# Kinetic Studies of the Reactions of Atomic Chlorine with N-Methylmethylenimine and 1,3,5-Trimethylhexahydro-1,3,5-triazine

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The reaction of  $Cl + CH_3N = CH_2 \rightarrow HCl + CH_2 = NCH_2$  has been studied with the very low pressure (VLPR) technique in the temperature range 303-363 K. The rate constant for the forward reaction is given by the expression  $k_1 = (7.54 \pm 1.60) \times 10^{-11} \exp(-826 \pm 240/RT)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> where R is expressed in cal mol<sup>-1</sup> K<sup>-1</sup>. The rate constant for the reaction of atomic chlorine with 1,3,5-trimethylhexahydro-1,3,5-triazine was also measured in the temperature range 303-363 K and found to be  $k_4 = (5 \pm 2) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at all temperatures. The conventional transition state theory suggests that the TS for reaction 1 is bent with the Cl atom forming a Cl···H···C angle ca. 160°, and placed away from the nitrogen lone pair. The heat of formation of CH<sub>2</sub>=NCH<sub>2</sub> radical is ca. 63 ± 3 kcal/mol, and reaction 1 is exothermic by ca. 5 ± 3 kcal/mol.

#### Introduction

Imines are rather unstable compounds that undergo efficient polymerization to cyclic compounds and hydrolysis to carbonyl compounds.1 They are generally considered as very reactive species, and they are mainly known as fast reactive intermediates. N-Methylmethylenimine and N-ethylmethylenimine are among the lowest members of the series and have been observed as reaction products in the IR multiphoton decomposition of dimethylnitramine and diethylnitramine,<sup>2,3</sup> the photochemistry of aliphatic amines.<sup>4,5</sup> and the thermal decomposition of alkylated ethylenediamines and methylhydrazines.<sup>6,7</sup> N-Methylmethylenimine has been reported as the primary reaction product in the reaction of atomic chlorine with dimethylnitramine.<sup>8</sup> There have been a number of studies concerning the geometrical and vibrational structure of these imines,<sup>9-12</sup> but there is very little known about their chemical reactivity and thermochemistry. It is important to determine the chemical reactivity of hydrogen atoms of the methyl group in N-methylmethylenimine and the strength of the C-H bond.

In this work we study the kinetics of the reaction of chlorine atoms with N-methylmethylenimine  $(CH_3N=CH_2)$  in the gas phase over the temperature range 303-363 K, using the VLPR (very low pressure reactor) technique.<sup>13</sup> This rate constant at room temperature has been estimated previously by our group.<sup>8</sup> Our kinetic measurements will determine the Arrhenius parameters and provide an estimate of the H--CH<sub>2</sub>N=CH<sub>2</sub> bond dissociation energy and the heat of formation of the H<sub>2</sub>C=NCH<sub>2</sub> · radical. The role of the nitrogen lone pair to the above kinetics will be investigated. Finally, the reaction kinetics of chlorine atoms with 1,3,5-trimethylhexahydro-1,3,5-triazine will be studied in order to estimate its contribution to the original reaction, since a small percentage of undecomposed triazine molecules are contained in the imine mixtures.

#### **Experimental Section**

The very low pressure reactor (VLPR) technique has been discussed in great detail by Benson et al.,<sup>14</sup> and our experimental apparatus has been described in a previous work.<sup>15</sup> The main features of the technique are as follows: The gas phase reaction occurs in a Knudsen cell at a total steady-state pressure less than 5 mTorr. The reactants are introduced into the reactor through two separate capillary inlets and are allowed to react for a short period of time, since they are also discharged through a variable aperture into the first stage of a differentially pumped system. Thus, a continuous molecular flow is maintained leading to a collimated molecular beam that is sampled with a quadrupole mass spectrometer which is mounted in the second stage vacuum chamber. The molecular beam is modulated with a tuning fork chopper at the entrance of the second vacuum chamber, in order to achieve amplification of the mass spectrometric signal.

