# Absolute Rate Constant for the Reaction of CI(<sup>2</sup>P) with CINO

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The room temperature rate constant for the reaction  $Cl + ClNO \rightarrow Cl_2 + NO$  has been measured by the method of discharge flow mass spectrometry. The rate constant was determined from the decay of CINO in the presence of an excess of CI atoms at a total pressure of 1 Torr. The rate constant obtained was  $(7.6 \pm 0.8) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. This result is compared with previous determinations, the values of which ranged by more than an order of magnitude and all of which depended on knowledge of the absolute concentration of CINO. We suggest that the lack of agreement is attributable principally to uncertainties in [CINO] resulting from absorption of this reactive species on glass and metal surfaces. Our result does not depend directly on [CINO] and supports the highest values published for this rate constant.

# Introduction

Current interest in possible ozone depletion in the stratosphere due to chlorofluorocarbons and other sources of chlorine<sup>1,2</sup> has generated considerable interest in rate constants of atomic chlorine reactions. In the present study we report measurements of the rate constant for the reaction of atomic chlorine with ClNO.

$$Cl + ClNO \rightarrow Cl_2 + NO$$
 (1)

Although this reaction is a relatively minor loss process for both Cl and ClNO in the stratosphere, the number of reactions considered by kineticists, modelers, and data evaluators has been greatly increased in order to obtain as complete a description of atmospheric chemistry as possible.<sup>2</sup> The reaction of Cl with ClNO is important not only to ClNO photochemistry<sup>3,4</sup> but also in the recombination of Cl atoms catalyzed by NO.5,6 The primary photolysis process is the production of Cl atoms followed by the reaction of Cl with ClNO. The recombination process occurs via the reaction<sup>7,8</sup>

$$Cl + NO + M \rightarrow ClNO + M$$
 (2)

followed by reaction 1. The determination of Cl concentrations in flow tube experiments has been accomplished using reaction 1 as a titration reaction.<sup>8-12</sup>

Reaction 1 has been studied by both direct and indirect methods. In 1952 Burns and Dainton<sup>13</sup> measured the inhibition of the photochemical formation of phosgene from CO and Cl<sub>2</sub> by added CINO. They derived a value for  $k_1$  of  $3.2 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> at 298 K. Clyne and Cruse<sup>14</sup> made the first direct measurement of  $k_1$ 

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using a discharge flow atomic resonance fluorescence system to obtain a room temperature value of  $3.0 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. A study by Grimley and Houston<sup>15</sup> using pulsed photolysis infrared NO fluorescence obtained a value of  $5.4 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>. Nelson and Johnston<sup>16</sup> reported a room temperature value of  $1.65 \times 10^{-11}$  cm<sup>3</sup>  $s^{-1}$  using laser flash photolysis resonance fluorescence. A study by Kita and Stedman<sup>17</sup> in 1982 employing discharge flow resonance fluorescence gave a value of  $7.2 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. Thus, over a 30-year period, the measured values of  $k_1$  have ranged from 3.2  $\times$  10<sup>-12</sup> to 7.2  $\times$  10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>. Even the more recent direct determinations ranged between  $5.4 \times 10^{-12}$  and  $7.2 \times 10^{-11}$  cm<sup>3</sup>  $s^{-1}$  and all depended on a knowledge of the absolute concentration of ClNO. This compound has a propensity for absorption on glass and metal surfaces 12,14,16 and is difficult to handle quantitatively. By way of contrast, the present experiments were performed by monitoring the decay of CINO in an excess of atomic chlorine in an effort to better establish the value for  $k_1$ . Measurements were made in a discharge flow system with monitoring of ClNO via collision-free sampling mass spectrometry. Our study is the first measurement of this rate constant via discharge flow mass spectrometry and the first that does not depend directly on the absolute concentration of CINO. The present approach is expected to generate rate data of high reliability.

