Kinetics of the gas-phase reaction of atomic chlorine with selected monoterpenes

Qadir K. Timerghazin and Parisa A. Ariya

Abstract

Halogens may play an important role in the chemistry of hydrocarbons in certain regions of the troposphere. We have studied Cl-atom-initiated reactions of several monoterpenes (α-pinene, 2-carene, 3-carene, myrcene and γ-terpinene) at atmospheric pressure of *ca*. 760 Torr over the temperature range 283–323 K in N_2 and air. The decay of the terpenes was followed using a gas chromatograph with a flame ionisation detector (GC-FID) and the rate constants were determined using the relative rate technique with n-nonane as a reference compound. The Cl atoms were generated by UV photolysis of trichloroacetylchloride (CCl_3COCl) at $\lambda \cong 250$ nm. Room temperature rate constants are found to be (in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, with uncertainties representing $\pm 2\sigma$) 5.3 ± 0.1 for α-pinene, 5.8 ± 0.1 for 2-carene, 5.2 ± 0.1 for 3-carene, 8.5 ± 1.8 for myrcene, and 10.4 ± 0.6 for γ-terpinene. No temperature dependence was observed for the reactions within our experimental uncertainties with the exception of Cl + γ-terpinene ($\ln k = (-27.9 \pm 0.8) - (2100 \pm 200)/T$). Data on the rate constants of the Cl reactions with monoalkenes and dienes, obtained in this work and taken from the literature were correlated with alkene HOMO energies within the framework of PFMO theory. The calculated semi-empirical parameters can be used to predict Cl-atom rate constants for alkenes in the troposphere. To gain a deeper insight into the reaction mechanism, several *ab initio* and DFT quantum chemical calculations were also carried out.

Introduction

Various types of non-methane volatile organic compounds (VOC) are emitted into the troposphere. Anthropogenic activities release mostly saturated and aromatic compounds, whereas the natural biosphere produces larger quantities of alkenes and dienes.[1,2] Isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) produced significantly from vegetation are among the most abundant natural VOC.[2] Terpenes and terpinoids are implicated in the formation of aerosols in the atmosphere.[1,3] It is now well established that during the daytime isoprene and terpenes are removed by reactions with HO radicals, while at night they may be oxidized by NO_3 radicals, and by O_3 all day long. A large set of laboratory kinetic data has been obtained on the reactions of biogenic and anthropogenic alkenes[4] initiated by atmospheric oxidants. In addition to laboratory experiments, theoretical calculations have been implemented to further understand the fate of unsaturated hydrocarbons in the atmosphere through analysis of the measured pool of rate constants using perturbation molecular orbital theory,[5–7] structure–reactivity relationships[8,9] and linear free energies.[9]

During the last decade scientists have revealed that in certain coastal regions and the Arctic, in addition to the “traditional” atmospheric oxidants such as HO,[10] atomic chlorine can play an important role in the oxidation of VOCs in the troposphere. Relatively significant concentrations of Cl have been suspected to exist in the marine boundary layer in the Arctic region (*e.g*. ref. 11).

However, the sources of Cl atoms are still subject to investigation. Although the concen tration of atomic chlorine can be lower than the HO concentration, Cl reacts with some hydrocarbons faster than the HO, implying that chlorine can play an important role in atmospheric chemistry. Extensive kinetic and mechanistic studies on the oxidation reactions involving Cl are therefore required to properly describe the fate of VOC in coastal regions as well as in the Arctic. At present, kinetic data are available for a number of the reactions of Cl with simple alkenes.[12–16] Among the biogenic alkenes, isoprene ($CH_2{=}C(CH_3){-}CH{=}CH_2$) oxidation by Cl has received much attention.[14,17–19] Limited data are also available for selected monoterpenes ($C_{10}H_{16}$).[20,21]

The aim of the present study was to investigate the kinetics of the oxidation of several monoterpenes (α-pinene, 2-carene, 3-carene, γ-terpinene and myrcene, see (Fig. 1) initiated by Cl atoms. The rate constants of these reactions were measured at 281 ± 1 K and at near atmospheric pressure, 760 ± 5 Torr, and the results combined with existing literature data were analyzed in the framework of perturbation molecular orbital theory. To mimic tropospheric conditions, we studied the temperature dependence of these reactions within the range 283 to 323 K. To gain a deeper insight into the reaction mechanism, several *ab initio* and DFT quantum chemical calculations were also performed.

Methodology

The rate constants were determined using the relative rate technique,[3] which has been employed to study the kinetics of various Cl-initiated reactions of organic compounds.[16,20]n-Nonane was used as the reference compound. The simultaneous loss of the organic compound of interest and the reference compound (due to their reaction with Cl) was monitored with a gas chromatograph with flame ionization detection (GC/FID, Hewlett Packard 6890). Chlorine atoms were generated by photolysis of trichloroacetylchloride (CCl_3COCl) at $\lambda \simeq 250$ nm. Photolysis of molecular chlorine was not used as a source of Cl, since dark reactions of terpenes with Cl_2 have

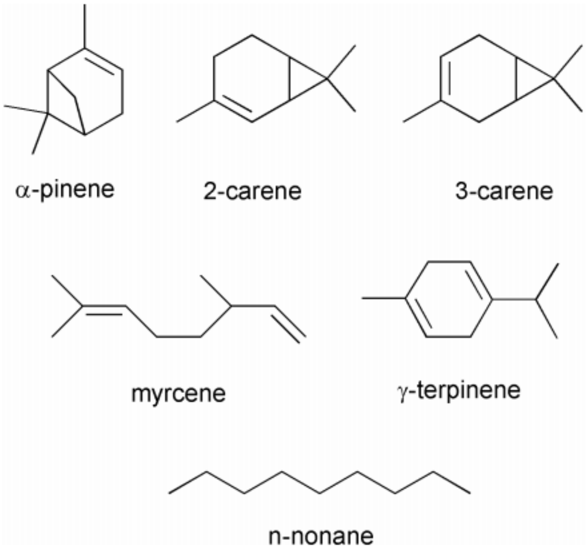


Fig. 1 Structures of the terpenes studied and the reference compound.