Chlorine atoms were generated by flowing 5%  $Cl_2$  in helium (ultrahigh purity) through a quartz tube coated with a dried slush of boric and phosphoric acid mixture and enclosed in a 2.45-GHz microwave cavity operating at 30 W. The complete dissociation of  $Cl_2$  was checked by mass spectrometry. *N*-Methylmethylenimine (IMI) was produced by thermal decomposition (at 300 °C) of a mixture (5% or 10%) of 1,3,5-trimethylhexahydro-1,3,5-triazine (TRZ) in He. The decomposition was achieved by flowing the mixture either through an externally heated quartz tube or past a heated filament placed before the reaction cell. Flow rates of all gases were determined by following the pressure drop in a known volume (700 cm<sup>3</sup>) as the gases flowed through a 1 mm × 20 cm capillary.

The reaction cell was mounted on a stainless-steel flange containing a 5-mm aperture. The interior surfaces of the cell ( $V = 168 \text{ cm}^3$ ) were coated with halocarbon wax in order to inhibit wall recombination. The escape constant of the cell (5 mm orifice) was measured by following the first-order decay curve (monitored by the mass spectrometer) for various gases after a fast halt of the flow.  $k_{esc}$  was found to be  $1.86(T/M)^{1/2} \text{ s}^{-1}$ , where T is the absolute temperature and M is the molecular weight. The temperature of the reactor was held constant by circulating a thermostated liquid (water) through an outer jacket surrounding the reactor. The temperature was controlled and monitored by a heater bath-circulator with an accuracy  $\pm 1 \text{ K}$ .

The electron energy of the ionizer was kept low at 19 eV, where the fragmentation of HCl (m/e 36) to Cl<sup>+</sup> (m/e 35) was less than 1%. Therefore, the formation of HCl reaction product did not interfere with the monitoring of Cl atom concentration (mass peak m/e 35). The IMI and TRZ concentrations were determined from their prominent mass spectrum peaks,  $I_{\rm IMI}$  (m/e43) and  $I_{\rm TRZ}$  (m/e 44), and accurate calibration curves,  $I_{\rm M}$  versus [M], were taken prior to each run. This was necessary since the calibration curves were varying from day to day (especially for imine), as can be seen in Table II. The uncertainty in  $I_{\rm M}$ measurements was  $\pm 5\%$ , and the precision of  $R_1 = [Cl]_0/[Cl]$ determination was  $\pm 7\%$ . The initial [IMI]<sub>0</sub> and [TRZ]<sub>0</sub> concentrations, without the presence of Cl atoms, were estimated from flow and escape rates, and from mass spectrometric verification that  $[IMI]_0 = 3\{[TRZ]_0 - [TRZ]\}$ .

Our VLPR system was initially tested by measuring the rate constant of the well-known reaction of Cl with  $CH_4$ , and the obtained rate constants at 303 K were in excellent agreement with the accepted value.<sup>16</sup>

#### Results

The mass spectrometric analysis of the reaction products reveals the formation of HCl (mass peaks m/e 36, 38) and CH<sub>2</sub>—NCH<sub>2</sub>• (mass peaks m/e 42). Therefore, the chemical reaction under study is

$$Cl + CH_3N = CH_2 \xrightarrow{\kappa_1} HCl + CH_2 = NCH_2 \cdot (1)$$

The secondary reactions

$$Cl + CH_2 = NCH_2 \rightarrow CH_2 = NCH_2Cl^*$$
 (2)

$$2CH_2 = NCH_2 \rightarrow (CH_2 = NCH_2)_2 \qquad (3)$$

were not occurring under our experimental conditions, since no traces of  $CH_2NCH_2Cl$  (mass peaks m/e 77, 79) and  $(CH_2=NCH_2)_2$  (mass peaks 84, 56) could be detected in the reaction products. The reverse reaction could not also compete since the exothermicity of the forward reaction is ca. 5 kcal/mol, as will be proven in the discussion.