#### Experimental Section

The apparatus consisted of a Pyrex discharge flow system linked via a two-stage collision-free sampling system to a quadrupole mass spectrometer. The flow tube was constructed of Pyrex, 50 cm long and of 28 mm internal diameter. The flow system had a moveable Teflon injector (6 mm o.d.) for the addition of ClNO. A more detailed description of the technique and its associated apparatus has been given in a previous publication from this laboratory.18

Typical flow conditions were 680–700  $\mu$ mol/s of helium carrier gas near 1 Torr total pressure at a flow velocity  $\leq 2200 \text{ cm}^3 \text{ s}^{-1}$ . A side arm, at the end of the flow tube, contained a microwave discharge (50 W, 2450 MHz) by which chlorine atoms were generated in a dilute mixture of  $\sim 1\%$  molecular chlorine in helium. The walls of the discharge tube were treated with  $H_3PO_4$ to minimize atom recombination. The walls of the flow tube were left untreated. The flow tube walls were exposed to chlorine atoms for up to 1 h before kinetic runs were performed each day.

A crucial part of these measurements was the determination of absolute Cl atom concentration. The chlorine atom concentration was determined by measuring the decrease in the  $Cl_2^+$  ion peak at mass 70 when the discharge was initiated.<sup>19</sup> The Cl

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Figure 1. Calibration curve for the NCl<sup>+</sup> peak as a function of CINO concentration. The electron energy was 26 eV.

concentration is given by  $[Cl] = 2([Cl_2]_{off} - [Cl_2]_{on})$ . This method measures Cl concentration at the downstream end of the flow tube and would be subject to error if there were wall recombination of Cl to re-form Cl<sub>2</sub>. To eliminate this possibility, C<sub>2</sub>H<sub>6</sub> was added downstream of the discharge to scavenge Cl atoms by the rapid reaction<sup>2</sup>

$$Cl + C_2H_6 \rightarrow C_2H_5 + HCl$$
(3)

This is essentially methods I and III described by Ray et al.<sup>19</sup> except that they used  $Br_2$  instead of  $C_2H_6$  to scavenge Cl. Our experience was essentially the same as theirs: with an uncoated flow tube pretreated by exposure to Cl atoms, the difference between [Cl] measured by method III ( $\Delta Cl_2$  in the presence of  $C_2H_6$ ) and method I ( $\Delta Cl_2$ ) was small and within the experimental uncertainty  $(\pm 10\%)$ . This indicates a relatively low loss of atomic chlorine at the wall. The validity of our method of determining [Cl] is verified by the determination of the rate constant for the reaction of atomic chlorine with methanol at 298 K. Our discharge flow mass spectrometry study<sup>20</sup> with atomic chlorine in excess gives  $k = (5.1 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , in reasonable agreement with our previous flash photolysis-resonance fluorescence value<sup>21</sup> (methanol in excess) of  $k = (6.3 \pm 0.7) \times 10^{-11} \text{ cm s}^{-1}$ .

The electron-impact mass spectrum of ClNO has an extremely low contribution from the parent CINO<sup>+</sup> peak.<sup>22</sup> Because of the lack of a significant parent peak even at low electron energies, we monitored the relative CINO concentration using the NCl<sup>+</sup> fragment peak at mass 49 with an electron energy of 26 eV. The more abundant NO<sup>+</sup> fragment peak was not used to monitor CINO since NO is a product of reaction 1. Although it was originally concluded<sup>12</sup> that it was not possible to make quantitative measurements of CINO consumption mass spectrometrically, improvements in sensitivity in the intervening years have made the experiment possible although difficult. A calibration curve was obtained for NCl<sup>+</sup> by monitoring the counts at mass 49 vs. the concentration of ClNO; this is shown in Figure 1. Although the absolute CINO concentration is uncertain due to possible wall losses, the calibration data demonstrate that the NCl<sup>+</sup> peak is linearly related to [CINO] as calculated from pressure and flow-meter readings. The sensitivity obtained was  $1.2 \times 10^9$  cm<sup>-3</sup> counts<sup>-1</sup> s. At signal/noise = 1 this corresponds to  $\sim 6 \times 10^{10}$ cm<sup>-3</sup>.