been observed in the literature[16,20] and are confirmed in the present study. The studied reactions were:

$$Cl + reference \xrightarrow{\mathrm{k_R}} products$$

$$Cl + substrate \xrightarrow{\mathrm{K_X}} products$$

the ratio of the rate constants k_X/k_R was determined from the following equation:

$$ln\frac{[substrate]_0}{[substrate]_t} = \frac{k_{substrate}}{k_{reference}}\,ln\frac{[reference]_0}{[substrate]_t} \tag{1}$$

where $[\mathrm{substrate}]_0$ and $[\mathrm{reference}]_0$ are the initial concentrations, and $[\mathrm{substrate}]_t$ and $[\mathrm{reference}]_t$ are the concentrations after photolysis. A plot of $\ln([\mathrm{substrate}]_0/[\mathrm{substrate}]_t)$ *vs.* $\ln([\mathrm{reference}]_0/[\mathrm{reference}]_t)$ should give a straight line with zero intercept; the slope of this line is k_X/k_R. The rate constant for the reaction of Cl with the reference compound (n-nonane)k_R = $(4.29 \pm 0.12) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, has been measured by Aschmann and Atkinson.[22] This reference molecule was chosen after our preliminary studies indicated that the rate constant of the Cl + n-butane, a reaction for which a large body of kinetic data is available, was much slower than those of Cl + terpenes. Cl + n-nonane was found to be close enough to the corresponding reactions of terpenes of interest, and hence was used as the reference reaction.

Experiments were carried out in a thermostatted 2 L double-walled Pyrex vessel. The outer jacket of the flask was connected to a Neslab RTE 111 circulator, the temperature was kept constant to ± 1 K. Typical concentrations of terpenes were *ca*. 35 ppmv; n-nonane: 30 ppmv; and trichloroacetylchloride: from 100 to 400 ppmv. To prepare reaction mixtures, the reaction chamber was evacuated to a pressure of *ca*. 10^{-4} Torr, the reactants were directly injected using liquid or gas-tight syringes. The total pressure was raised to 760 ± 5 Torr by the addition of N_2 or ultra-pure air. To prevent undesired reactions of reagents on the walls of the flask, the reaction chamber was coated with Halocarbon Wax (Supelco).

Photolysis was performed using a 100 W mercury arc lamp (Oriel Inc, λ = 254 nm) *via* a home-made quartz well. The reaction system was irradiated for between 5 and 10 min after which the reaction mixture was sampled. This was repeated for a total of 70–100 min. Gas samples were transferred into a GC/FID system after each irradiation using a gas-tight syringe (Hamilton 84889). The GC column used in this study was a 5% phenyl-methyl-siloxane capillary column (Hewlett Packard model 1909J-413). The sample volume was typically 250 µL. The column was operated at a constant head pressure of 25 psi. During chromatographic runs, the oven temperature was increased at 15°C min^{-1} from 35 to 160°C. Chlorobenzene was used as an internal standard, as its rate of reaction with Cl can be neglected due to its low rate constant.[23] At each sampling, the ratio of concentration of the reference molecule or terpenes of interest against the concentration of internal standard was used in further calculation of rate constants, in addition to direct calculation according to eqn. (1). This method allowed us to identify the errors associated with sample transfer, and was found to be less than ± 5%. The accumulated systematic and random errors, for such a system were estimated to be *ca*. 20%.[24]

Chemicals: α-pinene (purity 99%), γ-terpinene (97%), myrcene (96%), 2-carene (97%), 3-carene (90%) and trichloroacetyl chloride (99%) were purchased from Aldrich. n-Nonane (99%)

was supplied by Sigma, and chlorobenzene (99 + %) was obtained from Fisher Scientific. All the reagents were used as received. The nitrogen (certified oxygen content <5 ppmv) and the ultra-pure air (total hydrocarbons as CH_4<0.1%) were purchased from Matheson. Helium, air and hydrogen used for the GC were obtained from Matheson, with an activated charcoal trap for hydrocarbons (Hewlett Packard 5060-9096) on the air cylinder.

GAUSSIAN98[25] and PC GAMESS[26] packages were used for the quantum chemical calculations. The correlation of the rate constants with highest occupied molecular orbital (HOMO) energies of the alkenes was done in the framework of perturbation molecular orbital (PFMO) theory and E_{HOMO} energies were obtained using semi-empirical AM1[27] and *ab initio* RHF/6-31G(d,p)[28] calculations. Thermochemical effects of the reactions were calculated at the B3LYP/6-311 + G(2df,2p) and G2,[29] and G2(MP2)[30] levels of theory.

Results and discussion

Kinetic study of the reactions with Cl atoms

Terpenes were found to be stable in the halocarbon-wax-coated reaction chamber at room temperature, and the stability of the terpenes was also confirmed at 323 ± 1 K. Preliminary experiments showed that there is no dark reaction between the Cl atom source, trichloroacetyl chloride, and the terpenes of interest, or the reference molecule. Therefore the loss of the terpenes and n-nonane is assumed to be entirely due to the reaction with Cl atoms. Preliminary experiments carried out in reaction chambers of volume between 1 and 6 L indicated that the relative reaction rates of the compounds of interest were not affected by the different surface to volume ratios under the experimental conditions.

As depicted in Fig. 2, plots of the relative loss of terpenes and reference compound upon reaction led to straight lines with almost zero intercepts. We also aged the samples between irradiation to investigate the reformation of reactants or any significant secondary reactions induced by the reaction products, however we did not observe such phenomena under our experimental conditions, and linearity of the lines shown in Fig. 2 supports this. The data on relative rate constants k_X/k_R and absolute rate constants k_X at room temperature (298 K) are presented in Table 1. Each rate constant was obtained as the combination of at least three experiments. The slopes were calculated using a linear least squares analysis, and the uncertainties represented 2σ. The values of R^2 were in the range 0.98 to 0.99—the best correlation was observed for α-pinene, 2-carene and 3-carene. For myrcene and γ-terpinene the deviations of experimental points from a straight line are larger, but R^2 is still found to be no lower than 0.97. The experimental reaction system was also modelled using the ACCUCHEM program,[31] and it was found that the extent of secondary reactions was negligible under the stated experimental conditions.

