

APPLIED CHEMISTRY

Kinetics of the Reaction of Methyl Iodide with Hydroxylamine in an Aqueous Solution within the Framework of Nuclear Spent Fuel ReprocessingCéline Cau Dit Coumes,[†] Josette Chopin-Dumas,[‡] and Frédéric Devisme^{*,§}

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Within the scope of investigations carried out to find a new reactant for dissolution off-gas scrubbing in spent fuel reprocessing, this paper reports the study of the reaction between hydroxylamine and methyl iodide in an aqueous solution. The products with an excess of hydroxylamine were ascribed to be iodide and *N*-methylhydroxylamine. The main contribution of this work was the kinetics investigations from 25 to 55 °C within a pH range of 2.2–13.6 (analytical data obtained by ion chromatography), operating conditions for which no sufficient data were available from the literature. NH_2OH^+ was found to be nonreactive. The $\text{NH}_2\text{OH}/\text{CH}_3\text{I}$ and $\text{NH}_2\text{O}^-/\text{CH}_3\text{I}$ reactions, the second one having not been investigated so far, were first order with respect to each reactant, with second-order rate constants of respectively $(4.30 \pm 0.25) \times 10^{-3}$ and $(2.05 \pm 0.25) \times 10^{-1} \text{ mol}^{-1} \text{ L s}^{-1}$ at 55 °C and activation energies of 98.3 ± 3.4 and $67.4 \pm 2.9 \text{ kJ mol}^{-1}$. These results are consistent with estimations from a Brönsted correlation established for nitrogen nucleophiles. Edwards and Swain–Scott nucleophilic constants, not reported in the literature up to now, were calculated in water at 25 °C and compared to hydrazine and inorganic anions of potential interest within the scope of spent fuel reprocessing. An Ampac computational study of the transition state of the $\text{NH}_2\text{OH}/\text{CH}_3\text{I}$ reaction was performed in gaseous media.

Introduction

The Puretex Program run by the French Atomic Energy Commission aims at reducing the amounts of wastes generated by reprocessing according to the Purex process operated in COGEMA La Hague plants. One of the objectives is the vitrification of the low- and medium-activity effluents, which requires a significant reduction of their saline load. Both sulfur and sodium should be precluded from the vitrification facility: sulfur is prohibited because it leads to severe corrosion in the vitrification crucible, and sodium amounts should be reduced to ensure a low leachability of the glass.

Within this framework, studies have been undertaken to modify the dissolution off-gas treatment which currently consists of a countercurrent absorption of nitrogen oxides and iodine into sodium hydroxide. Nitrogen oxides result from the dissolution of uranium and plutonium into nitric acid. Iodine is a fission product, the radioisotope of which is ^{129}I in reprocessing (period of 1.6×10^7 years). This compound is mainly present

as I_2 ; however, a small fraction, lower than 6%, has been identified as organic iodides.^{1,2} The detected compounds are short-chain alkyl iodides, the most abundant being methyl iodide.^{2–4} They mainly result from free-radical reactions of I_2 with impurities from the recycled nitric acid or traces of oil carried out by the airlifts.^{5–7}

The alkaline scrubbing solution causes dismutation of volatile I_2 into nonvolatile I^- and IO_3^- , and hydrolysis of nitrogen oxides into nitrites, but is ineffective in trapping alkyl iodides.

The objective is to find a substitute to sodium hydroxide which would meet the following requirements: (i) to be a sulfur- and sodium-free organic compound destructible without generating any saline effluents, (ii) to trap iodine and alkyl iodides into solution, (iii) to convert nitrites into nonreactive species such as dinitrogen or dinitrogen monoxide, so as to prevent a new release of nitrogen oxides in a later step of the process, and (iv) to be involved in fast reactions, because the average residence time of gases in the scrubber is estimated to be 8 s.

As shown by preliminary studies,⁸ hydroxylamine is a scrubbing reagent of potential interest because it can reduce I_2 into I^- and HNO_2 into N_2O . In addition, it is already used in reprocessing for uranium/plutonium partitioning. It was thus decided to investigate the

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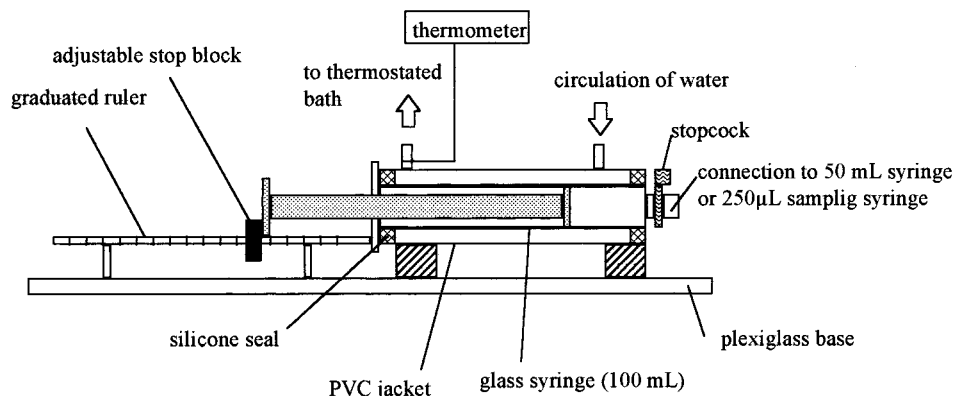


Figure 1. Experimental device.

reactions of hydroxylamine with nitrous acid or nitrogen oxides⁹ and with iodine as I_2 ¹⁰ or as methyl iodide. This paper deals with the kinetic study of the latter reaction in an aqueous solution.

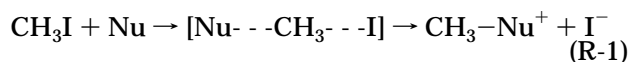
Literature Review

Reaction of nucleophiles with alkyl halides has been studied extensively since the development of the well-known Menshutkin reaction ($Et_3N + CH_3X$).¹¹ Nevertheless, only limited information (rate constant $k = 2.0 \times 10^{-2} \text{ mol}^{-1} \text{ L min}^{-1}$ at 30 °C in an aqueous solution of pH 6.87, ionic strength of 1.0 mol L^{-1} set up with KCl) was available on reaction between methyl iodide and hydroxylamine,¹² which justified this experimental study.

A characteristic property of methyl halides (CH_3X) is the polarization of the C–X bond. Halogens Cl (3.2), Br (3.0), and I (2.7) are more electronegative than C (2.6).¹³ The resulting dipole moment is thus appreciable [in the gaseous phases $CH_3\text{--}Cl$ (1.87 D), $CH_3\text{--}Br$ (1.81 D), $CH_3\text{--}I$ (1.62 D)]¹⁴ and governs a substantial part of the chemical behavior of CH_3X . With their saturated carbon, the methyl halides are substrates of low electrophilicity, or HL substrates [HL: high lowest unoccupied molecular orbitals (LUMOs)].¹⁵

The rate of reaction of methyl iodide with a variety of nucleophiles follows second-order kinetics, which indicates a bimolecular nucleophilic substitution (S_N2).

$$-\frac{d[CH_3I]}{dt} = k[CH_3I][Nu] \quad (E-1)$$



The hydrolysis of methyl iodide is extremely slow at ambient temperature¹⁶ (reaction half-life $t_{1/2}$ of 103 days at 25 °C). The formation of methanol is accelerated in an alkaline medium ($t_{1/2}$ of 3 h) but remains too slow to be significant in the current dissolution off-gas scrubbing process. The second-order rate constant for the hydrolysis of methyl iodide remains almost constant when methyl iodide is varied from 0 to about 2 mol L^{-1} but has been shown to be dependent on the ionic strength, increasing, for example, with the sodium sulfate concentration. This phenomenon is unusual because no significant electrolyte effect has been observed for reactions of methyl iodide with nucleophiles in water.¹⁷

The pH of the reactive medium does not seem to be an important parameter of the kinetics either, even when the nucleophile is a weak base which can be protonated. The rate of the reaction between methyl iodide and thiourea ($pK_a = 2.03$ at 25 °C¹⁸) is independent of pH within the range 0–9.¹⁹ Similar results have been obtained with hydrazine ($pK_a = 8$ at 25 °C¹⁴): a variation in pH within the range 10–13 has no effect on the rate²⁰ and, in an acidic medium at pH 1.6, the second-order rate constant k is only decreased by 7%, despite the protonation of hydrazine.²¹

Experimental Section

Experimental Device. With methyl iodide being highly volatile (partition coefficient $[CH_3I]_{aq}/[CH_3I]_{gas}$ ranging from 6.63²² to 3.43²³ at 25 °C and increasing with temperature²³), the experimental setup was designed to minimize its loss by transfer to the gaseous phase. Experiments were performed in a jacketed vapor-free reaction vessel made of a 100 mL glass syringe closed with a stopcock, to which either a 250 μL sampling syringe or a 50 mL syringe could be connected (Figure 1). The vessel was opaque to avoid photodegradation of methyl iodide. The reactor volume was defined by the position of the piston. An adjustable stop block sliding on a ruler allowed one to get repeatable volumes from one run to another. At the beginning of an experiment, the volume of the vessel was zero. Then, 50 mL volumes of hydroxylamine and methyl iodide preheated solutions were successively injected. The progress of the reaction was monitored by regularly taking 250 μL aliquots of the reactive medium and analyzing the produced iodide ions by ionic chromatography. Because of pressure adjustment, the volume of the reactor decreased after each sampling, which prevented the formation of a gaseous phase.