The ClNO was prepared by mixing excess NO with  $Cl_2$  (3:1). The gases were initially condensed at 77 K and held at this temperature for approximately 1 h. The gas mixture was then allowed to stand at room temperature overnight. Excess NO as well as unreacted Cl<sub>2</sub> was removed by pumping on the sample at 145 K (n-pentane slush). The final vapor pressure above the ClNO sample at 145 K was less than 1 mTorr. NO (99% Matheson) and Cl<sub>2</sub> (99.9% Matheson) were degassed at 77 K. NO<sub>2</sub> (99.5% Matheson) was purified by distillation from  $\sim 145$  to 77 K to remove NO. A small correction (<5%) was made to the NO<sub>2</sub> flow rate to account for the rapid dissociation of the  $N_2O_4$  dimer. He (99.9995%, Air Products) was drawn through a molecular sieve trap held at 77 K. C<sub>2</sub>H<sub>6</sub> (99.96% Matheson) was degassed at liquid nitrogen temperature.

## Results

The rate constant for reaction 1 was determined under pseudo-first-order conditions with  $[Cl]_0 > [ClNO]_0$ . The decay of ClNO is given by

$$\ln [\text{CINO}] = -k_{\text{obsd}}(d/v) + \ln [\text{CINO}]_0$$
(4)

where [ClNO] is proportional to the NCl<sup>+</sup> signal, d is the distance from the reactant injector probe tip to the detector, and v is the linear flow velocity. A potential complication in these experiments would be the presence of atomic hydrogen or oxygen in the products of the discharge. These species could be formed from residual impurities in the system and contribute to the decay of CINO due to the occurrence of the reactions H + CINO and O + ClNO. To check on this possibility, we added  $3 \times 10^{13}$  cm<sup>-3</sup> NO<sub>2</sub> to scavenge H and O. The NO<sub>2</sub> was added approximately 35 cm upstream of the probe through which the ClNO was added and any H and O would be removed by  $NO_2$  in less than 2 and 21 cm, respectively (3 decay lifetimes). We detected no effect within experimental uncertainty on the observed pseudo-first-order decay rate for CINO for experiments with and without added NO<sub>2</sub> (see Figure 3). The formation of OH in the scavenging of H by  $NO_2$  is of little consequence since the rate constant for the reaction of OH with ClNO<sup>23</sup> is  $3.2 \times 10^{-13}$  cm<sup>3</sup> s<sup>-1</sup>, at least 2 orders of magnitude slower than that for Cl + ClNO. We conclude from this that CINO decays only via reaction with Cl and loss at the walls of the flow tube (see below). The experimental first-order decay constant,  $k_{obsd}$ , was obtained by linear least-squares analyses of first-order plots according to eq 4. The diffusion-corrected first-order constant,  $k_{cor}$ , was then calculated from

$$k_{\rm cor} = k_{\rm obsd} (1 + k_{\rm obsd} D / v^2) \tag{5}$$

where D is the diffusion coefficient of ClNO in helium. The diffusion coefficient for CINO in helium was taken to be 0.78D (He-Ar), where the factor 0.78 equals the ratio of the square roots of the molecular weights of Ar and ClNO. D(He-Ar) was taken to be 486 cm<sup>2</sup> s<sup>-1</sup> at 1 Torr and 298 K.<sup>24</sup>

The bimolecular rate coefficient,  $k_1$ , is related to  $k_{cor}$  through the expression

$$k_{\rm cor} = k_1[{\rm Cl}] + k_{\rm w} \tag{6}$$

where  $k_w$  is the first-order rate constant for loss of ClNO on the wall. The bimolecular rate coefficient was determined from linear least-squares analyses of the data according to eq 6. A small stoichiometric correction was made to [Cl] to allow for depletion of [Cl]

$$[Cl]_{mean} = [Cl]_0 - \frac{1}{2} [ClNO]_0$$
(7)

The uncertainty in [CINO] mentioned above is of little consequence here since the stoichiometric correction to [Cl] was typically  $\sim 6\%$ . Table I summarizes the experimental conditions employed and the measured values of  $k_{cor}$ . ClNO was added at

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TABLE I: Rate Constant Data for the Reaction Cl + ClNO  $\rightarrow$  Cl\_2 + NO^a

