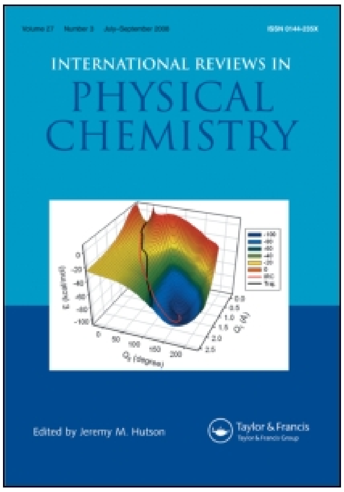

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Time-resolved infrared absorption measurements of product formation in Cl atom reactions with alkenes and alkynes

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The reactions of Cl with hydrocarbons have been the subjects of study since the early days of experimental chemical kinetics. The reactions of Cl atoms with alkanes are prototypical atom abstractions; the reactions with alkenes and alkynes display a richer chemistry because of the possibility of addition to form a chlorinated hydrocarbon radical. This review discusses recent infrared absorption investigations of the reactions of Cl with unsaturated hydrocarbons, with an emphasis on deconvolution of the addition and metathesis (i.e. abstraction or addition–elimination) pathways. These experiments are described in relation to other Cl + hydrocarbon reactions, and several examples illustrate the sensitivity of the kinetic and mechanistic behaviour of the Cl + alkene reactions to the thermochemistry of the individual systems. In the Cl + C_2H_4 reaction, where metathesis is endothermic, addition dominates except at elevated temperatures or low pressures, but the exothermic metatheses of Cl with C_3 unsaturated species effectively compete with addition even at room temperature. An example of thermochemical differences creating qualitatively different kinetic behaviours is given by the reactions of Cl with the C_3H_4 isomers allene ($CH_2{=}C{=}CH_2$) and propyne ($CH{\equiv}C{-}CH_3$). Whereas Cl + propyne displays kinetics similar to other Cl + alkene systems, the Cl + allene reaction shows unusual behaviour driven by the formation of the resonance-stabilized chloroallyl radical. Characterization of the nature of abstraction in Cl + alkene systems and examination of the role of addition–elimination in exothermic reactions are suggested as important areas for further investigation.

1. Introduction

Recent impetus for investigating chlorine chemistry has come from the discovery that Cl atoms arising from the solar photolysis of man-made chlorinated compounds, especially chlorofluorocarbons (CFCs), contribute to the depletion of stratospheric ozone [1–3]. The reaction of Cl atoms with hydrocarbons is one of the chain-terminating reactions in the ozone destruction cycle. Further, it has been recently proposed that atomic Cl is an important oxidizing species in the troposphere, especially in the marine boundary layer [4, 5]. The release of Cl atoms into the troposphere is thought to be initiated by reactions of NaCl from sea spray, for example $N_2O_5 + NaCl \rightarrow ClNO_2 + NaNO_3$ or by direct oxidation reactions at sea-salt particles [6, 7]. The importance of the atmospheric chemistry of Cl compounds has fuelled study of reactions with many atmospherically important species under conditions analogous to the stratospheric or tropospheric environments, that is room temperature and below, and near atmospheric pressure. The chemistry of Cl atoms at higher temperatures has applications in the chlorination of hydrocarbons [8] and the incineration of municipal wastes, chemical weapons and CFCs [9, 10].

Additionally, Cl atom reactions are of importance as prototypical reactions for understanding fundamental classes of chemical reactions. The photoinitiated chain reaction of Cl_2 and alkanes is a paradigm of two-centre chain chemistry [11]. Abstraction of a H atom from a hydrocarbon by a Cl atom is a standard problem for studying direct atom abstraction. The dynamical importance of these reactions is emphasized by a recent flurry of studies using state-selected and product state-resolved techniques [12–25]. Finally, the reactions of Cl atoms can be used to gain thermochemical information about hydrocarbon radicals via the $Cl + RH \leftrightarrow HCl + R$ reaction, using the well known thermochemistry of Cl, HCl and many stable hydrocarbons [26].

The reactions of Cl with hydrocarbons, discussed in this review, were first studied in connection with chain chlorination reactions [27, 28]. The Cl_2–alkane chain reaction is literally a textbook example of chain chemistry [29]; the reactions with unsaturated species were also extensively studied because of their importance in photochlorination and in Cl-sensitized photo-oxidation of alkenes [30–35]. Many early investigations of the chlorination chemistry of hydrocarbons used product analysis of chain chlorination to deduce information about individual reaction steps [36–38], and many studies of elementary reactions of Cl atoms with hydrocarbons are still carried out using competitive chlorination of hydrocarbon species [39–46]. In the intervening years, more direct methods such as discharge-flow and flash photolysis techniques have provided increasingly detailed information on Cl+ hydrocarbon reaction kinetics [47–52]. Most recently, the technique of laser photolysis–continuous-wave (CW) long-path absorption has been applied to the study of several Cl+ hydrocarbon reactions [53–57]. This review describes those experiments in the larger context of Cl+ unsaturated hydrocarbon kinetics.

Whereas the reactions of Cl atoms with alkanes have been extensively studied, at every level of detail from thermal rate studies to state-to-state reaction dynamics, the reactions of Cl with alkenes and alkynes have drawn markedly less experimental attention. Cl atom addition to unsaturated species is the initiation step in important chain processes such as the chlorine-sensitized photo-oxidation of alkenes and haloalkenes, chlorine-induced pyrolysis and photochlorination which have a long history of study [28]. The central reaction underlying the chemistry of these systems is the ability of alkenes to undergo addition reactions with electrophiles.

Electrophilic addition of halogens or HX to double bonds is a characteristic reaction of alkenes [29]. The mechanism proceeds via a formally ionic intermediate; the X_2 or HX attacks the double bond to produce a carbocation and a halide anion, which subsequently react. The initial step occurs in a manner to produce the more stable carbocation, following what is called Markovnikov's rule; in HX addition the proton will add to the less substituted C in the double bond. A free-radical mechanism for addition is the source of 'anti-Markovnikov' addition that occurs during certain reactions of HBr with terminal alkenes. The free-radical mechanism is in a two-step chain mechanism initiated by Br atom addition to the alkene:

$$Br + RCH = CH_2 \rightarrow R\dot{C}HCH_2Br, \qquad (1a)$$

$$RCHCH_2Br + HBr \rightarrow RCH_2CH_2Br + Br. \qquad (1b)$$

The free-radical addition is catalysed by the presence of peroxides, whose reactions with HBr are a source of free Br atoms. The Br atoms add to the alkene to form the more stable radical. The cause of the 'anti-Markovnikov' HBr addition is in fact obedience to the same fundamental rule, namely that the initial addition to the alkene forms the most stable radical species.

A similar mechanism underlies the chlorine-sensitized photo-oxidation of alkenes, where the radical formed by addition to Cl to the alkene proceeds to react with molecular O_2 to form peroxy radicals, which are consumed by self-reaction or decomposition to OH, HO_2 or other chain carriers. The products of the photooxidation depend on the products of the initiating addition reaction. The early work on the addition of atoms to hydrocarbons has been summarized in several reviews [36, 37]. Understanding site specificity in the addition of Cl atoms is complicated somewhat by the existence of a relatively facile 1,2 Cl atom shift which tends to form the most stable radical regardless of the original site of Cl atom attack. Experiments from Rowland's group [58–62] in the 1970s and 1980s show that the product branching fractions from Cl addition to substituted ethenes and propene depend on the concentration of the radical scavenger. These results alter some conclusions of earlier work which measured site preferences in Cl atom addition using end product analysis.

In general, the course of reaction between a Cl atom and an alkene will include simultaneous contributions from addition, direct abstraction and addition–elimination channels, the relative importances of which will change with temperature and pressure. This review concentrates on recent experimental investigations of the competition between metathesis and addition channels in the kinetics of Cl atom reactions with alkenes. (Metathesis refers to any bimolecular reaction where an atom or group of atoms is transferred from one reactant to the other, and hence encompasses both direct abstraction and addition followed by HCl elimination.) First, the experimental method of laser photolysis–CW infrared long-path absorption is described and the particular suitability of HCl product detection for the Cl+ alkene reactions is analysed. An overview of abstraction reactions in Cl+ alkanes and of addition reactions in related systems is given in order to provide a background for the discussion of Cl+ alkene reactions. Several examples are given to illustrate how the competition between addition and metathesis depends on the thermochemistry of the individual reaction. The reaction of Cl with acetylene provides a straightforward separation of the two reactive channels, since the metathesis is considerably endothermic and becomes significant only at high temperatures, where the addition reaction is negligible. In the case of the reaction of Cl with ethene, where the metathesis is less endothermic, the competition between metathesis and addition is more difficult to separate, with the contribution from addition decreasing smoothly as the temperature is increased or the pressure decreased. Where the metathesis is exothermic, as with $Cl + C_3H_6$ and $Cl + C_3H_4$, both abstraction and addition–elimination mechanisms have been proposed, further complicating the reaction mechanism. Kinetic measurements of rate coefficients, branching fractions and vibrational energy disposal are presented, and the implications of these observations for the mechanism of the reactions are discussed. Finally, unanswered questions and opportunities for further study are examined.

2. Time-resolved infrared measurements of HCl product formation

For Cl reacting with unsaturated hydrocarbons both metathesis and addition pathways will in general be operative, and some means is required to disentangle the two channels. Several strategies are possible to distinguish the individual contributions. The pressure dependence of the total reaction rate coefficient can be modelled to try to separate addition from metathesis. The Finlayson-Pitts group [50, 63, 64] has used the differing kinetic isotope effects for addition and abstraction channels to estimate their relative contributions in reactions of Cl with several small alkenes. Another method is to detect directly the products of the reaction; end-product analysis by spectroscopic or chromatographic means has been used by several groups [35, 47, 65–67]. The technique of laser photolysis–CW infrared absorption, probing the time behaviour of HCl product formation via infrared absorption of the vibrational fundamental [57], is a powerful companion to these other methods.

Simply, the laser photolysis–CW infrared absorption method consists of pulsed photolytic initiation of the reaction and a continuous infrared probe, tuned in this case to a transition in the HCl product, which follows the course of the reaction. This technique builds on infrared kinetic spectroscopy [68–70] which has been used for years to gain spectroscopic and kinetic data on transient species. The continuous probe allows the entire time profile to be obtained on every laser shot, which facilitates signal averaging to improve the signal-to-noise ratio. By using multipass optics and frequency modulation techniques, the signal-to-noise ratio in such experiments can be further enhanced. In the reactions of Cl with hydrocarbons, the HCl product is detected; so the branching into HCl-producing channels can be determined by comparison with a reaction known to produce HCl with unity yield (e.g. Cl+ ethane or Cl+ propane). Since the infrared transition probes a population difference between vibrational levels, the technique is also inherently sensitive to the HCl product vibrational distribution. The vibrational energy disposal has been shown to reflect the mechanism of the reaction; in particular, a direct abstraction process typically produces more HCl vibrational excitation than a similar elimination reaction [71–73]. Probing the vibrational energy can therefore in principle help to decide between possible abstraction and addition–elimination mechanisms.

Multiple-pass detection is the simplest and most direct method for increasing the sensitivity of absorption measurements. Many designs for multipass cells have been used in kinetic experiments, with the White [74] cell possibly the most prevalent. Recently a design based on the Herriott cell has been developed for use in temperature-dependent kinetics measurements [75]. The Herriott cells uses off-axis paths in a spherical resonator; so the probe beam traces out a circle of spots on each mirror and a smaller circle in the centre of the cell [76]. By employing an on-axis photolysis pulse, the overlap between pump and probe beams is confined to the centre of the cell, where the temperature is well controlled. The optical arrangement is depicted in figure 1. Using linearly polarized lasers allows the path length to be doubled by reflection through a $\lambda/4$ plate or allows multiple probe beams to be copropagated.

Additional improvements in signal-to-noise ratio can be gained by the application of frequency modulation (FM) techniques [53]. The frequency modulation technique has a long history [77–79] but its application to kinetics experiments is surprisingly recent [80]. The enhanced signal-to-noise ratio in the FM is accomplished by shifting the detection frequency out of the region where most experimental noise occurs. In general this is accomplished by applying a periodic phase shift to the beam, typically at high frequencies. This phase shift places frequency side bands on the probe beam, spaced from the carrier by the modulation frequency. Therefore, phase modulation at 500 MHz of a laser with centre (carrier) frequency ω will produce side bands at $\omega \pm 500$ MHz. Differential absorption of one of these side bands relative to the carrier will produce a periodic change in the total intensity at the modulation frequency (i.e. 500 MHz), whose magnitude is proportional to the absorption. Because of the limitations on the frequency response of infrared detectors, a modification to this technique called two-tone frequency modulation is used in the infrared [81–83]. The phase of the probe beam is modulated at two closely spaced frequencies (e.g. 500 ± 1 MHz) in a $LiNbO_3$ crystal housed in an external resonant cavity. Differential attenuation of either the carrier of the side bands now generates a signal at both carrier

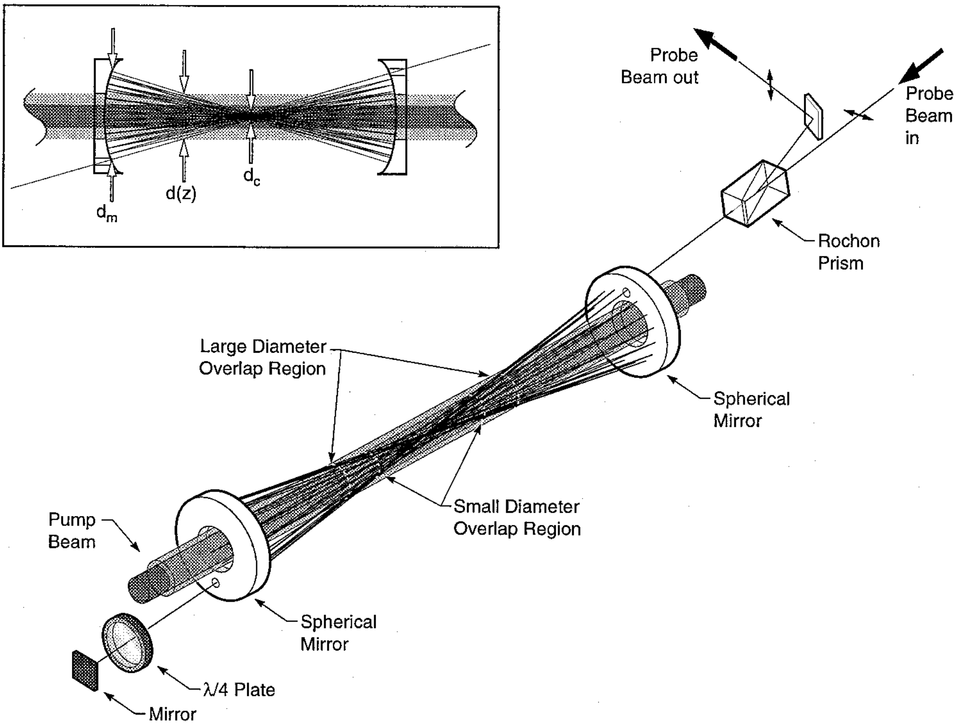

Figure 1. Optical arrangement of the modified Herriott cell used for temperature-dependent kinetics measurements. The inset shows a two-dimensional projection of the multiple-pass cavity. The probe laser rays define a circle whose diameter varies from a minimum in the centre to a maximum on the cavity end mirrors. Changing the diameter of the pump laser changes the linear extent of the overlap with the probe laser. (Reprinted with permission from [75].)

frequencies, and therefore also a beat note at the difference frequency. The detector photocurrent is then heterodyne detected at twice the intermodulation frequency (i.e. 2×1 MHz $= 2$ MHz) to provide the signal.

The absorption or FM signal as a function of time following pulsed photolytic initiation of the reaction (e.g. by photolysis of CF_2Cl_2 at 193 nm or photolysis of Cl_2 at 355 nm) is proportional to the time-resolved concentration of HCl in the reactor. The form of the time behaviour of the HCl concentration depends on the kinetics of the reaction producing it. In general, three qualitatively different types of time trace are observed in the reactions of Cl atoms with hydrocarbons. These typical traces are depicted in figure 2, and the detailed mathematical description is given in appendix A. The trace in figure 2(*a*) displays the behaviour for a simple reaction of Cl atom with a single channel producing HCl. The exponential rise of the HCl signal matches the decay of the Cl atom concentration and the final HCl concentration is the same as the initial Cl atom concentration. Such a trace is found, for example, in the reactions of Cl with alkanes, where abstraction is the only pathway available. In figure 2(*b*) an absorption trace is depicted which corresponds to a reaction with multiple channels, only one of which produces HCl. Now, since not all the Cl atoms are converted to HCl, the final HCl concentration is less than the initial Cl concentration. However, the rise time of the HCl signal once again matches the decay time of the Cl atom concentration; only the amplitude is affected. Figure 2(*c*) depicts the case where Cl atoms are

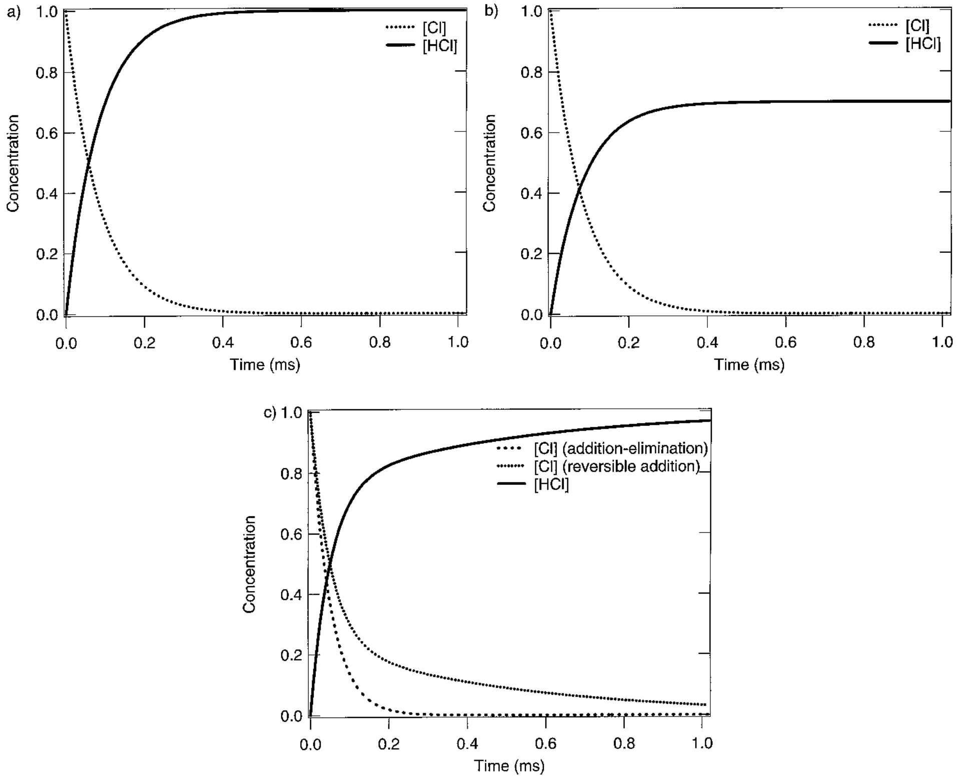

Figure 2. Schematic views of time-resolved product formation in Cl+ hydrocarbon reactions. (*a*) Simple one-step metathesis reaction $Cl + RH \rightarrow HCl + R$. Note that $[HCl]_\infty = [Cl]_0$. (*b*) Competition of simple metathesis with irreversible addition. While the rise time of HCl production matches the decay of the Cl concentration, $[HCl]_\infty \leqslant [Cl]_0$. (*c*) Biexponential traces produced by addition–elimination or by competition of metathesis with a reversible addition reaction. In this case $[HCl]_\infty \leqslant [Cl]_0$ and the time behaviour of HCl production does not necessarily match the removal of Cl atoms. See text for details.

regenerated by a reversible addition reaction, or where elimination of HCl from an adduct occurs. In both cases, Cl atoms are temporarily sequestered in an adduct, which later dissociates, generating a biexponential rise in the HCl concentration with time. The figure shows complete conversion of Cl to HCl, but the final concentration of HCl will be less than the initial Cl concentration if the adduct is permanently removed by stabilization or reaction before dissociation can occur.

