

KINETICS OF THE REACTION OF GROUND STATE OXYGEN ATOMS WITH TRICHLORO-ETHYLENE FROM 295 TO 1127 K; COMPARISON TO OTHER O + CHLORO-ETHYLENE REACTIONS

Jasmina Hranisavljevic and Arthur Fontijn
High-Temperature Reaction Kinetics Laboratory, The Isermann Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180-3590

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INTRODUCTION

Chlorinated hydrocarbons frequently occur in wastes and present a major pollution hazard from waste incinerators. Compounds such as chlorinated olefins are toxic and carcinogenic by themselves and their oxidation and pyrolysis products may be involved in the formation of highly toxic chloro-furans and -dioxins.¹⁻³ In order to influence the incineration process, such that hazardous emissions are reduced, kinetic models based on realistic kinetic data are needed.¹ Few measurements on individual oxidation reactions of chloro-ethylenes are available for the 700-1500 K regime of prime incineration interest. We have recently reported on the reactions of ground state oxygen atoms with monochloro-ethylene (1), 1,1-dichloro-ethylene (2) and *trans* 1,2-dichloro-ethylene (3) in the 290-1200 K range,⁴ and compared these to ethylene⁵. The series is now expanded to trichloro-ethylene (4), one of the compounds most commonly encountered in municipal wastes.

It is known that below about 500 K, in O-atom olefin reactions, addition to the double bond dominates.⁶ In the earlier study we found that, below about 700 K, the temperature dependences of the rate coefficients of the four reactions mentioned differ only slightly from each other. However, the magnitude of the rate coefficients was found to decrease substantially in the sequence $k_{C_2H_4}(T) > k_1(T) \approx k_2(T) > k_3(T)$, in agreement with the preferential attack of O-atoms at the site of the unsubstituted olefinic C-atom. While these trends were shown to continue at higher temperatures for the first three members of this sequence, a sharp increase was observed in $k_3(T)$ above about 700 K. It was thought that this increase may be attributed to H-atom abstraction from the weakened C-H bond. A method was developed for estimating rate coefficients, for H-abstraction from organic molecules by O-atoms, over wide temperature ranges.^{4,7} The sum of the $k_{ABS}(T)$ thus obtained, and the $k_{ADD}(T)$ based on the extrapolation of a transition state theory (TST) expression for addition,⁶ was shown to be in good agreement with the experimental data for reaction (3). The same type of calculations also suggested a negligible influence of abstraction on the other discussed reactions in the investigated temperature range, in agreement with the experiments.

These results, and those of a study of O-atom reactions with the four C_4H_8 butenes,⁷ suggested that it is possible to predict the high temperature rate coefficients for O-atom reactions with olefins, with good accuracy, by:

- i) taking a few experimental points below 500 K
- ii) using those points with the Singleton and Cvetanovic TST expression⁶ to obtain $k_{ADD}(T)$ over the temperature range of interest, and
- iii) adding the estimated $k_{ABS}(T)$ to the $k_{ADD}(T)$ to obtain the overall $k(T)$.

In the present work we check the validity of this approach for the trichloro-ethylene reaction.

EXPERIMENTAL TECHNIQUE

The measurements were performed in two different HTP (high-temperature photochemistry) reactors. The older design reactor,⁸ here referred to as reactor A, is shown in Fig. 1, while reactor B⁹ is shown in Fig. 2. The reactant gases were introduced into the heated bath gas through cooled inlets. Ground state oxygen atoms were produced by photolysis of O_2 through a MgF_2 window, or SO_2 through a Suprasil quartz window. Flash photolysis FP was used in reactor A, while both flash photolysis and laser photolysis LP were employed in reactor B. The relative concentrations of oxygen atoms were monitored by fluorescence of the 130.2-130.6 nm resonance triplet. The source of resonance radiation was a microwave discharge flow lamp through which He flowed at 2.0 mbar. The O-atom fluorescence was monitored with a photomultiplier tube through a CaF_2 window ($\lambda > 125$ nm).