$[Cl]_{mean}/$ 10 <sup>12</sup> cm <sup>-3</sup>	[CINO] <sub>0</sub> / 10 <sup>11</sup> cm <sup>-3</sup>	$k_{\rm cor}/{\rm s}^{-1}$	$[C1]_{mean}/$ 10 <sup>12</sup> cm <sup>-3</sup>	[CINO] <sub>0</sub> / 10 <sup>11</sup> cm <sup>-3</sup>	$k_{ m cor}/ m s^{-1}$
11.3	7	865	3.7	20	400
10.3	7	803	3.5	10	365
9.3	7	825	2.6	10	219
8.3	7	707	1.8	8	191
7.2	7	613	4.1	10	351
6.3	7	488	3.3	10	257
5.2	7	579	2.5	10	177
5.5	4	562	1.4	7	173
4.5	4	404	0.99	7	121
5.4	8	568	2.9	10	296

 ${}^{a}k_{1} = (7.64 \pm 0.86) \times 10^{-11} (2\sigma) \text{ cm}^{3} \text{ s}^{-1}; k_{w} = 66 \pm 25 \text{ s}^{-1}; \langle T \rangle = 300 \pm 1 \text{ K}; \langle P \rangle = 1.013 \pm 0.008 \text{ Torr}; v = 2173 \pm 14 \text{ cm} \text{ s}^{-1}.$ 



Figure 2. Kinetics of the Cl + ClNO reaction at 298 K. Typical firstorder logarithmic decay plots of ClNO in the presence of various excess concentrations of Cl atoms (cm<sup>-3</sup>):  $\blacklozenge$ , 8.3 × 10<sup>12</sup>;  $\circlearrowright$ , 4.1 × 10<sup>12</sup>;  $\blacklozenge$  1.8 × 10<sup>12</sup>.



Figure 3. Corrected first-order rates for reaction 1 vs. Cl atom concentration.  $\odot$ ,  $3 \times 10^{13}$  cm<sup>-3</sup> NO<sub>2</sub> added to scavenge H and O; see text.

reaction times from 1.5 to 12 ms and initial stoichiometries  $[Cl]_0/[ClNO]_0$  ranged from 1 to 16. Figure 2 shows typical logarithmic decay plots of [ClNO] vs. time. Figure 3 shows the variation of the pseudo-first-order rate constant  $k_{cor}$  with  $[Cl]_{mean}$  at 298 K. A linear least-squares analysis of the data (Table I) according to eq 6 gave a bimolecular rate constant of (7.64 ± 0.43) × 10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup> (1 $\sigma$ ). Allowing for possible systematic error in the Cl atom concentration gives the value  $k_1 = (7.6 \pm 0.8) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>.

The positive intercept in Figure 3 is  $66 \pm 25$  s<sup>-1</sup>. Experiments performed in the absence of atomic chlorine gave first-order CINO decays consistent with this value. Thus the intercept is real and not an artifact<sup>19</sup> caused by uncertainties in the method used to determine atomic chlorine concentrations. This constant CINO loss is most likely associated with removal of ClNO on the Cl treated Pyrex wall of the flow tube. Other as yet unidentified loss processes could also be occurring.

TABLE II: Comparison of Direct Measurements of the Rate Constant for the Reaction  $Cl + CINO \rightarrow Cl_2 + NO$  at 298 K

$k/10^{-11}$ cm <sup>3</sup> s <sup>-1</sup>	excess species	concn of excess species/cm <sup>-3</sup>	species monitored	method <sup>a</sup>	ref
3.00	CINO	1012-1013	Cl	DF-RF	14
0.54	CINO	1016	NO	LFP-CL	15
1.62	CINO	1013-1014	Cl	LFP-RF	16
7.2	CINO	$(2-7) \times 10^{11}$	Cl	DF-RF	17, 26
11	CINO	$10^{12} - 10^{13}$	Cl	LFP-RF	25
7.6	Cl	1012-1013	CINO	DF-MS	this study

 ${}^{a}DF$  = discharge flow; RF = resonance fluorescence; LFP = laser flash photolysis; CL = chemiluminescence (IR fluorescence); MS = mass spectrometry.