A key difference between elimination and reversible addition is the relationship of the HCl rise to the Cl decay. In the case of a reversible addition, adduct dissociation regenerates Cl atoms; so the Cl decay would display biexponential behaviour similar to the HCl rise. In the case of delayed elimination, however, HCl is produced by a sequential mechanism, addition followed by elimination, and the Cl concentration decays with a single exponential despite the biexponential rise in the HCl concentration. Since the Cl decay is unobserved in the infrared measurements, reversible addition and addition–elimination mechanisms are largely indistinguishable.

Infrared absorption probes a difference in population between the vibrational states that are linked by the optical transition. If the vibrations are in thermal equilibrium, this absorption is also proportional to the total HCl population. For

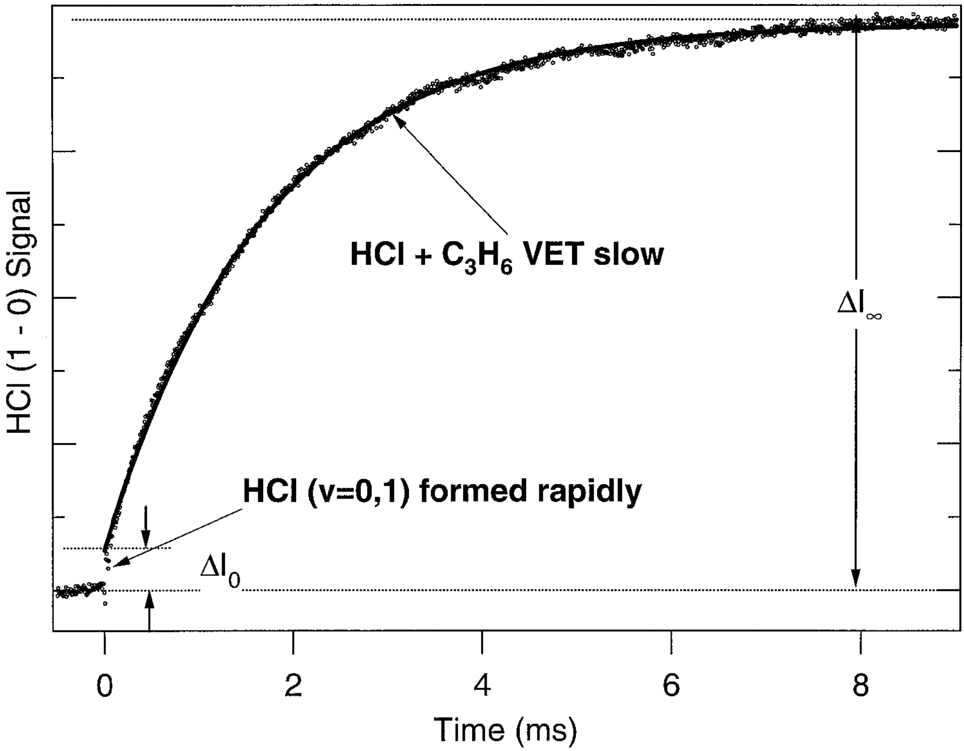

Figure 3. A schematic view of the determination of HCl ($v = 1$) branching fractions using infrared absorption on a ($1 \leftarrow 0$) transition, taken for the Cl+ propene reaction at 600 K and 10 Torr (Ar buffer). The initial rise in the HCl absorption reflects the initial population of HCl ($v = 1$) and HCl ($v = 0$) formed in the reaction, and the slower rise is due to collisional vibrational relaxation of the $v = 1$ population. The final absorption is therefore proportional to the total HCl produced in the reaction.

reactions which produce vibrationally excited HCl, this correspondence does not occur unless vibrational relaxation is significantly faster than the reaction timescale. In the case where the vibrational excitation is limited to $v = 1$, HCl can be treated essentially as a two-level system, since rotational redistribution is rapid. With an Ar or He buffer gas, vibrational relaxation is often slow relative to the reaction producing HCl. By comparison of measurements on the ($1 \leftarrow 0$) transition under different conditions of vibrational relaxation (e.g. with CO_2 versus Ar as a buffer), the vibrational branching between HCl ($v = 1$) and HCl ($v = 0$) can be directly determined, as depicted in figure 3. This method is similar in spirit to the measurements of the absorption against the gain of spin–orbit branching fractions performed by Leone and co-workers [84]. Measurement of branching fractions where more than two vibrational levels are populated generally requires measurement and calibration of multiple vibrational transitions.

Time-resolved infrared probing of HCl product formation offers a range of information concerning the course of the Cl+ hydrocarbon reaction. The form of the time behaviour is a qualitative indicator of the reaction mechanism. By measuring the amplitude of the signal relative to that from a reference reaction which completely converts Cl to HCl (e.g. Cl+ alkane reactions), the branching fraction into HCl-producing channels can be determined. Vibrational distributions can also be ascertained under favourable conditions. The infrared absorption method is well suited to investigate the competition between addition and metathesis channels in Cl+ alkene and alkyne reactions. As an introduction to these reactions it is instructive to first consider several similar reactions where one channel dominates. In particular, the nature of the abstraction in Cl+ alkane reactions has been examined in some detail, and Cl addition has been measured for several reactions under conditions where metathesis is negligible.

3. Abstraction reactions of Cl with hydrocarbons

The abstraction of a H atom to form HCl is the prototypical reaction of Cl atoms with hydrocarbons. The chain reaction of Cl_2 and a saturated hydrocarbon RH is well known:

$$Cl_2 \xrightarrow{h\nu} 2Cl \text{ (initiation)}, \tag{2}$$

$$Cl + RH \xrightarrow{k_a} HCl + R, \tag{3a}$$

$$R + Cl_2 \xrightarrow{k_b} RCl + Cl, \tag{3b}$$

$$R + R, Cl + R \rightarrow \text{products (termination)}. \tag{4}$$

The study of chain chlorination reactions has a long history [11, 28] but the detailed dynamics of the elementary reactions continue to provide fertile areas for study.

The metathesis reaction (3*a*) is slightly exothermic for abstraction of primary ($\Delta H \approx -2$ kcal mol^{-1}), secondary ($\Delta H \approx -4$ kcal mol^{-1}) or tertiary ($\Delta H \approx -5$ kcal mol^{-1}) H [26]. The Cl+ methane reaction is by far the most thoroughly studied reaction of Cl atom with a hydrocarbon. The activation energy for the reaction is approximately 3 kcal mol^{-1} near room temperature, slightly larger than the 1.75 kcal mol^{-1} endothermicity. The exothermic abstractions in alkanes typically display zero or small positive activation energies. The activation energy of the Cl+ ethane reaction ($\Delta H = -2.0$ kcal mol^{-1}) is 270 cal mol^{-1}, but a zero activation energy is found in the reaction of Cl with propane ($\Delta H = -4.6$ kcal mol^{-1} for abstraction of a secondary H atom) [57]. The temperature dependence of several Cl+ hydrocarbon metathesis rate coefficients is given in table 1. Prominent curvature exists in a simple Arrhenius plot of both the Cl+ methane and Cl+ ethane abstraction reactions. This curvature can be described as a temperature dependence of the *A* factor, which arises from changes in the heat capacity between the reactants and the transition state. Simple thermochemical transition-state analysis qualitatively reproduces the curvature in the Cl+ CH_4 Arrhenius plot, underpredicting the rate coefficient by 40% at $T = 500$ K [88]. Possible vibrational contributions to the observed Arrhenius curvature have also been proposed on the basis of detailed dynamical studies (see below).

Competitive studies of abstraction reactions from different hydrocarbon sites have been performed and structure–activity relationships have been put foward to parameterize Cl atom reactivity with many species [51, 89]. The degree of exothermicity affects the relative rates of H abstraction in Cl+ hydrocarbon reactions. For example, the reaction of Cl with propane has been shown to produce only about 50% *n*-propyl radicals at room temperature, despite the predominance of primary H abstraction sites. The more exothermic secondary and tertiary sites also dominate the reaction with butanes [51]. Chlorination tends to decrease the overall reactivity and increase the branching to the α-C. A similar effect has been observed for OH substitution, with the

Table 1. Temperature dependence of metathesis rate coefficients for reactions of Cl with hydrocarbons.

Reaction (temperature)	A (cm^3 molecule^{-1} s^{-1})	E_a (cal mol^{-1})	Reference
Cl+ CH_4 (292–800 K)	$(3.7^{+8.2}_{-2.5}) \times 10^{-13}\ (T/298)^{(2.6 \pm 0.7)}$	770 ± 640	[57]
Cl+ CH_4 (200–500 K)	$1.37 \times 10^{-12}\ (T/298)^{1.96}$	1490	[85]
Cl+ CH_4 (200–300 K)	9.6×10^{-12}	2680 ± 510	[86]
	1.1×10^{-11}	2780 ± 306	[87]
Cl+ C_2H_6 (292–600 K)	$(8.6 \pm 0.5) \times 10^{-11}$	170 ± 50	[57]
Cl+ C_2H_6 (292–800 K)	$(3.4 \pm 1.4) \times 10^{-11}\ (T/298)^{(0.7 \pm 0.3)}$	-300 ± 220	[57]
Cl+ C_2H_6 (200–300 K)	7.7×10^{-11}	180 ± 180	[87]
Cl+ C_2H_6 (200–600 K)	8.2×10^{-11}	200 ± 200	[86]
Cl+ C_2H_4 (500–800 K)	$(6.2 \pm 1.4) \times 10^{-11}$	6800 ± 900	[55]
Cl+ C_2H_4 (300–383 K)	$(1.2^{+8}_{-0.9}) \times 10^{-11}$	5430 ± 1400	[66]
Cl+ C_3H_8 (292–700 K)	$(1.38 \pm 0.03) \times 10^{-10}$	0 ± 100	[57]
Cl+ C_3H_8 (220–600 K)	1.2×10^{-10}	80 ± 400	[86]
Cl+ C_3H_8 (200–300 K)	1.2×10^{-10}	80 ± 500	[87]
Cl+ C_3H_6 (290–800 K)	$(4.9 \pm 0.5) \times 10^{-11}$	170 ± 100	[54]
Cl+ propyne (400–800 K)	$(3.7 \pm 1.0) \times 10^{-11}$	1360 ± 300	[53]
Cl+ propyne (292–800 K)	$(1.25 \pm 0.21) \times 10^{-12}\ (T/298)^2$	995 ± 185	
Cl+ allene (292–800 K)	$(3.7 \pm 1.7) \times 10^{-10}$	3300 ± 600	[53]
	$(1.25 \pm 0.68) \times 10^{-11}\ (T/298)^2$	1050 ± 640	
Cl+ isoprene	$8.2 \pm 5.1 \times 10^{-11}$	220 ± 350	[47]

$-CH_2-$ group in ethanol contributing about 90% of the reactivity at room temperature [90].

Deuterium kinetic isotope effects have been measured for several H abstraction reactions of Cl atoms. The reaction of Cl with methane shows a substantial tunnelling contribution and a large normal kinetic isotope effect [91, 92], with $k_{CH_4}/k_{CD_4} = 16.4$ at 298 K [43]. Various measurements of the kinetic isotope effect for the reaction with ethane have established the kinetic isotope effect $k_{C_2H_6}/k_{C_2D_6}$ to be 2.8–3.0 [39, 93, 94]. Cl or F substitution on the neighbouring C changes the kinetic isotope effect non-monotonically, but a significant normal isotope effect is maintained. Tschuikow-Roux *et al.* [39] investigated the rate coefficient ratios for H- and D-atom abstraction from the methyl groups in $CH_3CH_{3-n}Cl_n$. They measured isotope effects of 2.79, 6.20, 4.13 and 1.46 for $n = 0, 1, 2$ and 3. The abstraction reactions, even those without an energy barrier to reaction, tend to display a marked normal kinetic isotope effect. This normal kinetic isotope effect is characteristic of the Cl+ hydrocarbon abstraction and is in contrast with Cl+ alkene addition reactions, which tend to show an inverse isotope effect [64].

In the last few years, the techniques of chemical dynamics have also been brought to bear on the study of Cl+ hydrocarbon reactions. Laser photolytic production of Cl atoms and state-of-the-art detection techniques have been applied to examine these reactions at the single quantum state level. Fundamental information on the energy disposal in the abstraction reaction and on the influence of initial reagent energy has great value in interpreting the results of thermal kinetic experiments. The energy disposal in Cl+ alkane reactions has been shown to favour low rotational levels, which is generally taken as an indication that the transition state for abstraction is nearly linear. However, Kandel *et al.* [24] have pointed out that the equivalence between low rotational excitation and linear transition state is strictly valid only for impulsive energy release and have proposed kinematic constraints as an explanation for cold rotational distributions. Under the conditions of most dynamical experiments, the bulk of the excess energy in the reaction is translational energy. Transferring this translational energy into HCl vibration is unlikely on kinematic grounds; indeed, all the dynamical experiments on Cl+ ground-state alkane reactions have shown minimal vibrational excitation.

A clear enhancement in the reaction rate by vibrational excitation of the hydrocarbon has been shown by Zare and co-workers [19] for the Cl+ methane reaction. At a collision energy of 0.16 eV, excitation of the ν_3 mode in methane was found to enhance reactivity by a factor of 30. On the other hand, stretch excitation in ethane was found to have a much smaller effect, increasing the reactivity by 5–10% at 0.28 eV [22]. Kandel and Zare [23] recently measured the speed distributions of state-selected methyl radical products from the Cl+ methane reaction at collision energies from 0.13 to 0.29 eV. They observed products which contained more energy than could be explained by the reaction of vibrationless methane with Cl [$^2P_{3/2}$] and concluded that a large increase in reactivity from low-lying bending and torsional vibrations was responsible for the anomalously high-energy products. Thermal excitation of these modes at higher temperatures was suggested by these workers as a possible source of the curvature in the Arrhenius plot of Cl+ methane.

The effect of spin–orbit excitation on the reaction with hydrocarbons is less clear. Although the spin–orbit-excited Cl atom has 2.5 kcal mol^{-1} excess energy, the adiabatic correlation is to repulsive electronic states which do not correspond to product channels. The facility of curve crossing determines the reactivity of the excited state, and in most similar reactions the excited spin–orbit state is thought to exhibit a much lower reactivity. A certain amount of discrepant evidence exists concerning the reactivity of Cl [$^2P_{1/2}$] with hydrocarbons. Ravishankara and Wine [95] measured an unusual dependence of the reaction of Cl+ CH_4 on buffer gas composition in a flash photolysis measurement, observing a higher rate coefficient at low temperatures for He than for Ar. They suggested that this may be due to insufficient quenching of Cl [$^2P_{1/2}$] by He, which must then be more reactive than the ground state. However, this interpretation relied on Cl [$^2P_{1/2}$] quenching rates from Fletcher and Husain [96], which have been shown by more recent measurements to be in error [97*a*, *b*]. Direct measurements on the thermal reaction of Cl [$^2P_{1/2}$] with methane have shown that the removal of spin–orbit-excited Cl by CH_4 proceeds predominantly by quenching to the ground state Cl [$^2P_{3/2}$], with a rate coefficient of about $(2–3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. A precise estimate of the rate coefficient for reactive removal of Cl [$^2P_{1/2}$] with methane is not available although Matsumi *et al.* [97*b*] gave an upper limit of 10^{-11} cm^3 molecule^{-1} s^{-1}.

Additional detail about the transition state in Cl abstractions is provided by a growing number of state-resolved dynamical measurements for Cl+ alkane reactions. Zare and co-workers [17–24] have measured product angular, energy and alignment distributions in the reactions of Cl with CH_4, CD_4, C_2H_6 and C_2D_6. Varley and Dagdigian [14–16] have carried out studies of HCl product distributions in the reactions of Cl with methane, ethane, propane and isobutane. The scattering angular distributions are broader for the higher alkanes than for methane, which is consistent with a looser transition state. Suits and co-workers [25, 98] have measured translational and angular distributions for Cl+ propane and Cl+ *n*-pentane using a crossed-beam apparatus. They have observed distinctly different behaviours for forward- and backward-scattered alkyl radical products in the two reactions. In particular, the backward-scattered products in the reaction with *n*-pentane showed evidence of C skeletal excitation in the reaction, in marked contrast with previous investigations of reactions with smaller alkanes, where the alkyl radical was treated as a spectator to the reaction.

Given the extensive kinetic and dynamic data on Cl+ alkane reactions, especially for Cl+ methane, theoretical analysis has been able to uncover much of the mechanism for H abstraction. Analysis of the magnitude of the pre-exponential factor carried out using simple transition-state theory suggests a tight and linear transition state for Cl+ CH_4, which becomes less constrained for larger hydrocarbons and for the more exothermic secondary and tertiary abstractions. The dynamics measurements are broadly consistent with this simple interpretation, and high-level calculations, most notably on the Cl+ CH_4 reaction, bear this out [88, 99–102]. However, a number of unanswered questions regarding details of the transition state remain. Progress continues rapidly on the dynamics of these reactions and investigations to uncover the details of the transition state are sure to produce exciting data in the future.

