

Kinetics of Silane Decomposition by Atomic and Molecular Nitrogen Metastables

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We have studied the reactions of a number of metastable nitrogen species with silane in a discharge-flow reactor. By monitoring the decays in the metastable number densities both as a function of time and as a function of silane number density, we have determined reaction rate coefficients, in units of 10^{-11} cm³ molecule⁻¹ s⁻¹, for the following species: N₂(A³Σ_u⁺, v'=0), 0.84 ± 0.16; N₂(A³Σ_u⁺, v'=1), 1.23 ± 0.24; N₂(a¹Σ_u⁻, v'=0), 20.7 ± 5.0; N(²D), 5.9 ± 1.3; N(²P), 0.09 ± 0.03; and N(⁴S), <0.008. When silane is added to a flow containing only N₂(A³Σ_u⁺), we observe no spectral features of any kind between 220 and 850 nm. Adding silane to a flow of atomic nitrogen excites several atomic lines of silicon, the SiN and SiH bands between 400 and 430 nm, and a continuum extending between 270 and 450 nm, all very weakly. Adding N₂(A) to the flow of N(⁴S) atoms upstream from the silane addition inlet enhances the number densities of N(²P) and N(²D) in the flow and, in addition, the previously observed UV emissions. The UV spectral features are further enhanced when silane is added to the orange afterglow of active nitrogen, which is a mix of all the metastables studied and, in addition, vibrationally excited, ground-electronic-state nitrogen. We suggest that the decomposition of silane is initiated by absorbing several quanta from vibrationally excited nitrogen, followed by H atom stripping in reactions of SiH₄[†] and its fragments with N atoms. The observed excitations result from energy-transfer reactions between the various nitrogen metastables and the silane fragments in the flow.

Introduction

Silicon nitride films, which are important in various semiconductor applications, can be generated by plasma vapor deposition processes. Typical plasmas are created by either microwave or radio-frequency discharges through mixtures of silane and nitrogen. Developing models of such plasmas, so that the plasma deposition process can be better understood, requires a knowledge of the kinetics of various nitrogen species with silane and its fragments. Such kinetic information is sparse.

Horie et al.¹ reported chemiluminescence from various spectral features when silane was added to active nitrogen in a discharge-flow reactor. In addition, they monitored decay profiles of atomic nitrogen and silane. However, they made no quantitative estimates of kinetic rates.

We have measured the rate coefficients for the interactions of silane with a number of nitrogen species quantitatively. These studies include the atomic and molecular metastables N₂(A³Σ_u⁺, v'=0,1), N₂(a¹Σ_u⁻, v'=0), N(²D), and N(²P). In addition, we have estimated an upper limit to the rate coefficient for the reaction between N(⁴S) and silane. We have also observed chemiluminescent emissions from mixtures of silane with active nitrogen that was produced under several different sets of conditions. These observations permit us to speculate on the mechanisms of silane decomposition in active nitrogen.

Experimental Section

These experiments were all done in the 2-in.-diameter discharge-flow reactor that we have described in detail previously.²⁻⁵ The nitrogen species were generated by various discharge techniques at the upstream end of the reactor and detected further downstream. We have documented our procedures for generating and detecting the nitrogen species previously.²⁻⁵ Table I summarizes these techniques and documents the relevant publications. Three of these species, N₂(a¹Σ_u⁻), N(²D), and N(⁴S), are formed inside a discharge. The other two species, N₂(A) and N(²P), are generated by energy-transfer processes. The precursor species for these two metastables are consumed completely in the upstream portion of the flow reactor, above the silane injector. In all cases, conditions downstream from the silane injector are such that additional production mechanisms for all species studied are in-

significant. Table I also lists the range of experimental conditions under which we studied each metastable.

The silane was added to the reactor through a movable injector. The rate coefficients were determined by monitoring the decay of the nitrogen species as a function of silane number density and of reaction time.

Chemiluminescent emissions were observed by recording spectra between 200 and 850 nm under the different sets of operating conditions. We used a 0.5-m scanning monochromator that was equipped with a thermoelectrically cooled photomultiplier and a photon-counting rate meter. A computer-based, data acquisition system digitized the output of the photon counter and stored the data for subsequent analysis.