#### Discussion

Previous published studies of the reaction Cl + ClNO were reviewed in the Introduction. Since completion of the present experiments, we have learned of a recent direct study by Margitan<sup>25</sup> which employed laser flash photolysis-resonance fluorescence. A summary of all the direct determinations of  $k_1$ at 298 K is given in Table II. As mentioned in the Introduction, all previous direct studies (including the most recent one by Margitan) depend directly on knowledge of the absolute concentration of ClNO as the species in excess. In the absence of direct monitoring of [CINO] in the reaction cell under reaction conditions, the tendency for CINO to be lost by absorption on glass and metal surfaces could lead to an overestimation of [CINO]. This in turn could lead to an underestimation of  $k_1$  since, under pseudo-first-order conditions with [ClNO] > [Cl],  $k_{1st}$  =  $k_1$ [ClNO]. An inspection of the results summarized in Table II reveals that the two lowest values of  $k_1$  are associated with the highest values of [ClNO]. It could be that experiments with very high values of [CINO] had the most serious problem with loss of CINO.

The very low value of Grimley and Houston<sup>15</sup> might be rationalized by assuming that the reaction channel leading to NO (the reaction product monitored in their experiment) is a relatively minor one ( $\sim 5\%$  of the total reaction) and the low rate constant is attributable to only this minor channel. This assumption is, however, not consistent with the results of Clyne, Cruse, and Watson<sup>12</sup> who showed in a very direct manner that the ratio of [NO] produced to [Cl] reacted is equal to  $1.04 \pm 0.06$  for reaction 1. This clearly requires that the major product channel for reaction 1 is NO + Cl<sub>2</sub>.

The two previous high values for  $k_1$  listed in Table II came from experiments which avoided loss of ClNO or allowed for its occurrence. Thus, Kita and Stedman<sup>17</sup> used very low<sup>26</sup> [ClNO] while Margitan<sup>25</sup> monitored [ClNO] in his reaction cell. In the present study we had Cl in excess and therefore our value for  $k_1$  does not depend on the absolute [ClNO] in our system. These three studies probably represent the best present estimate of  $k_1$  and we may take the simple mean value of  $k_1 = (8.6 \pm 1.7) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> as the recommended value. This is nearly 4 times faster than the 1985 NASA Panel recommendation.<sup>2</sup>

The value of  $k_1$  recommended here may be compared with other fast Cl reactions with molecules such as Cl<sub>2</sub>O<sup>2</sup> and ClOO<sup>2</sup> (Cl abstraction), Br<sub>2</sub><sup>27</sup> (Br abstraction), C<sub>2</sub>H<sub>4</sub>S<sup>28,29</sup> (S and H abstraction), and H<sub>2</sub>S<sup>28</sup> (H abstraction). All these molecules, including ClNO, react with atomic chlorine with a rate constant within a factor of 2 of 1 × 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup>. Further, the rate constants have been shown (C<sub>2</sub>H<sub>4</sub>S, H<sub>2</sub>S) or assumed (Cl<sub>2</sub>O, ClOO, Br<sub>2</sub>) to be temperature independent. It is reasonable to assume that  $k_1$  also has little or no temperature dependence.

Consideration of the present suggested value, which still precludes reaction 1 from providing but a relatively minor loss process

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for stratospheric Cl and ClNO, may be useful to providing information concerning ClNO photochemistry, NO-catalyzed Cl atom recombination, and more accurate Cl calibrations in flow tube studies.

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# Absolute Rate Constants for Silylene Reactions with Hydrocarbons at 298 K

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We report absolute removal rate constants for silylene by reaction with alkanes, olefins, 1,3-butadiene, and acetylene at ambient temperature and 5-Torr total pressure. Rate constants were determined by laser resonance absorption flash kinetic spectroscopy. The results show that silylene is unreactive with alkanes and reacts rapidly and unselectively with unsaturated hydrocarbons.

# Introduction

Silylenes are widely recognized as important intermediates in silicon hydride and organosilicon chemistry. Evidence for their importance comes largely from classical mechanistic studies, and information on silylene reactivity comes almost exclusively from relative rate studies under pyrolysis, shock tube, or nuclear recoil conditions.<sup>1,2</sup> Recently, two direct absolute measurements of SiH<sub>2</sub> reaction rate constants<sup>3,4</sup> and two relative rate studies, <sup>5,6</sup> all based on generation of silylene by photolysis of phenylsilane, have appeared. The results of these studies do not agree well with previous estimates of relative or absolute silylene reactivity, for a number of reaction partners. These discrepancies require further investigation, and reliable direct measurements of absolute rate data are essential to conclusively unraveling the chemistry of these reactive intermediates.