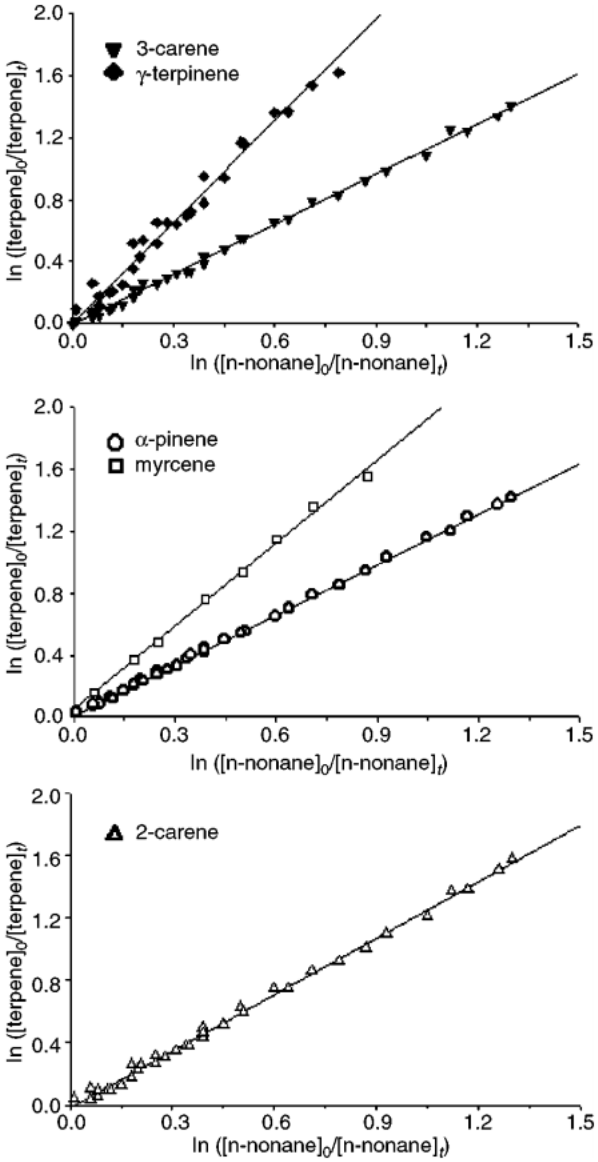


Fig. 2 Relative rate plots for the terpenes and the reference molecule.

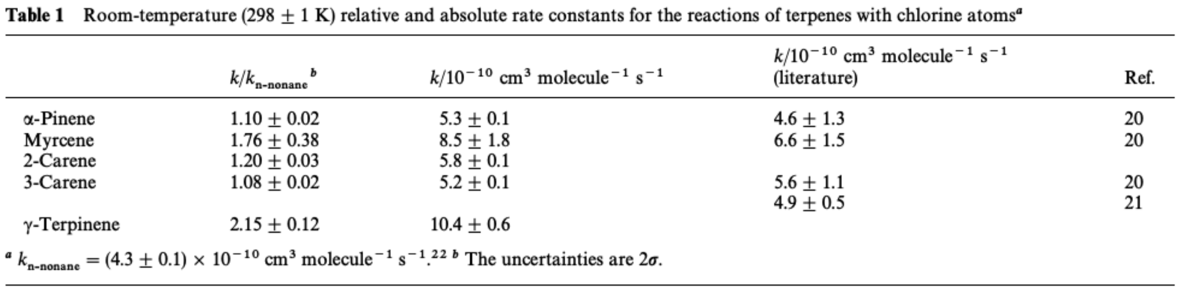


Table 1 Room-temperature (298 ± 1 K) relative and absolute rate constants for the reactions of terpenes with chlorine atoms[a]

	$k/k_{\text{n-nonane}}$ [b]	$k/10^{-10}$ cm^3 molecule^{-1} s^{-1}	$k/10^{-10}$ cm^3 molecule^{-1} s^{-1} (literature)	Ref.
α-Pinene	1.10 ± 0.02	5.3 ± 0.1	4.6 ± 1.3	20
Myrcene	1.76 ± 0.38	8.5 ± 1.8	6.6 ± 1.5	20
2-Carene	1.20 ± 0.03	5.8 ± 0.1		
3-Carene	1.08 ± 0.02	5.2 ± 0.1	5.6 ± 1.1 4.9 ± 0.5	20 21
γ-Terpinene	2.15 ± 0.12	10.4 ± 0.6		

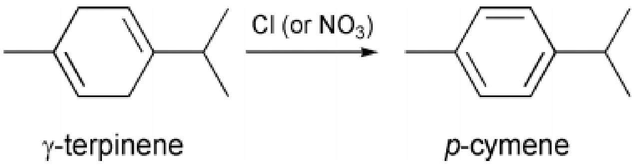
[a] $k_{\text{n-nonane}} = (4.3 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[22] [b] The uncertainties are 2σ.

The rate constants of the terpene oxidation by chlorine atoms, relative to the reaction of Cl with n-nonane, varied from 1.08 for 3-carene, to 2.15 for γ-terpinene. The absolute values varied from 5.2×10^{-10} to 10.4×10^{-10} cm^3 molecule^{-1} s^{-1}. These data are in good agreement with reported literature values for several terpenes.[20,21] For α-pinene and 3-carene. Finlayson-Pitts *et al.*[20] have reported rate constant values of $(4.6 \pm 1.3) \times 10^{-10}$ and $(5.6 \pm 1.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively. For 3-carene the rate constant for the reaction with Cl was also measured by Canosa-Mas *et al.*[21] as $(4.9 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. All the reported values, including ours for 3-carene, are in good agreement. The value of $(8.5 \pm 1.8) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} obtained here for myrcene is in agreement within uncertainty limits, with the value of $(6.6 \pm 1.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} reported by Finlayson-Pitts *et al.*[20] The present results provide the first kinetic data for Cl-atom-initiated reactions of 2-carene and γ-terpinene. The collision limits for the terpenes and n-nonane are estimated to be approximately $(7 \pm 2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. As seen in Table 1, only the calculated rate constant for Cl + γ-terpinene reaction seems to exceed slightly this calculated collision limit. However, it should be noted that in addition to errors in this study (*ca.* ± 20%), all of our reaction rates are calculated using the absolute value of the reference molecule, n-nonane. The calculation of the absolute rate constant for the reaction of Cl + reference molecule was also by the relative technique, and hence it includes errors (*ca.* ± 20%). If we incorporate the additional accumulated systematic and random errors associated with calculation of the absolute value of Cl + n-nonane with the reported absolute value of Cl + γ-terpinene, our reported rate constant for this reaction does not then exceed the collision limits. Our calculated rate constants, as well as previous literature data (see Table 1), indicate that the rate constants for all Cl + terpene reactions studied are very close to their collision limits.