The abstraction reactions for Cl+ alkanes have been extensively studied and the fundamentals of these reactions are understood at a considerable level of detail. Abstraction of allylic and vinylic H atoms may be different from abstraction from an alkane, since changes in orbital hybridization and the presence of the competing addition channel may influence the dynamics and mechanism of the metathesis. The effect of neighbouring double and triple bonds on the site specificity of abstractions from alkyl side chains also remains to be investigated. Nevertheless, given the relative paucity of experimental and theoretical information on the metathesis reactions of Cl with unsaturated hydrocarbons, the Cl+ alkane abstractions must form the basis for understanding the reactions of Cl with alkenes.

4. Addition reactions of Cl with unsaturated hydrocarbons

Early investigations of the 'free-radical' mechanism of HX addition and the photochlorination of alkenes necessitated the study of the addition reactions of Cl to alkenes and haloalkenes. Early work on addition reactions of a number of atoms and polyatomic radicals, including Cl, to unsaturated hydrocarbons has been summarized [36]. Just as the radical chain chlorination reaction opened the door to detailed studies of the elementary reactions in the chain mechanism, photochlorination and chlorine-sensitized photo-oxidation form the historic basis for investigations of the reactions of Cl with unsaturated hydrocarbons.

The reactions of Cl atoms with alkenes proceed largely by addition at low temperatures and moderate pressures. The addition is exothermic, typically by about 20 kcal mol^{-1}, as formation of the C–Cl bond provides more energy than the difference between the C=C double bond of the alkene and the single C–C bond of the chloroalkyl radical [36]. Addition reactions characteristically display a negative temperature dependence and a dependence on the total pressure (fall-off). The pressure dependence of the addition reaction is often parameterized using the Troe [103, 104] formulation [105]:

$$k = \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_\infty} F_{\mathrm{c}}^{\{1+[\log(k_0[\mathrm{M}]/k_\infty)]^2\}^{-1}} \tag{5}$$

where k_0 is the low-pressure limiting third-order rate coefficient, k_∞ is the high-pressure limiting second-order rate coefficient and F_{c}, referred to as the broadening parameter, is related to the efficiency of stabilizing collisions. The low-pressure limiting rate coefficient is largely governed by collisional relaxation of the excited adduct, and the high-pressure limiting rate coefficient reflects the total probability of adduct formation. There is accordingly a difference in low-pressure reaction rate coefficients (but not in the high-pressure limit) for third-body colliders of different energy transfer efficiencies.

The shape of the overall pressure dependence of the reaction is controlled by the adduct density of states, which tends to increase with increasing well depth and adduct size [105, 106]. An increase in the adduct state density increases the lifetime relative to redissociation to reactants as well as enhancing vibrational energy relaxation because of the larger bath of receptor states. This change in lifetime and collisional relaxation affect the shape of the fall-off and the low-pressure rate coefficients, which are dominated by energy-transfer constraints. For two adduct molecules with similar numbers and frequencies of vibrational modes, the molecule with the larger well depth will have the higher density of states at the energy of the initially formed complex. This higher state density will enhance collisional relaxation, hence increasing the low-pressure limiting rate coefficient k_0 and move the fall-off towards a lower pressure. Likewise, for similar well depths, addition to larger molecules tends to show a larger low-pressure limiting rate coefficient and to reach the high-pressure limit at a lower pressure than for smaller molecules. Therefore, in comparing two addition reactions, the reaction which forms the adduct with the higher density of states will have the larger low-pressure limiting rate k_0 but, because its fall-off is at lower total densities, will usually have the *shallower* pressure dependence for a given pressure range.

Addition of Cl to an unsaturated hydrocarbon is the reverse of the thermal dissociation of the corresponding chlorinated radical. Therefore, the addition reactions can be used to gain thermochemical information about the adduct radical. The heat of formation of the radical adduct can be ascertained from measurements of the addition and the dissociation reaction rate coefficients, using the relationship of the equilibrium constant to the change in free energy and the (usually) well known thermochemistry of the hydrocarbon reactant. Often such measurements are performed by investigating the addition reaction under conditions where the adduct dissociation and subsequent establishment of quasi-equilibrium takes place on a similar time scale to the initial addition reaction. Extraction of the thermochemistry of the adduct in principle requires only the determination of the forward (addition) and reverse (dissociation) rate coefficients at a given temperature. However, the typical measurements of addition and redissociation in the fall-off regime may not directly measure a true thermal equilibrium. The possibility of steady-state measurements that do not reflect a thermal population has been treated by several workers and has been seen experimentally in an apparent pressure dependence of equilibrium constants for addition reactions, notably for $OH + C_2H_4$ [107]. Whereas this time-resolved approach to measurements of forward-reverse equilibration in addition reactions has been extensively applied, for example, in reactions of alkyl radicals with O_2, and in reactions of OH with alkenes, it has found more limited use in Cl+ alkene additions.

One example of this approach is found in the investigation of the reversible addition of Cl to C_2Cl_4, where metathesis is negligible, by Wine and co-workers [108] using the flash-photolysis resonance fluorescence technique. The decay of Cl atoms in a large excess of C_2Cl_4 was observed to follow simple pseudo-first-order kinetics at temperatures of 300 K or lower. At temperatures above 330 K, regeneration of Cl atoms by dissociation of the C_2Cl_5 adduct was observed. The thermochemistry of the

Table 2. Rate coefficients at room temperature for addition reactions of Cl atoms with alkenes and alkynes.

Reaction	k_0 (cm^6 $molecule^{-2}$ s^{-1})	k_∞ (cm^3 $molecule^{-1}$ s^{-1})	Reference
Cl+ C_2H_2	$(6.1 \pm 0.2) \times 10^{-30}$	$(2.0 \pm 0.1) \times 10^{-10}$	[112]
Cl+ C_2H_4	$(1.42 \pm 0.05) \times 10^{-29}$	$(3.2 \pm 0.15) \times 10^{-10}$	[112]
Cl+ C_3H_6	$(4.0 \pm 0.2) \times 10^{-28}$	$(2.7 \pm 0.1) \times 10^{-10}$	[65]
Cl+ CH_3CCH	$> 2.4 \times 10^{-29}$ (4.4 Torr rate coefficient divided by total density)	$\geqslant 2.68 \times 10^{-10}$ (760 Torr rate coefficient)	[42, 53]
Cl+ CH_2CCH_2	$> 1.3 \times 10^{-27}$ (5 Torr rate coefficient divided by total density)	$\geqslant 4.38 \times 10^{-10}$ (760 Torr rate coefficient)	[42, 53]
Cl+ isoprene		$(2.8 \pm 0.7) \times 10^{-10}$ $(3.9 \pm 0.5) \times 10^{-10}$ (760 Torr rate coefficient)	[47] [63]

pentachloroethyl radical could then be estimated by study of the reversible addition. In this way they obtained an experimental enthalpy for the addition reaction of Cl to C_2Cl_4 of $\Delta H^\circ_{298\ K} = -18.6 \pm 0.5$ kcal mol^{-1}, similar to other Cl+ alkene additions.

Studies of the pressure and temperature dependences have been carried out for Cl additions to ethene, acetylene, isoprene and several chlorinated and fluorinated ethenes. In many of these reactions, metathesis is a significant competing channel, as will be discussed in the next section. However, it is instructive to consider a number of cases where the reaction proceeds essentially exclusively via addition to gain an idea of the pressure and temperature dependences typically associated with Cl atom addition.

The metathesis reaction $Cl + C_2H_2 \rightarrow HCl + C_2H$ is endothermic by 29.7 kcal mol^{-1} [26, 109]; so, except under high-temperature conditions, the reaction proceeds exclusively by addition. Both the temperature dependence and the pressure dependence of the addition reaction have been studied. Brunning and Stief [110] performed flash photolysis resonance fluorescence measurements between 210 and 361 K for a range of pressures and fitted the results to the Troe fall-off expression to deduce the temperature-dependent low- and high-pressure limiting rate coefficients. Kaiser [111] extended the pressure range of the measurements made by Brunning and Stief using a relative rate technique to measure rate coefficients between 230 and 370 K at pressures up to 1300 Torr. The room-temperature pressure dependence was measured up to 5800 Torr by Wallington *et al.* [44]. Kaiser and Wallington [66] combined the results of these studies with additional measurements between 0.3 and 700 Torr and fitted them to a Troe formulation to obtain low- and high-pressure limiting rate coefficients at 298 K of $k_0 = (6.1 \pm 0.2) \times 10^{-30}$ cm^6 $molecule^{-2}$ s^{-1} and $k_\infty = (2.0 \pm 0.1) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Rate coefficients for a number of Cl+ unsaturated hydrocarbon additions are collected in table 2. The theoretical modelling of the temperature- and pressure-dependent data was considered by Zhu *et al.* [113], who used the reaction as a test case for different treatments of angular momentum in Rice–Ramsperger–Kassel–Marcus calculations. Rather vexingly, various formalisms for treating the *K* quantum number were found to give different microcanonical rate coefficients and fitted collision efficiencies, and none was able to model successfully the available experimental Cl+ C_2H_2 measurements.

Ethene is the next larger unsaturated hydrocarbon, and its addition reaction with

Cl should be similar to that of acetylene. The metathesis channel in the Cl+ C_2H_4 reaction has been the subject of some degree of controversy, which will be addressed later; however, there have been a number of studies on the addition reaction alone. The most extensive investigation of the pressure dependence is that of Wallington *et al.* [44], who measured the pressure dependence in air between 10 and 3000 Torr. Kaiser and Wallington [66] extended the measurements of the pressure dependence of this reaction down to 0.2 Torr. On the basis of the combined measurements they fitted the pressure dependence, using $F_c = 0.6$ in the Troe expression for the fall-off, to extract the limiting rate coefficients $k_0 = (1.42 \pm 0.05) \times 10^{-29}$ cm^6 molecule^{-2} s^{-1} and $k_\infty = (3.2 \pm 0.15) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The high-pressure limiting rate coefficient is similar to that found in the investigations of the Cl+ C_2H_2 reaction. In addition, the dependence of the third-body collision partner has been reported by Kaiser and Wallington [114], who estimate the third-body efficiency in He to be approximately 60% of that for N_2. The low-pressure limiting rate coefficient is larger for Cl+ C_2H_4 than for Cl+ C_2H_2, because the increased number of vibrational degrees of freedom, and concomitantly higher adduct state density, enhances collisional stabilization.

A consequence of the dependence of the addition reaction on collisional energy transfer in the adduct is an inverse deuterium kinetic isotope effect for Cl atom addition [106]. An increase in the density of states of the adduct upon deuteration tends to increase its lifetime, making it more likely to suffer collisional deactivation before redissociation. This phenomenon is most pronounced at lower pressures, since the high-pressure limiting value of the addition rate coefficient does not depend on energy transfer and is expected to have an insignificant kinetic isotope effect. The Finlayson-Pitts group has recently published a series of measurements which demonstrate the inverse kinetic isotope effect in Cl+ alkene addition reactions. For example, Stutz *et al.* [64, 115] have measured the kinetic isotope effect for Cl atom addition to C_2H_4 and C_2D_4 to be $k_{C_2H_4}/k_{C_2D_4} = 0.74 \pm 0.06$ at 1 atm and 0.33 ± 0.09 at 1 Torr. The inverse isotope effect can be well modelled by the predictions of the Troe theory. In measurements of the kinetic isotope effect for a series of alkenes, they were able to demonstrate that, while the kinetic isotope effect is inverse for addition in the low-pressure limit, it tends towards unity as the pressure increases. Measurements at 1 Torr show that the reactions of Cl with alkenes larger than ethene display a kinetic isotope effect nearer unity, as the high-pressure limit is reached at lower pressures [50]. The kinetic isotope effect has been used to infer qualitatively the relative contributions of abstraction and addition channels in Cl+ alkene reactions.

The site specificity and stereo-specificity of Cl addition reactions with alkenes has been extensively explored, although some questions remain. The rule that addition forms the more stable radical would predict, in general, terminal additions to double bonds. A special case is allene, where addition to the central C is vastly favoured energetically, but the addition of H and alkyl radicals has been found nonetheless to favour terminal addition [36, 116–118]. Rowland and co-workers [58–62] carried out an extensive study on Cl atom additions to propene, propyne and a number of substituted ethenes. Their work served to show that the initial addition of Cl to alkenes did not show as high a preference for addition to the less-substituted C as had previously been assumed. This series of studies utilized radioactive ^{38}Cl reacting with normal reagents in the presence of a radical scavenger such as HI which served to stabilize the initially formed radical product. The product fraction for addition to the less-substituted site was seen to increase with decreasing concentration of HI, indicating that some process interconverts the initially formed radical products. This process was postulated to be a facile 1,2 Cl atom shift which produces the more stable radical product preferentially, regardless of the initial radical adduct; in fact, the formation of a 'bridged' structure in Cl atom addition has been proposed. Even accounting for this shift, a preference for addition to the less-substituted C remains in most Cl atom additions.

In summary, while the addition of Cl to alkenes generally takes place at the site which will produce the most stable adduct radical, this preference is by no means exclusive. Rearrangement of the initially formed adduct, which interconverts chloroalkyl radicals, is facile for many Cl+ alkene reactions. The addition is nearly barrierless; although extensive studies of the temperature dependence of k_∞ are rare, the large values at room temperature ($k_\infty > 10^{-10}$ cm^3 molecule^{-1} s^{-1}) preclude any sizeable positive activation energy. The formation of a C–Cl bond is approximately 20 kcal mol^{-1} exothermic for most Cl+ alkene additions. An inverse kinetic isotope effect is observed for several Cl+ hydrocarbon additions at low pressures, because of the increased adduct state density upon deuteration.

5. Competition between addition and metathesis in Cl+ alkene reactions

It is generally accepted that the abstraction reactions of Cl with alkanes proceed through a linear or nearly linear transition state. However, the abstraction channels in the reactions of Cl atoms with alkenes have been less well studied than their alkane counterparts, and the nature of the transition state to abstraction of an allylic H atom (i.e. from a methyl group adjacent to a double bond) or vinylic H atom (from a terminal double-bonded C atom) may be different from that for abstraction from a saturated hydrocarbon. The addition reactions of Cl atoms with alkenes proceed by direct attack of the Cl atom and simple C–Cl bond formation. However, in most reactions of Cl atoms with unsaturated hydrocarbons, the addition channel operates in competition with metathesis channels, the presence of which may affect the addition reaction. In order to obtain a full description of these reactions a method is necessary to distinguish the various contributions to the reaction rate.

In the simplest case, a direct abstraction channel with an energy barrier competes with an addition channel. This is the case where the abstraction is endothermic, as in the reaction of Cl with ethene. The reactions of OH with alkenes provide excellent examples of this situation. For a given pressure, the temperature behaviour of the OH–alkene reactions displays three distinct characteristic regions [119]. At low temperatures, the rate coefficient falls with increasing temperature as the reaction is dominated by addition; at high temperatures, the reaction proceeds entirely by abstraction, and the rate coefficient rises with increasing temperature. At intermediate temperatures, the alkene·OH adduct thermally dissociates and the kinetics became complex, with the apparent rate coefficient for OH removal changing dramatically with temperature [120, 121]. Since *A* factors for OH abstraction reactions are lower than the corresponding addition reactions, and the activation energies for abstraction are significant, the rate coefficient often falls precipitously as the adduct begins to dissociate.

In the case of Cl atom reactions, the competition between addition and metathesis is on a more even footing. The *A* factors for abstraction by a Cl atom are larger than for abstraction by an OH molecule, and the activation energies are smaller. In fact, many exothermic Cl abstraction reactions with hydrocarbons have nearly negligible activation energies. The endothermicities of the abstraction reactions of Cl with acetylene and with ethylene, 29.7 and 7.3 kcal mol^{-1} respectively [26], allow relatively easy experimental separation of the addition and metathesis channels. As discussed above, the reaction with acetylene proceeds purely by addition except at high temperatures; the addition reaction has been investigated as a function of pressure and temperature without interference from metathesis. The addition channel of the Cl atom reaction with ethene dominated the reaction at room temperature and has also been discussed above. The $Cl + C_2H_4 \rightarrow C_2H_3 + HCl$ abstraction channel is most readily investigated at low pressures or elevated temperatures. This reaction is of interest because of its relation to the heat of formation of the vinyl radical.

For Cl atoms reacting with alkenes larger than ethene, the two channels will have similar rate coefficients at moderate temperatures and pressures. The relative contributions of addition and metathesis reactions of Cl with larger alkenes therefore display a more complex dependence on temperature and pressure. The reactions of propene and propyne, each of which has an exothermic direct abstraction at the methyl site, show a prominent addition channel below about 500 K, above which direct abstraction appears to dominate the reaction. The Cl+ isoprene reaction also obeys the general pattern of other Cl+ alkene reactions. The reaction with allene, however, appears to be controlled by the addition to form the chloroallyl radical and thus displays an unusual pressure and temperature dependence.

5.1. *Ethene*

The metathesis reaction of Cl atom with C_2H_4 has attracted recent interest because of a discrepancy in determinations of the heat of formation of the vinyl radical (CH_2CH) by different methods. The vinyl radical is an important intermediate in hydrocarbon combustion and also plays a role in the chemistry of planetary atmospheres. Measurements using photoelectron spectroscopy and ion cycles determined a bond energy $D_{298\ K}(CH_2CH{-}H)$ of 111.2 ± 0.8 kcal mol^{-1}, which corresponds to a standard heat of formation of C_2H_3 of $\Delta H^{\circ}_{f,298\ K} = 71.6 \pm 0.8$ kcal mol^{-1} [109]. Recent work by Knyazev and Slagle [122] on the unimolecular decomposition of C_2H_3 yields $\Delta H^{\circ}_{f,298\ K}(C_2H_3)$ of 71.4 ± 1.6 kcal mol^{-1}. However, kinetic measurements using the equilibrium $Cl + C_2H_4 \leftrightarrow HCl + C_2H_3$ by Benson and co-workers [123, 124] generated a heat of formation of the vinyl radical of $\Delta H^{\circ}_{f,298\ K} = 66.9 \pm 0.8$ kcal mol^{-1}. This is a far greater discrepancy than is generally expected in such measurements, and this disagreement has led to recent reinvestigations of the Cl+ ethene reaction. Because the metathesis is endothermic, an addition–elimination mechanism is not relevant to the Cl+ ethene reaction, and the metathesis must proceed by direct abstraction. In order to investigate the abstraction reaction, some means must be used to isolate it from the addition channel which also contributes to the total reactivity. Since the addition becomes less important as the temperature increases or the pressure decreases, investigations designed to probe the abstraction have typically been carried out at low pressures or elevated temperatures.