Analytical Methods. Iodide ions were analyzed by ion chromatography with a Dionex 500 chromatograph equipped with a 25 μL injection valve, a 50 mm length of 4 mm i.d. AS7 Dionex Ionpac column operated under isocratic conditions, and an electrochemical ED40 Dionex detector. The mobile phase was nitric acid at $2 \times 10^{-1} \text{ mol L}^{-1}$, with a flow rate of 1.5 mL min^{-1} . With iodide being electroactive, the detection was performed by amperometry (which revealed a much more selective and sensitive technique than conductimetry) at a Pt electrode polarized at 0.8 V vs the reference electrode (Ag–AgCl/KCl 3.5 mol L^{-1}). Figure 2A gives a typical chromatogram obtained when analyzing a $5 \times 10^{-5} \text{ mol L}^{-1}$ iodide solution in the presence of 4 orders of

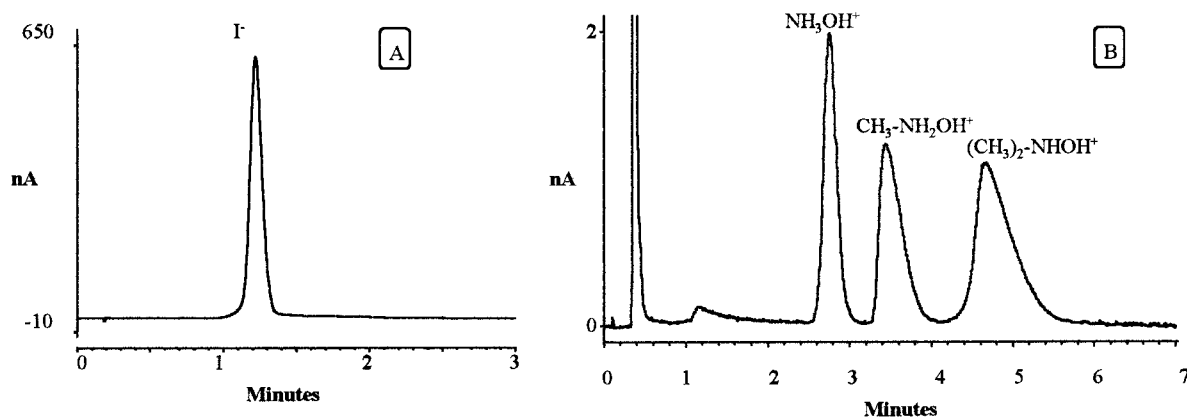


Figure 2. Analyses by ion chromatography (conditions given in the text): (A) of iodide ($[I^-] = 5 \times 10^{-5} \text{ mol L}^{-1}$, $[NH_3OH^+] = 1 \text{ mol L}^{-1}$, $[SO_4^{2-}] = 5 \times 10^{-1} \text{ mol L}^{-1}$); (B) of hydroxylamines ($[NH_3OH^+] = 5 \times 10^{-4} \text{ mol L}^{-1}$, $[CH_3-NH_2OH^+] = [(CH_3)_2-NHOH^+] = 2.5 \times 10^{-3} \text{ mol L}^{-1}$).

Table 1. Thermodynamic Acidity Constants (μ = Ionic Strength) of Hydroxylamine and *N*-Methyl- and *N,N*-Dimethylhydroxylamine

reaction	pK_a	conditions	author	ref
$NH_3OH^+ \rightleftharpoons NH_2OH + H^+$	6.04	20 °C, $\mu = 0 \text{ M}$	Robinson and Bower (1961)	<i>a</i>
	5.96	25 °C, $\mu = 0 \text{ M}$	Robinson and Bower (1961)	<i>a</i>
			Smith and Martell (1976)	<i>b</i>
			Bissot et al. (1957)	<i>c</i>
	6.0	25 °C, $\mu = 0.5 \text{ M}$	Lumme et al. (1965)	<i>d, e</i>
	5.80	25 °C	Acharya et al. (1983)	<i>f</i>
	5.84	30 °C	Robinson and Bower (1961)	<i>a</i>
	6.85	35 °C	Sharma et al. (1992)	<i>g</i>
	6.60	40 °C	Sharma et al. (1992)	<i>g</i>
	14.21 ± 0.03	10 °C	Bonner and Wang (1986)	27
$NH_2OH \rightleftharpoons NH_2O^- + H^+$	14.01 ± 0.06	15 °C	Bonner and Wang (1986)	27
	13.83 ± 0.06	20 °C	Bonner and Wang (1986)	27
	13.70 ± 0.06	25 °C	Bonner and Wang (1986)	27
	13.71	25 °C	Hughes et al. (1971)	<i>h</i>
	13.74	25 °C	Hughes et al. (1971)	<i>h</i>
$CH_3-NH_2OH^+ \rightleftharpoons CH_3-NHOH + H^+$	5.97	25 °C	Bissot et al. (1957)	<i>c</i>
$(CH_3)_2NHOH^+ \rightleftharpoons (CH_3)_2NOH + H^+$	≈ 6	25 °C	Bissot et al. (1957)	<i>c</i>

^a Robinson, R. A.; Bower, V. E. The Ionization Constant of Hydroxylamine. *J. Phys. Chem.* **1961**, *65*, 1279. ^b Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1976; Vol. 4. ^c Bissot, T. C.; Parry, R. W.; Campbell, D. H. The Physical and Chemical Properties of the Methyl-Hydroxylamines. *J. Am. Chem. Soc.* **1957**, *79*, 796. ^d Lumme, P.; Laherno, P.; Tummavouri, J. Thermodynamics of the Ionization of Hydroxylamine and Nitrous Acid in Water. *Acta. Chem. Scand.* **1965**, *19*, 2175. ^e Briegleb, G. Proton Affinity, Base Strength and Resonance Energy of Simple Nitrogen Bases. *Z. Elektrochem.* **1949**, *53*, 350. ^f Acharya, S.; Neogi, G.; Panda, R. K.; Ramaswamy, D. Studies in Nickel(IV) Chemistry. V. Kinetics of Electron Transfer in Redox Systems Containing Tris(dimethylglyoximate)nickelate(IV), Hydroxylamine and Catalytic Amounts of Copper(II) in Aqueous Alkaline Media. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2814. ^g Sharma, M.; Prasad, D. S. N.; Gupta, K. S. Kinetics and Mechanism of Oxidation of Hydroxylamine by Peroxomonosulfate. *Int. J. Chem. Kinet.* **1992**, *24*, 665. ^h Hughes, M. N.; Nicklin, H. G.; Shrimanker, K. Autoxidation of Hydroxylamine in Alkaline Solutions. II. Kinetics. Acid Dissociation Constant of Hydroxylamine. *J. Chem. Soc. A* **1971**, *22*, 3485.

magnitude more concentrated sulfate ions. The limit of detection was determined to be $10^{-6} \text{ mol L}^{-1}$. The relative standard deviation values, between 1 and 2%, were achieved by repeating five times the analysis of 10^{-5} , 7.6×10^{-5} , and $2 \times 10^{-4} \text{ mol L}^{-1}$ iodide solutions.