The formation of  $CH_3N$ — $CH_2$  by thermal decomposition of triazine was not complete; thus the remaining small fraction of triazine molecules will react with Cl atoms via the reaction

$$CI + \bigvee_{H_{3}C}^{CH_{3}} \bigvee_{CH_{3}}^{k_{4}} HCI + \bigvee_{H_{3}C}^{N} \bigvee_{CH_{3}}^{N} (4)$$

In our system, the mass balance of chlorine atoms concentration gives the expression

$$R_{1} = \frac{[\text{Cl}]_{0}}{[\text{Cl}]} = 1 + \frac{k_{1}[\text{IMI}] + k_{4}[\text{TRZ}]}{k_{\text{escCl}}}$$
(I)

where  $[Cl]_0$  is the initial chlorine atom concentration in the absence of *N*-methylmethylenimine and  $k_{escCl}$  is the escape constant of chlorine atoms. Expression I can be written in the form

$$(R_1 - 1)k_{\text{escCl}} = k_1[\text{IMI}] + k_4[\text{TRZ}]$$
(II)

Thus, a plot of  $(R_1 - 1)k_{escCl} - k_4[TRZ]$  versus [IMI] should yield a straight line with slope equal to  $k_1$  and zero intercept. However, the contribution of reaction 4 can be ignored for concentrations [IMI] > 100[TRZ], but otherwise it has to be estimated by measuring the rate constant  $k_4$  independently.

Hence, the reaction of Cl atoms with triazine molecules was studied over the temperature range 303-363 K. The steadystate concentration of triazine molecules is given by the expression

$$R_4 = \frac{[\text{Cl}]_0}{[\text{Cl}]} = 1 + \frac{k_4 [\text{TRZ}]}{k_{\text{escCl}}}$$
(III)

or

$$(R_4 - 1)k_{escCl} = k_4[TRZ]$$
(IV)

A plot of  $(R_4 - 1)k_{escCl}$  versus [TRZ] should yield a straight line with slope equal to  $k_4$  and zero intercept. Least-squares fits of the data yield straight lines, and a typical plot at 303 K is shown in Figure 1. The obtained rate constants  $k_4$  at 303, 333, and 363 K were found to be the same within experimental error 10% (2 $\sigma$ ), and the resultant value is  $k_4 = (5 \pm 2) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.



Figure 1. Plot of  $(R_4 - 1)k_{escCl}$  versus [TRZ] at 303 K. Symbol size reflects the propagated errors  $(2\sigma)$ .



Figure 2. Plot of  $(R_1-1)k_{escCl}-k_4$  [TRZ] versus [IMI] at 303 K. Symbol size reflects the propagated errors  $(2\sigma)$ .

TABLE I: Measured Values of Rate Constant  $k_1$  at Various Temperatures

<i>T</i> , K	$k_1 (\pm 2\sigma), 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
303	$1.90 \pm 0.15$			
333	2.18 • 0.12			
363	$2.38 \pm 0.19$			

The plots of  $(R_1 - 1)k_{escCl} - k_4[TRZ]$  versus [IMI] and the least-squares fits of the data yield straight lines with zero intercept, as shown in Figure 2. Experiments were performed at three different temperatures, 303, 333, and 363 K, and the obtained rate constants  $k_1$  are listed in Table I. The precision of the  $k_1$ rate constant measurements was ca. 10% ( $2\sigma$ ). Typical flow rates, signal intensities, and steady-state concentrations of all reactants at three different temperatures are presented in Table II. The contribution of reaction 4 to the overall reaction was very minor and always less than 5%.