The measurements of Benson and co-workers were performed using their very-low-pressure reactor (VLPR) method, which uses a Knudsen cell reactor coupled with a mass spectrometer to measure second-order kinetics in the millitorr pressure range. Under these conditions the contribution of three-body collisions should be negligible, and in fact the rate of wall collisions can approach the rate of bimolecular collisions [125]. The first measurements to move the kinetic data into into closer agreement with the negative ion–photoelectron data were performed by Kaiser and Wallington [66]. They measured the total rate coefficient for the reaction of Cl atom with ethene as a

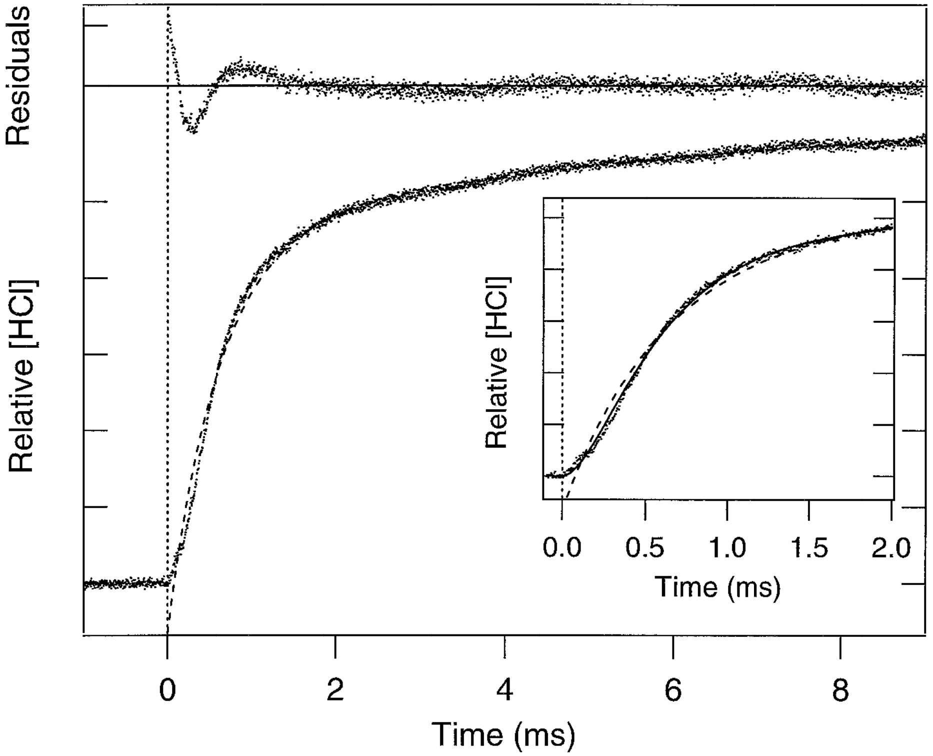

Figure 4. Time behaviour of HCl production after photolysis of CF_2Cl_2 (2×10^{14} molecule cm^{-3}) in the presence of 4×10^{15} molecule cm^{-3} C_2H_4 at 10 Torr total pressure and 292 K, which displays sigmoidal behaviour characteristic of a secondary reaction product: (– – –), best fit to a biexponential, with residuals displayed above. The inset shows the early time behaviour of the HCl signal, with a simulation (——) based on secondary HCl production by Cl+ C_2H_4Cl. (Adapted from [55], copyright 1997 American Chemical Society. Used with permission.)

function of pressure, and noted that the rate coefficient at low pressures was much smaller than the abstraction rate coefficient measured by Dobis and Benson [123, 126]. By performing a careful product analysis, Kaiser and Wallington were able to extract the contribution of the abstraction channel as a function of temperature between 300 and 383 K. These measurements yielded a rate coefficient for the abstraction more than a factor of 500 smaller than the results of Dobis and Benson. The activation energy for the reaction was also measured to be larger in the experiments of Kaiser and Wallington. Using a third-law method in conjunction with measurements of the reverse reaction by Russell *et al.* [127], a vinyl radical heat of formation of $\Delta H^{\circ}_{f,298\ K} = 70.6 \pm 0.4$ kcal mol^{-1} was determined, in good agreement with the bond strength measured by Ervin *et al.* [109].

Subsequently, the reaction was also investigated using infrared absorption detection of the HCl product [55, 56]. At room temperature and 5–10 Torr total pressure, the time behaviour of the HCl production was dominated by secondary reactions, making it impractical to measure a room-temperature rate coefficient. Only at higher temperatures was direct formation of HCl observed. However, even at temperatures above 500 K the addition channel continues to contribute, requiring that the measured rate coefficients be corrected for the HCl yield in order to extract the abstraction rate coefficient. The time behaviour at room temperature is shown in figure 4. The time trace is at first glance similar to a biexponential trace; however, there is a clear induction period which indicates that the formation of HCl proceeds by a secondary mechanism. One possible mechanism is addition of Cl to ethene, forming a 2-chloroethyl radical (CH_2CH_2Cl), followed by reaction with remaining Cl atoms [55]. As shown in figure 4, modelling of the HCl production using such a mechanism can reproduce the qualitative features of the experimental traces; however, it is unreasonable to attempt to extract rate coefficients from such a speculative mechanism. The reaction of Cl with the chloroethyl radical may be rapid; the reaction of Cl with ethyl radicals has been measured to be as high as about 3×10^{-10} cm^3 molecule^{-1} s^{-1} [128–130] although there is some dispute about these results based on simple collision theory arguments and on VLPR studies [123, 126, 131].

At higher temperatures the addition reaction is expected to contribute less, as the reverse reaction becomes fast. Above about 500 K, exponential HCl production is observed in the time-resolved infrared absorption experiments. Consideration of a reaction mechanism which includes direct abstraction and secondary reaction of chloroethyl radicals shows that near-exponential behaviour is possible even with a moderate contribution of secondary reactions. However, the abstraction quickly dominates HCl production. The yield of HCl is nonetheless less than 100% in the Cl+ ethene system even up to 750 K. This is somewhat unexpected, given that the decomposition of the initially formed 2-chloroethyl radical should be extremely rapid at these temperatures [132]. Tunnelling of an excited adduct (through what is expected to be a significant barrier) to form the more stable 1-chloroethyl radical (CH_3CHCl) could contribute, if 3×10^{-4} of the initially formed adduct species tunnel before collisional stabilization. Since any removal of the chloroethyl radical would yield indistinguishable results, this suggestion should be regarded as conjecture. Any competing Cl atom removal will also reduce the measured yield, for example radical–radical recombination such as Cl+ CF_2Cl or Cl atom reaction with buffer gas impurities.

The experimental results for the Cl+ ethene system are shown in figure 5. The activation energy for the metathesis reaction as measured in the time-resolved infrared experiments is 6.2 kcal mol^{-1} [55]. Using a second-law method and the negative activation energy for the reverse reaction measured by Russell *et al.* [127], this yields a heat of formation of the vinyl radical of 70.6 kcal mol^{-1} [56] in reasonable agreement with the determination of Kaiser and Wallington [66]. However, there is no region of temperature overlap between the determinations of Pilgrim and Taatjes and any literature measurements of the reverse reaction; so a second-law determination requires extrapolation of the vinyl+ HCl results to a higher temperature. It should also be noted that Benson and Dobis [131] have questioned the observation of negative activation energies in alkyl radical+ HX reactions; measurements of C_2H_3 + HCl at higher temperatures could help to resolve remaining issues concerning $Cl + C_2H_4 \leftrightarrow HCl + C_2H_3$ thermochemistry. A third-law analysis is also possible using the forward reaction at 500 K and the reverse reaction at 495 K from Russell *et al.* [127]. The heat of formation determined in this way is 71.3 ± 0.3 kcal mol^{-1} [56], in excellent agreement with the second-law determination and with the ion cycle measurements of Ervin *et al.* [109] and the kinetic measurements of Kaiser and Wallington [66]. Note that the activation energy of the total reaction rate coefficient of Cl with ethene is lower than the metathesis; correction of the rate coefficient for the HCl yield is a significant factor in determining the correct rate coefficient.

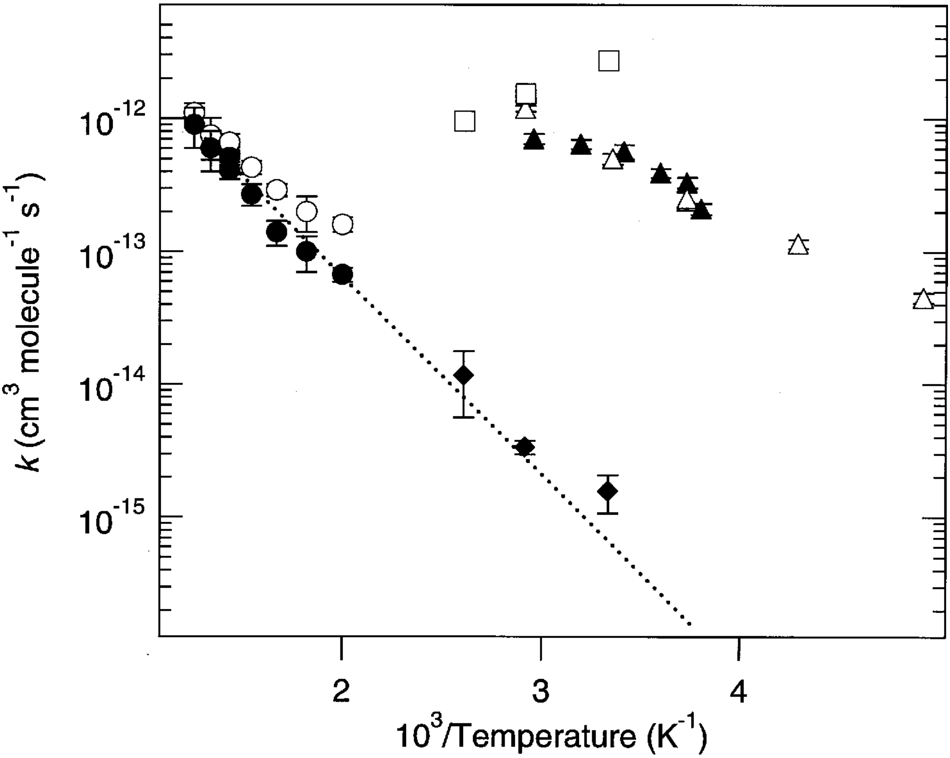

Figure 5. Rate coefficients for the reaction of Cl atoms with ethene: (△), results for the metathesis from Dobis and Benson [123]; (▲), metathesis rate coefficients of Parmar and Benson [124]; (●), metathesis rates obtained by Pilgrim and Taatjes [55]; (◆), methathesis rates obtained by Kaiser and Wallington [66]; (○), total rate coefficients at 10 Torr determined by Pilgrim and Taatjes [55]; (□), total rate coefficients at 10 Torr determined by Kaiser and Wallington [66]. The dotted line represents an Arrhenius fit to the high temperature data of [55].

In most respects the reaction of Cl atom with ethene is typical of what would be expected for an endothermic abstraction reaction in competition with an addition. The metathesis channel appears similar to the abstraction reaction in saturated hydrocarbons. The *A* factor is approximately (1–2) × 10^{-11} cm^3 molecule^{-1} s^{-1} per available H atom, as has been observed in Cl+ saturated hydrocarbon abstraction reactions [51, 57]. The contribution of the addition reaction of course falls off to higher temperatures and to lower pressures; in the case of Cl+ ethene, the redissociation of the chloroethyl radical has little effect on the time behaviour of HCl production above 500 K. The activation energy of the abstraction is large enough that its contribution becomes significant only at these higher temperatures where addition is unimportant, and the competition does not produce biexponential time traces. However, in the case of the reaction of Cl with C_3 unsaturated hydrocarbons, the metatheses are significantly exothermic because of resonance stabilization in the hydrocarbon radical products. The difference in the thermodynamics produces qualitatively different kinetic behaviour in these reactions.

5.2. *Propene*

In contrast with the endothermic abstraction reaction of Cl with C_2H_4, the abstraction of the allylic H atom from the methyl group in Cl+ propene is highly exothermic ($\Delta H_{298\ \mathrm{K}} = -(14.3 \pm 0.6)\ \mathrm{kcal\ mol^{-1}}$) [26, 133, 134], because of the formation of the resonance stabilized allyl radical product. Removal of the allylic H atom in propene is therefore relatively facile and competes with addition over a wide temperature range. Also, because of the exothermicity of the reaction, an addition–elimination mechanism for HCl production may now be feasible. Compared with Cl+ ethene, the competition between addition and metathesis is shifted in favour of metathesis even at lower temperatures. However, the higher density of states in the chloropropyl radical over the chloroethyl radical also increases the importance of the addition reaction at lower pressures. As a result, the laboratory investigations of the Cl+ propene reaction can be expected to display addition, abstraction and addition–elimination channels.

Kaiser and Wallington [65] have measured the total rate coefficient for the reaction of Cl with propene relative to Cl+ ethane over a large pressure range. They used Fourier transform infrared (FTIR) and gas chromatography product analysis to deduce the yields of allyl radical in the reaction and therefore to separate the addition and metathesis contributions. Their measured rate coefficients are in reasonable agreement with the few previous relative rate determinations, taken at room temperature and near atmospheric pressure [42, 45], although the early determination of Wallington *et al.* [42] relative to *n*-butane now appears to be somewhat high. Using their results Kaiser and Wallington fitted a Troe curve to the fall-off behaviour and estimated high- and low-pressure limiting rate coefficients for the addition reaction. The values obtained for $k_\infty = 2.7 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ and $k_0 = 4.0 \times 10^{-28}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}}$ were based on an assumed centre broadening factor $F_c = 0.6$. The low-pressure limiting rate coefficient is larger than for Cl+ ethene, again reflecting the increased density of states in the larger molecule.

The addition reaction for Cl+ propene competes with the exothermic metathesis reaction to form HCl and the allyl radical. Several measurements have addressed this competition. Kaiser and Wallington [65] measured the rate coefficient for allyl production at room temperature for pressures ranging from 1 to 100 Torr. They observed an increase in the metathesis rate coefficient with decreasing pressure, a signature of an addition–elimination mechanism. The low-pressure limiting (less than 30 Torr) metathesis rate coefficient was found to be $3.7 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. Using the pressure dependence of the metathesis rate coefficient, they were able to make an estimate of the abstraction contribution of $(2.3 \pm 0.3) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K. Lee and Rowland [58] investigated the reaction of thermal ^{38}Cl with propene and found an upper limit of (14±4)% contribution of the abstraction reaction at room temperature and 3000 Torr. Lee and Rowland reported no absolute rate coefficients, but using their product ratio at 3000 Torr with the high-pressure limiting rate coefficient of Kaiser and Wallington [65] would give a value of $3.8 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ for the abstraction. Stutz *et al.* [50] measured the rate coefficient and kinetic isotope effect for Cl+ propene at room temperature and pressures of 1 and 760 Torr. Their rate coefficient determinations are in reasonable agreement with those of Kaiser and Wallington. Unfortunately, the kinetic isotope effect is insufficiently sensitive to distinguish fine changes in the relative contributions of abstraction and addition; Stutz *et al.* reported a kinetic isotope effect of $k_{\mathrm{C_3H_6}}/k_{\mathrm{C_3D_6}} = 1.1 \pm 0.2$ at 1 Torr and of 0.99 ± 0.09 at 760 Torr.

Absolute rate coefficients for Cl+ propene between 292 and 750 K have been measured using the laser photolysis–CW long-path absorption technique [54]. Measurements of the HCl yield were carried out using Cl+ propane as a reference

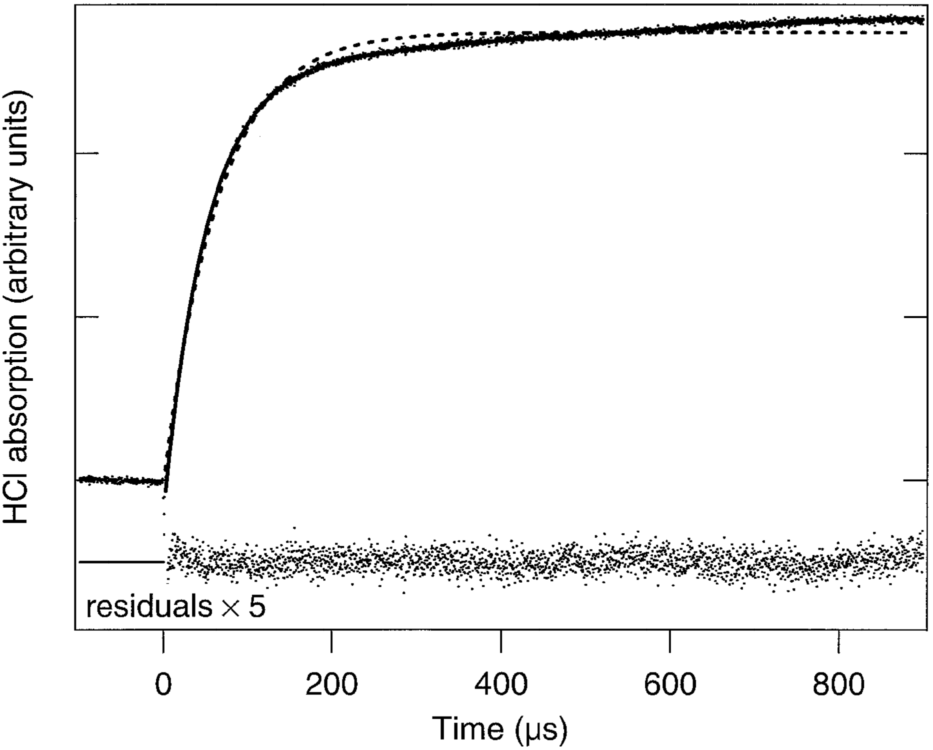

Figure 6. Biexponential time-resolved HCl production from the reaction of Cl atoms with propene at 10 Torr total pressure and 298 K: (——), fit to a biexponential, with residuals (× 5) displayed below; (– – –), best fit to a single exponential, which clearly does not correctly model the time behaviour of the HCl signal. (Reprinted with permission from [54], copyright 1997 American Chemical Society.)

reaction, enabling separation of metathesis and addition channels. The total metathesis rate coefficient at 292 K and 10 Torr, $(3.7 \pm 0.6) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, agrees well with the measurements by Kaiser and Wallington at the same pressure. The metathesis channel, which is a combination of direct abstraction and addition–elimination pathways, shows a simple Arrhenius behaviour with temperature. Because addition, dissociation and abstraction all compete, the time behaviour of the HCl production near room temperature is biexponential, as shown in figure 6, and determination of the rate coefficients is complicated. Pilgrim and Taatjes extracted the rate coefficients by plotting the sum of the fitted time constants against the concentration of propene, as described in appendix A. This plot gives a line, the slope of which is the total effective rate coefficient for the removal of Cl atoms by propene. The metathesis rate coefficient is this rate coefficient multiplied by the HCl yield. The available rate coefficient data are displayed in figure 7.