Cl-initiated oxidation reactions of monoterpenes proceed faster than reactions of other atmospheric oxidants such as NO_3, HO and O_3. For instance, the rate constants for α-pinene reactions with NO_3, HO and O_3 are equal to 6.2×10^{-12}, 5.4×10^{-11} and 8.7×10^{-17} cm^3 molecule^{-1} s^{-1},[4] respectively. The rate constant of Cl atom with α-pinene is hence about one order of magnitude larger than for HO, about two orders higher than for NO_3 and *ca.* seven orders larger than O_3-initiated oxidation rates. Values of the rate constants for reactions of Cl + alkenes vary within a narrow range, from 1.1×10^{-10} (ethene) to 10.4×10^{-10} cm^3 molecule^{-1} s^{-1} (γ-terpinene). However, HO reaction rate constants for the same alkenes (ethene and γ-terpinene) vary within two orders of magnitude (8.5×10^{-12} and 3.6×10^{-10} cm^3 molecule^{-1} s^{-1}),[4] NO_3 reaction within six orders (2.5×10^{-16} and 1.4×10^{-10}),[4] and O_3 within four (1.6×10^{-18} and 2.1×10^{-14} cm^3 molecule^{-1} s^{-1}) orders of magnitude.[4]

It is noteworthy that in the course of the experiments, we did not observe the appearance of any significant chromatographic peaks within the given GC program, which could be attributed to products, except in the case of the oxidation of γ-terpinene. Seemingly, the products formed have low vapour pressure and condense on the walls of the flask. Thus, the oxidation of terpenes by Cl, similarly to the oxidation by ozone,[3] may contribute to the formation of condensed matter. For γ-terpinene, we observed that a chromatographic peak with a retention time characteristic for *p*-cymene appeared. The increase of *p*-cymene coincided with the decay of the γ-terpinene peak. It is noteworthy that formation of *p*-cymene upon reaction of γ-terpinene with the NO_3 radical has been observed previously.[32]

This suggests that the reaction between γ-terpinene and chlorine atoms may proceed *via* abstraction or addition–elimination, a subject that is examined in the following part of this study.



(2)

PFMO correlations

Previous research on the reactions of hydroxyl radicals, nitrate radicals and ozone with alkene has indicated[5–7] that the rate constants can be well correlated with the energy gap between frontier molecular orbitals in the framework of perturbation molecular orbital theory (PFMO).[33] PFMO claims that the logarithm of the rate constant correlates with ΔE between the HOMO of alkene and the single occupied MO (SOMO) in the case of radicals (HO, NO_3, Cl, *etc*.) or the lowest unoccupied MO (LUMO) in the case of molecular oxidants such as O_3:

$$\ln k = \frac{a}{E_{LUMO} - E_{HOMO}} + b \tag{3}$$

where k is the rate constant, E_{LUMO} and E_{HOMO} correspond to the energies of the HOMO and LUMO, and a and b are constants. It has been shown[5] that if the E_{HOMO} values do not vary over a large range then this equation may be reduced to:

$$\ln k = a'^{E_{HOMO}} + b' \tag{4}$$

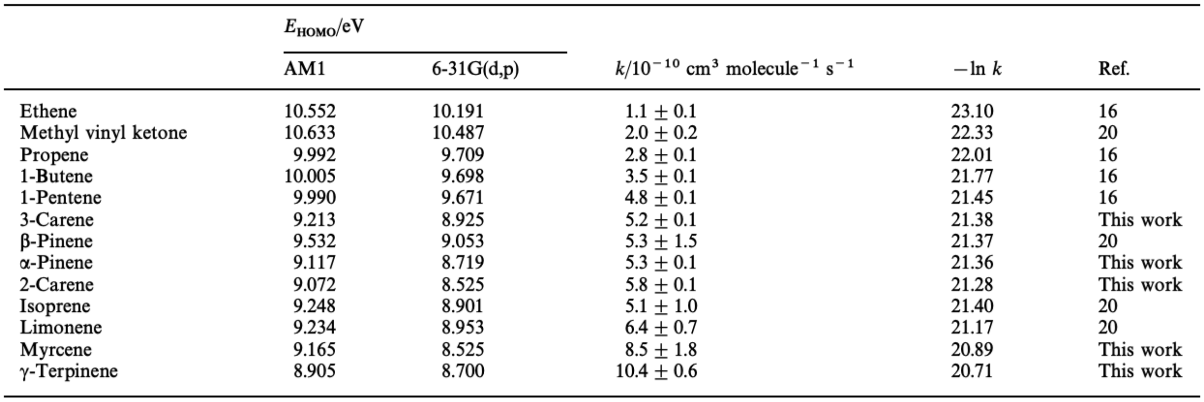
Even though this theory is currently being reconsidered on the basis of density functional theory (DFT),[34] PFMO still remains an effective tool for the estimation of rate constants for chemical reactions, including reactions of atmospheric importance.[5–7] We attempted to apply PFMO-based ln k–E_{HOMO}(alkene) correlation to the kinetic data existing for Cl reactions with alkenes obtained in our group or elsewhere. We used E_{HOMO}(alkene) values obtained both from semi-empirical (AM1) and *ab initio* (RHF/6-31G(d,p)) quantum-chemical calculations. The collected rate constants from the literature and this work, their logarithms and HOMO energies (AM1 and *ab initio*) are given in Table 2. Fig. 3 shows the plots of − ln k as a function of E_{HOMO}(alkene). Despite the fact that the values did not change significantly over a wide range, as is the case for the NO_3 radical, rate constants for Cl atom reactions with alkenes depicted a relatively good linear dependence on the energy of the HOMO of alkene. Using AM1 values of E_{HOMO}(alkene) we obtained the following correlation using least-squares analysis (Fig. 3):

$$\ln k = (1.0 \pm 0.3)E_{HOMO} - (12.3 \pm 2.9), R^2 = 0.79 \qquad (5)$$

Ab initio calculations RHF/6-31G(d,p) give a very similar result:

$$\ln k = (0.8 \pm 0.3)E_{HOMO} - (13.8 \pm 2.8), R^2 = 0.74 \qquad (6)$$

Table 2 The HOMO energies of selected organic molecules calculated by AM1 and RHF/6-31G(d,p) methods and corresponding rate constants for their reactions with chlorine atoms