The variation in the response of the monochromator as a function of wavelength was determined by scanning the output of standard quartz-halogen and deuterium lamps. A BaSO₄ screen reflected the lamp emission into the monochromator, thereby ensuring that the optics were filled. Calibrations obtained from the two lamps agreed excellently in the region of spectral overlap, 300-400 nm.

Results

Kinetic Measurements. The rate of change of the nitrogen species, N_x^{*}, as a function of reaction time is

$$d[N_x^*]/dt = -(k_{\text{wall}} + k_{\text{rxn}}[\text{SiH}_4])[N_x^*] \quad (1)$$

where k_{wall} is the effective first-order rate of diffusion to the reactor walls. The reactor walls quench the metastables with near unit efficiency.^{6,7} Other species in the reactor such as N₂ and Ar are not significant quenchers under the conditions employed. In all instances, the number density of added silane is much greater than that of the various nitrogen metastables. Removal of the metastables by silane, therefore, is effectively first order, and eq 1 can be solved to give

$$\ln \{ [N_x^*] / [N_x^*]_0 \} = -(k_{\text{wall}} + k_{\text{rxn}}[\text{SiH}_4])t \quad (2)$$

where the subscript 0 implies the number density prior to SiH₄ addition.

In flow-reactor studies of this type the effective reaction time is given by 0.62 times the ratio of the distance between the injector and the detection region, z , to the bulk flow velocity of the gas, \bar{v} . The factor of 0.62 corrects for fluid mechanical effects.⁸⁻¹⁰ In

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TABLE I: Metastable Nitrogen Production Techniques

species	excitation energy, eV	production	detection	$[N^*]_0$ or $[N_2^*]_0$, particles cm^{-3}	$[SiH_4]_{max}$, molecules cm^{-3}	range of mixing times, ^a ms	bulk flow velocity, $cm\ s^{-1}$	press., Torr	ref
$N_2(A^3\Sigma_u^+)$	6.17	$Ar^* + N_2 \rightarrow N_2^* + Ar$; Ar^* produced in dc discharge	$N_2(A-X)$ emission (220–350 nm)	4×10^8 ($v'=0$) 3×10^8 ($v'=1$)	4×10^{13}	10–18	1500	2.0	2
$N_2(a'^1\Sigma_u^-)$	8.3	dc discharge through N_2/Ar mixture	$N_2(a'-X)$ emission (140–180 nm)	$\sim 10^8$	1×10^{13}	2–4.5	2800	1.5	5
$N(^2D)$	2.38	microwave discharge through 3% N_2 in Ar	vacuum-UV resonance fluorescence	4×10^{10}	2×10^{13}	3–8	3200	1.5	4
$N(^2P)$	3.58	$N_2(A) + N(^4S) \rightarrow N(^2P) + N_2(X)$	$N(^2P-^4S)$ emission at 347 nm	1×10^9	5×10^{13}	9–16	1650	1.8	3
$N(^4S)$		microwave discharge through N_2/Ar followed by passage through glass wool plug	$N_2(B-A)$	8×10^{12}	3×10^{13}	16	1650	1.8	3

^a Effective reaction time = $0.62z/\bar{v}$.

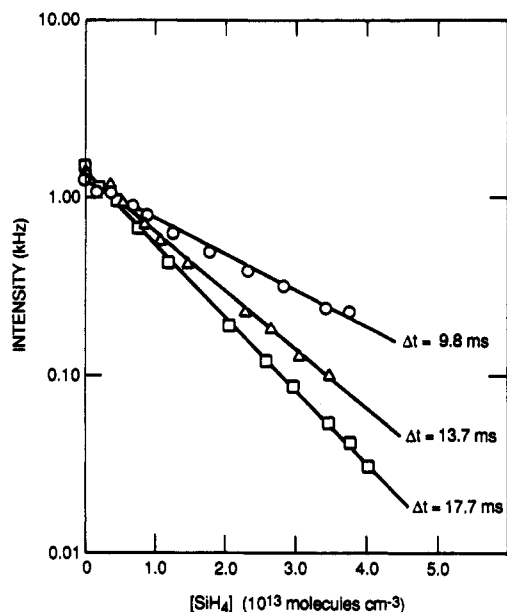


Figure 1. Decay of $N_2(A, v'=0)$ as a function of SiH_4 number density at three different reaction times.

practice, we fix the reaction distance and measure the decay coefficient, Γ , at constant flow velocity and total pressure

$$\Gamma = -\frac{d \ln [N_x^*]}{d[SiH_4]} = 0.62k_{rxn}z/\bar{v} \quad (3)$$

The slope of a plot of Γ as a function of reaction time, $0.62z/\bar{v}$, then, will give the desired rate coefficient. This procedure also corrects for imperfect mixing at the injector.