As discussed in appendix A, biexponential traces can arise from either an elimination or a reversible addition reaction. The biexponential traces were analysed using both formulations and the extracted rate coefficients were found to be indistinguishable [54]. However, pressure-dependent apparent equilibrium coefficients would be obtained from forward and reverse rates for chloropropyl radical formation extracted under the assumption of a pure reversible addition mechanism. This suggests

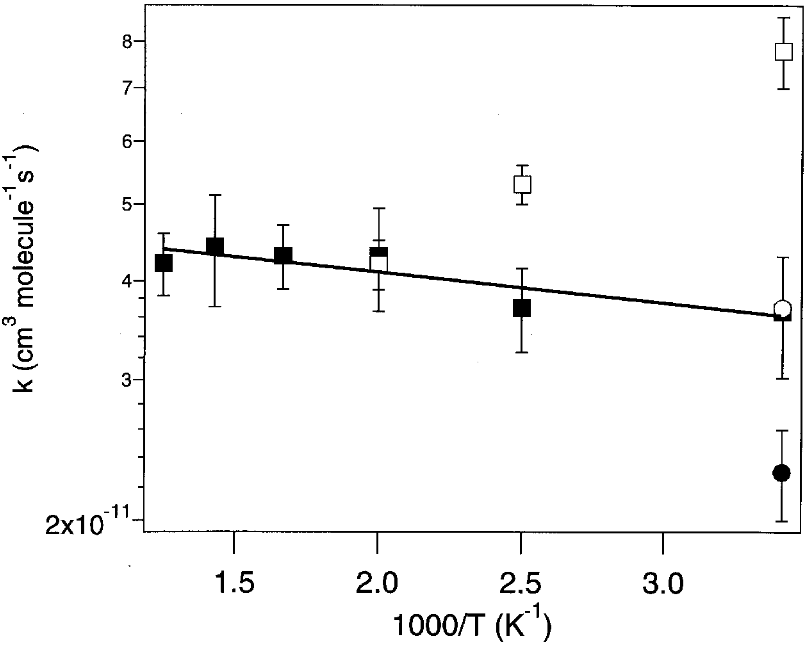

Figure 7. Rate coefficients for Cl+ propene reactions; (□), total rate coefficient at 10 Torr from Pilgrim and Taatjes [54]; (■), metathesis rate coefficient at 10 Torr from Pilgrim and Taatjes [54]; (○), total metathesis rate from Kaiser and Wallington [65]; (●), abstraction rate coefficient from Kaiser and Wallington [65].

that thermal dissociation of chloropropyl is not the sole origin of the biexponential behaviour and is consistent with an elimination contribution.

Biexponential traces are observed at 293 and 400 K; at higher temperatures (500 K or above), single-exponential behaviour is observed. Since the pseudo-first-order time constants are (1–3) × 10^4 s^{-1}, the observation of single-exponential traces implies that the redissociation of a chloropropyl adduct occurs on a significantly faster time scale. Such an observation is consistent with a well depth of 15–20 kcal mol^{-1} for adduct formation, as would be expected for terminal addition of Cl atom to propene. No direct observations of the thermal dissociation of chloropropyl radicals have been reported. However, a simple estimate can be performed using an A factor for C–Cl bond fission of 3.9×10^{13} s^{-1} from calculations of the similar CH_2CH_2Cl dissociation by Barat and Bozzelli [132] and taking a typical chloroalkyl C–Cl bond energy of 20 kcal mol^{-1} as the activation energy. This yields a chloropropyl dissociation rate coefficient of about 7×10^4 s^{-1} at 500 K, supporting the proposition that rapid dissociation of the chloropropyl radical is responsible for the change to single-exponential behaviour above 500 K. Finally, above 500 K the HCl yield is unity, indicating that no stable chloropropyl radical is produced at these temperatures.

The activation energy of the metathesis channel observed in the infrared experiments is nearly zero (0.17 ± 0.10 kcal mol^{-1}), similar to exothermic abstraction reactions of Cl with alkanes [57]. However, the abstraction of the allylic H atom in propene may differ from abstraction reactions in alkanes because of the large exothermicity associated with the formation of the resonance stabilized allyl product. The HCl product energy distribution offers another point of comparison with other Cl+ hydrocarbon reactions. Linear transition-state geometries, as observed in the

Cl+ alkane reactions, tend to produce low rotational excitation. Halogen atom abstraction reactions H+ RX→ HX+ R place significant amounts of energy into vibration of the diatomic HX product, suggesting that the transition state lies at a larger H–X distance than in the product. Pilgrim and Taatjes [54] measured the HCl vibrational energy disposal in the reaction of Cl with propene by comparing the signals taken in Ar buffer, a poor relaxer of vibrationally excited HCl, and in CO_2, which relaxes HCl ($v = 1$) rapidly [135]. A significant amount of the reaction exothermicity, $(28 \pm 3)\%$, was found to be channelled into HCl vibration, with nearly half of the HCl product formed vibrationally excited [54]. This large degree of vibrational excitation is similar to that observed in the highly exothermic abstraction reactions of H atoms with halogenated hydrocarbons, for example [71, 72]. However, there is as yet only a limited set of energy disposal measurements for Cl+ alkane reactions that are directly comparable with the Cl+ propene reaction.

Different forms of available energy in a reaction (e.g. translational energy, vibrational energy and reaction exothermicity) are channelled differently into product energy. Dynamical experiments have shown that excess translational energy in Cl+ alkane reactions is not effectively transferred to HCl product vibration. In contrast, Zare and co-workers have shown that vibrational excitation in CH_4 does tend to increase HCl ($v > 0$) populations in the Cl+ CH_4 reaction. The channelling of reaction exothermicity into HCl vibration, as occurs in Cl+ propene, has received less study, because Cl+ alkane abstraction reactions are in general not energetic enough to populate HCl ($v = 1$). Park *et al.* [136] measured DCl from the reaction of Cl with deuterated cyclohexane, which is sufficiently exothermic (8 kcal mol^{-1}) to populate DCl ($v = 1$) (6.1 kcal mol^{-1}). They determined that less than 5% of the DCl was formed vibrationally excited, implying that a maximum of 3.8% $[0.05 \times (6.1\ \text{kcal mol}^{-1}/8\ \text{kcal mol}^{-1})]$ of the reaction exothermicity appears in DCl vibration. This fraction is much smaller than the $f_v = 0.28$ observed for Cl+ propene; in fact, the contribution of addition–elimination in the Cl+ propene metathesis (see below) implies that the vibrational excitation for the abstraction channel must be even higher. The results therefore suggest that the abstraction transition state differs for Cl+ propene and Cl+ cyclohexane. Further experiments, for example, to measure HCl rotational distributions from the Cl+ propene reaction or DCl vibrational distributions from reactions such as Cl+ C_3D_8 and Cl+ C_4D_{10} would facilitate more detailed mechanistic comparisons between Cl+ alkene and Cl+ alkane reactions.

5.3. *Isoprene*

Because of the presence of Cl in the marine boundary layer, there has been recent interest in reactions of Cl atoms with biogenic hydrocarbons such as isoprene (2-methyl-1,3-butadiene, which is produced by phytoplankton). The products of Cl-initiated oxidation of isoprene have been measured by the Finlayson-Pitts group [63, 137], and markers for the atmospheric degradation of isoprene have been devised based on their work. Since isoprene is essentially a vinyl-substituted propene, and the thermochemistries of the two systems are similar, the reactivity of isoprene to Cl atoms should follow the pattern of the Cl+ propene reaction. Abstraction of an allylic H atom at the methyl group can be expected to compete with addition, similar to the allylic abstraction pathway in Cl+ propene. No addition site in the butadienes produces a resonance-stabilized adduct; so the well depths for addition to isoprene should be similar to Cl+ other alkenes. However, the addition channel at low pressures should be enhanced in isoprene relative to the reaction with propene because of the increased density of states available in the larger molecule.

Because of the larger density of states in Cl+ isoprene, the fall-off should occur at significantly lower pressure than for Cl+ propene, corresponding to a shallower pressure dependence at the usual 1–760 Torr range of laboratory experiments. The Finlayson-Pitts group has studied the pressure dependence of the kinetic isotope effect and the rate coefficient for Cl+ isoprene at room temperature. Ragains and Finlayson-Pitts [63] measured the 298 K rate coefficients for Cl+ isoprene and isoprene-d_8 relative to *n*-butane ($k_{\mathrm{Cl}+n\text{-butane}} = (2.11 \pm 0.18) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) between 0.16–5 Torr and at 760 Torr. They also determined the HCl yield in the atmospheric pressure Cl+ isoprene reaction using FTIR detection. Abstraction was found to contribute (15 ± 4)% to the reaction at 298 K and atmospheric pressure. The addition reaction is near its high-pressure limit at 298 K and 1 atm. Ragains and Finlayson-Pitts reported an extremely shallow fall-off with pressure, with a rate coefficient of $(4.6 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 760 Torr, $(4.01 \pm 0.42) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 5 Torr, and $(2.64 \pm 0.26) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 0.16 Torr. Absolute rate coefficient determinations by Stutz *et al.* [50], using a fast-flow method, of $(3.7 \pm 1.0) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 1 Torr and by Notario *et al.* [48], using flash photolysis resonance fluorescence, of $(3.61 \pm 0.10) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} between 15 and 60 Torr confirmed that the fall-off is extremely shallow between 0.16 and 760 Torr. By comparison, the addition of Cl+ propene changes by a factor of 20 between 1 and 760 Torr [65].

The metathesis in the Cl+ isoprene, removing an allylic H atom from the methyl group, is analogous to the metathesis in Cl+ propene. Bedjanian *et al.* [47] measured the rate coefficients and branching fractions for the Cl+ isoprene reaction relative to Cl+ $\mathrm{Br_2}$ using a discharge-flow mass spectrometry technique between 233 and 320 K. They found that the total rate coefficient changed by less than 10% between 0.25 and 3 Torr at room temperature and measured the temperature dependence of the Cl+ isoprene reaction at 1 Torr to be $k_{\mathrm{total}} = (6.7 \pm 2.0) \times 10^{-11} \exp[(485 \pm 85)/T]$ cm^3 molecule^{-1} s^{-1}. They also measured the temperature-dependent yield of HCl in the reaction, using the BrCl signal from titration of the initial Cl concentration by $\mathrm{Br_2}$ as a reference. The reported branching fraction at 1 Torr is $\phi_{\mathrm{HCl}} = (1.22 \pm 0.4) \exp[-(595 \pm 90)/T]$ between 233 and 320 K. Using this information in conjunction with the overall rate coefficient, the rate coefficient for the metathesis could also be deduced, as $\phi_{\mathrm{HCl}}\, k_{\mathrm{total}} = (8.2 \pm 5.1) \times 10^{-11} \exp[-(110 \pm 175)/T]$ cm^3 molecule^{-1} s^{-1}. The small activation energy is consistent with the similar exothermic metathesis reaction of Cl with propene. The pre-exponential factor is large for an abstraction reaction with three abstractable H atoms, but the sizeable error bars encompass the propene A factor of $(4.9 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Their measured low-pressure value for the metathesis rate coefficient at 298 K, $(5.7 \pm 1.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, is in agreement with the number calculated from the atmospheric pressure yield and rate coefficient measurements of Ragains and Finalyson-Pitts, $(0.15 \pm 0.04) \times (4.6 \pm 0.5) = (6.9 \pm 2.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

The general picture of the Cl+ isoprene reaction is in fact very similar to that of Cl+ propene, with removal of an allylic H atom competing effectively with addition across the double bond. Product measurements have been used to evaluate the rate coefficients for metathesis, which are in good agreement with the similar allylic abstractions in propene. Ragains and Finlayson-Pitts [63] measured a normal kinetic isotope effect in the reaction at 1 atm, consistent with an abstraction contribution; however, they unexpectedly found a negligible kinetic isotope effect at lower pressures, which may indicate a more complicated reaction mechanism. While there is approximate conformity in the absolute values of the rate coefficient measurements, there is slight disagreement as to the details of the pressure dependence. Bedjanian *et al.* [47] observed a pressure-independent addition reaction in their 0.25–3 Torr measurements and quoted $k_\infty = (2.8 \pm 0.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} as simply $k_{\text{total}} - k_{\text{metathesis}}$ from their results. This high-pressure limit estimate is approximately 40% lower than the 1 atm measurements of the addition rate coefficient from the Finlayson-Pitts group.

5.4. *Allene and propyne*

The two C_3H_4 isomers allene ($CH_2{=}C{=}CH_2$) and propyne ($CH_3C{\equiv}CH$) are nearly isoenergetic, and abstraction of a H atom from either will produce propargyl+ HCl with about 14 kcal mol^{-1} excess energy [26, 138]. It might be expected therefore that the C_3H_4 isomers would react similarly with Cl atoms and, furthermore, that the reactions would be analogous to the Cl+ alkene reactions described above. It will be seen that the reaction with propyne is in fact similar to that with propene, since the energy for C–Cl bond formation is similar in the two reactions and since the densities of states are similar. However, the reaction with allene is different from other Cl+ alkene reactions, a difference which reflects the possibility of addition to the central C atom to form a reasonantly stabilized chloroallyl radical. Although other radical additions to allene have been measured to proceed via attack at the terminal site, there is strong indirect evidence that the reaction of chlorine with allene forms the chloroallyl radical.

The reaction with propyne is almost completely analogous to the reaction of Cl with propene. In both cases abstraction of a methyl H atom gives rise to the resonance-stabilized form of the hydrocarbon radical product. Wallington *et al.* [42] measured rate coefficients for Cl+ propyne and propene relative to *n*-butane at 298 K and 760 Torr (air). The rate coefficient for Cl+ propyne was measured to be $(83 \pm 6)\%$ of that for Cl+ propene. Using a rate coefficient of 2.25×10^{-10} cm^3 molecule^{-1} s^{-1} for Cl+ *n*-butane, Wallington *et al.* reported a rate coefficient for Cl+ propyne of $(2.68 \pm 0.16) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Addition of Cl to neither of the possible C atom sites in propene produces a resonantly stabilized adduct, and the binding energy for Cl addition is expected to be about 15–20 kcal mol^{-1}, similar to other Cl+ unsaturated hydrocarbon additions. The contribution of the addition reaction should diminish with increasing temperature in an equivalent manner to the cases of Cl+ ethene and Cl+ propene, where biexponential time traces cease to be observed above 500 K.

Absolute rate coefficients for Cl+ propyne and allene between 292 and 850 K have been measured by Farrell and Taatjes [53] using laser photolysis–infrared frequency modulation methods. Similar to the earlier direct absorption experiments, the FM experiments probed the time behaviour of HCl product formation and determined HCl yields by comparison with a reference reaction. At the 5–10 Torr pressure range of these measurements, the addition channel in Cl+ propyne ceases to contribute significantly above about 500 K. As in the case of Cl+ propene, the metathesis can in principle proceed either by abstraction or by addition–elimination. The redissociation of the C_3H_4Cl adduct, either back to reactants or by elimination of HCl, produces biexponential time traces for HCl production below 500 K, as in the Cl+ propene reaction. An identical analysis was used to extract rate coefficients from the

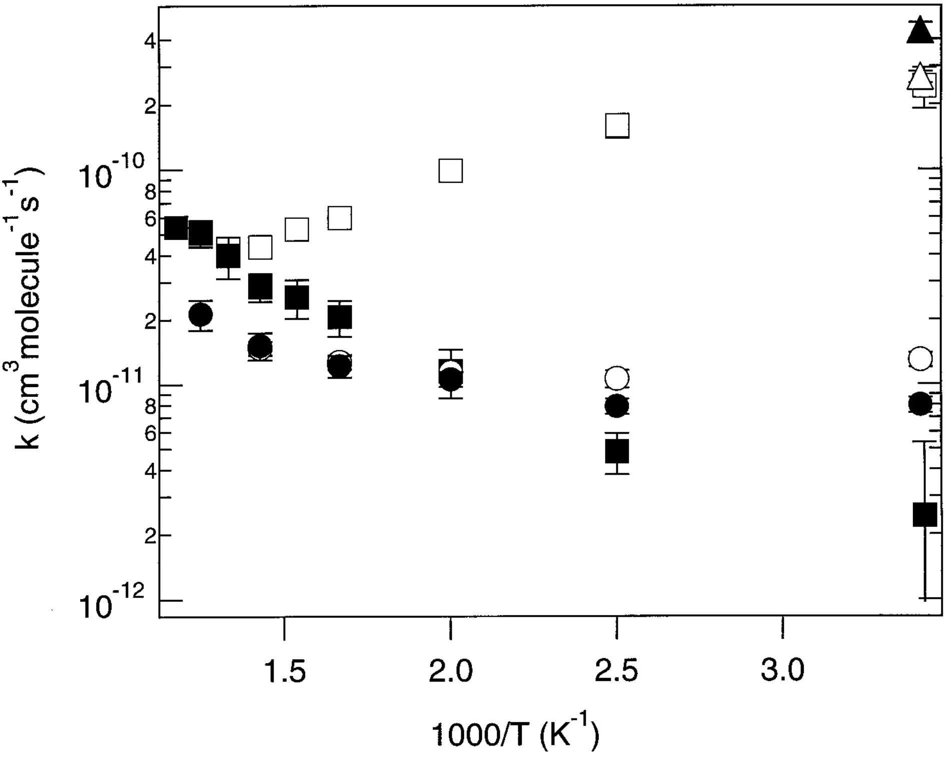

Figure 8. Rate coefficients for the reactions of Cl with allene and propyne: (●), metathesis rate coefficients (Ar at 10 Torr) for Cl+ propyne obtained by Farrell and Taatjes [53]; (○), rate coefficients (Ar at 10 Torr) for Cl+ propyne obtained by Farrell and Taatjes [53]; (■), metathesis rate coefficients (Ar at 10 Torr) for Cl+ allene obtained by Farrell and Taatjes [53]; (□), total rate coefficients (Ar at 10 Torr) for Cl+ allene obtained by Farrell and Taatjes [53]; (▲), total rate coefficient for Cl+ allene measured relative to *n*-butane by Wallington *et al.* [42] and scaled using $k_{n\text{-butane}} = 2.15 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} from Tyndall *et al.* [51]; (△), total rate coefficient for Cl+ propyne measured relative to *n*-butane by Wallington *et al.* [42] and scaled using $k_{n\text{-butane}} = 2.15 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} from Tyndall *et al.* [51].

Cl+ propyne biexponential data as for Cl+ propene. At 4.4 Torr total pressure and temperatures of 500 K and above, single-exponential time behaviour of HCl production was observed and HCl yields were found to be unity. These observations indicate a rapid dissociation of the C_3H_4Cl adduct above 500 K and is consistent with a well depth for adduct formation similar to that in Cl+ propene and Cl+ ethene. The available rate coefficients for Cl+ propyne and Cl+ allene are shown in figure 8.