	E_{HOMO}/eV				
	AM1	6-31G(d,p)	$k/10^{-10}$ cm^3 molecule^{-1} s^{-1}	$-\ln k$	Ref.
Ethene	10.552	10.191	1.1 ± 0.1	23.10	16
Methyl vinyl ketone	10.633	10.487	2.0 ± 0.2	22.33	20
Propene	9.992	9.709	2.8 ± 0.1	22.01	16
1-Butene	10.005	9.698	3.5 ± 0.1	21.77	16
1-Pentene	9.990	9.671	4.8 ± 0.1	21.45	16
3-Carene	9.213	8.925	5.2 ± 0.1	21.38	This work
β-Pinene	9.532	9.053	5.3 ± 1.5	21.37	20
α-Pinene	9.117	8.719	5.3 ± 0.1	21.36	This work
2-Carene	9.072	8.525	5.8 ± 0.1	21.28	This work
Isoprene	9.248	8.901	5.1 ± 1.0	21.40	20
Limonene	9.234	8.953	6.4 ± 0.7	21.17	20
Myrcene	9.165	8.525	8.5 ± 1.8	20.89	This work
γ-Terpinene	8.905	8.700	10.4 ± 0.6	20.71	This work

These expressions can be used for the estimations of the rate constants of the alkene and diene oxidation reactions by chlorine atoms. We compared our calculated expressions on the Cl system with literature results on HO, NO_3 and O_3.[6] Cl reactions appear to behave analogously to HO reactions, *i.e.*, the *k* for monoalkenes and dienes obey the same ln *k*–E_{HOMO}(alkene) dependence, whereas for NO_3 and O_3, the rate constants for the reactions with monoalkenes and dienes show different dependences on E_{HOMO}(alkene).[6] It has been noted[6] that *ab initio* (RHF/6-31G(d,p)) calculations are required to describe the influence of subtle changes due to alkene structure upon reactions with HO, NO_3 and O_3. In this study, *ab initio* and semi-empirical calculations perform similarly, and since the AM1 method is to be preferred from the computational point of view, especially for large molecules such as terpenes, we recommend its use for prediction of the rate constant of the Cl reactions + terpenes.

Temperature dependence study

The temperature dependence of the reaction of Cl atoms with α-pinene, 2-carene, 3-carene, γ-terpinene and myrcene was investigated over the range 283–323 K at a nearly constant pressure of 760 Torr. The relative rate constants measured at 283, 290, 298, 313 and 323 K are presented in Table 3. It has been shown that the reaction of Cl atoms with simple alkanes has an insignificant temperature dependence,[35] so we used the room temperature rate constant $k_{\text{n-nonane}} = (4.3 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}[22] for the reference reaction over the temperature range 283–323 K. For α-pinene, 2-carene, 3-carene and myrcene, we observed no temperature dependence within our experimental uncertainties. A slight temperature dependence can be attributed to the potential change in the rate constant of the reference reaction, which cannot be neglected if the reaction of interest exhibits a slight dependence on temperature.

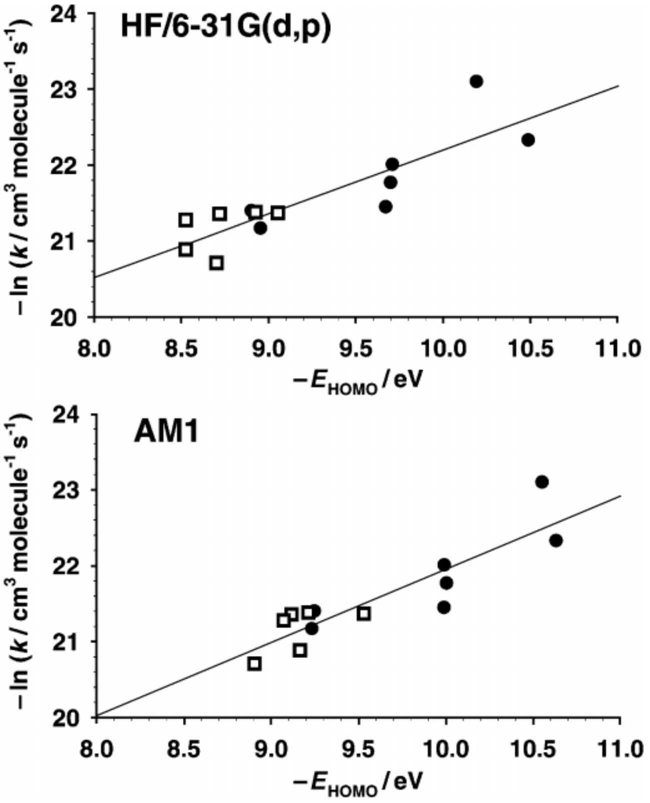


Fig. 3 The dependence of the rate constant on the energy of the highest occupied molecular orbital, calculated by *ab initio* and AM1 methods (open squares: terpenes; closed circles: other organic compounds).