An Arrhenius plot for  $k_1$  is presented in Figure 3. Linear least-squares analysis of the  $k_1$  temperature-dependence data yields the activation energy and the Arrhenius A factor for reaction 1:

$$E_{\rm a} = 826 \pm 240 \ (2\sigma) \ {\rm cal/mol}$$

$$= (7.54 \pm 1.60) \times 10^{-11} (2\sigma) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

# A = (Discussion

The thermochemical kinetics version of conventional transitionstate theory<sup>17</sup> has been applied to reaction 1, in order to provide some insight about the transition-state geometry. Thus, the

TABLE II: Typical Flow Rates, Signal Intensities, and Concentrations of Helium Carrier Gas, Chlorine, N-Methylmethylenimine (IMI), and 1,3,5-Trimethylhexahydro-1,3,5-triazine (TRZ) at Three Temperatures<sup>4</sup>

$[Cl]_0 (\times 10^{11})$	$F_{IMI} (\times 10^{14})$	$F_{TRZ}$ (× 10 <sup>13</sup> )	$F_{\rm He total}$ (× 10 <sup>17</sup> )	$[Cl] (\times 10^{11})$	ITR 7	[TRZ] (× 10 <sup>9</sup> )	Іімі	[IMI] (× 10 <sup>11</sup> )
					- IKE			· · · · · ·
			Tempera	ture 303 K				
4.74	22.2	4.72	0.91	0.41	0.0015	4.94	0.58	30.8
7.66	15.5	3.30	1.28	1.52	0.0008	2.64	0.17	9.10
7.65	9.87	2.10	1.12	2.67	0.0007	2.31	0.10	5.36
5.87	9.08	1.93	0.87	1.91	0.0004	1.32	0.13	6.71
3.59	2.49	0.53	0.95	2.35	0.0001	0.34	0.01	0.60
			Tempera	ture 333 K				
3.72	6.78	15.06	1.09	0.94	0.0008	2.52	0.29	8.33
3.53	2.07	4.60	0.99	2.52	0.0002	1.89	0.07	1.95
3.31	2.04	4.52	0.93	2.25	0.0004	1.26	0.07	1.90
3.28	1.21	2.70	1.02	2.99	0.0003	0.94	0.03	0.98
3.06	1.20	2.66	0.95	2.71	0.0002	0.63	0.04	1.14
			Tempera	ture 363 K				
2.45	14.84	32.97	2.17	0.46	0.0031	10.4	0.63	9.03
1.68	4.55	10.10	1.38	0.97	0.0012	3.01	0.16	2.24
1.55	4.45	9.88	1.28	0.86	0.0006	1.81	0.16	2.32
1.96	3.03	6.75	1.65	1.64	0.0002	0.60	0.06	0.84
1.81	2.99	6.64	1.52	1.42	0.0001	0.36	0.08	1.08

a Flows are in molecules s<sup>-1</sup>, concentrations are in molecules cm<sup>-3</sup>. Signal intensities are in arbitrary units normalized relative to the mass spectrometer and lock-in amplifier sensitivities used.



**Figure 3.** Arrhenius plot of  $\ln k_1$  versus 1/T. Symbol size reflects the propagated errors  $(2\sigma)$ .

entropy change  $\Delta S^*$  for forming one mole of transition state complex from the two reactants has to be estimated, and this is given by the expression

$$\Delta S^* = S^{\circ}(\text{complex}) - S^{\circ}(\text{IMI}) - S^{\circ}(\text{Cl})$$
$$= \Delta S^{\circ}(\text{difference}) - S^{\circ}(\text{Cl})$$

where  $\Delta S^{\circ}$  (difference) is the difference in entropies between transition state and reactant imine and includes changes in translation, vibration, rotation, internal rotation, electronic, symmetry, and optical isomerism entropies. The calculation of  $\Delta S^{\circ}$  (difference) requires knowledge of the geometries as well the vibrational frequencies of both ground and transition states. However, only the ground state data are known in the literature,<sup>12</sup> while the transition-state data have to be adjusted in order to reproduce the experimental data.