The metathesis channel in Cl+ propyne exhibits a significant activation energy $E_a = 1.36 \pm 0.30$ kcal mol^{-1}. The activation energy in Cl+ hydrocarbon reactions appears to depend on the hybridization of the β-C. Comparison of the propane ($E_a = 0$), propene ($E_a = 0.170 \pm 0.1$ kcal mol^{-1}) and propyne data suggests that increasing hybridization correlates with a slight increase in abstraction barrier. Like the reaction of Cl with propene, the HCl product from the Cl+ propyne reaction shows significant vibrational excitation. In the infrared FM measurements, $(55 \pm 9)\%$ of the HCl is found to be formed in $v = 1$, corresponding to $(35 \pm 10)\%$ of the reaction exothermicity in HCl vibration [53]. The reaction of Cl with propyne seems analogous in every significant way with the thermochemically similar Cl+ propene reaction.

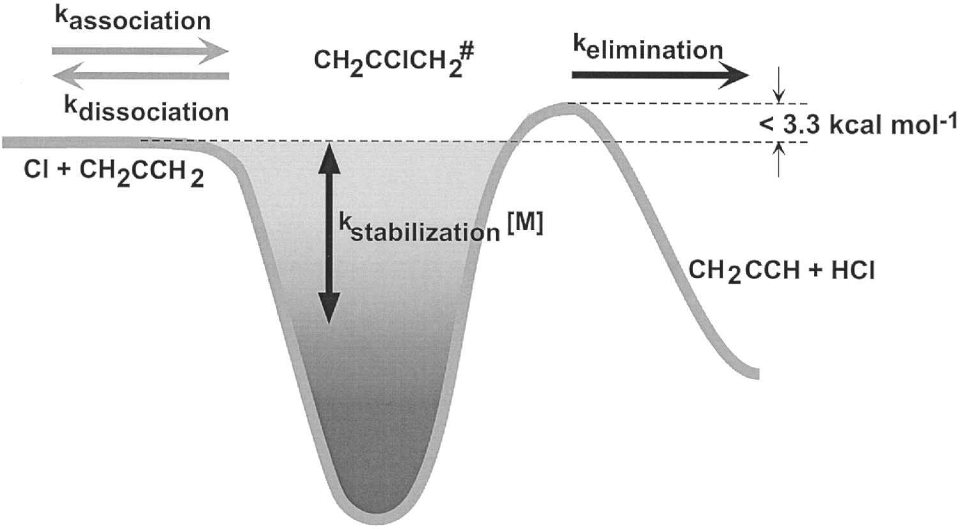

Figure 9. Schematic diagram of the proposed addition–elimination mechanism for the Cl+ allene reaction. The reaction is dominated by the stabilization to chloroallyl at low temperatures and, as the temperature increases, the branching begins to favour the metathesis channel. The phenomenological activation energy reflects the temperature dependence of the competition between stabilization and elimination. The observed value of 3.3 kcal mol^{-1} is therefore an upper limit for the barrier to the metathesis although, since the transition state for elimination should be relatively constrained, the actual barrier is expected to be much smaller.

The reaction of Cl with allene, however, displays qualitatively different kinetic behaviour from other Cl+ hydrocarbon reactions, as can be seen from the rate coefficient data in figure 8. The reaction proceeds almost entirely by addition at room temperature and moderate pressures. Wallington *et al.* measured the rate coefficient relative to *n*-butane at 298 K and 760 Torr (air). Using $k_{\mathrm{Cl}+n\text{-}\mathrm{C_4H_{10}}} = 2.25 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, they reported a rate coefficient of 4.38×10^{-10} cm^3 molecule^{-1} s^{-1} for Cl+ allene. In the infrared experiments the Cl+ allene rate coefficient was found to be a factor of less than two smaller at 10 Torr, $k = 2.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and to have a slight pressure dependence between 5 and 10 Torr. The addition channel dominates the reaction and continues to be a significant part of the reactivity up to 800 K. The metathesis channel has a substantial activation energy, 3.3 ± 0.6 kcal mol^{-1}, greater than that observed for C_3H_8, C_3H_6 or CH_3CCH. Furthermore, a simple Arrhenius fit to the metathesis rate coefficients yields an improbably large pre-exponential factor of 3.7×10^{-10} cm^3 molecule^{-1} s^{-1}. Assuming a pre-exponential factor of $(1\text{–}2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} per abstractable H atom, based on the abstraction reactions of the saturated hydrocarbons with Cl, would produce a value five to ten times smaller. It is difficult to rationalize such a large pre-exponential based on any plausible model for an abstraction.

The reaction with allene has an important thermochemical difference from other Cl atom+ hydrocarbon reactions, since addition to the central C atom produces a resonantly stabilized chloroallyl radical, CH_2CClCH_2. The well depth for this addition is estimated to be about 40 kcal mol^{-1} by density functional theory methods [53, 139]. This suggests that the metathesis channel in Cl+ allene is dominated by an addition–elimination mechanism, driven by the deep well for central Cl addition, over the 292–850 K temperature range of the infrared studies [53]. This mechanism is depicted schematically in figure 9. Under this interpretation, the reaction is dominated by addition to form an excited chloroallyl radical. Production of HCl arises by elimination from the high-energy radical adduct, which is in competition with collisional stabilization. The pre-exponential factor of the reaction thus is determined by the initial addition step. The phenomenological activation energy reflects the energy dependence of this competition between redissociation to products, elimination of HCl and collisional stabilization. The increase in the metathesis rate coefficient with increasing temperature is principally attributable to a change in the branching fraction for HCl elimination. If this interpretation of the data is accepted, the observed activation energy places an upper limit on the barrier to elimination of 3.3 kcal $\mathrm{mol^{-1}}$ above the Cl+ C_3H_4 asymptote. However, since the transition state for elimination is expected to be tighter than that for C–Cl bond fission, the barrier may be much smaller.

Other addition reactions with allene, for example CH_3 + allene and H+ allene, have shown evidence of addition to the terminal C atom. Wagner and Zellner [117] measured a propensity for production of CH_3CCH_2 over CH_2CHCH_2 of about 7 : 1 for the H atom reaction with allene. Scherzer *et al.* [116] reported essentially exclusive (more than 99%) production of $CH_3CH_2CCH_2$ from CH_3 + allene addition. A similar conclusion was made for other alkyl radical additions [118]. The unique hybridization of allene requires an electronic rearrangement before the allyl configuration can be realized. It has therefore been postulated that the energy associated with the resonance structure is unavailable in the transition state for addition and does not affect the rate coefficient.

An explanation assuming terminal addition for the Cl+ allene reaction (with an approximately 20 kcal $\mathrm{mol^{-1}}$ well depth) appears impossible to reconcile with the data. Stabilization must again compete with an addition–elimination or an abstraction process with an effective barrier of 3.3 kcal $\mathrm{mol^{-1}}$. Such a rationalization cannot explain the factor of ten increase in the rate coefficient between Cl+ propyne and Cl+ allene. The 292 K results of Farrell and Taatjes show a Cl+ allene addition rate coefficient of 2.0×10^{-10} $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$ at 5 Torr, compared with 5.1×10^{-12} $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$ for Cl+ propyne at 4.4 Torr. The 5 Torr Cl+ allene rate coefficient places a strict lower limit on k_0 of 1.3×10^{-27} $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$. The true value for k_0 must be significantly larger, since the Cl+ allene reaction is not at all near the low-pressure limit at 5 Torr (He), but this lower limit is already more than three times larger than the low-pressure limiting rate coefficient for Cl+ propene [65]. In order to generate the observed difference in the pressure dependence for Cl+ propyne and Cl+ allene under the assumption of terminal addition, an implausibly large difference between the density of states for CH_2ClCCH_2 and CH_3CCHCl must be postulated.

Evidently, unlike the case for addition of CH_3 radicals or H atoms, the allylic configuration does contribute to the transition state for Cl addition to allene. The increased well depth is responsible for the large rate coefficient for addition and for the shallow fall-off with pressure. The reaction with Cl displays other differences from the addition of H atom or CH_3. First, both H and CH_3 additions show a positive activation energy [116, 117]. Second, the *A* factors for the addition of H (1.4×10^{-11} $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$) [117] and CH_3 (9.55×10^{-14} $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$) [116] are considerably smaller than that for the Cl reaction ($k_{\mathrm{add}} = 4.38 \times 10^{-10}$ $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$ at 760 Torr and 295 K) [42]. It appears that the barrierless addition of Cl atom proceeds via a qualitatively different transition state than the energetically constrained and tighter transition states for CH_3 and H atom addition. The current results on the Cl+ allene reaction suggest that an investigation of the addition products for this and perhaps other halogen+ allene reactions would greatly enhance the understanding of these reactions.

6. The role of addition–elimination in exothermic metatheses

The previous sections have discussed the resolution of the competing metathesis and addition channels in the reactions of Cl with unsaturated species, which can be accomplished by time-resolved infrared absorption as well as by other methods. However, understanding the details of the metathesis reaction necessitates a further subdivision of the mechanism. In exothermic Cl+ alkene and Cl+ alkyne reactions a full consideration of the reaction must include the possibility of an addition–elimination path to HCl production. Most of the experiments performed to date are not equipped to distinguish unambiguously an addition–elimination mechanism from a simple abstraction mechanism. In particular, time-resolved product formation measurements can determine the total metathesis rate but do not directly establish the mechanism of the metathesis. Biexponential time traces, as seen in measurements of HCl production in Cl+ propene and Cl+ propyne reactions, can arise from a delayed elimination of HCl or from a reversible addition reaction with a competing abstraction pathway. The exact role that addition–elimination plays in these and other Cl+ alkene reactions is not yet clear, and further study is necessary. However, in at least two cases, the reactions of Cl with propene and with allene, evidence is seen for an addition–elimination component.

While an extensive body of literature exists on the elimination of HCl and HF from stable molecules, there is a marked lack of experimental or theoretical studies on elimination from radical species. Typical experimental investigations of HX elimination have utilized chemical activation (i.e. radical–radical recombination reactions) or photolysis to produce molecules which are excited above the threshold to elimination. Experiments on the effect of methyl and halogen substitution on HX elimination have suggested that ionic curves play a role in the elimination process and that electron donating substituents at either the α-C atom or the β-C atom (relative to the departing halogen atom) tend to lower the barrier to elimination [140, 141]. For example, the barrier to HF elimination in CHF_2CH_3 ($E_0 = 61$ kcal mol^{-1}) is reduced by 7 kcal mol^{-1} if an α-H atom is replaced by a methyl group ($E_0(CH_3CF_2CH_3) = 54$ kcal mol^{-1}) [140]. If in fact addition–elimination occurs in Cl+ alkene reactions, a radical centre evidently lowers the barrier even further. A typical energy barrier to four-centre HCl elimination is 50–60 kcal mol^{-1} (e.g. $E_0(CH_3CH_2Cl) = 55$ kcal mol^{-1}) [142]. Such a large barrier height in the chloropropyl radical, for example, which is bound by only 20 kcal mol^{-1} with respect to Cl+ propene, would preclude any role for addition–elimination in that reaction.

The plainest experimental evidence for an addition–elimination reaction is a decrease in the rate coefficient with increasing pressure, which arises as collisional stabilization of the adduct exceeds the elimination rate. Such a case arises, for example, in the reaction of C_2H_5 and C_3H_7 with O_2, where elimination of HO_2, either directly or via rearrangement to a hydroperoxy radical, competes with the formation of the alkylperoxy radical [112, 143–146]. The yield of the alkene in these reactions displays a strong inverse pressure dependence which has been measured by several investigators.

Auxiliary evidence for addition–elimination may be found in energy disposal into

HCl product vibration. The study of vibrational energy distributions from abstraction and from elimination has a long history, dating back to the first investigations of infrared chemiluminescence [71]. Qualitatively, abstraction is expected to result in more vibrational excitation of the HCl product, since the abstraction process proceeds via a direct removal of the H atom with the vibrations of the alkyl partner remaining relatively unaffected. In particular, in the case where the transition state for abstraction occurs at an extended H–Cl distance, much of the available energy is expected to be transferred to HCl vibration [147]. The highly exothermic abstraction reaction of H atoms with Cl_2 produces vibrational population inversions, which has been exploited in HCl chemical lasers [148]. An addition–elimination mechanism, on the other hand, presumes a kinetically significant lifetime for the RH–Cl adduct, allowing vibrational energy to be randomized in the adduct molecule and reducing preferential channelling into the H–Cl product. Nonetheless, significant vibrational excitation can result from an elimination process [71–73, 130, 140, 142, 149].

Setser and co-workers [72] have investigated the vibrational energy disposal in a number of abstraction and elimination reactions involving halogenated hydrocarbons. Elimination from chemically activated haloethanes shows typical vibrational fractions of $f_v \approx 0.1$–0.2, while abstractions tend to show higher vibrational excitation, $f_v \approx 0.4$. Setser and co-workers measured the vibrational distribution of HCl formed from $H + CH_2CH_2Cl$ and found a bimodal distribution from which they estimated separate abstraction and elimination contributions. The calculated elimination distribution is hot ($f_v = 0.155$) but is a monotonically decreasing function of v; the abstraction produces higher vibrational excitation ($f_v = 0.33$) and an inverted distribution. In explaining the vibrational distributions from elimination processes, a distinction is commonly made between the excess energy above the barrier to elimination (called E_X which equals the total energy minus the potential energy at the barrier), which is available for redistribution in the transition state, and the energy required to surmount the barrier (called E_P which equals the potential energy at the barrier minus the final potential energy), which is released only after proceeding through the transition-state region. Zamir and Levine [149] formulated a sum rule which proposed separate partitioning of these two amounts of energy, with E_P more likely to appear as HX product vibration. Setser and co-workers [73] applied this formulation in discussing HF elimination from fluoroalkanes. They found that the experimental results could be described by assuming statistical partitioning of E_X in the transition state, and placing approximately 25% and 35% of E_P into HF vibration for four-centre and three-centre eliminations respectively. The extensive studies of elimination and abstraction reactions in stable systems provided a background for consideration of the evidence for addition–elimination contributions in exothermic Cl + alkene reactions, which invoke elimination from a chloroalkyl adduct.

6.1. *Propene*

The reaction of Cl with propene exhibits a metathesis component that decreases with increasing pressure between 10 and 100 Torr. The rate coefficient for HCl formation has been shown by Kaiser and Wallington [65] to reach a plateau below 10 Torr, with an effective rate coefficient of $(3.7 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This number is in excellent agreement with the infrared absorption results of Pilgrim and Taatjes [54], who found $k_{\text{metathesis}} = (3.7 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 5 and 10 Torr total pressure (Ar). The reduction of the metathesis rate coefficient with increasing pressure is a clear mark of an addition–elimination process. Kaiser and

Wallington applied a Lindemann mechanism to estimate the ratio of simple redissociation to elimination of the initially formed chloropropyl adduct as 18 : 1, using their value for k_∞ as the rate coefficient for adduct formation. If the A factors for C–Cl bond scission and HCl elimination were equal, this ratio would imply an upper limit for the barrier to elimination of 1.7 kcal mol^{-1} above the entrance channel. Of course, the A factor for four-centre elimination can be expected to be considerably smaller than that for a direct C–Cl bond fission. If the A factor for HCl elimination were 100 times smaller, the elimination barrier could be about 1 kcal mol^{-1} below the Cl+ propene asymptote. In any case, the elimination barrier must be no more than a few kilocalories per mole larger than the Cl–propene well depth to permit significant addition–elimination contribution to the reaction.

As discussed above, direct abstraction is expected to produce more vibrational excitation in the HCl product than an addition–elimination. The vibrational energy disposal in the Cl+ propene reaction has been measured using infrared absorption probing [54]. The reaction of Cl with propene is sufficiently faster than the vibrational relaxation of HCl in the system that the biexponential production of HCl could be ignored. Comparison of the time-dependent signal with CO_2 buffer and with Ar buffer allowed extraction of the vibrational branching fraction and the vibrational energy transfer rate of HCl ($v = 1$) with propene. A significant fraction of the HCl produced was found to be formed in the vibrationally excited state. A branching fraction of 0.48 ± 0.06 into $v = 1$ was determined in the infrared absorption experiments, which corresponds to a vibrational energy disposal of $f_v = 0.28$. This sizeable partitioning of reaction exothermicity into HCl vibration is consistent with HCl formation from a direct abstraction mechanism. However, vibrational excitation is also possible from addition–elimination, and a clear mechanistic distinction is difficult based solely on the vibrational energy disposal.

The vibrational excitation in elimination systems can often be described using a modified statistical theory. Seakins *et al.* [130] used such a theory to describe the vibrational distribution resulting from the reaction of Cl atoms with ethyl radicals. In that work a statistical partitioning of vibrational energy was performed at the transition state for elimination, which was modelled as ethylene+ HCl, but with a reduced frequency for the HCl molecule. A similar treatment has been carried out by Pilgrim and Taatjes [54] for the Cl+ propene reaction, using an effective HCl vibrational frequency of 1400 cm^{-1} at the transition state and taking the other frequencies from published *ab initio* calculations on the allyl radical. Such a simple calculation would predict a fraction of vibrationally excited HCl of only about 15%, much smaller than the observed HCl ($v = 1$) fraction. A sum rule such as that proposed by Zamir and Levine [149] may give a larger predicted vibrational excitation in the elimination. Placing 25% of the energy E_P into HCl vibration, as suggested by Setser and co-workers [73], would require a barrier to elimination of about 16 kcal mol^{-1} above allyl+ HCl, or 1.7 kcal mol^{-1} above Cl+ propene, to produce the observed distributions. This energy is considerably larger than the observed activation energy of 0.17 kcal mol^{-1}; the vibrational energy distribution therefore implies some participation of a direct abstraction channel in the reaction.