With hydroxylamine and *N*-methyl- and *N,N*-dimethylhydroxylamine being protonated in an acidic medium (Table 1), these compounds were analyzed using the same ionic chromatographic technique (Figure 2B). The system differed only by the column used (a 50 mm length of 4 mm i.d. CG3 Dionex Ionpac column) and the flow rate (1 mL min^{-1}). Detection by conductimetry was unusable through lack of sensitivity (with the use of a suppressor being unsuitable because the analytes were weak bases). It was thus resorted to amperometry despite the inhibition of the oxidation signals of hydroxylamine and its derivatives noticed after a few analyses of solutions also containing iodide ions, which was attributed to the blocking of active sites by adsorption of atomic iodine on the platinum surface.²⁴ The method only provided qualitative information.

Solutions. All analytical-grade chemicals were used without further purification. The solutions were prepared with demineralized water. Stock solutions of hydroxylamine from the dissolution of crystalline hydroxylamine sulfate (Fluka 16139) were standardized by iodometry according to Bartousek.²⁵ Test solutions of *N*-methyl and *N,N*-dimethylhydroxylamine were obtained from the commercial reagents (Fluka 67545 and 40704). Methyl iodide (Fluka 67690) stock solutions were diluted from a solution saturated at room temperature (aqueous solubility of $9.58 \times 10^{-2} \text{ mol L}^{-1}$ at 22 °C²⁶). The pH was adjusted with concentrated nitric acid (Merck 456.1000) or sodium hydroxide (Fluka 72071).

Experimental Conditions and Data Handling. All kinetic experiments (35 runs, 800 chromatographic analysis) were performed with at least a 10-fold molar excess of hydroxylamine over methyl iodide. The initial concentration of methyl iodide was around $10^{-4} \text{ mol L}^{-1}$, and the temperature was varied between 25 and 55 °C and the pH between 2.2 and 13.6 (values at 25 °C). Most

runs were carried out at 55 °C so as to ensure fast enough kinetics.

With methyl iodide being highly volatile, there was appreciable loss of this compound during the preliminary operations (dilution of the stock solution and thermostating), so that its initial concentration in the reactor was deduced from the final concentration of iodide.

A kinetic run included three steps: (1) monitoring of the iodide concentration until the end of the reaction, (2) determination of the initial concentration of methyl iodide, and (3) calculation of the concentration of methyl iodide as a function of time.

Dependence of Hydroxylamine Thermodynamic Acidity Constants on Temperature. The published pK_a constants of $\text{NH}_3\text{OH}^+/\text{NH}_2\text{OH}$ and $\text{NH}_2\text{OH}/\text{NH}_2\text{O}^-$ at various temperatures are reported in Table 1.

Data relative to $\text{NH}_3\text{OH}^+/\text{NH}_2\text{OH}$ are rather inconsistent. In this work, the pK_a at 55 °C, which was required to estimate the reactivity of NH_3OH^+ , was assumed to be equal to 6 because no determination was available at this temperature and no empirical correlation could be drawn from data at other temperatures.

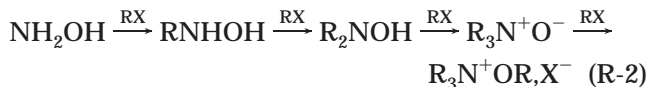
The pK_a of $\text{NH}_2\text{OH}/\text{NH}_2\text{O}^-$ was assumed to check the van't Hoff equation. Good correlation was achieved with the Bonner and Wang values²⁷ within the range 10–25 °C

$$pK_a = (2813.6/T) + 4.2592 \quad r^2 = 0.993 \quad (\text{E-2})$$

It was noted that eq E-2 was very close to the one between pK_w (water) and $1/T$ within the range 10–55 °C, calculated from data of ref 14 ($pK_w = (2890.5/T) + 4.3109$). Extrapolation of eq E-2 to higher temperatures gave pK_a ($\text{NH}_2\text{OH}/\text{NH}_2\text{O}^-$) = 13.39 ± 0.06 at 35 °C, 13.10 ± 0.06 at 45 °C, and 12.83 ± 0.06 at 55 °C.

Results

Products of the Reaction. The use of hydroxylamine as a nucleophile may be quite perplexing in view that, in reactions with carbonyl substrates, attack by nitrogen or oxygen can be considered. For example, acylation occurs almost exclusively on oxygen with relatively weak acylating agents but takes place at nitrogen with highly reactive acylating species. Because no O-alkylation product was found for hydroxylamine made to react with methyl iodide in water at room temperature,²⁸ the initial alkylation takes place at nitrogen.²⁹ The reaction can then proceed further and lead to a mixture of alkylated derivatives.



Our analysis of the reactive medium at the end of the reaction indicated the absence of *N,N*-dimethylhydroxylamine and the presence of *N*-methylhydroxylamine. A decrease was observed in the retention time (2.9 min) of *N*-methylhydroxylamine by comparison to the reference chromatogram of Figure 2, which may have resulted from a displacement of the *N*-methylhydroxylammonium ions by the hydroxylammonium ions in great excess. Within the framework of reprocessing, the large excess of hydroxylamine over methyl iodide would thus stop the reaction to *N*-monoalkylation.

Table 2. Calculation of the First-Order Rate Constant $k_{\text{corrected}}$ ($[\text{NH}_2\text{OH}]_0 = 10^{-1} \text{ mol L}^{-1}$, $[\text{CH}_3\text{I}]_0 = 3.1 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{SO}_4^{2-}]_0 = 5 \times 10^{-2} \text{ mol L}^{-1}$, pH 8, 55 °C)

$k_{\text{H}_2\text{O}}$ ($\text{mol}^{-1} \text{ L min}^{-1}$) at 55 °C	$5.17 \times 10^{-6} \text{ }^a$
$k_{\text{SO}_4^{2-}}$ ($\text{mol}^{-1} \text{ L min}^{-1}$) at 55 °C	$6.18 \times 10^{-4} \text{ }^b$
k_{OH^-} ($\text{mol}^{-1} \text{ L min}^{-1}$) at 55 °C	$1.22 \times 10^{-1} \text{ }^c$
$k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]$ (min^{-1})	2.87×10^{-4}
$k_{\text{SO}_4^{2-}}[\text{SO}_4^{2-}]$ (min^{-1})	3.09×10^{-5}
$k_{\text{OH}^-}[\text{OH}^-]$ (min^{-1})	variable with time $< 1.22 \times 10^{-7} \rightarrow$ negligible
$k_{\text{corrected}}$ (min^{-1})	$(2.72 \pm 0.13) \times 10^{-2}$
$k_{\text{corrected}}$ (min^{-1}) ^d	$(2.69 \pm 0.13) \times 10^{-2}$

^a $k_{\text{H}_2\text{O}}$ ($\text{mol}^{-1} \text{ L s}^{-1}$) = 1.66×10^{-9} at 25 °C; $\log(k_{\text{H}_2\text{O}}, \text{mol}^{-1} \text{ L min}^{-1}) = 5.605/T + 11.76$.¹⁶ ^b $k_{\text{SO}_4^{2-}}$ ($\text{mol}^{-1} \text{ L s}^{-1}$) = 1.81×10^{-7} at 25 °C; $\log(k_{\text{SO}_4^{2-}}, \text{mol}^{-1} \text{ L min}^{-1}) = 5.720/T + 12.44$.¹⁷ ^c k_{OH^-} ($\text{mol}^{-1} \text{ L s}^{-1}$) = 6.36×10^{-5} at 25 °C; $\log(k_{\text{OH}^-}, \text{mol}^{-1} \text{ L min}^{-1}) = 4.8517/T + 12.09$.³⁰ ^d $k_{\text{corrected}} = k - (k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{SO}_4^{2-}}[\text{SO}_4^{2-}])$ (eq E-5). $[\text{H}_2\text{O}]$ and $[\text{SO}_4^{2-}] \gg [\text{CH}_3\text{I}]$ were considered to be constant with time. The values of $k_{\text{H}_2\text{O}}$, $k_{\text{SO}_4^{2-}}$, and k_{OH^-} at the required temperature T were calculated from footnotes a–c.