It is very reasonable to assume that the reaction proceeds via a tight transition state, where C-H and H-Cl bond distances are elongated by 0.4 Å<sup>17</sup> relative to the normal covalent lengths. Most vibrational frequencies of the transition state are almost similar to those of the ground state, and only three bending frequencies associated with the abstracted hydrogen are lowered by ca. 50% from their ground-state values. The symmetric C-H stretching becomes reaction coordinate, and the three new degrees of freedom are the asymmetric C- $\cdot$ H $\cdot$ ··Cl stretching (450 cm<sup>-1</sup>), the C $\cdot$ ··H $\cdot$ ··Cl in-plane bending (700 cm<sup>-1</sup>), and the internal rotation about the C $\cdot$ ··H bond. All vibrational frequency assignments are presented in Table III. The external and internal

TABLE III:	Estimation of	of the	$\Delta S^{*}(298)$	for	the	Reaction
$CH_3N = CH_2$	+ Clª					

degrees of freedom	$\Delta S^{\circ}(diff),$ eu
translational $\Delta S = 3/2P \ln(M^{\frac{1}{2}}/M)$	1 70
classicational $\Delta S_{tr} = S/2K \ln(M/M)$	1.79
electronic $\Delta S_{el} = R \ln(2S \pm 1)$	1.40
symmetry $\Delta S_{\sigma} = R \ln(\sigma/\sigma^*), \sigma = \sigma^* = 1$	U
vibrational	
$\nu$ (C-H), 3000 cm <sup>-1</sup> $\rightarrow$ $\nu$ <sub>asym</sub> (C···H···Cl), 2100 cm <sup>-1</sup>	r.c.
$\nu_{\rm b}({\rm H-C-N}), 1100 {\rm ~cm^{-1}} \rightarrow \nu_{\rm b}({\rm HC-N}), 550 {\rm ~cm^{-1}}$	0.6
(2) $\nu_{\rm b}(\rm H-C-H)$ , 1440 cm <sup>-1</sup> $\rightarrow$	0.5
$(2) v_{\rm b} (\mathbf{H} \cdots \hat{\mathbf{C}} - \mathbf{H}), 750  {\rm cm}^{-1}$	
(new) $v_{sym}$ (CĤCl), 450 cm <sup>-1</sup>	0.85
(new) in-plane bend (C…Ĥ…Cl), 700 cm <sup>-1</sup>	0.3
$\Delta S_{\rm tr} + \Delta S_{\rm el} + \Delta S_{\rm sym} + \Delta S_{\rm vib} = 5.44 \ \rm eu$	
external rotations	
$\Delta S_{\text{ext,rot}} = 1/2R \ln\{(I_A I_B I_C)^*/(I_A I_B I_C)\}$	4.88
internal rotations	
about the N-C single bond, $\Delta S_f = 1/2R \ln(I_r^*/I_r)$	1.93
(new) about the (Cl···H)···C bond, $S_{f}(I_{r} = 10.8 \text{ amu } \text{Å}^{2})$	6.96
$\Delta S_{\text{ext,rot}} + \Delta S_{\text{int,rot}} = 13.77 \text{ eu}$	
	19.21

 ${}^{a}\Delta S^{*}(298) = 19.2 - 39.5 = -20.3$  eu.  $A_{300}$  (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) =  $10^{-5.72}(T/298)^{2} \exp(\Delta S^{*}/R) = 10^{-10.14}$ .

rotations are treated as free rotors, and their contributions to the entropy difference depend strongly on the transition-state geometry. Furthermore, the Cl atom position in the transition state is limited by the van der Waals radii of the adjacent H atoms. This restriction is presented as missing area in the surface of Figure 4, where the rotational entropy difference is plotted as a function of Cl...H...C angle and dihedral angle  $\varphi$  between Cl...H...C and H...C-N planes. The internal rotation about the C...H bond is considered as free for Cl...H...C angles higher than 150° and becomes restricted for lower angles due to the central nitrogen atom.