Figure 1 shows the decay of $N_2(A, v'=0)$ as a function of silane number density at three different reaction times. The slopes of the three lines are decay coefficients at the different reaction times. Figure 2 shows a plot of the decay coefficients for $N_2(A, v'=0)$ removal by silane as a function of reaction time for five different reaction times. The slope of this line is the rate coefficient for $N_2(A)$ quenching by SiH_4 . The intercept in Figure 2 shows that reagents, under the conditions employed, take approximately 1.5 ms to mix. The effective mixing time is a function of flow velocity, pressure, and injector design. It must be determined for each set of experimental conditions.

Table II summarizes all of the rate coefficient measurements. The error limits include the statistical errors in the data analysis as well as estimated systematic uncertainties resulting from such

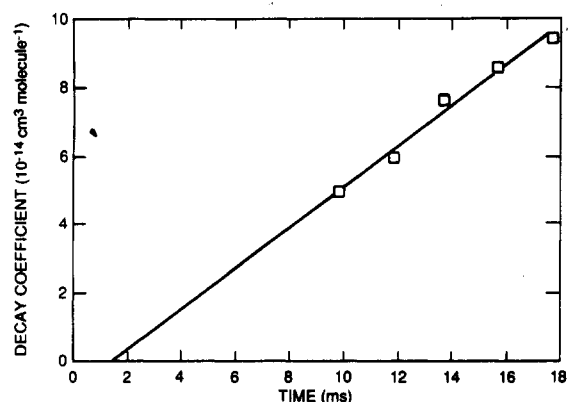


Figure 2. Decay coefficients as a function of reaction time for $N_2(A^3\Sigma_u^+, v'=0) + SiH_4$.

TABLE II: Rate Coefficients for Metastable Nitrogen Reactions with Silane

nitrogen species	rate coefficient, $10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$
$N_2(A^3\Sigma_u^+, v'=0)$	0.84 ± 0.16
$N_2(A^3\Sigma_u^+, v'=1)$	1.12 ± 0.24
$N_2(a'^1\Sigma_u^-, v'=0)$	20.7 ± 5.0
$N(^2D)$	5.7 ± 1.3
$N(^2P)$	0.09 ± 0.03
$N(^4S)$	<0.008

things as errors in calibrations of flow meters, pressure transducers, reproducibility, etc.

Chemiluminescence Observations. Spectra were measured under four sets of conditions: (1) in the afterglow containing only $N_2(A)$, (2) in the presence of recombining N atoms, (3) in the presence of recombining N atoms to which $N_2(A)$ has been added and fully consumed upstream from the silane injector, and (4) in the short-lived, orange afterglow generated by a microwave discharge through a mixture of N_2 dilute in argon. The recombining N atom afterglow is produced by passing the effluents of discharged N_2/Ar mixtures through a glass wool plug. This procedure deactivates any nitrogen metastables produced in the discharge and generally deactivates vibrationally excited, ground-state nitrogen.¹¹ After finishing these studies, however, we performed some Penning ionization experiments¹² on this afterglow and discovered the vibrational deactivation to be incomplete. About a third of the molecular nitrogen was vibrationally excited with about 12% of the $N_2(X, v)$ in vibrational levels five and above. The role of $N_2(X, v)$ in the silane fragmentation

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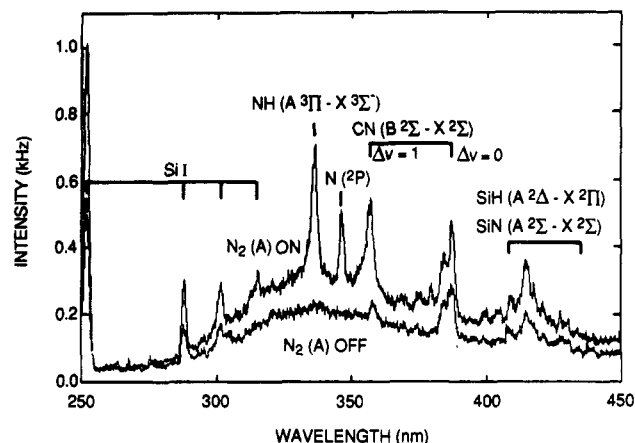


Figure 3. Spectra excited by adding SiH_4 to flow of N atoms with and without $\text{N}_2(\text{A})$ addition to N atom flow upstream from point of SiH_4 injection.