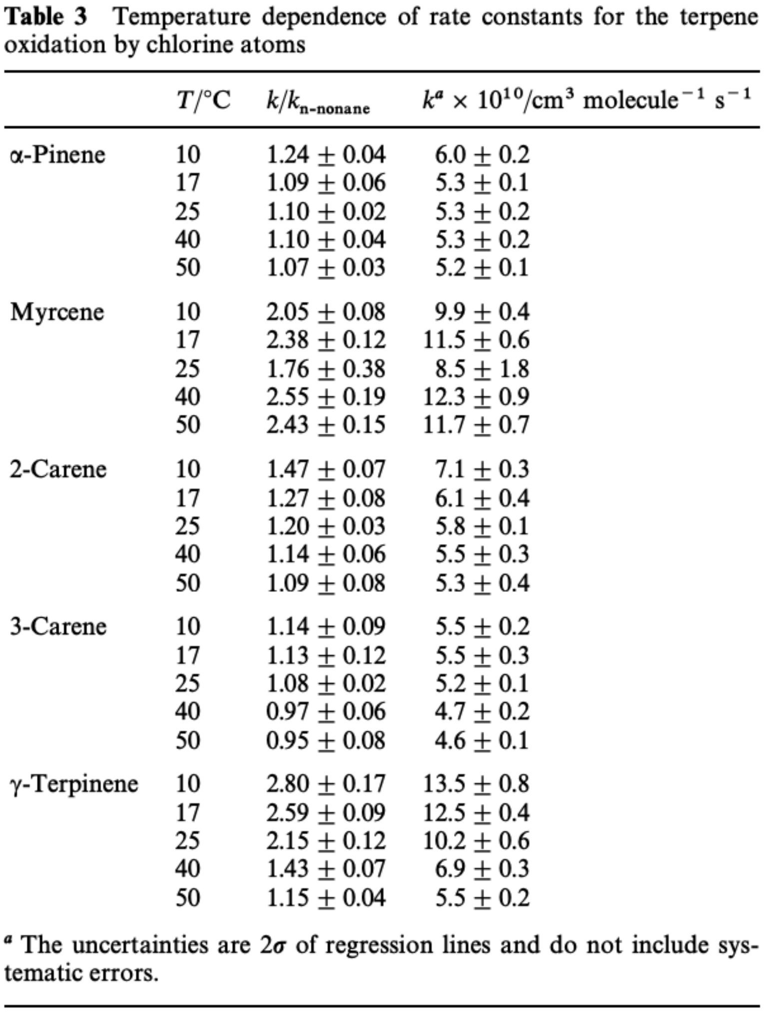
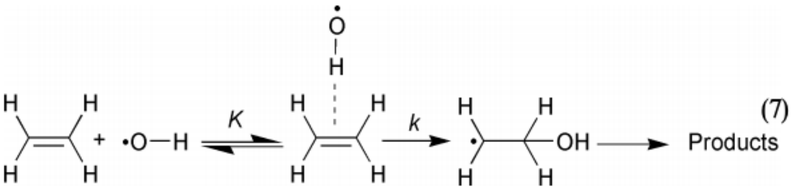


Table 3 Temperature dependence of rate constants for the terpene oxidation by chlorine atoms

	T/°C	$k/k_{\text{n-nonane}}$	$k^a \times 10^{10}$/cm^3 molecule^{-1} s^{-1}
α-Pinene	10	1.24 ± 0.04	6.0 ± 0.2
	17	1.09 ± 0.06	5.3 ± 0.1
	25	1.10 ± 0.02	5.3 ± 0.2
	40	1.10 ± 0.04	5.3 ± 0.2
	50	1.07 ± 0.03	5.2 ± 0.1
Myrcene	10	2.05 ± 0.08	9.9 ± 0.4
	17	2.38 ± 0.12	11.5 ± 0.6
	25	1.76 ± 0.38	8.5 ± 1.8
	40	2.55 ± 0.19	12.3 ± 0.9
	50	2.43 ± 0.15	11.7 ± 0.7
2-Carene	10	1.47 ± 0.07	7.1 ± 0.3
	17	1.27 ± 0.08	6.1 ± 0.4
	25	1.20 ± 0.03	5.8 ± 0.1
	40	1.14 ± 0.06	5.5 ± 0.3
	50	1.09 ± 0.08	5.3 ± 0.4
3-Carene	10	1.14 ± 0.09	5.5 ± 0.2
	17	1.13 ± 0.12	5.5 ± 0.3
	25	1.08 ± 0.02	5.2 ± 0.1
	40	0.97 ± 0.06	4.7 ± 0.2
	50	0.95 ± 0.08	4.6 ± 0.1
γ-Terpinene	10	2.80 ± 0.17	13.5 ± 0.8
	17	2.59 ± 0.09	12.5 ± 0.4
	25	2.15 ± 0.12	10.2 ± 0.6
	40	1.43 ± 0.07	6.9 ± 0.3
	50	1.15 ± 0.04	5.5 ± 0.2

[a] The uncertainties are 2σ of regression lines and do not include systematic errors.

The rate constant of the reaction of γ-terpinene with chlorine atoms has a pronounced tendency to decrease with increasing temperature and shows simple Arrhenius behaviour (see Fig. 4). The values for the activation energy (E_A), and pre-exponential factor (A) were calculated: $E_A = -4.2 \pm 0.5$ kcal mol^{-1}, $\log(A/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = -12.2 \pm 0.4$. Previously, negative activation energies were observed for the reactions of Cl atoms with simple alkenes:[16]ethene, − 1.9 kcal mol^{-1}; propene, − 1.7 kcal mol^{-1}; 1-butene, − 2.0 kcal mol^{-1} and 1-pentene, − 1.5 kcal mol^{-1}. Reactions of other atmospheric oxidants of a radical nature (HO and NO_3) with alkenes also frequently show negative temperature dependences.[36] For reactions of HO radicals, this negative temperature dependence was explained by reversible formation of the pre-reactive complex in analogous systems:[37–39]



(7)

In this case, the rate of the reaction is determined by:

$$w = k_{eff}[Alkene][OH] = kK[Alkene][OH] \tag{8}$$

Where *w*, *K*, *k* are total rate, equilibrium constant and rate constant. The effective rate constant (k_{eff}), depends on temperature according to the following equations:

$$k_{eff} = A\exp\left(\frac{-E_A}{RT}\right)\exp\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right) = A' exp\left(\frac{-E_{eff}}{RT}\right) \tag{9}$$

$$E_{eff} = E_A + RT \tag{10}$$

Where ΔH (enthalpy change) and ΔS (entropy change) are the thermodynamic characteristics of the formation of pre-reactive complex formation, and E_{A} is the activation energy of the reactive transformation of the complex. If $E_{\mathrm{A}}<|\Delta H|$, then the experimentally observed activation energy E_{eff} will be negative.