However, the experimental value of  $A = 10^{-10.12}$  at 303 K corresponds to  $\Delta S^* = -20.3$  eu, and  $\Delta S^\circ$ (difference) = 19.2 eu since

$$A = 10^{-5.72} (T/298)^2 \exp(\Delta S^*/R)$$

This value of  $\Delta S^{\circ}$  (difference) corresponds to a  $\Delta S_{\text{ext,r}} + \Delta S_{\text{int,r}}$ value equal to ca. 13.8 eu, which consequently correlates to a Cl···H···C angle ca. 160°, according to Figure 4. Thus, the average transition state geometry is shown in Figure 5. The Cl atom is approaching a methylic hydrogen atom of imine along a direction that comes with a 160° angle to the C···H bond.



Figure 4. Rotational entropy difference  $(\Delta S_{\text{ext,rot}} + \Delta S_{\text{int,rot}})$  as a function of dihedral angle  $\varphi$ , and Cl···H···C angle.



Figure 5. Bent model of transition state for  $Cl + CH_3N = CH_2$ .

This bent transition state geometry is consistent with the following analysis. The incoming Cl atom is initially experiencing the permanent dipole moment interaction of imine ( $\mu = 1.53$  D), and preferentially approaches along the tail of dipole moment vector, that is almost crossing the N atom and is directed toward the nitrogen lone pair. Therefore, the Cl atom approaches the imine molecule from the opposite direction of the nitrogen lone pair and toward a methyl group hydrogen atom along a direction that forms an angle of ca. 160° with the C...H bond. Thus, the most effective encounters occur only when Cl approaches within a cone of ca. 20° surrounding a methylic hydrogen atom (Figure 5).

The obtained Arrhenius parameters can be compared with those of similar known reactions of Cl atom with molecules of the general formula  $CH_3R$ , where  $R = CH_3$ , N= $CH_2$ , OH, OCH<sub>3</sub>, CH=CH<sub>2</sub>, ONO<sub>2</sub>, N(CH<sub>3</sub>)NO<sub>2</sub>, and CN,<sup>18-24</sup> which are presented in Table IV. The derived A factor is in agreement with those of ethane and methanol and smaller by a factor of 2 with the rest. However, the activation energies vary depending on the strength of the C-H bond and the polarity of the adjacent R group. For ethane the activation energy is only 0.180 kcal/mol, since there are no polar effects from the CH3 group, although the C-H bond strength is high,  $101 \pm 0.4$  kcal/mol.<sup>25</sup> For methanol there is no activation energy, since the C-H bond strength is only 93 kcal/mol,<sup>26</sup> but there is a contribution from the polar OH group. Similarly, for dimethyl ether there is no activation energy, since the C-H bond strength is 95 kcal/mol<sup>26</sup> and there are polar effects from the methoxy group. Thus for N-methylmethylenimine, where the activation energy is 0.820 kcal/mol and the  $N=CH_2$  group is polar, the C-H bond strength must be between 94 and 101 kcal/mol. Assuming that BDE[H<sub>2</sub>C=NCH<sub>2</sub>-H]  $\approx$ 97.5  $\pm$  3.5 kcal/mol, and taking  $\Delta H_{\rm f}^{\circ}(\rm CH_3N=CH_2) = 17.3$ kcal/mol,<sup>29</sup> we obtain  $\Delta H_1^{\circ}(CH_2 = NCH_2^{\circ}) = (63 \pm 3)$  kcal/

**TABLE IV:** The Arrhenius Parameters for the Reaction of Cl Atoms with Molecules of the General Formula CH<sub>3</sub>R

