the adjustment variable $[EA]_0/[NH_2Cl]_0$ will be at least higher than 20.

CONCLUSION

During this work, a separate kinetic study of formation and degradation reactions permitted identifying the products obtained and establishing a model composed of a system of differential equations. The resolution of this model can be used to determine the optimal conditions of HEH formation.

A kinetic and mechanistic comparison of HEH synthesis by the Raschig process with alkylation by CletOH and the CH_2OCH_2 process was performed.

Compared with MMH, HEH synthesis by the Raschig process has two disadvantages: The nucleophilic power of the corresponding amine is lower, and oxidation of the hydrazine is easier. These properties are linked to the electroattractive effect of the terminal OH function. The kinetic parameters obtained are in agreement with the spatial conformation of the molecule promoting the interaction between the OH end group and hydrogen atoms that are potentially oxidizable.

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