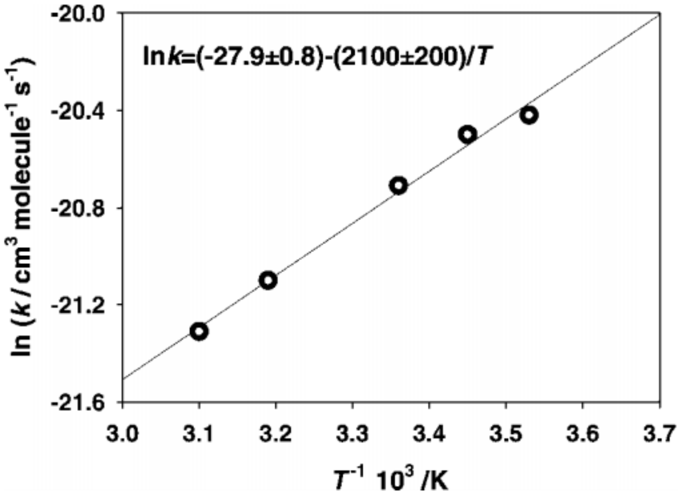
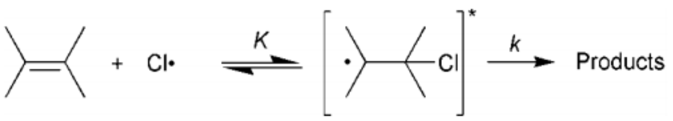


Fig. 4 Arrhenius plot for the reaction of Cl with γ-terpinene.

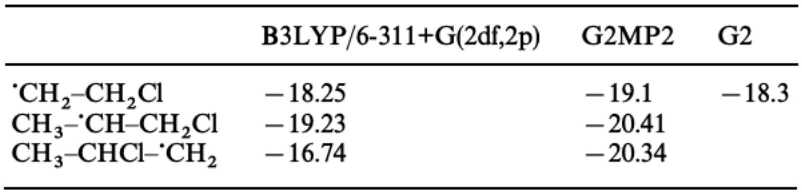
In the case of the chlorine atom–alkene reaction, a negative temperature dependence can also be explained by reversible formation of a pre-reactive complex: according to recent theoretical results by Brana *et al.*,[40] the stabilisation energy of such a complex is about − 3 to − 7 kcal mol^{-1}. Another possibility is the reversible formation of an unstable radical adduct:



(11)

The pressure dependence of the rate constants of these reactions, along with negative activation energies supports this suggestion.[14,15,41,42] According to our calculations (see Table 4), the enthalpy of formation of a radical adduct from the reaction of Cl atom with ethene and propene is about − 16 to − 21 kcal mol^{-1}, depending on the alkene and level of theory. The Cl–alkene radical-adduct is thus unstable enough and may indeed be in equilibrium with reactants.

Table 4 Enthalpy of Cl–alkene adduct formation at different levels of theory (kcal mol^{-1})



	B3LYP/6-311+G(2df,2p)	G2MP2	G2
$^{\bullet}CH_2–CH_2Cl$	−18.25	−19.1	−18.3
$CH_3–^{\bullet}CH–CH_2Cl$	−19.23	−20.41	
$CH_3–CHCl–^{\bullet}CH_2$	−16.74	−20.34	

Due to the complexity of alkene reactions with Cl atoms, which involve addition, abstraction and addition–elimination channels, it is difficult to predict all the activation energies for these reactions by theoretical methods. The observed negative value of activation energy for the γ-terpinene–Cl reaction may suggest that the direct abstraction channel is not of significant importance, since the abstraction pathway generally exhibits very little temperature dependence. Potential formation of *p*-cymene may suggest that the addition–elimination process can take place. This process seems to have a very low activation barrier, since allylic hydrogens in the γ-terpinene ring are surrounded by two C═C double bonds and should be very active. In this case, the difference between E_A and enthalpy for adduct formation from reagents should be larger than for other alkenes studied here, leading to more negative E_{eff}.

Further theoretical investigations of addition–elimination processes are required to evaluate this suggestion, and at this stage, no definite conclusion on the detailed mechanism can be drawn, based on the present study.

Conclusions

Rate constants for the reactions of Cl atoms with several monoterpenes were obtained over the temperature range 283–323 K in N_2 and in air at an atmospheric pressure of 760 Torr. Room temperature rate constants were found to be generally in good agreement with available literature values. Data on the rate constants of the Cl reactions with monoalkenes and dienes, obtained in this study and from the literature were correlated with alkene HOMO energies within the framework of PFMO theory. The calculated correlation can be used to calculate Cl-atom rate constants for alkenes for which no laboratory data exist, including various alkenes observed in the troposphere. Rate constants for the reactions of chlorine atoms with α-pinene, 2-carene, 3-carene and myrcene were found to exhibit no definite temperature dependence under our experimental conditions, whereas for γ-terpinene clear temperature dependence was observed and Arrhenius parameters were calculated. Although not studied here, some of the products of Cl-atom initiated reactions of terpenes, appear to be in a condensed form. Further research is needed to characterize the chemical composition of these products and their impact on the formation of aerosols in the atmosphere.

Acknowledgements

We would like to cordially thank the Natural Science and Engineering Research Council of Canada (NSERC), the Fond pour la Formation de Chercheurs et l'Aide a la Recherche (FCAR), the Canadian Foundation for Innovation (CFI) and Environment Canada for financial support. We thank Alexei Khalizov and Elena Avzyanova for fruitful discussions, and the reviewers for their helpful comments and suggestions.