R	$k_{300}, cm^3$ molecule <sup>-1</sup> s <sup>-1</sup>	A, cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	E <sub>α</sub> , kcal/ mol	BDE(C-H), kcal/mol	μ,ª D	ref
CH <sub>3</sub>	5.7 × 10-11	7.7 × 10-11	0.180	$101 \pm 0.4$ [25]	0	16
	6.1 × 10-11	8.2 × 10 <sup>-11</sup>	0.170			18
$N=CH_2$	1.9 × 10-11	7.5 × 10 <sup>-11</sup>	0.830	97 ± 3	1.53	this work
ОН	6.33 × 10-11	6.33 × 10-11	0	94 ± 2 [26]	1.7	19, 20
OCH <sub>3</sub>	$1.76 \times 10^{-10}$	1.76 × 10 <sup>-10</sup>	0	93 ± 1 [26]	1.69	19, 20
$CH = CH_2$	$3.22 \times 10^{-10}$			88.7	0.37	21
-	$2.44 \times 10^{-10}$					22
ONO <sub>2</sub>	$2.62 \times 10^{-13}$				3.12	23
N(CH <sub>3</sub> )NO <sub>2</sub>	$1.86 \times 10^{-11}$	$1.4 \times 10^{-10}$	1.20	98 ± 2 [8]	5.2	8
CN	$3.25 \times 10^{-14}$	3.5 × 10 <sup>-10</sup>	5.57	93 ± 2.5 [26]	3.92	24

<sup>*a*</sup> Dipole moments taken from ref 28. <sup>*b*</sup> Estimation by taking  $\Delta H_{f}^{\circ}$  (allyl) = 41.5 kcal/mol from ref 27.

mol, and  $\Delta H_1^{\circ} = -(5 \pm 3)$  kcal/mol. The heat of formation of  $CH_2$ =NCH<sub>2</sub>• radical is about 46 kcal/mol higher than that of imine molecule, as in the case of allyl radical relative to propene (40.1 and 4.9 kcal/mol,<sup>17</sup> respectively). Therefore, the  $\dot{C}H_2$ -NCH<sub>2</sub> product undergoes a large resonance stabilization similar to that of allyl radical, which results in rather high reaction rates. This resonance stabilization is due either to the  $\pi$  bond or to the nitrogen lone pair,<sup>30</sup> but their relative contributions cannot be estimated.

The rate constant for the analogous reaction of Cl atoms with CH<sub>3</sub>CH=CH<sub>2</sub> molecules has been reported as  $(3.22 \pm 0.13) \times$  $10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1 21</sup> and (2.44 ± 0.07) × 10<sup>-10</sup> cm<sup>3</sup> molecule  $^{-1}\,s^{-1}\,\,^{22}$  at 298 K and atmospheric pressure. Those rates have been determined relative to the reaction of Cl with ethane and are an order of magnitude higher than  $k_1$ . The reaction of Cl with  $CH_3N = CH_2$  is expected to have a lower rate constant partially due to the strong repulsive interaction between the electrophilic Cl atom and the nitrogen lone pair. Ab initio SCF calculations at 3-21G base have shown that the relative atomic charges in N-methylmethylenimine are N (-0.48), double bond carbon (-0.08), methylene hydrogens (0.18 and 0.14), C (-0.28), and methyl hydrogens (0.18, 0.18, and 0.13).<sup>31</sup> However, if the previously used transition state model is applied to the analogous reaction of Cl with propene, it should yield a similar A factor ca.  $10^{-10.12}$ , which is lower by a factor of 4 in relation to the experimental rates.<sup>21,22</sup> Therefore, either the experimental rates have been overestimated, which is probably the case since the measurements were performed by monitoring only the reactants with no knowledge of the products, or the proposed transition state model has a higher uncertainty and underestimates the Afactor.

The obtained rate constant value for the reaction of Cl atoms with triazine molecules is rather high and in agreement within a factor of 2 with similar reactions of Cl atoms with cyclohexane,  $k = (3.11 \pm 0.16) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and  $n \cdot C_7 H_{16}$ ,  $k = 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  $(3.40 \pm 0.14) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, at room temperature.<sup>22</sup>

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