However, there must also be an addition–elimination component to the Cl+ propene reaction, as indicated by the pressure dependence of the metathesis rate coefficient. Since this component presumably produces less HCl ($v = 1$), the vibrational excitation in the 'pure' abstraction reaction must be greater than the $f_v = 0.28$ observed for the total reaction. By combining results from the various experimental investigations, an estimate can be made of the vibrational excitation from the abstraction itself. Using the measurement of 2.3×10^{-11} cm^3 molecule^{-1} s^{-1} obtained by Kaiser and Wallington for the abstraction rate coefficient and the low-pressure metathesis rate coefficient of 3.7×10^{-11} cm^3 molecule^{-1} s^{-1}, 38% of the reaction proceeds by addition–elimination at room temperature and 10 Torr. If this portion is assumed to obey the modified statistical prediction of 15% vibrational energy disposal, the fraction of the exothermicity which must be channelled to HCl vibrational energy in the abstraction would be $f_v = 0.37$, similar to that observed in H+ halocarbon abstraction reactions. A calculation based on sum rules gives a similar picture. As discussed above, the barrier height of 1.7 kcal mol^{-1} above Cl+ propene, required to make a sum rule model of addition–elimination reproduce the observed vibrational energy distribution, is much larger than the observed activation energy. Furthermore, this barrier height would be consistent with the 18:1 ratio of C–Cl fission to HCl elimination inferred by Kaiser and Wallington only under the implausible assumption that the *A* factors for elimination and C–Cl bond fission are identical. For comparison, using a barrier height of 1 kcal mol^{-1} below the reactant channel, a similar sum rule would predict $f_v = 0.23$ for the addition–elimination, and hence (with 38% addition–elimination) would require $f_v = 0.33$ for the abstraction. Taken together, the measurements of vibrational energy disposal and of the pressure dependence of the metathesis rate both indicate a prominent role for abstraction in Cl+ propene, with a secondary but significant addition–elimination contribution.

6.2. *Allene*

As discussed above, the reaction of Cl with allene is unusual among Cl+ alkene reactions [53]. The availability of a deep well corresponding to chloroallyl formation is manifested in a reduced dependence on the total pressure compared with that of the Cl+ propyne reaction. The metathesis shows an activation energy of 3.3 ± 0.6 kcal mol^{-1}, significantly larger than that of other exothermic metatheses. By comparison, Cl+ propane has zero activation energy, Cl+ propene 0.17 ± 0.10 kcal mol^{-1} and Cl+ propyne 1.3 ± 0.5 kcal mol^{-1}. More tellingly, the *A* factor for the metathesis channel is $(3.7\pm1.7)\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, an order of magnitude larger than expected, and far too large to be explained by an abstraction mechanism. This suggests that an addition–elimination mechanism may dominate HCl formation in this reaction.

If addition–elimination dominates the metathesis channel, the vibrational energy distribution should be consistent with an elimination mechanism. The vibrational energy disposal in this reaction has not been definitively measured because of the small HCl yield at room temperature, but preliminary measurements have been reported at elevated temperatures. For Cl+ allene at 600 K, an effective $v = 1$ yield of 0.42 has been measured, giving $f_v = 0.25$, similar to results for Cl+ propene and Cl+ propyne [53]. These measurements did not consider possible formation of $v = 2$ in the reaction, which might lead to a slight underestimate of vibrational excitation. At 600 K, approximately 12% of the collisions have sufficient energy to produce propargyl+ HCl ($v = 2$). The $v = 1$ yield of 0.42 can be modelled using the rule of thumb that about 25% of the energy below the barrier E_P is parcelled into HCl vibration. A barrier for elimination in the Cl+ allene system lying above the propargyl+ HCl asymptote by 14.2 kcal mol^{-1}, that is at the energy of the Cl+ allene reactants, could reproduce the observed vibrational energy disposal. This value for the barrier height is consistent with the observed activation energy of 3.3 kcal mol^{-1} for the metathesis. In the

Cl+ allene reaction an addition–elimination mechanism accounts for all the experimental observations.

The nature of the metathesis reactions of Cl with alkenes and alkynes remains imperfectly understood. The related reactions of Cl with alkanes have been extensively studied by molecular beam scattering, and these dynamical studies have created a set of stringent tests for sophisticated calculations. Similar studies on the Cl+ unsaturated hydrocarbon reactions could be instrumental in unravelling the richer chemistry in these systems. For example, both the vibrational energy distribution and the differential cross-section should be different for abstraction and addition–elimination. The HCl ($v = 0$) and HCl ($v = 1$) products of the Cl+ propene reaction may therefore display markedly different angular distributions in molecular scattering measurements. Vibrational energy disposal alone, as discussed above, is an inexact measure of the reaction mechanism of these reactions, since the expected differences between addition–elimination and abstraction can be subtle for the small exothermicities involved. More detailed investigations of rotational as well as vibrational energy disposal in the exothermic Cl+ alkene reactions, perhaps by FTIR absorption techniques, would be valuable in distinguishing their mechanisms. However, accurate theoretical estimates of the vibrational and rotational excitation expected in the various pathways will probably be critical to interpreting these measurements.

7. Conclusions

The reactions of Cl atoms with alkenes display a range of kinetic behaviours which depends sensitively on the thermochemistry and mechanistic details of the reactions. The technique of time-resolved infrared absorption probing of product formation has been able to provide a great deal of information, often complementary to other kinetic techniques, which contributes to the effort to unravel the cases where metathesis and addition compete. There remains a great deal of uncertainty concerning the nature of the metathesis reaction in these systems, whether addition–elimination is a significant pathway, and whether the abstraction channel resembles the more thoroughly investigated Cl+ saturated hydrocarbon reactions. Further kinetic and dynamical studies will be required to understand these reactions in detail.

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Appendix A. Time-resolved kinetics of competing addition and metathesis

A.1. *Time-resolved HCl product formation*

The kinetics governing a simple one-step reaction where time-resolved product formation rates are measured are quite straightforward. For Cl atoms reacting with a hydrocarbon to form HCl plus an alkyl radical, the kinetics scheme is as follows:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Cl}] &= -k_1[\mathrm{RH}][\mathrm{Cl}], \\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{HCl}] &= k_1[\mathrm{RH}][\mathrm{Cl}]. \end{aligned} \qquad (\mathrm{A}\ 1)$$

In practice, it is often necessary to include removal of species by diffusion or reaction with impurities, but these details are neglected for the present treatment. The HCl time profile is then given by

$$[\mathrm{HCl}]_t = [\mathrm{Cl}]_0 [1 - \exp(-k_1[\mathrm{RH}]t)]. \tag{A 2}$$

Where addition and metathesis channels compete, the kinetic equations governing the reaction must be expanded. For the simplest case, where an irreversible addition competes with a direct abstraction, the modification is minimal:

$$\left.\begin{aligned}
&\mathrm{Cl} + \mathrm{C}_n\mathrm{H}_m \xrightarrow{k_1} \mathrm{HCl} + \mathrm{C}_n\mathrm{H}_{m-1},\\
&\mathrm{Cl} + \mathrm{C}_n\mathrm{H}_m \xrightarrow{k_2} \mathrm{C}_n\mathrm{H}_m\mathrm{Cl},\\
&[\mathrm{Cl}]_t = [\mathrm{Cl}]_0 \exp\{-(k_1 + k_2)[\mathrm{C}_n\mathrm{H}_m]t\},\\
&[\mathrm{HCl}]_t = \frac{[\mathrm{Cl}]_0 k_1}{k_1 + k_2}(1 - \exp\{-(k_1 + k_2)[\mathrm{C}_n\mathrm{H}_m]t\}).
\end{aligned}\right\} \tag{A 3}$$

The production of HCl follows single-exponential behaviour with the rate coefficient $k_1 + k_2$ for total removal of Cl atoms. The metathesis rate is simply this total rate coefficient times the HCl yield, which is defined as $[\mathrm{HCl}]_\infty/[\mathrm{Cl}]_0 = k_1/(k_1 + k_2)$. However, if the addition becomes reversible (i.e. if redissociation of the adduct is significant on the time scale of the experiments), then the kinetic behaviour can become more complex.

A.2. *Addition–elimination competing with stabilization*

The production of HCl in some Cl+ alkene systems can occur by two pathways, either direct abstraction with rate coefficient k_A or addition with rate coefficient k_B followed by HCl elimination (k_E). In these cases the data can be modelled using a modified Lindemann mechanism, taking into account both collisional stabilization (k_M) and addition–elimination:

$$\mathrm{Cl} + \mathrm{C}_n\mathrm{H}_m \xrightarrow{k_A} \mathrm{HCl} + \mathrm{C}_n\mathrm{H}_{m-1}, \tag{A 4}$$

$$\xrightarrow{k_E} \mathrm{HCl} + \mathrm{C}_n\mathrm{H}_{m-1}$$

$$\mathrm{Cl} + \mathrm{C}_n\mathrm{H}_m \xrightarrow{k_B} \mathrm{C}_n\mathrm{H}_m\mathrm{Cl}^{\#} \tag{A 5}$$

$$\xrightarrow{k_M} \mathrm{C}_n\mathrm{H}_m\mathrm{Cl},$$

where $\mathrm{C}_n\mathrm{H}_m\mathrm{Cl}^{\#}$ designates an energized adduct. The solution to the kinetic equations corresponding to this mechanism gives a biexponential expression for the HCl concentration as a function of time:

$$[\mathrm{HCl}]_t = [\mathrm{Cl}]_0 (A - B\exp\{-(k_A + k_B)[\mathrm{C}_n\mathrm{H}_m]t\} - C\exp[-(k_E + k_M)t]). \tag{A 6}$$

(Note that the previously reported expression for Cl+ propene has an erroneous factor of $\frac{1}{2}$ in the exponents) [54].) Since the HCl yield is the ratio of the effective rate coefficients for the channels producing HCl to the rate coefficient for removal of Cl atoms, that is

$$\phi_{\mathrm{HCl}} \equiv \frac{[\mathrm{HCl}]_\infty}{[\mathrm{Cl}]_0} = A = \frac{k_A + k_B k_E/(k_E + k_M)}{k_A + k_B} \equiv \frac{k_1}{k_1 + k_2}, \tag{A 7}$$

the observed time constants can be straightforwardly related to the rate coefficients k_1 and k_2. The quantity $k_A + k_B$ is readily identified as the total rate coefficient $k_1 + k_2$, and the effective rate coefficient k_1 for HCl production is then given by $\phi_{\mathrm{HCl}}\,(k_A + k_B)$. The rate coefficient k_1 can be deduced by fitting a biexpoential to the observed data and plotting the sum of the two fitted time constants (since it is not known *a priori* which time constant is larger) as a function of alkene concentration. The slope of such a plot is then the total rate coefficient $k_1 + k_2$, which yields k_1 when multiplied by the HCl yield.

A.3. *Reversible addition competing with direct metathesis*

A similar treatment is possible for the case where the initial addition step is thermally reversible. In this case the system is expected to reach a quasisteady state when thermal dissociation of the adduct has the same rate as collisional formation of the adduct. This situation also produces a biexponential time profile for HCl product formation, where the fast exponential corresponds to establishment of a quasisteady state for addition and the longer time constant corresponds to production of HCl by dissociation and subsequent metathesis reaction. The kinetic scheme is as follows:

$$\mathrm{Cl} + \mathrm{C}_n\mathrm{H}_m \xrightarrow{k_A} \mathrm{HCl} + \mathrm{C}_n\mathrm{H}^{m-1}, \tag{A 8}$$

$$\mathrm{Cl} + \mathrm{C}_n\mathrm{H}_m \overset{k_{\pm B}}{\longleftrightarrow} \mathrm{C}_n\mathrm{H}_m\mathrm{Cl}^{\#} \xrightarrow{k_M} \mathrm{C}_n\mathrm{H}_m\mathrm{Cl}. \tag{A 9}$$

Note that this formulation is equivalent to that for an addition with rate coefficient k_B and a thermal dissociation with rate coefficient k_{-B} in competition with some reactive removal process represented by the rate coefficient k_M. Solving the related differential equations for the HCl concentration yields

$$[\mathrm{HCl}]_t = [\mathrm{Cl}]_0\{A + C_+ \exp[-\tfrac{1}{2}(k+\kappa)\,t] + C_- \exp[-\tfrac{1}{2}(k-\kappa)\,t]\}, \tag{A 10}$$

where $k = (k_A + k_B)[\mathrm{C}_n\mathrm{H}_m] + k_B + k_M$ and

$$A = \frac{k_A(k_{-B} + k_M)}{k_B k_M + k_A(k_{-B} + k_M)}, \tag{A 11}$$

$$C_\pm = \frac{k_A[(k_{-B} + k_M)(k_A[\mathrm{C}_n\mathrm{H}_m] + k_B[\mathrm{C}_n\mathrm{H}_m] - k_{-B} - k_M \pm \kappa) - 2k_B[\mathrm{C}_n\mathrm{H}_m]k_{-B}]}{2\kappa[k_B k_M + k_A(k_{-B} + k_M)]}, \tag{A 12}$$

$$\kappa = \{k^2 - 4[\mathrm{C}_n\mathrm{H}_m][k_B k_M + k_A(k_{-B} + k_M)]\}^{1/2}. \tag{A 13}$$

Since the two situations both produce a biexponential it is difficult to distinguish contributions from addition–elimination and reversible addition followed by abstraction on the basis of a simple product formation measurement. The two pathways may be distinguishable by other means, such as product energy distributions and pressure dependences, as discussed above.

As the temperature increases, the dissociation of the adduct is sufficiently fast that a steady-state approximation can be made for the energized adduct, $\mathrm{C}_n\mathrm{H}_m\mathrm{Cl}^{\#}$. The

HCl concentration then exhibits simple exponential behaviour, with a rise time constant equal to the pseudo-first-order rate coefficient for Cl atom removal, that is

$$[\mathrm{HCl}]_t \propto 1 - \exp\{-(k_1 + k_2)[\mathrm{C}_n\mathrm{H}_m]\,t\} \qquad \text{(A 14)}$$

This situation is equivalent to the case of an irreversible addition, since thermal dissociation of the chlorinated adduct has been neglected. Under these conditions, the rate coefficient for HCl production can again be directly extracted as the slope of a plot of the HCl rise time against $[\mathrm{C}_n\mathrm{H}_m]$ multiplied by the HCl yield.

A.4. *Vibrationally excited HCl*

For reactions where a significant fraction of the HCl product is produced vibrationally excited, the metathesis reaction can be expressed as

$$\mathrm{Cl} + \mathrm{C}_n\mathrm{H}_m \xrightarrow{k_1[\mathrm{C}_n\mathrm{H}_m]} f\,\mathrm{HCl}(v=1) + (1-f)\,\mathrm{HCl}(v=0) + \mathrm{C}_n\mathrm{H}_{m-1}, \qquad \text{(A 15)}$$

where f is the fractional HCl population formed in $v = 1$. The full kinetics system now must include collisional vibrational relaxation. If (as is often the case) the relaxation by the buffer and photolyte are negligible, the vibrational relaxation will proceed predominantly by collisions with the hydrocarbon reactant:

$$\mathrm{HCl}(v=1) \xrightarrow{k_{\mathrm{VET}}[\mathrm{C}_n\mathrm{H}_m]} \mathrm{HCl}(v=0). \qquad \text{(A 16)}$$

If HCl formation is much faster than vibrational relaxation, the kinetics for the metathesis is described by equations (A 15) and (A 16). These equations form a simple A → B → C type reaction scheme which is easily solved by standard methods to give the populations in HCl ($v = 0$) and HCl ($v = 1$). Absorption on the $v = 1 \leftarrow 0$ transition will be proportional to

$$\frac{F_{\mathrm{B,lower}}}{g_{\mathrm{lower}}}[\mathrm{HCl}(v=0)]_t - \frac{F_{B,\mathrm{upper}}}{g_{\mathrm{upper}}}[\mathrm{HCl}(v=1)]_t, \qquad \text{(A 17)}$$

where F_B is the rotational Boltzmann fraction and g is the rotational degeneracy $2J + 1$ for the upper or lower state of the transition. The time behaviour of the observed adsorption signal is thus given by

$$\begin{aligned} \text{absorption} \propto 1 &- \frac{(1+\varepsilon) f (k_1 + k_2)}{(k_1 + k_2) - k_{\mathrm{VET}}} \exp\{-k_{\mathrm{VET}}[\mathrm{C}_n\mathrm{H}_m]\,t\} \\ &+ \left(\frac{(1+\varepsilon) f (k_1 + k_2)}{(k_1 + k_2) - k_{\mathrm{VET}}} - 1 \right) \exp\{-(k_1 + k_2)[\mathrm{C}_n\mathrm{H}_m]\,t\}, \end{aligned} \qquad \text{(A 18)}$$

where ε is a correction for the different rotational Boltzmann fractions in the upper and lower levels:

$$\varepsilon = \frac{Q_{\mathrm{rot}}^{v=1} \exp[-J_{\mathrm{lower}}(J_{\mathrm{lower}} + 1) B_{v=0}/kT]}{Q_{\mathrm{rot}}^{v=0} \exp[-J_{\mathrm{upper}}(J_{\mathrm{upper}} + 1) B_{v=1}/kT]} \approx \exp\left(\frac{85.4}{T}\right) \quad \text{for HCl R(2).} \qquad \text{(A 19)}$$

Here Q is a rotational partition function and B is a rotational constant. Using this expression the $(1 \leftarrow 0)$ signal as a function of hydrocarbon concentration can be used to extract vibrational branching fractions directly without the need to calibrate absorption signals on different vibrational transitions.

References

[1] Finlayson-Pitts, B. J., and Pitts, J. N., Jr, 1986, *Atmospheric Chemistry: Fundamentals and Experimental Techniques* (New York: Wiley–Interscience).

[2] Rowland, F. S., 1991, *A. Rev. phys. Chem.*, **42**, 731.

[3] Molina, M. J., Molina, L. T., and Kolb, C. E., 1996, *A. Rev. Phys. Chem.*, **47**, 327.

[4] Finlayson-Pitts, B. J., 1993, *Res. Chem. Intermediates*, **19**, 235.

[5] Spicer, C. W., Chapman, E. G., Finlayson-Pitts, B. J., Plastridge, R. A., Hubbe, J. M., Fast, J. D., and Berkowitz, C. M., 1998, *Nature*, **394**, 353.

[6] Keene, W. C., 1995, *Naturally-Produced Organohalogens*, edited by A. Grimvall and E. W. B. de Leer (Dordrecht: Kluwer), p. 363.

[7] Oum, K. W., Lakin, M. J, DeHaan, D. O., Brauers, T., and Finlayson-Pitts, B. J., 1998, *Science*, **279**, 74.

[8] Tirtowidjojo, M. M., Colegrove, B. T., and Durant, J. L., 1995, *Ind. Engng Chem.*, **34**, 4202.

[9] Tsang, W., 1990, *Combust. Sci. Technol.*, **74**, 99.

[10] Frenklach, M., 1990, *Combust. Sci. Technol.*, **74**, 283.

[11] Benson, S. W., 1960, *Foundations of Chemical Kinetics* (New York: McGraw-Hill).

[12] Alagia, M., Balucani, N., Casavecchia, P., Stranges, D., and Volpi, G. G., 1995, *J. chem. Soc., Faraday Trans.*, **91**, 575.

[13] Yen, Y., Wang, Z., Xue, B., and Koplitz, B., 1994, *J. phys. Chem.*, **98**, 4.

[14] Varley, D. F., and Dagdigian, P. J., 1995, *J. phys. Chem.*, **99**, 9843.

[15] Varley, D. F., and Dagdigian, P. J., 1996, *Chem. Phys. Lett.*, **255**, 393.