References

1. J. H. Seinfeld and S. N. Pandis , *Atmospheric Chemistry and Physics* , Wiley, New York, 1998,
2. C. N. Hewitt *Reactive Hydrocarbons in the Atmosphere* , Academic Press, New York, 1999,
3. B. J. Finlayson-Pitts and J. N. J. Pitts , *Atmospheric Chemistry: Fundamentals and Experimental Techniques* , Wiley, New York, 1986,
4. R. Atkinson *J. Phys. Chem. Ref. Data*, 1997, **26** , 215
5. R. W. S. Aird , C. E. Canosa-Mas , D. J. Cook , G. Marston , P. S. Monks and R. P. Wayne , *J. Chem. Soc., Faraday Trans.*, 1992, **88** , 1093
6. M. D. King , C. E. Canosa-Mas and R. P. Wayne , *Phys. Chem. Chem. Phys.*, 1999, **1** , 2231
7. D. Johnson , A. R. Rickard , C. D. McGill and G. Marston , *Phys. Chem. Chem. Phys.*, 2000, **2** , 323
8. M. D. King , C. E. Canosa-Mas and R. P. Wayne , *Phys. Chem. Chem. Phys.*, 1999, **1** , 2239
9. D. Grosjean and E. L. Williams , *Atmos. Environ., Part A*, 1992, **26** , 1395 .
10. B. J. Finlayson-Pitts , M. J. Ezell and J. N. J. Pitts , *Nature*, 1989, **337** , 241 .
11. P. A. Ariya , B. T. Jobson , R. Sander , H. Niki , J. F. Hopper , K. G. Anlauf and G. W. Harris , *J. Geophys. Res.*, 1998, **103** , 13169 .
12. R. Atkinson and S. R. Aschmann , *Int. J. Chem. Kinet.*, 1985, **17** , 33 .
13. T. J. Wallington , L. M. Skewes and W. O. Siegl , *J. Photochem. Photobiol. A*, 1988, **45** , 167 .
14. J. Stutz , M. J. Ezell , A. A. Ezell and B. J. Finalyson-Pitts , *J. Phys. Chem. A*, 1998, **102** , 8510 .
15. E. W. Kaiser and T. J. Wallington , *J. Phys. Chem.*, 1996, **100** , 4111 .
16. S. Coquet and P. A. Ariya , *Int. J. Chem. Kinet.*, 2000, **32** , 478 .
17. M. L. Ragains and B. J. Finlayson-Pitts , *J. Phys. Chem. A*, 1997, **101** , 1509 .
18. J. S. Pilgrim and C. A. Taatjes , *J. Phys. Chem. A*, 1997, **101** , 5776 .
19. I. Suh and R. Zhang , *J. Phys. Chem. A*, 2000, **104** , 6590 .
20. B. J. Finlayson-Pitts , C. J. Keoshian , B. Buehler and A. A. Ezell , *Int. J. Chem. Kinet.*, 1999, **31** , 491 .
21. C. E. Canosa-Mas , H. R. Hutton-Squire , M. D. King , D. J. Stewart , K. C. Thompson and R. P. Wayne , *J. Atmos. Chem.*, 1999, **34** , 163 .
22. S. M. Aschmann and R. Atkinson , *Int. J. Chem. Kinet.*, 1995, **27** , 613 .
23. J. Shi and M. J. Bernhard , *Int. J. Chem. Kinet.*, 1997, **29** , 349 .
24. P. A.Ariya, Ph.D. Thesis, York University, 1996..
25. M. J.Frisch, G. W.Trucks, H. B.Schlegel, G. E.Scuseria, M. A.Robb, J. R.Cheeseman, V. G.Zakrzewski, J. A.Montgomery, R. E.Stratmann, J. C.Burant, S.Dapprich, S.Millam, A. D.Daniels, K. N.Kudin, M. C.Strain, O.Farkas, J.Tomasi, V.Barone, M.Cossi, R.Cammi, B.Mennucci, C.Pomelli, C.Adamo, S.Clifford, J.Ochterski, G. A.Petersson, P. Y.Ayala,

Q.Cui, Q.Morokuma, D. K.Malick, A. D.Rabuck, K.Raghavachari, J. B.Foresman, J.Cioslowski, J. V.Ortiz, B. B.Stefanov, G.Liu, A. Liashenko, P.Piskorz, I.Komaromi, R.Gomperts, R. L.Martin, D. J.Fox, T.Keith, M. A.Al-Laham, M. A.Peng, A.Nanayakkara, C.Gonzalez, M.Challacombe, P. M. W.Gill, B. G.Johnson, W.Chen, W.Wong, J. L.Andres, M.Head-Gordon, E. S.Replogle and J. A.Pople, GAUSSIAN 98 (Revision A.7), Gaussian Inc., Pittsburgh, PA, 1998..

26. M. W. Schmidt , K. K. Baldridge , J. A. Boatz , S. T. Elbert , M. S. Gordon , J. H. Jensen , S. Koseki , N. Matsunaga , K. A. Nguyen , S. Su , T. L. Windus , M. Dupuis and J. A. Montgomery , *J. Comput. Chem.*, 1993, **14** , 1347 .
27. M. J. S. Dewar , E. G. Zoebisch , E. F. Healy and J. J. P. Stewart , *J. Am. Chem. Soc.*, 1985, **107** , 3902 .
28. W. Hehre , P. v. R. Schleier , L. Radom and J. Pople , *Ab initio Molecular Orbital Theory* , Wiley, New York, 1986, .
29. L. A. Curtiss , K. Raghavachari , G. W. Trucks and J. A. Pople , *J. Chem. Phys.*, 1991, **94** , 7221.
30. L. A. Curtiss , K. Raghavachari and J. A. Pople , *J. Chem. Phys.*, 1993, **98** , 1293 .
31. W. Braun , J. T. Herron and D. K. Kahaner , *Int. J. Chem. Kinet.*, 1988, **20** , 51 .
32. E. Martinez , B. Cabanas , A. Aranda , P. Martin and S. Salgado , *J. Atmos. Chem.*, 1999, **33** , 265 .
33. I. Fleming *Frontier Orbitals and Organic Chemical Reactions* , Wiley, Chichester, 1976, .
34. F. Jensen *Introduction to Computational Chemistry* , Wiley, New York, 1999, .
35. R. S. Lewis , S. P. Sander , S. Wagner and R. T. Walson , *J. Phys. Chem.*, 1980, **84** , 2009 .
36. R. Atkinson *Chem. Rev.*, 1986, **86** , 69 .
37. D. L. Singelton and R. J. Cvetanovic , *J. Am. Chem. Soc.*, 1976, **98** , 6812 .
38. M. Mozurkewich and S. W. Benson , *J. Phys. Chem.*, 1984, **88** , 6429 .
39. J. R. Alvarez-Idaboy , N. Mora-Diez and A. Vivier-Bunge , *J. Am. Chem. Soc.*, 2000, **122** , 3715 .
40. P. Brana , B. Menendez , T. Fernandez and J. A. Sordo , *J. Phys. Chem. A*, 2000, **104** , 10842 .
41. T. J. Wallington , J. M. Andino , I. M. Lorkovic , E. W. Kaiser and G. Marston , *J. Phys. Chem.*, 1990, **94** , 3644 .
42. J. M. Ncovich , S. Wang , M. L. McKee and P. H. Wine , *J. Phys. Chem.*, 1996, **100** , 680