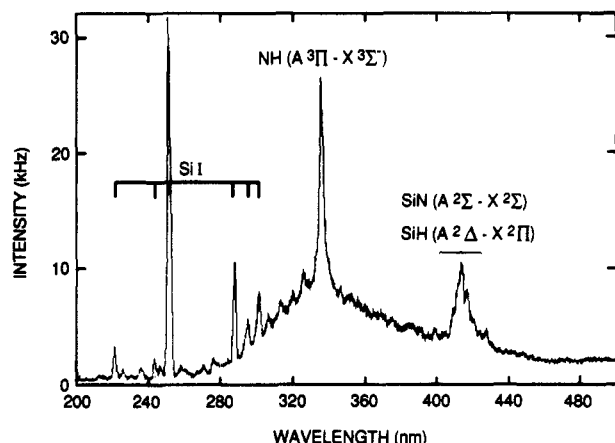


Figure 4. Spectrum from adding SiH_4 to active nitrogen.

processes observed in this afterglow, therefore, cannot be discounted and indeed seems likely.

No spectral features were observed between 200 and 850 nm when silane was added directly to $\text{N}_2(\text{A})$ with the exception, of course, of the $\text{N}_2(\text{A}^3\Sigma_u^+ - \text{X}^1\Sigma_g^+)$, Vegard-Kaplan, bands. Figure 3 shows the UV spectra generated under conditions 2 and 3, given above, while Figure 4 shows the UV spectrum excited under condition 4. All three sets of conditions result in essentially similar spectral features related to SiH_4 addition except that the intensities increase substantially from condition 2 to 4. Major emissions include a number of lines of atomic silicon, an apparent continuum emission between 250 and 450 nm, and the A-X bands of SiH, SiN, and NH. All three spectra imply substantial decomposition of the silane.

The spectra in the 500–850-nm region for conditions 2 and 4 consisted primarily of the nitrogen first-positive bands, $\text{N}_2 - (\text{B}^3\Pi_g - \text{A}^3\Sigma_u^+)$, with an apparent underlying continuum when silane was introduced into the reactor. No spectrum was taken for condition 3, since it should be similar to that of condition 2. For condition 2, the vibrational distribution of the first-positive bands was characteristic of that generated by N atom recombination,¹³ while that for condition 4 was characteristic of the excitation of $\text{N}_2(\text{B}^3\Pi_g)$ generated in the energy-transfer reaction between $\text{N}_2(\text{A}^3\Sigma_u^+)$ and $\text{N}_2(\text{X}, v' \geq 5)$.¹⁴

The position of silane injection for condition 3, the addition of $\text{N}_2(\text{A})$ to recombining N atoms, was somewhat downstream from the point at which the N atoms had quenched all of the $\text{N}_2(\text{A})$. Thus, the major difference between condition 3 compared to condition 2 should be the presence of $\text{N}(\text{2P}, \text{2D})$ metastables in

TABLE III: Possible Reactions Leading to Silane Decomposition in Active Nitrogen

reaction	enthalpy, eV
$\text{N}(\text{4S}) + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{NH}$	+0.45
$\text{N}(\text{2D}) + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{NH}$	-1.93
$\rightarrow \text{SiH}_3 + \text{H} + \text{N}$	+1.58
$\rightarrow \text{SiH}_2 + \text{H}_2 + \text{N}$	+0.10
$\text{N}(\text{2P}) + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{NH}$	-3.13
$\rightarrow \text{SiH}_3 + \text{H} + \text{N}$	+0.38
$\rightarrow \text{SiH}_2 + \text{H}_2 + \text{N}$	-1.10
$\text{N}_2(\text{A}) + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H} + \text{N}_2$	-2.21
$\rightarrow \text{SiH}_2 + \text{H}_2 + \text{N}_2$	-3.33
$\text{N}_2(\text{X}, v=15) + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H} + \text{N}_2(\text{X}, v=0)$	+0.002
$\text{N}_2(\text{X}, v=9) + \text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2 + \text{N}_2(\text{X}, v=0)$	+0.008