The operational procedures have been previously described.^{8,10,11} The experiments were carried out under pseudo-first-order conditions $[O] \ll [C_2HCl_3]$, for which the fluorescence intensity I , proportional to $[O]$, can be written as

$$I = I_0 \exp(-k_{ps1}t) + B \quad (5)$$

Here, $I_0 + B$ is the intensity at time $t=0$, k_{ps1} is the pseudo-first-order rate coefficient, and B is the background due to scattered light. The values of k_{ps1} were obtained by fitting¹² the observed $\ln I$ vs. t profiles to eq. 5. In all cases exponential $\ln I$ vs. t plots were obtained, as verified by a two stage residual analysis.¹³ Plots of typically five or six k_{ps1} obtained over a range of C_2HCl_3 concentrations were used to obtain rate coefficients k_4 for the temperature of the experiment; uncertainty analysis was used as previously described.¹¹

RESULTS

The experimental conditions were varied over wide ranges of the flash or laser energy, total gas concentration (pressure), average gas velocity, cooled inlet to observed reaction zone distance, and residence time. Residual analyses showed the independence of the results of these implicit parameters. The rate coefficients obtained are shown in Figs. 3 and 4. There is a good agreement between the data obtained from the two reactors and from the different O-atom production arrangements, as shown in these figures. A four-parameter fit was found to give the best fit to the data:

$$k_4(295-1127 \text{ K}) = 1.1 \times 10^{-12} \exp(-695 \text{ K/T}) + 1.5 \times 10^{-9} \exp(-7508 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6).$$

As in previous work^{4,7-10} the results of a covariance matrix analysis were combined¹⁴ to determine precision limits. 2σ precision limits obtained vary from a minimum of $\pm 3\%$ at 393 K to a maximum of $\pm 12\%$ at 1127 K. Allowing, probably exaggeratedly, for $\pm 20\%$ systematic errors leads to corresponding accuracy limits of $\pm 20\%$ to $\pm 23\%$. A three-parameter fit of the format $k(T) = a (T/K)^n \exp(-e \text{ K/T})$ was also attempted, but led to higher 2σ precision limits, varying from a minimum of $\pm 6\%$ at 541 K to a maximum of $\pm 16\%$ at 295 K.

There has been only one previous measurement of the O-atom trichloro-ethylene reaction. This relative room temperature measurement, as assessed in the evaluation of Cvetanovic,¹⁵ is shown in Fig. 4. and is in good agreement with the present work.

DISCUSSION

In Fig. 5 the rate coefficient plot of reaction (4) is compared to those of the other discussed ethylenic reactions. The trends that were observed⁴ are continued. Below about 700 K the plots have similar slopes, indicating that Cl-substitution does not strongly affect the activation energies. The rate coefficients of reactions (3) and (4) are approximately equal near room temperature and differ only slightly at higher temperatures. This confirms that rate coefficients do not change much with further Cl-substitution of an already mono-substituted C-atom. The sequence of rate coefficients can now be extended to read: $k_{C_2H_4}(T) > k_1(T) = k_2(T) > k_3(T) = k_4(T)$. The sharp curvature of the $k_4(T)$ plot above 700 K, similar to, but stronger than, that of $k_3(T)$, can again be attributed to H-abstraction and is shown below to be in agreement with the predictive method described in the Introduction.

The rate coefficient expression for the addition channel used is:⁶

$$k_{ADD}(T) = A T^{-0.5} [1 - \exp(-1.439 \omega/T)]^{-2} \exp(-E_0/RT) \quad (7),$$

Here A is a temperature independent pre-exponential factor, ω is the vibrational frequency of the degenerate bending mode in the O-olefin transition state, and E_0 is the energy barrier. The parameters A, ω and E_0 are selected such that the best fit is obtained with the experimental values of the rate coefficients at three temperatures in the 300-500 K range. This yields:

$$k_{ADD}(295-1460) = 1.0 \times 10^{-11} (T/K)^{-0.5} [1 - \exp(-423 \text{ K/T})]^{-2} \exp(-729 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (8)$$

The previously described method for estimating rate coefficients for H-atom abstraction^{4,7} gives for O + trichloro-ethylene:

$$k_{ABS}(295-1460) = 2.4 \times 10^{-16} (T/K)^{1.55} \exp(-2801 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (9).$$

In Fig. 6 the estimated rate coefficient values are compared to the experimental points. It may be seen that the addition channel expression alone yields at higher temperatures values lower than those measured, but that the sum of the $k_{ABS}(T)$ and $k_{ADD}(T)$ expressions again^{4,7} yields good agreement with experimental results.