Kinetics. (i) Order with Respect to Methyl Iodide. The hydroxylamine concentration could be considered as constant in the course of the reaction. Under these conditions, if the reaction were first order with respect to iodine, the rate should check eq E-3, which gave eq E-4 by integration:

$$v = -d[\text{CH}_3\text{I}]/dt = k[\text{CH}_3\text{I}] \quad (\text{E-3})$$

$$\ln [\text{CH}_3\text{I}] = \ln [\text{CH}_3\text{I}]_0 - kt \quad (\text{E-4})$$

In all runs, the $\ln [\text{CH}_3\text{I}]$ vs time curves were linear, which confirmed the first order with respect to methyl iodide. The first-order rate constant $k_{\text{corrected}}$ of the reaction between methyl iodide and hydroxylamine was deduced from slope k of the curve, corrected from the contributions of the byreactions between methyl iodide and water, sulfate, or hydroxide ions.

$$k_{\text{corrected}} = k - (k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{SO}_4^{2-}}[\text{SO}_4^{2-}] + k_{\text{OH}^-}[\text{OH}^-]) \quad (\text{E-5})$$

Second-order rate constants $k_{\text{H}_2\text{O}}$,¹⁶ $k_{\text{SO}_4^{2-}}$,¹⁷ and k_{OH^-} ³⁰ were estimated at the required temperatures from literature values at 25 °C and activation parameters. The calculation of $k_{\text{corrected}}$ is exemplified in Table 2 at 55 °C.

(ii) Dependence of the Rate on pH. A series of experiments was performed at 55 °C with constant initial concentrations of hydroxylamine and variable pH. The dependence of the first-order rate constant on pH is illustrated in Figure 3. No reaction occurred at pH 2.2 during the 12-h-long investigation. The reaction proceeded very slowly at pH 3.8. The rate gradually increased when the pH was raised from 3.8 to 8 (Figure 3A), remained almost constant within the pH range 8–10.5, and increased again in a more basic medium (Figure 3B). This influence of the pH could be connected to the predominant form of hydroxylamine in the reactive medium. The reaction was faster when hydroxylamine was in a more nucleophilic form, $\text{NH}_2\text{O}^- > \text{NH}_2\text{OH} > \text{NH}_3\text{OH}^+$.

(iii) Reactivity of NH_2OH . The $k_{\text{corrected}}$ rate constant was determined for various initial concentrations of hydroxylamine. The experiments were carried out at pH 8, so that hydroxylamine was almost exclusively in the NH_2OH form. The $k_{\text{corrected}}$ constant from eq E-5 was proportional to the hydroxylamine concentration, which

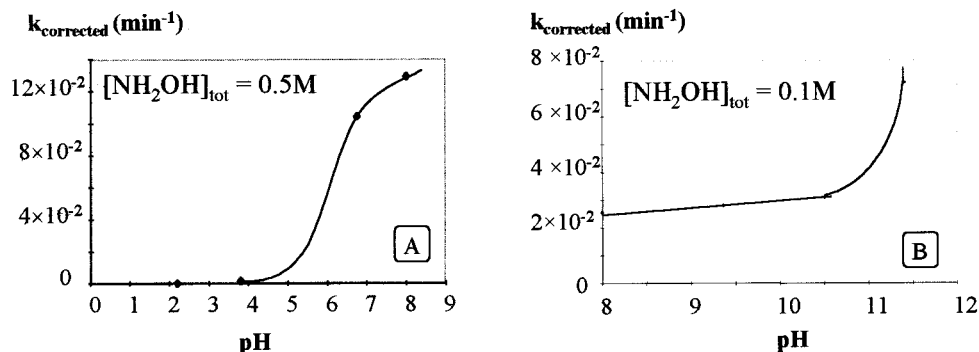


Figure 3. Dependence of the first-order rate constant on pH. 55 °C, $[\text{NH}_2\text{OH}]_{\text{tot}} = [\text{NH}_3\text{OH}]^+ + [\text{NH}_2\text{OH}] + [\text{NH}_2\text{O}^-]$. $k_{\text{corrected}} = k - (k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{SO}_4^{2-}}[\text{SO}_4^{2-}] + k_{\text{OH}^-}[\text{OH}^-])$.

Table 3. First-Order Rate Constants in a Basic Medium at 55 °C

pH ^a	$[\text{NH}_2\text{OH}]_{\text{tot}}^b$ (mol L ⁻¹)	$k_{\text{corrected}}^c$ (min ⁻¹)	$k_{\text{NH}_2\text{OH}}[\text{NH}_2\text{OH}]$ (min ⁻¹)	$(k_{\text{corrected}} - k_{\text{NH}_2\text{OH}}[\text{NH}_2\text{OH}])$ (min ⁻¹)
10.5	10^{-1}	3.06×10^{-2}	2.56×10^{-2}	$(4.97 \pm 1.10) \times 10^{-3}$
11.4	9.78×10^{-2}	7.02×10^{-2}	2.41×10^{-2}	$(4.62 \pm 0.67) \times 10^{-2}$
12.1	4.76×10^{-2}	1.47×10^{-1}	9.52×10^{-3}	$(1.38 \pm 0.16) \times 10^{-1}$
12.3	9.62×10^{-3}	4.50×10^{-2}	1.66×10^{-3}	$(4.33 \pm 0.69) \times 10^{-2}$
12.7	9.62×10^{-3}	3.25×10^{-2}	6.20×10^{-4}	$(3.19 \pm 0.56) \times 10^{-2}$

^a pH values at 55 °C. ^b $\text{p}K_a = 12.83$ at 55 °C is used to calculate $[\text{NH}_2\text{OH}]$ and $[\text{NH}_2\text{O}^-]$ from $[\text{NH}_2\text{OH}]_{\text{tot}}$. ^c $k_{\text{corrected}} = k - (k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{SO}_4^{2-}}[\text{SO}_4^{2-}] + k_{\text{OH}^-}[\text{OH}^-])$ (eq E-5).

Table 4. Second-Order Rate Constants at Temperatures 25–55 °C

<i>T</i> (K)	$k_{\text{NH}_2\text{OH}}$ (mol ⁻¹ L min ⁻¹)	$k_{\text{NH}_2\text{O}^-}$ (mol ⁻¹ L min ⁻¹) ^a
298.2	$(7.06 \pm 0.15) \times 10^{-3}$	1.07 ± 0.02
308.2	$(2.25 \pm 0.03) \times 10^{-2}$	2.26 ± 0.04
318.2	$(8.13 \pm 0.19) \times 10^{-2}$	5.93 ± 0.14
328.2	$(2.58 \pm 0.15) \times 10^{-1}$	12.3 ± 0.7

^a The $\text{p}K_a$ values of $\text{NH}_2\text{OH}/\text{NH}_2\text{O}^-$ required to evaluate $[\text{NH}_2\text{O}^-]$ from $[\text{NH}_2\text{OH}]_i$ are 13.69 ± 0.06 at 25 °C, 13.39 ± 0.06 at 35 °C, 13.10 ± 0.06 at 45 °C, and 12.83 ± 0.06 at 55 °C, from the modeling values of ref 14, leading to $\text{p}K_a = 2813.6/T + 4.2592$.

Table 5. Summary of Kinetic Results

nucleophile	NH_2OH	NH_2O^-
k (mol ⁻¹ L s ⁻¹) at 25 °C	1.12×10^{-4}	1.71×10^{-2}
ΔE (kJ mol ⁻¹)	98.2 ± 3.4	67.4 ± 2.9
$\log[A$ (mol ⁻¹ L s ⁻¹)]	13.25 ± 0.28	10.04 ± 0.49
Edwards nucleophilic constant E_n (V)	1.72 ± 0.05	2.49 ± 0.09
Swain–Scott nucleophilic constants	$s = 1.05, n = 4.64$	$s = 1.05, n = 6.73$

indicated that the reaction was also first order with respect to hydroxylamine. The second-order rate constant $k_{\text{NH}_2\text{OH}}$ was given by the slope of the $k_{\text{corrected}}$ vs $[\text{NH}_2\text{OH}]$ curve.

$$k_{\text{NH}_2\text{OH}} = (2.58 \pm 0.15) \times 10^{-1} \text{ mol}^{-1} \text{ L min}^{-1} \text{ at } 55 \text{ °C} \quad (\text{E-6})$$

Additional experiments were performed at 25, 35, and 45 °C (Table 4). The rate constants followed an Arrhenius law, $\ln(k_{\text{NH}_2\text{OH}}, \text{mol}^{-1} \text{ L min}^{-1}) = (-11817/T) + 34.62$ ($r^2 = 0.9988$), the parameters of which (activation energy and preexponential term) are summarized in Table 5. The k value of Gregory and Bruce¹² ($2.0 \times 10^{-2} \text{ mol}^{-1} \text{ L min}^{-1}$ at 30 °C) is consistent with that of our set of data ($1.29 \times 10^{-2} \text{ mol}^{-1} \text{ L min}^{-1}$ at 30 °C).