In this paper we present a survey of absolute rate constants for the reaction of  $SiH_2$  with hydrocarbons. Direct measurements of absolute rate constants for the removal of silylene by methane, ethane, ethylene, propylene, 1,3-butadiene, and acetylene have been measured at 5-Torr total pressure and 298 K using laser resonance absorption flash kinetic spectroscopy (LRAFKS). The results demonstrate that  $SiH_2$  is unreactive with saturated hydrocarbons but extremely reactive and rather unselective with unsaturated hydrocarbons. Since the anticipated products of these reactions are chemically activated organosilanes, the results may also provide some information on the decomposition chemistry of these molecules.

#### **Experimental Section**

A schematic of the LRAFKS apparatus has been published previously.<sup>4</sup> Briefly, transient concentrations of silylene are produced in a flowing gas cell by excimer laser (Lambda Physik EMG-102E) photodissociation of a suitable precursor. Silylene concentrations are monitored in real time by transient absorption of light from a single-frequency Rhodamine 6G ring dye laser tuned to single rotational lines of the  ${}^{1}B_{1}(0,2,0) \leftarrow {}^{1}A_{1}(0,0,0)$ electronic transition of SiH<sub>2</sub>. The only modifications of the apparatus for the present study were the addition of fast preamplifiers (LeCroy VVB100, 2-ns risetime) to the photodiodes and the addition of an automatic throttle valve to the exhaust port of the flow cell. The throttle valve is controlled by the output from a capacitance manometer (MKS Baratron Model 221A, 10 Torr full scale) which monitors the cell pressure. This allows operation of the flow system at constant total pressure and constant total flow as the composition of the gas mixture changes.

Silylene was generated by photodissociation of phenylsilane or disilane with ArF excimer laser radiation at 193 nm or by photodissociation of SiH<sub>3</sub>I by KrF excimer laser radiation at 248 nm. The different silylene sources are necessary since not all of the hydrocarbon reaction partners are suitably transparent at 193 nm. Phenylsilane (Petrarch) was degassed prior to use. Disilane (Airco or Matheson) was used as received. Iodosilane was prepared by HI cleavage of phenylsilane or chlorophenylsilane.<sup>7</sup> Silylene transient absorption was monitored by using the <sup>R</sup>Q<sub>0,J</sub>(5) or the <sup>R</sup>Q<sub>0,J</sub>(7) rotational lines when phenylsilane or disilane was used as a precursor. The <sup>R</sup>Q<sub>0,J</sub>(7) line was used exclusively when iodosilane was used as a precursor in order to avoid possible complications owing to the near coincidence between the <sup>R</sup>Q<sub>0,J</sub>(5) silylene transition and a molecular iodine absorption line.

Gas flow rates were measured and controlled with calibrated electronic mass flow controllers (Vacuum General UV series, 10-, 100-, or 1000-sccm full flow) with the exception of phenylsilane and iodosilane, for which a needle valve was used. In a typical experiment a flow of silvlene precursor in helium buffer gas at 300 sccm and 5-Torr total pressure was established. Hydrocarbon reactant flow was then added and the helium flow decreased to maintain a total flow rate of 300 sccm while the vacuum pump throttle valve maintained the total pressure at 5 Torr by maintaining a constant pumping speed independent of the gas composition. Under these conditions, the average residence time in the cell volume is  $\sim 1-2$  s. This procedure guarantees that the partial pressure of silylene precursor is constant. Phenylsilane flow rates through the needle valve were determined by measuring pressure rise in a fixed volume as a function of time. The partial pressure of phenylsilane in kinetic experiments was less than 1  $\times 10^{-4}$  Torr. The mass flow rate of iodosilane was not determined. We estimate that the partial pressure of iodosilane in the kinetic experiments for which it was a precursor was less than  $1 \times 10^{-3}$ Torr. Hydrocarbon partial pressures were calculated from the total pressure by using the total gas flow rate and the flow rate of the hydrocarbon. The estimated absolute uncertainty in the hydrocarbon partial pressure is  $\pm 5\%$  as determined from the stated accuracy of the capacitance manometer and the accuracy of the mass flow controllers.

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