[16] Varley, D. F., and Dagdigian, P. J., 1996, *J. phys. Chem.*, **100**, 4365.

[17] Simpson, W. R., Orr-Ewing, A. J., and Zare, R. N., 1993, *Chem. Phys. Lett.*, **212**, 163.

[18] Simpson, W. R., Rakitzis, T. P., Kandel, S. A., Orr-Ewing, A. J., and Zare, R. N., 1995, *J. chem. Phys.*, **103**, 7313.

[19] Simpson, W. R., Rakitzis, T. P., Kandel, S. A., Lev-On, T., and Zare, R. N., 1996, *J. phys. Chem.*, **100**, 7938.

[20] Orr-Ewing, A. J., Simpson, W. R., Rakitzis, T. P., Kanel, S. A., and Zare, R. N., 1997, *J. chem. Phys.*, **106**, 5961.

[21] Rakitzis, T. P., Kandel, S. A., Lev-On, T., and Zare, R. N., 1997, *J. chem. Phys.*, **107**, 9392.

[22] Kandel, S. A., Rakitzis, T. P., Lev-On, T., and Zare, R. N., 1997, *Chem. Phys. Lett.*, **265**, 121.

[23] Kandel, S. A., and Zare, R. N., 1998, *J. chem. Phys.*, **109**, 9719.

[24] Kandel, S. A., Rakitzis, T. P., Lev-On, T., and Zare, R. N., 1998, *J. phys. Chem.* A, **102**, 2270.

[25] Blank, D. A., Hemmi, N., Suits, A. G., and Lee, Y. T., 1998, *Chem. Phys.*, **231**, 261.

[26] Berkowitz, J., Ellison, G. B., and Gutman, D., 1994, *J. phys. Chem.*, **98**, 2744.

[27] Semenov, N. N., 1958, *Some Problems in Chemical Kinetics and Reactivity*, Vol. 1 (Princeton University Press).

[28] Semenov, N. N., 1959, *Some Problems in Chemical Kinetics and Reactivity*, Vol. 2 (Princeton University Press).

[29] Streitweiser, A., Jr, and Heathcock, C. H., 1985, *Introduction to Organic Chemistry* (London: Macmillan).

[30] Franklin, J. A., Goldfinger, P., and Huybrechts, G., 1968, *Ber. Bunsenges. phys. Chem.*, **72**, 173.

[31] Ayscough, P. B., Cocker, A. J., Dainton, F. S., and Hirst, S., 1962, *Trans. Faraday Soc.*, **58**, 318.

[32] Ayscough, P. B., Cocker, A. J., Dainton, F. S., and Hirst, S., 1962, *Trans. Faraday Soc.*, **58**, 295.

[33] Hagopian, A. K. E., Knox, J. H., and Thompson, E. A. 1962, *Bull. Soc. chim. Belg.*, **71**, 764.

[34] Sanhueza, E., and Heicklen, J., 1975, *J. Photochem.*, **4**, 17.

[35] Catoire, V., Ariya, P. A., Niki, H., and Harris, G. W., 1997, *Int. J. chem. Kinetics*, **29**, 695.

[36] Kerr, J. A., and Parsonage, M. J., 1972, *Evaluated Kinetic Data on Gas Phase Addition Reactions* (London: Butterworth).

[37] Cvetanovic, R. J., 1963, *Adv. Photochem.*, **1**, 115.
[38] Fettis, G. C., and Knox, J. H., 1964, *Progress in Reaction Kinetics*, Vol. 2, edited by G. Porter (Oxford: Pergamon), p. 1.
[39] Tschuikow-Roux, E., Niedzielski, J., and Faraji, F., 1985, *Can. J. Chem.*, **63**, 1093.
[40] Tschuikow-Roux, E., Yano, T., and Niedzielski, J., 1985, *J. chem. Phys.*, **82**, 65.
[41] Tschuikow-Roux, E., and Niedzielski, J., 1984, *J. Photochem.*, **27**, 141.
[42] Wallington, T. J., Skewes, L. M., and Siegl, W. O., 1988, *J. Photochem. Photobiol.* A, **45**, 167.
[43] Wallington, T. J., and Hurley, M. D., 1992, *Chem. Phys. Lett.*, **189**, 437.
[44] Wallington, T. J., Andino, J. M., Lorkovic, I. M., Kaiser, E. W., and Marston, G., 1990, *J. phys. Chem.*, **94**, 3644.
[45] Atkinson, R., and Aschmann, S. M., 1985, *Int. J. chem. Kinetics*, **17**, 33.
[46] Atkinson, R., and Aschmann, S. M., 1987, *Int. J. chem. Kinetics*, **19**, 1097.
[47] Bedjanian, Y., Laverdet, G., and LeBras, G., 1998, *J. phys. Chem.* A, **102**, 953.
[48] Notario, A., LeBras, G., and Mellouki, A., 1997, *Chem. Phys. Lett.*, **281**, 421.
[49] Park, J.-Y., Slagle, I. R., and Gutman, D., 1983, *J. phys. Chem.*, **87**, 1812.
[50] Stutz, J., Ezell, M. J., Ezell, A. A., and Finlayson-Pitts, B. J., 1998, *J. phys. Chem.* A, **102**, 8510.
[51] Tyndall, G. S., Orlando, J. J., Wallington, T. J., Dill, M., and Kaiser, E. W., 1997, *Int. J. chem. Kinetics*, **29**, 43.
[52] Davis, D. D., Braun, W., and Bass, A. M., 1970, *Int. J. chem. Kinetics*, **2**, 101.
[53] Farrell, J. T., and Taatjes, C. A., 1998, *J. phys. chem.* A, **102**, 4846.
[54] Pilgrim, J. S., and Taatjes, C. A., 1997, *J. phys. Chem.* A, **101**, 5776.
[55] Pilgrim, J. S., and Taatjes, C. A., 1997, *J. phys. Chem.* A, **101**, 4172.
[56] Pilgrim, J. S., and Taatjes, C. A., 1997, *J. phys. Chem.* A, **101**, 8741.
[57] Pilgrim, J. S., McIlroy, A., and Taatjes, C. A., 1997, *J. phys. Chem.* A, **101**, 1873.
[58] Lee, F. S. C., and Rowland, F. S., 1977, *J. phys. Chem.*, **81**, 1222.
[59] Lee, F. S. C., and Rowland, F. S., 1980, *J. phys. Chem.*, **84**, 1876.
[60] Subramonia Iyer, R., Rogers, P. J., and Rowland, F. S., 1983, *J. phys. Chem.*, **87**, 3799.
[61] Subramonia Iyer, R., Chen, C.-Y., and Rowland, F. S., 1985, *J. phys. Chem.*, **89**, 2042.
[62] Subramonia Iyer, R., and Rowland, F. S., 1985, *J. phys. Chem.*, **89**, 3730.
[63] Ragains, M. L., and Finlayson-Pitts, B. J., 1997, *J. phys. Chem.* A, **101**, 1509.
[64] Stutz, J., Ezell, M. J., and Finlayson-Pitts, B. J., 1997, *J. phys Chem.* A, **101**, 9187.
[65] Kaiser, E. W., and Wallington, T. J., 1996, *J. phys. Chem.*, **100**, 9788.
[66] Kaiser, E. W., and Wallington, T. J., 1996, *J. phys. Chem.*, **100**, 4111.
[67] Zhu, T., Yarwood, G., Chen, J., and Niki, H., 1994, *J. phys Chem.*, **98**, 5065.
[68] Kanamori, H., Butler, J. E., Kawaguchi, K., Yamada, C., and Hirota, E., 1985, *J. molec. Spectrosc.*, **113**, 262.
[69] Petek, H., Nesbitt, D. J., Ogilby, P. R., and Moore, C. B., 1983, *J. phys. Chem.*, **87**, 5367.
[70] Unfried, K. G., Glass, G. P., and Curl, R. F., 1991, *Chem. Phys. Lett.*, **177**, 33.
[71] Sloan, J. J., 1988. *J. phys. Chem.*, **92**, 18.
[72] Arunan, E., Rengarajan, R., and Setser, D. W., 1994, *Can. J. Chem.*, **72**, 568.
[73] Arunan, E., Wategaonkar, S. J., and Setser, D. W., 1991, *J. phys. Chem.*, **95**, 1539.
[74] White, J. U., 1942, *J. opt. Soc. Am.*, **32**, 285.
[75] Pilgrim, J. S., Jennings, R. T., and Taatjes, C. A., 1997, *Rev. scient. Instrum.*, **69**, 1875.
[76] Herriott, D., Kogelnik, H., and Kompfner, R., 1964, *Appl. Optics*, **3**, 523.
[77] Supplee, J. M., Whittaker, E. A., and Lenth, W., 1994, *Appl. Optics*, **33**, 6294.
[78] Hall, J. L., Hollberg, L., Baer, T., and Robinson, H. G., 1981, *Appl. Phys. Lett.*, **39**, 680.
[79] Bjorklund, G. C., 1980, *Optics Lett.*, **5**, 15.
[80] North, S. W., Fei, R., Sears, T. J., and Hall, G. E., 1997, *Int. J. chem. Kinetics*, **29**, 127.
[81] Powers, P. E., Taatjes, C. A., and Kulp, T. J., 1996, *Appl. Optics*, **35**, 4735.
[82] Janik, G. R., Carlisle, C. B., and Gallagher, T. F., 1986, *J. opt. Soc. Am.* B, **3**, 1070.
[83] Cooper, D. E., and Warren, R. E., 1987, *Appl. Optics*, **26**, 3726.
[84] Haugen, H. K., Weitz, E., and Leone, S. R., 1985 *J. chem. Phys.*, **83**, 3402.
[85] Baulch, D. L., Duxbury, J., Grant, S. J., and Montague, D. C., 1981, *J. phys. Chem. Ref. Data*, **10**, Suppl. 1.
[86] Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Jr, Kerr, J. A., Rossi, M. J., and Troe, J., 1997, *J. phys. Chem. Ref. Data*, **26**, 521.

[87] DeMore, W. B., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J., Ravishankara, A. R., Kolb, C. E., and Molina, M. J., 1997, *Chemical Kinetics Photochemical Data for Use in Stratospheric Modeling. Evaluation Number 12*, JPL Publication 97-4 (Pasadena, CA: Jet Propulsion Laboratory).

[88] Heneghan, S. P., Knoot, P. A., and Benson, S. W., 1981, *Int. J. chem. Kinetics*, **13**, 677.

[89] Senkan, S. M., and Quam, D., 1992, *J. phys. Chem.*, **96**, 10837.

[90] Taatjes, C. A., Christensen, L., Hurley, M. D., and Wallington, T. J., 1999, (to be published).

[91] Roberto-Neto, O., Coitiño, E. L., and Truhlar, D. G., 1998, *J. phys. Chem.* A, **102**, 4568.

[92] Espinosa-García, J., and Corchado, J. C., 1996, *J. chem. Phys.*, **105**, 3517.

[93] Wallington, T. J., and Hurley, M. D., 1992, *Chem. Phys. Lett.*, **194**, 309.

[94] Dobis, O., Benson, S. W., and Mitchell, T. J., 1994, *J. phys. Chem.*, **98**, 12264.

[95] Ravishankara, A. R., and Wine, P. H., 1980, *J. chem. Phys.*, **72**, 25.

[96] Fletcher, I. S., and Husain, D., 1977, *Chem. Phys. Lett.*, **49**, 516; 1978, *J. chem. Soc. Faraday Trans.* II, **74**, 203.

[97] (*a*) Tyndall, G. S., Orlando, J. J., and Kegley-Owen, C. S., 1995, *J. chem. Soc., Faraday Trans.*, **91**, 3055; (*b*) Matsumi, Y., Izumi, K., Skorokhodov, V., Kawasaki, M., and Tanaka, N., 1997, *J. phys. Chem.* A, **101**, 1216.

[98] Hemmi, N., and Suits, A. G., 1998, *J. chem. Phys.*, **109**, 5338.

[99] Yu, H.-G., and Nyman, G., 1999, *Phys. Chem. chem. Phys.*, **1**, 1181.

[100] Nyman, G., Yu, H.-G., and Walker, R. B., 1998. *J. chem. Phys.*, **109**, 5896.

[101] Dobbs, K. D., and Dixon, D. A., 1994, *J. phys. Chem.*, **98**, 12584.

[102] Duncan, W. T., and Truong, T. N., 1995, *J. chem. Phys.*, **103**, 9642.

[103] Troe, J., 1977, *J. chem. Phys.*, **66**, 4745.

[104] Troe, J., 1977, *J. chem. Phys.*, **66**, 4758.

[105] Gilbert, R. G., and Smith, S. C., 1990, *Theory of Unimolecular and Recombination Reactions* (Oxford: Blackwell Scientific).

[106] Holbrook, K. A., Pilling, M. J., and Robertson, S. H., 1996, *Unimolecular Reactions* (Chichester, West Sussex: Wiley).

[107] Fulle, D., Hamann, H. F., Hippler, H., and Jansch, C. P., 1997, *Ber. Bunsenges. phys. Chem.*, **101**, 1433.

[108] Nicovich, J. M., Wang, S., McKee, M. L., and Wine, P. H., 1996, *J. phys. Chem.*, **100**, 680.

[109] Ervin, K. M., Gronert, S., Barlow, S. E., Gilles, M. K., Harrison, A. G., Bierbaum, V. M., DePuy, C. H., Lineberger, W. C., and Ellison, G. B., 1990, *J. Am. chem. Soc.*, **112**, 5750.

[110] Brunning, J., and Stief, L. J., 1985, *J. chem. Phys.*, **83**, 1005.

[111] Kaiser, E. W., 1992, *Int. J. chem. Kinetics*, **24**, 179.

[112] Kaiser, E. W., 1995, *J. phys. Chem.*, **99**, 707.

[113] Zhu, L., Chen, W., Hase, W. L., and Kaiser, E. W., 1993, *J. phys. Chem.*, **97**, 311.

[114] Kaiser, E. W., and Wallington, T. J., 1998, *J. phys. Chem.* A, **102**, 6054.

[115] Stutz, J., Ezell, M. J., and Finlayson-Pitts, B. J., 1998, *J. phys. Chem.* A, **102**, 6056.

[116] Scherzer, K., Claus, P., and Dabbagh, M., 1983, *J. prakt. Chem.*, **325**, 680.

[117] Wagner, H. G., and Zellner, R., 1972, *Ber. Bunsenges. phys. Chem.*, **76**, 667.

[118] Getty, R. R., Kerr, J. A., and Trotman-Dickenson, A. F., 1967, *J. chem. Soc.* A, 979.

[119] Atkinson, R., 1989, *Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds*, *J. phys. Chem. Ref. Data*, Monograph 1 (Washington, DC: American Chemical Society).

[120] Tully, F. P., and Goldsmith, J. E. M., 1985, *Chem. Phys. Lett.*, **116**, 345.

[121] Tully, F. P., 1983, *Chem. Phys. Lett.*, **96**, 148.

[122] Knyazev, V. D., and Slagle, I. R., 1996, *J. phys. Chem.*, **100**, 16899.

[123] Dobis, O., and Benson, S. W., 1991, *J. Am. chem. Soc.*, **113**, 6377.

[124] Parmar, S. S., and Benson, S. W., 1988, *J. phys. Chem.*, **92**, 2652.

[125] Dobis, O., and Benson, S. W., 1987, *Int. J. chem. Kinetics*, **19**, 691.

[126] Dobis, O., and Benson, S. W., 1990, *J. Am. chem. Soc.*, **112**, 1023.

[127] Russell, J. J., Senkan, S. M., Seetula, J. A., and Gutman, D., 1989, *J. phys. Chem.*, **93**, 5184.

[128] KAISER, E. W., RIMAI, L., and WALLINGTON, T. J., 1988, *J. phys. Chem.*, **93**, 4094.

[129] MARICQ, M. M., SZENTE, J. J., and KAISER, E. W., 1994, *J. phys. Chem.*, **97**, 7970.

[130] SEAKINS, P. W., WOODBRIDGE, E. L., and LEONE, S. R., 1993, *J. phys. Chem.*, **97**, 5633.

[131] BENSON, S. W., and DOBIS, O., 1998, *J. phys. Chem.* A, **102**, 5175.

[132] BARAT, R. B., and BOZZELLI, J. W., 1992, *J. phys. Chem.*, **96**, 2494.

[133] ELLISON, G. B., DAVICO, G. E., BIERBAUM, V. M., and DEPUY, C. H., 1996, *Int. J. Mass Spectrom. Ion Processes*, **156**, 109.

[134] WENTHOLD, P. G., POLAK, M. L., and LINEBERGER, W. C., 1996, *J. phys. Chem.*, **100**, 6920.

[135] LEONE, S. R., 1982, *J. phys. Chem. Ref. Data*, **11**, 953.

[136] PARK, J., LEE, Y., HERSHBERGER, J. F., HOSSENLOPP, J. M., and FLYNN, G. W., 1992, *J. Am. chem. Soc.*, **114**, 58.

[137] NORDMEYER, T., WANG, W. H., RAGAINS, M. L., FINLAYSON-PITTS, B. J., SPICER, C. W., and PLASTRIDGE, R. A., 1997, *Geophys. Res. Lett.*, **24**, 1615.

[138] ROBINSON, M. S., POLAK, M. L., BIERBAUM, V. M., DEPUY, C. H., and LINEBERGER, W. C., 1995, *J. Am. chem. Soc.*, **117**, 6766.

[139] FARRELL, J. T., and DURANT, J. L. (unpublished data).

[140] MCDONIEL, J. B., and HOLMES, B. E., 1997, *J. phys. Chem.* A, **101**, 1334.

[141] FERGUSON, H. A., FERGUSON, J. D., and HOLMES, B. E., 1998, *J. phys. Chem.* A, **102**, 5393.

[142] MCDONIEL, J. B., and HOLMES, B. E., 1996, *J. phys. Chem.*, **100**, 3044.

[143] WAGNER, A. F., SLAGLE, I. R., SARZYNSKI, D., and GUTMAN, D., 1990, *J. phys. Chem.*, **94**, 1853.

[144] KAISER, E. W., and WALLINGTON, T. J., 1996, *J. phys. Chem.*, **100**, 18 770.

[145] KAISER, E. W., 1998, *J. phys. Chem.* A, **102**, 5903.

[146] DOBIS, O., and BENSON, S. W., 1993, *J. Am. chem. Soc.*, **115**, 8798.

[147] LEVINE, R. D., and BERNSTEIN, R. B., 1987, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford University Press).

[148] PARKER, J. V. V., and PIMENTEL, G. C., 1965, *Phys. Rev. Lett.*, **14**, 352.

[149] ZAMIR, E., and LEVINE, R. D., 1980, *Chem. Phys.*, **52**, 253.