(iv) Reactivity of NH_3OH^+ . The absence of a noticeable reaction at pH 2.2 12 h after starting the experi-

ment seemed to indicate that the acidic form of hydroxylamine NH_3OH^+ was nonreactive toward methyl iodide. The $k_{\text{corrected}}$ rate constants were determined experimentally at various acidities and compared to the constants calculated under the hypothesis that NH_2OH be the only reactive species. It was assumed that the equilibrium between NH_3OH^+ and NH_2OH was always achieved, that the NH_2OH concentration was constant in the reactive medium, and that the $\text{p}K_a$ of $\text{NH}_3\text{OH}^+/\text{NH}_2\text{OH}$ was equal to 6. Given the good agreement between the experimental and calculated rate constants for 6 out of 8 runs, it was concluded that, within the experimental conditions, NH_3OH^+ was nonreactive.

(v) Reactivity of NH_2O^- . If pH could be easily adjusted so that hydroxylamine existed mainly in the NH_2OH or NH_3OH^+ form, it was more difficult to isolate NH_2O^- . The runs were performed within the pH range 10.5–12.8 (values at 55 °C) where both NH_2OH and NH_2O^- coexisted.

The concentrations of these two species were inferred from the total hydroxylamine concentration using eqs E-7 and E-8, where K'_a is linked to thermodynamic

$$[\text{NH}_2\text{OH}] = \frac{[\text{NH}_2\text{OH}]_t}{1 + K'_a/[\text{H}^+]} \quad (\text{E-7})$$

$$[\text{NH}_2\text{O}^-] = \frac{[\text{NH}_2\text{OH}]_t}{1 + [\text{H}^+]/K'_a} \quad (\text{E-8})$$

acidity constant K_a by eq E-9 and the activity coefficients were calculated from the Debye–Hückel equation (E-10).³¹

$$K'_a = K_a \frac{\gamma_{\text{NH}_2\text{OH}}}{\gamma_{\text{NH}_2\text{O}^-} \gamma_{\text{H}^+}} \quad (\text{E-9})$$

$$\log \gamma_i = \frac{-Az_i^2 I^{1/2}}{1 + 3BI^{1/2}} \quad (\text{E-10})$$

The reactivity of NH_2O^- was evaluated by $k_{\text{corrected}} - k_{\text{NH}_2\text{OH}}[\text{NH}_2\text{OH}]$ (Table 3). This difference, which takes into account the new contribution from NH_2OH in addition to those from water, sulfate, and hydroxide ions, was proved to be proportional to the concentration of NH_2O^- , which means that the reaction was first order with respect to that compound. The second-order rate constant was inferred from the slope of the $k_{\text{corrected}} - k_{\text{NH}_2\text{OH}}[\text{NH}_2\text{OH}]$ vs $[\text{NH}_2\text{O}^-]$ curve.³²

$$k_{\text{NH}_2\text{O}^-} = 12.4 \pm 1.5 \text{ mol}^{-1} \text{ L min}^{-1} \text{ at } 55^\circ\text{C}^{32} \quad (\text{E-11})$$

Kinetic experiments were completed at 25, 35, and 45 °C (Table 4). The plot of $\ln(k_{\text{NH}_2\text{O}^-})$ vs $1/T$ gave a straight line, $\ln(k_{\text{NH}_2\text{O}^-}, \text{mol}^{-1} \text{ L min}^{-1}) = (-8112.1/T) + 27.227$ ($r^2 = 0.9964$). The Arrhenius activation energy and preexponential term calculated from the slope and intercept are given in Table 5.

Discussion

These results demonstrate the direct dependence of the rate on the hydroxylamine and methyl iodide concentrations, as is assumed for a $\text{S}_{\text{N}}2$ reaction. The rate is strongly dependent on pH, which differs from the results obtained for hydrazine and thiourea. This is probably due to the fact that protonation of molecules with two NH_2 groups, like N_2H_4 or $\text{CS}(\text{NH}_2)_2$, still preserves one active NH_2 group. Thus, the reaction of methyl *p*-nitrophenyl sulfate with a hydrazine–hydrazine hydrochloride system in methanol generates different types of behaviors depending on the state of protonation of the reagent ($\text{H}_2\text{N}-\text{NH}_2/\text{H}_2\text{N}-\text{NH}_3^+$ or $\text{H}_2\text{N}-\text{NH}_3^+/\text{H}_3\text{N}-\text{NH}_3^+$ and $^+\text{H}_3\text{N}-\text{NH}_3^+$).³³

Correlations and Nucleophilic Scales. (i) Water–Methanol Correlation. The rates of reaction between methyl iodide and a number of nucleophiles have been measured in methanol.³⁴ The rates in methanol and water do not strongly differ, with these two protic solvents leading to heavy solvation of the nucleophiles through hydrogen bonds. The plot of the logarithms of the rate constants in methanol vs the ones in water gives a straight line (Figure 4).

$$-\log(k_{\text{CH}_3\text{OH}}) = -a \log(k_{\text{H}_2\text{O}}) + b \quad a = 1.02 \pm 0.05 \\ b = -0.19 \pm 0.21 \quad (\text{E-12})$$

The data relative to hydroxylamine ($-\log k_{\text{CH}_3\text{OH}} = 3.30$; $-\log k_{\text{H}_2\text{O}} = 3.94$) do not check eq E-12 accurately, with the calculated $\log(k_{\text{CH}_3\text{OH}})$ being 3.83. A Student's *t* test shows that, with a confidence level of 99%, the difference between these two values is significantly different from zero. This distinctive behavior of hydroxylamine will be discussed later.

Linear free energy equations have been often proposed to compare and rationalize values of rate constants of similar reactions.

(ii) Brønsted Relationship. The Brønsted relationship,³⁵ which was first established for acid ($\log k = \alpha \text{p}K_{\text{A}} + C$) and base ($\log k = \beta \text{p}K_{\text{B}} + C$) catalysis, was demonstrated to be valid for various $\text{S}_{\text{N}}2$ reactions since 1933.³⁶ It correlates the logarithm of the second-order rate constant of the reaction between a basic nucleophile and a substrate *S* to the $\text{p}K_{\text{A}}$ of the conjugate acid of the nucleophile. The Brønsted correlation is only valid for a limited series of nucleophiles. Thus, primary, secondary, and tertiary amines check different equations.³⁷

When the Brønsted relationship is rewritten as eq E-13, with $\beta_{\text{Nu}} \equiv \alpha$ and $b \equiv C - \log(k_{\text{H}_2\text{O}})$:³⁸

$$\log(k_{\text{Nu}}/k_{\text{H}_2\text{O}})_S = \beta_{\text{Nu}} \text{p}K_{\text{A}} + b \quad (\text{E-13})$$

and fitted to kinetic data of $\text{S}_{\text{N}}2$ reactions involving methyl iodide at 25 °C, parameters $\beta_{\text{Nu}} = 0.29 \pm 0.02$ and $b = 1.48 \pm 0.13$ were obtained for *oxygen-containing* nucleophiles.¹⁷ For *nitrogen-containing* nucleo-

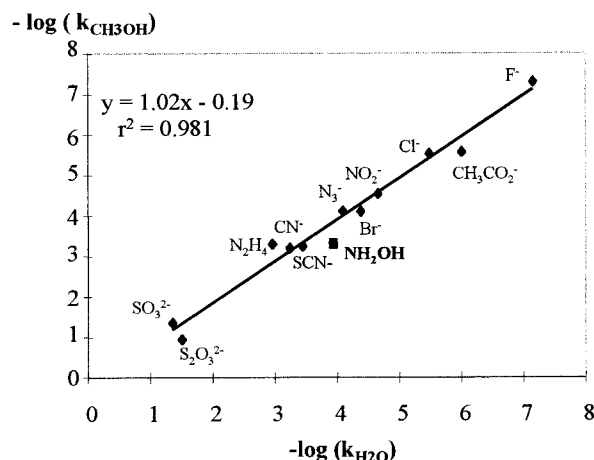


Figure 4. Correlation between the second-order rate constants in water and methanol.