the flow.³ The presence of $\text{N}(\text{2P})$ under condition 3 is evident in Figure 3 by the $\text{N}(\text{2P}-\text{4S})$ emission line at 347 nm. (While $\text{N}(\text{2P})$ is also a constituent of the flow under condition 4, the 347-nm line is too weak to register on the scale of Figure 4.) Some small enhancement to the number density of vibrationally excited, ground-state molecular nitrogen is also likely under condition 3 compared to condition 2 because the energy-transfer reaction between $\text{N}_2(\text{A})$ and $\text{N}(\text{4S})$ to make $\text{N}(\text{2P})$ is exoergic by 2.6 eV. This excess energy is likely to be retained as internal energy in $\text{N}_2(\text{X})$.

Discussion

Table II shows that the rate coefficients for quenching $\text{N}_2(\text{A})$, $\text{N}_2(\text{a}')$, and $\text{N}(\text{2D})$ are all tenth gas kinetic or faster. The most probable result of the quenching of $\text{N}_2(\text{A})$ and $\text{N}_2(\text{a}')$ by silane will be SiH_4 fragmentation. Both molecular metastables contain enough energy to fragment the silane into either SiH_3 and H or SiH_2 and H_2 (see Table III). The atomic metastable $\text{N}(\text{2D})$ can only react with silane to give SiH_3 and NH as the products. Our results show it must do this quite efficiently unless the quenching mechanism is just E-V transfer to vibrational modes of SiH_4 . The higher energy atomic metastable, $\text{N}(\text{2P})$, reacts some 2 orders of magnitude more slowly in spite of having a reactive channel similar to that for $\text{N}(\text{2D})$ and, in addition, a possible quenching channel that results in the generation of SiH_2 and H_2 . Ground-state nitrogen atoms have no exoergic channel for reacting with silane, in accord with our failure to observe any signs of $\text{N}(\text{4S})$ removal when silane was added to the reactor.

The energetics of silane decomposition by nitrogen metastables are such that no simple elementary reaction can be responsible for the observed fragment excitation.¹⁵⁻¹⁷ What must be happening instead is that the constituents in the active nitrogen decompose the silane, and the resultant fragments are then excited in subsequent energy-transfer reactions. Table III lists a number of likely first steps in the silane decomposition along with the associated exoergicities of the decomposition reactions. Since ground-state atomic nitrogen does not react with silane, some other species in the recombining-nitrogen afterglow must be responsible for the first step in the decomposition. One possibility for these other species would be the $\text{N}_2(\text{A})$ and $\text{N}_2(\text{X}, v)$ which are generated in the homogeneous recombination of the N atoms in the afterglow. Given that the N atom number density in the afterglow was only 8×10^{12} atoms cm^{-3} , the steady-state number densities of these species will be quite small, $\leq 10^9$ molecules cm^{-3} . Silane decomposition by these species, therefore, should be minimal.

More likely is fragmentation by vibrationally excited $\text{N}_2(\text{X}, v)$ that was produced in the discharge. Our Penning ionization observations^{12b} indicated a likely number density of $\text{N}_2(\text{X}, v' \geq 5)$ in excess of 10^{13} molecules cm^{-3} . The role of $\text{N}_2(\text{X}, v')$ can follow two pathways. Both cases involve transferring vibrational energy from the $\text{N}_2(\text{X}, v')$ to SiH_4 . Such an energy-transfer process should be highly probable given that one-quantum transfer from

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$N_2(X, \nu')$ to both ν_1 and ν_3 of SiH_4 is resonant to within kT up to $\nu'' = 15$.

The most likely pathway for silane decomposition would involve having $N_2(X, \nu')$ supply sufficient vibrational energy to the SiH_4 to allow H atom stripping by $N(^4S)$ to become exoergic. Only two $N_2(X, \nu')$ quanta need to be supplied for this process to become possible, although several more quanta may be required before the stripping process becomes efficient.