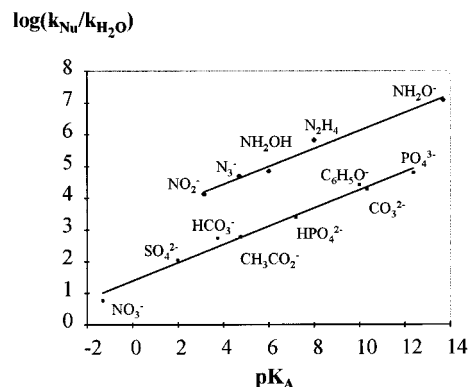


Figure 5. Brønsted-type correlations for nitrogen- or oxygen-containing nucleophiles.

philes^{12,17,21,20} including hydroxylamine, a more appropriate correlation was achieved at 25 °C (Figure 5), which gave $\beta_{\text{Nu}} = 0.27 \pm 0.03$ and $b = 3.35 \pm 0.20$. Both correlations have the same slope, but the intercept of the second is larger by $\Delta b = b_{\text{N}} - b_{\text{O}} = 1.87$. Nitrogen-containing nucleophiles are, hence, more reactive than oxygen-containing nucleophiles of equal basicity, as previously observed with other methyl substrates³⁹ [methyl perchlorate $\Delta b = 0.96$ (0 °C), methyl nitrate $\Delta b = 0.87$ (90 °C), methyl benzene sulfonate $\Delta b = 1.09$ (25 °C)]. The β_{Nu} value of 0.27 is characteristic of a small effect of nucleophile basicity. A similar trend has been observed when nucleophiles are made to react with a sp^3 carbon, with the β_{Nu} values, almost independent of temperature, being 0.235 (methyl perchlorate, 0 °C), 0.228 (methyl nitrate, 90 °C), 0.236 (methyl benzene sulfonate, 25 °C),³⁹ 0.27 (methyl *p*-toluenesulfonate, 30 °C),⁴⁰ and 0.22 (methyl iodide, 30 °C).¹² In contrast, the aminolysis of acyl groups of esters exhibits a marked dependency on the basicity ($\beta_{\text{Nu}} = 0.80-1.0$).^{41,42}

(iii) Swain–Scott Correlation. In 1953, Swain and Scott⁴³ set up a relative scale of nucleophilicity.

$$\log(k_{\text{Nu}}/k_{\text{H}_2\text{O}})_S = sn \quad (\text{E-14})$$

Substrate constant *s*, which is a measure of the discrimination of the substrate among various nucleophiles, is arbitrarily fixed to unity for methyl bromide. Nucleophilic constant *n* is characteristic of the nucleophile only ($n = 0$ for H_2O). This correlation gives good results for substrates whose electrophilic center is a

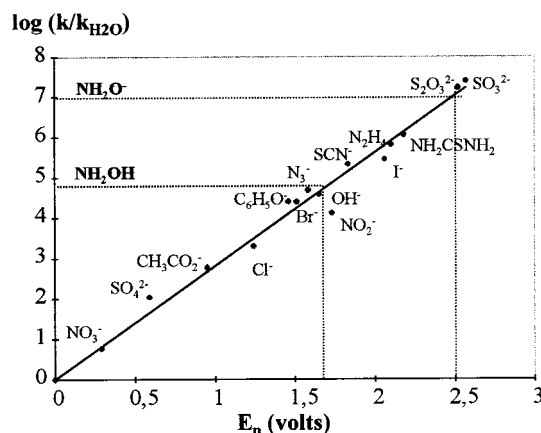


Figure 6. Correlation between the Edwards nucleophilic constant and the second-order rate constant.

tetrahedral carbon in a hydroxylic medium. The s values have been found within the range 0.6–1.2.⁴⁴ Constant n has been determined as 6.6 for hydroxylamine in methanol at 25 °C³⁴ [close to that of hydrazine (6.61), SCN^- and CN^- (6.70)] but is unknown in water. This value was estimated as $n_{\text{NH}_2\text{OH}} = 4.64$ from Pearson and Songstag⁴⁵ correlations.⁴⁶ From our kinetic results,⁴⁷ the s value of the substrate constant for CH_3I in water at 25 °C was then calculated as $s = 1.05$. This value is consistent with that deduced from the rate constants of various nucleophiles (Cl^- , OH^- , I^- , SCN^- , CN^- , and $\text{S}_2\text{O}_3^{2-}$), reacting a little faster with CH_3I than with CH_3Br and giving an s value ranging from 1.01 to 1.19.^{39,48} Finally, $\log(k_{\text{NH}_2\text{O}^-}/k_{\text{H}_2\text{O}})$ was calculated as 7.03 from our results, providing $n_{\text{NH}_2\text{O}^-} = 7.03/1.046 = 6.72$ as the nucleophilic constant of NH_2O^- (Table 5).

(iv) Edwards Correlation. The Edwards equation (1954) has been quite successful in correlating a very wide range of data, including both kinetic and thermodynamic results from organic and inorganic systems.^{49,50} Davis has shown that eq E-15 (referred as the “oxybase scale” because it takes into account oxidative dimerization potentials and basicities) gives good correlation for nucleophilic displacements on tetrahedral carbons.⁵¹

$$\log(k_{\text{Nu}}/k_{\text{H}_2\text{O}}) = \alpha E_n + \beta H \quad (\text{E-15})$$

E_n is a nucleophilic constant, characteristic of the nucleophile, which is calculated from the standard potential E° for the oxidative dimerization $2\text{Nu}^- \rightarrow \text{Nu}_2 + 2e^-$ ($E_n = E^\circ + 2.60$ V). H is the relative basicity of the nucleophile to protons ($H = \text{p}K_a + 1.74$), and α and β are the substrate constants. Constant α measures the easiness of reduction of the substrate and increases steadily with the softness of the leaving group X in CH_3X ($\alpha = 2.50$ for CH_3Br and 2.92 for CH_3I in water at 25 °C⁵¹). Constant β is a measure of the acidity of the substrate; the more positive the center being attacked, the larger is β ($\beta = 0.002$ for CH_3Br and -0.0134 for CH_3I in water at 25 °C⁵²). For substituted methanes, α is generally about 100 times greater than β , and the ratio of rate constants is essentially controlled by the αE_n term in eq E-15. Because a reasonably good correlation was obtained using only the αE_n term (Figure 6) when eq E-16 was fitted to the literature data,^{49,50} the unknown Edwards nucleophilic constants of NH_2OH and NH_2O^- could be estimated from our kinetics results: $E_n = 1.72 \pm 0.05$ for NH_2OH and 2.49 ± 0.09 for NH_2O^- at 25 °C. The nucleophilicities of NH_2OH and

$$\log(k_{\text{Nu}}/k_{\text{H}_2\text{O}}) = \alpha E_n \quad \alpha = 2.81 \pm 0.10 \quad (\text{E-16})$$

NH_2O^- are thus respectively close to the ones of SCN^- and $\text{S}_2\text{O}_3^{2-}$. Both of these compounds are more reactive toward methyl iodide than hydroxide ions ($E_n = 1.65$).

α Effect. The “ α effect” denomination has been used in 1962⁵³ to describe the high reactivity of nucleophiles possessing an unshared pair of electrons adjacent to the nucleophilic atom, like hydroxylamine and RONH_2 , hydrazine, hydroxamic acids, N -hydroxyphthalimide, isonitrosoacetone, the anions of hydrogen peroxide and substituted peroxides, hypochlorite ion, oxime anions, and others. The nucleophiles leading to an α effect have been divided into two groups: anionic nucleophiles, such as ROO^- , ClO^- , RSS^- , and some of the N -methylhydroxamic acids, which show enhanced reactivity whatever the substrate, and other nucleophiles, such as hydrazine and hydroxylamine,^{40,54,55} which exhibit increased reactivity only with a limited range of substrates. A common practice is to express the α effect as a rate constant ratio such as $k_{\text{HOO}^-}/k_{\text{HO}^-}$, $k_{\text{H}_2\text{NNH}_2}/k_{\text{NH}_3}$ or $k_{\text{H}_2\text{NNH}_2}/k_{\text{gly-gly}}$ of an α nucleophile to a normal nucleophile having almost identical basicity [$\text{p}K_a = 8.11$ (hydrazine), 8.25 (glycylglycyl), and 8.10 (glycinamide)].

There is a link between the α effect and the Brönsted coefficient.^{40,56–59} Large variations in the α effect (from 2 to 50) have been reported for nucleophiles involved in substitutions at unsaturated centers, the rates of which also strongly depend on the basicity of the attacking nucleophile (β_{Nu} has been found to range from 0.12 to 1).

The α effect also depends on the hybridization type of the electrophilic carbon center.^{57,60} The largest α effect has been observed for HOO^- reaction at the sp carbon of benzonitriles. Nucleophilic attack on sp^2 carbon centers is typically associated with α effects ranging from 50 to 100 (and sometimes even larger^{54,61}). Data on increased reactivity at the sp^3 carbon in various solvents are highly variable, ranging from 0⁶² to 1500.⁶³ Most of them seem, however, to be below 35, a value for benzyl transfer in 50% aqueous acetone ($k_{\text{HOO}^-}/k_{\text{HO}^-} = 34$).⁶⁴ In methyl transfer reactions, α effects in the range 2–11 are obtained in methanol from methyl phenyl sulfates (mixed alkyl aryl sulfate with ArOSO_3^- as a leaving group) with a HO_2^- anion ($k_{\text{HOO}^-}/k_{\text{CH}_3\text{O}^-} = 5.7$ –11)⁶² or with NH_2NH_2 ($k_{\text{NH}_2\text{NH}_2}/k_{\text{gly-ester}} = 3.0$ –5.2)⁵⁷ and from methyl arenesulfonates (with ArSO_3^- as a leaving group) with N -methylbenzohydroxamate anions ($k_{\text{GPhCON(Me)O}^-}/k_{\text{GPhO}^-} = 2.5$ –3.5)⁶⁵ or N -phenylhydroxylamines ($k_{\text{GPhNHOH}}/k_{\text{GPhNHMe}} = 1.5$ –3.0).⁵⁹ Larger α effects for methyl transfer in methanol (13–75) are observed with N -methylbenzohydroxamate anions and aryl dimethylsulfonium cations.⁶⁶ Recent studies on the magnitude of the α effect at the sp^3 carbon have led their authors⁶⁷ to identify three significant factors, that is, (i) ability of the α nucleophile to transfer a single electron (single-electron-transfer character), (ii) ability for the leaving group to take the excess charge away, and (iii) ability of the group being transferred to modify (weakening or strengthening) the bond to the leaving group.

In the aqueous aminolysis (including hydroxylamine, methoxyamine, and hydrazine) of methyl iodide, the α effect has been found to be either 0¹² (as estimated from the deviation from the Brönsted plot for primary amines) or 5⁵⁶ (as calculated by $k_{\text{hydrazine}}/k_{\text{glycinamide}}$). Our results confirm that both NH_2OH and NH_2O^- check the

Brönsted equation for primary amines reacting with methyl iodide in water, which thus shows the absence of α effect under these conditions. In methanol, however (Figure 4), the rate of the reaction between hydroxylamine and methyl iodide is higher than the expected rate from the water–methanol correlation (eq E-12), which indicates an α effect in methanol. The rate enhancement is estimated to be 3.7, as given by the ratio of the experimental rate constant in methanol to the theoretical one calculated assuming that hydroxylamine checks the Brönsted equation established for nitrogen-containing nucleophiles (NO_2^- , N_3^- , aniline, and hydrazine) in methanol.

Transition State. Two propositions in the Brönsted original exposition of 1924³⁵ are that the linear relationship should hold over only a limited range and that the proportionality constant should vary between limiting values of zero and unity. At the same time, the Bell–Evans–Polanyi (BEP; 1936) principle⁶⁸ has stated that an increase δ of the reaction energy ΔE , brought about by some substituent perturbation in a series of related reactions, results in a partial reduction of the energy barrier ΔE^\ddagger . With additional assumptions, the statement has been extended to free energy, activation free energy ΔG^\ddagger , and standard free energy ΔG° , resulting in eq E-17 and leading to a physical model of the Brönsted relationship.

$$\delta(\Delta G^\ddagger) = \beta \delta(\Delta G^\circ) \quad (\text{E-17})$$

The Leffler–Hammond postulate (LHP; 1953)⁶⁹ suggests that coefficient β ($0 < \beta < 1$) may be used as a measure of the progress along the reaction coordinate axis and, therefore, as a measure of the structure of the transition state. This is expressed quantitatively by eq E-18, which relates changes in the transition state energy resulting from a perturbation (for example, a substituent change in one of the reactants) to the free energy changes brought about by those same substituents in reactants (R) and products (P). A β value

$$\delta G^\ddagger = \beta \delta G_p + (1 - \beta) \delta G_R \quad (\text{E-18})$$

approaching zero indicates a reactant-like transition state, characteristic of an exergonic and unselective reaction because the rate constant is too large to be sensitive to substituents effects; conversely, a value approaching unity indicates a product-like transition state, characteristic of an endergonic and selective reaction. This is the reactivity–selectivity principle, which underlines that reactivity and selectivity are inversely related. The Marcus theory of 1968⁷⁰ is an attempt to relate the free energy of activation ΔG^\ddagger for a given reaction to the intrinsic barrier ΔG_0^\ddagger (ΔG_0^\ddagger is the extrapolation of $\Delta G^\ddagger = f(\Delta G^\circ)$ to $\Delta G^\circ = 0$) and the free energy change ΔG° of the reaction. Any change in the free energy of the reaction [$\Delta(\Delta G^\circ)$] is only partially reflected in the transition state [$\Delta(\Delta G^\ddagger)$], with factor $\beta = \Delta(\Delta G^\ddagger)/\Delta(\Delta G^\circ)$ being a function of the curve form and slope and lying within the range $0 < \beta < 1$. On the basis of Marcus theory, β is calculated as $1/2 + \Delta G^\circ/8\Delta G_0^\ddagger$. The deviation of β from $1/2$ reflects variations in the intrinsic barrier rather than Leffler–Hammond variations in the transition state structure,⁷¹ and the variation of this intrinsic barrier in $\text{S}_\text{N}2$ systems would result in non-reactivity–selectivity principle behavior.^{72,73} From Abraham and McLennan⁷³ thermodynamic data, Alberty and Kreevoy⁷⁴ calculated β values for the transition

state of methyl transfer reactions in water involving anionic nucleophiles: β was close to $1/2$ for many reactions, with the exception of nucleophilic attack by HO^- and CN^- , where β was significantly lower than $1/2$.

The $\text{S}_\text{N}2$ reaction of methyl derivatives generally obeys the rate–equilibrium relationship.^{74,75} Diagrams plotting the geometry of the transition state against more than one coordinate have been first introduced by Alberty.⁷⁶ A third dimension is the free energy surface (potential energy surface diagrams).⁷⁷ The transition state is viewed as a species which varies, geometrically and electronically, in a continuous manner among the well-defined structures of reactants, products, and potential intermediates. The characterization of the transition state and reaction mechanisms based on the interpretation of Brönsted (Hammett) or Marcus coefficient has been questioned^{72,78–80} with various conclusions. One is that the precise magnitude of the Brönsted parameter cannot be given a simple and quantitative molecular interpretation;⁸⁰ another is that $\text{S}_\text{N}2$ reactions occur in two stages, with the size of β_Nu determined in the first stage where an ion–dipole complex is formed and the rate determined largely in the second stage where bonds are formed and cleaved.⁸¹ It has also been suggested that structure–reactivity coefficients may be indicators of reaction progress if transition states can be treated in the same way as ground states.⁷⁹ Recently, the $\text{S}_\text{N}2$ barrier has been generated from an avoiding crossing of two electronic curves which contains the reactant-like and product-like Heitler–London valence bond forms $\text{N}:\text{R}\cdots\text{X}$ and $\text{N}\cdots\text{R}:\text{X}$ (VBCM, valence bond configuration mixing).⁸² The avoiding crossing state is a well-defined point on the reaction surface in the immediate vicinity of the transition state and may be used as a transition state model. For the $\text{S}_\text{N}2$ reaction profile of methyl derivatives, the avoiding crossing is simply represented from two configurations, one being $\text{N}:\text{H}_3\text{C}\cdots\text{X}$ and the other $\text{N}^+\cdots\text{H}_3\text{C}:\text{X}^-$.⁸³ It has been demonstrated for a range of ionic and Menschutkin $\text{S}_\text{N}2$ reactions of CH_3X ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) that there is no simple linkage between transition state charge and geometry, the former being largely governed by the extent of mixing of the intermediate configuration and the latter being governed by reaction exothermicity.⁸⁴