The other possible pathway would be SiH_4 dissociation by $N_2(X, \nu')$. Formation of either SiH_3 and a hydrogen atom or SiH_2 and a hydrogen molecule could occur in one step for collisions with N_2 in vibrational levels 15 or 9, respectively. More probable, of course, would be a stepwise excitation of silane by a number of successive collisions with molecular nitrogen containing lower amounts of vibrational energy. With an $N_2(X, \nu)$ number density on the order of a milliTorr, each silane molecule will undergo roughly 15 collisions within a millisecond. Thus, even single-quantum transfers would be sufficiently frequent to effect the decomposition of the silane on the time scale of the experiments, 10–20 ms, were not intramode relaxation within the silane likely to redistribute the absorbed energy. A number of successive single- and multiple-quantum transfers would be necessary to dissociate the silane.

After the first decomposition step, atomic nitrogen can react exoergically with the SiH_x fragments to generate smaller fragments. If these reactions are moderately fast, this further decomposition can occur rapidly even at the modest $N(^4S)$ number densities of the present experiments ($\sim 10^{13}$ atoms cm^{-3}). The final decomposition step, that between SiH and $N(^4S)$, is endoergic to produce Si atoms and NH but is exoergic by 1.5 eV for generating SiN and H atoms. The channel producing Si and NH is exoergic if the nitrogen atoms are electronically excited. Atomic silicon also can be produced in an exoergic reaction between H atoms and SiH.

Once the silane is fragmented, the observed emissions can be excited in energy-transfer reactions with the nitrogen metastables which are generated by N atom recombination. Even at number

densities as low as 10^7 – 10^8 molecules cm^{-3} , metastable $N_2(A)$ can excite strong emissions from fragments such as NH, SiH, and Si given number densities of these latter species on the order of 10^9 – 10^{10} molecules cm^{-3} .

The much larger intensity in the spectrum excited under condition 4 compared to those excited under conditions 2 and 3 can be rationalized by the fact that the $N_2(X, \nu)$ and $N_2(A)$ number densities are much larger for condition 4. These larger number densities will greatly increase the rates of both silane decomposition and fragment excitation. The slight increase in the intensities in changing from condition 2 to condition 3 most likely results from a somewhat more rapid fragmentation that is possible with the metastable nitrogen atoms that result when $N(^4S)$ quenches $N_2(A)$. In addition, although the $N_2(A)$ has been quenched by the atomic nitrogen to levels below our detection limit, 10^7 molecules cm^{-3} , the $N_2(A)$ number density might still be somewhat in excess of the steady-state number density generated in N atom recombination. Clearly these effects are small because the intensity enhancement is only about a factor of 2.

Summary

Atomic and molecular metastable nitrogen, $N(^2D)$, $N_2(A)$, and $N_2(a')$, react rapidly with silane, leading to SiH_4 fragmentation. In addition, silane appears to be decomposed efficiently by vibrationally excited, ground-electronic-state molecular nitrogen. This latter fragmentation most probably occurs when $N(^4S)$ strips H atoms from silane molecules that have absorbed two or more $N_2(X, \nu')$ quanta. Also possible would be silane dissociation by $N_2(X, \nu')$ either in one step with many quanta (on the order of 10) transferred to the SiH_4 or by a series of successive transfers a few quanta at a time.

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New Features of Stirring Sensitivities of the Belousov–Zhabotinskii Reaction

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The sensitivity to stirring shown by the oscillatory Belousov–Zhabotinskii (BZ) reaction when carried out in batch mode has been experimentally examined. Different series of experiments were designed in order to test the influence of both the flow rate of a deaerating agent and the reactant initial concentrations on the observed stirring susceptibility. In addition, distinctive stirring effects associated with the different phases of the oscillatory reaction were analyzed. The experimental results indicate that stirring effects strongly depend on the initial concentrations of the BZ mixture and on the detailed chemical dynamics inherent in each phase of the reaction.

I. Introduction

Chemical instabilities, as paradigms of nonlinear effects corresponding to dynamics operating in far from equilibrium regimes, have been mostly described in past years in terms of homogeneous models, avoiding any reference to heterogeneities. Yet it is presently well-documented that effects originated in nonideal mixing conditions not only exist under the usual operating modes of real experiments but may also exert noticeable influences enhancing, suppressing, or modifying normal patterns of behavior such as temporal oscillations or multistability.¹ Even recently,

features of irreproducibility likely mediated by stirring, which have been observed in certain chemical systems, have motivated preliminary experimental² and theoretical studies.³ Commonly, stirring effects within the context of oscillatory or multistable chemical dynamics have attracted the attention of both theoreticians^{4–10} and experimentalists.^{6,11–22} The existing literature refers

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