We report computational results on the transition structure of the hydroxylamine– CH_3I reaction using parametric quantum mechanical molecular model AM1⁸⁵ of the AMPAC software (version 6.55). Both starting reactants (hydroxylamine and methyl iodide) and products (CH_3NHOH and HI) structure energies were minimized. Heats of formation of reactants and products in gaseous phase were found to be -17.47 and -13.42 kcal mol^{-1} , respectively. The transition state was reached by the following procedure: (i) the highest transition state between reactant and product geometry was localized using the CHAIN algorithm, (ii) the saddle points were determined using the Newton algorithm, and (iii) the intrinsic reaction coordinate (IRC) algorithm was used to connect the transition state with reactants and products by following the transition vector in both directions. The energy profile is shown in Figure 7, together with the charge evolution on atom I. The heat of formation of the transition state (point of abscissa 20) was evaluated as 53.04 kcal mol^{-1} , which gave an activation energy ΔE_A of $53.04 + 17.47 = 70.51$ kcal mol^{-1} . After the transition point, a plateau in the energy values (abscissa range from 22 to 25) was

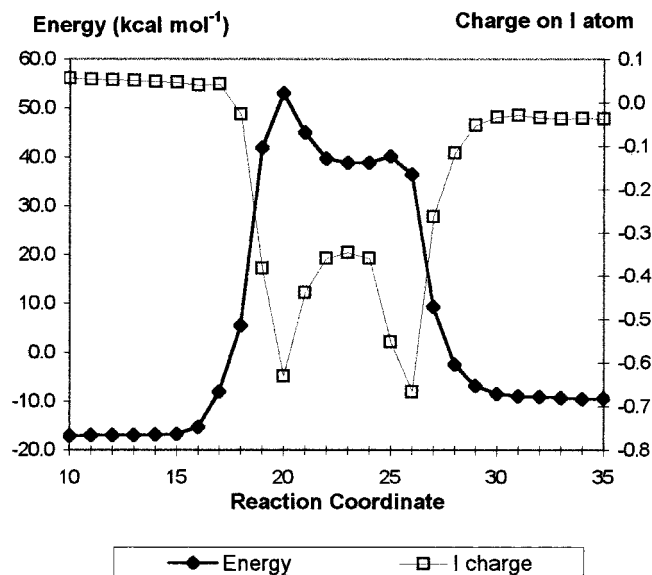


Figure 7. Energy profile (heat of formation) and evolution of the charge on the I atom versus reaction coordinate.

Table 6. Summary of Computational Results in the Gas Phase

reaction coordinate	reactants number 15 ^a	T.S. number 20 ^b	products ^c number 45
d_{N-O}	1.342	1.363	1.346
d_{C-I}	2.051	2.608	5.335
d_{C-N}		1.558	1.460
d_{C-H}		1.157	
d_{I-H}		2.089	1.592
$\alpha(\text{ONC})$	112.18	117.47	110.54
$\beta(\text{ICN})$		162.05	
$\gamma(\text{NOH})$	104.77	107.49	
$D(\text{ICNO})$	169.84	178.32	
$D(\text{CNOH})$		2.47	-108.72
I charge	0.046	-0.630	0.004

^a Reactants are $\text{N}(\text{H}(2)\text{H}(3))\text{-O-H}(5) + \text{C}(\text{H}(8)\text{H}(9)\text{H}(10))\text{-I}$.

^b Transition state is $\text{I-H}(10)\text{-C}(\text{H}(8)\text{H}(9))\text{-N}(\text{H}(2)\text{H}(3))\text{-O-H}(5)$.

^c Products are $\text{C}(\text{H}(8)\text{H}(9)\text{H}(10))\text{-N}(\text{H}(3))\text{-O-H}(5) + \text{I-H}(2)$.

observed, which was reached by the IRC algorithm from the transition state. The assumption that abscissa number 26 is another transition point was not confirmed by application of the IRC algorithm from abscissa number 23. Charges on the N, C, and I (Figure 7) atoms changed drastically for abscissa numbers within the range 18–28. The charge on atom I presented two minima: one at the transition state (−0.630) and the other at the end of the energy plateau (−0.667). This second minimum peak could be correlated with charge variation and movement of the H(2) atom (one of the NH_2 initial group) to form the I–H bond. The most interesting structural parameters of reactants, products, and transition state are reported in Table 6. In the transition state, atoms I, C, N, O, and H(5) are coplanar [$D(\text{ICNO}) \approx 180^\circ$ and $D(\text{CNOH}) \approx 0^\circ$].

To understand the small evolution of the rate of hydrazinolysis of CH_3I with the pH (−7% in an acidic medium), compared to hydroxylaminolysis, the charges on the two N atoms of the hydrazine were calculated with the result that the charge on unprotonated N was little changed by protonation of the other N. For unprotonated hydrazine, both nitrogen atoms have the same charge of −0.48. When the acidity is raised, the charge on the N protonated atom of $\text{NH}_2\text{-NH}_3^+$ is drastically reduced to −0.052, whereas that of the unprotonated N is weakly raised to −0.54.

Conclusion

This work brings new data, summarized in Table 5, on the reactivity of hydroxylamine with methyl iodide in alkaline aqueous solutions, with temperature up to 55 °C (particularly the first Edwards nucleophilic constant assessment). These reaction conditions had not been investigated so far, with most studies being devoted to the acidic medium and ambient temperature, the current conditions of use of hydroxylamine as a reductant in spent fuel reprocessing for uranium/plutonium partitioning.

From the process standpoint, the results show that dissolution off-gas scrubbing with acidic hydroxylamine would be ineffective to trap iodoalkanes. There would thus be no improvement compared to the current process with sodium hydroxide. In neutral hydroxylamine solutions, a reaction would occur, but with a slow kinetic at ambient temperature. With a molar solution of hydroxylamine and a temperature of 25 °C, the methyl iodide half-life would be 101 min at pH 8, 20 min at pH 12, and 3 min at pH 13. It would decrease to 29 s provided that hydroxylamine be only in the NH_2O^- form. Fast kinetics would thus require very basic media. Very basic media may generate other difficulties such as the degradation of hydroxylamine in ammonia, dinitrogen, and dinitrogen monoxide.^{86–88}

However, the use of a moderately basic aqueous solution of hydroxylamine remains an interesting solution to eliminate methyl iodide when reaction time is not a criterion, as is the case for a batch process, and when temperature can be raised a little. As an example, within the framework of nuclear reactor safety, the introduction of hydroxylamine in the containment (either directly in the sump or as a spray) in the case of a severe accident might both limit the formation of organic iodides and prevent the volatilization of iodine.⁸⁹

Acknowledgment

The authors thank Professor R. Gallo for his helpful suggestions on the manuscript and Dr. C. Marchi, who performed the computational calculations on molecular modeling with aid of Dr. M. Rajzmann on IBM RSCOOO 43P140. This work was performed with the financial support of COGEMA.

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(46) Kinetic data for nucleophiles (F^- , $HOCCO^-$, Cl^- , N_3^- , Br^- , SCN^- , CN^- , I^- , and $S_2O_3^{2-}$) reacting with methyl iodide in methanol at 25 °C have enabled Pearson and Songstad⁴⁵ to calculate (i) $\log(k_{Nu}/k_{CH_3OH}) = n_{CH_3I}$ and (ii) slope $s = 1.42$ of the linear curve obtained by plotting n_{CH_3I} in methanol vs n_{CH_3I} in water,⁴³ that is, the substrate constant for CH_3I in a CH_3OH medium referred to the substrate constant for CH_3Br in water. From the nucleophilic constant, $n_{CH_3I} = 6.585$, of hydroxylamine with CH_3I in methanol at 25 °C, it is inferred that $n_{CH_3Br} = 6.585/1.42 = 4.637$, that is, the nucleophilic constant of hydroxylamine with CH_3I , referred to CH_3Br in water at 25 °C.

(47) From our results, $n_{CH_3I} = \log(k_{NH_2OH}/k_{H_2O}) = \log(1.178 \times 10^{-4}/1.66 \times 10^{-9}) = 4.851$ is the nucleophilic constant of hydroxylamine reacting with CH_3I in water at 25 °C. The substrate constant for CH_3I referred to CH_3Br in water at 25 °C is $s = 4.851/4.637 = 1.046$.

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Received for review August 27, 1999

Revised manuscript received February 4, 2000

Accepted September 14, 2000

IE990645B