CONCLUSIONS

Rate coefficients for the O + trichloro-ethylene reaction have been measured for the first time above room temperature. They follow the trends established for the O-atom reactions with the less substituted ethylenes and confirm the usefulness of our recently developed method for estimating high temperature rate coefficients for O-atom olefin reactions. It would appear that the method can be extended to other reactions of O-atoms with aliphatic hydrocarbons.

REFERENCES

- 1) Tsang, W.; *Combust. Sci. and Tech.* **1990**, *74*, 99
- 2) Oppelt, E. T.; *J. Air Poll. Contr. Assoc.*, **1987**, *37*, 558
- 3) Penner, S. S.; Report from NSF sponsored Workshop, **1988**, La Jolla, California
- 4) Hranisavljevic, J.; Adusei, G. Y.; Xun, Y.; Fontijn, A.; *Combust. Sci. and Tech.*, submitted
- 5) Klemm, R. B.; Sutherland, J. W.; Wickramaaratchi, M. A.; Yarwood, G.; *J. Phys. Chem.* **1990**, *94*, 3354
- 6) Singleton, D. L.; Cvetanovic, R. J.; *J. Am. Chem. Soc.* **1976**, *98*, 261
- 7) Adusei, G. Y.; Fontijn, A.; *J. Phys. Chem.*, submitted

- 8) Ko, T.; Marshall, P.; Fontijn, A.; *J.Phys.Chem.* **1990**,*94*,1401
- 9) Mahmud, K.; Kim, J. S.; Fontijn, A.; *J.Phys.Chem.* **1990**,*94*,2994
- 10) Marshall, P.; Ko, T.; Fontijn, A.; *J.Phys.Chem.* **1989**,*93*,1922
- 11) Fontijn, A.; Futerko, P. M.; in Fontijn, A. (Ed.), *Gas-Phase Metal Reactions*, North Holland, Amsterdam, 1992, Chapter 6.
- 12) Marshall, P.; *Comput.Chem.* **1987**,*11*,219
- 13) Ko, T.; Adusei, G. Y.; Fontijn, A.; *J.Phys.Chem.* **1991**,*95*,8745
- 14) Wentworth, W. E.; *J.Chem.Educ.* **1991**,*95*,8745
- 15) Cvetanovic, R. J.; *J.Phys.Chem.Ref.Data* **1987**,*16*,261

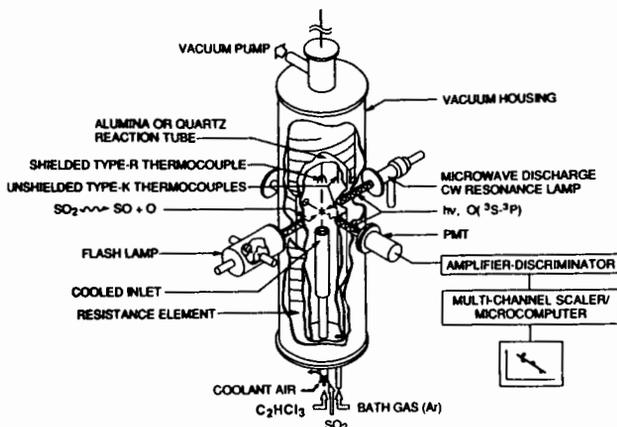


Figure 1. HTP reactor - older design (reactor A), for details see Ref. 8

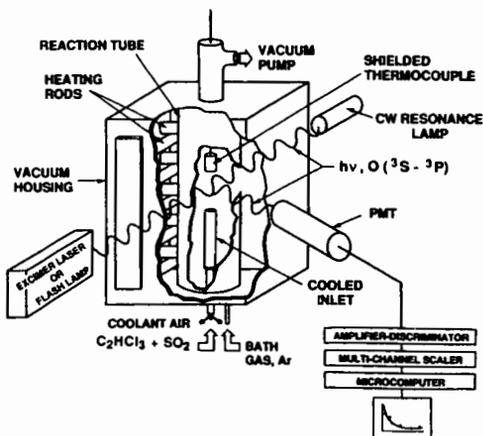


Figure 2. HTP reactor - newer design (reactor B), for details see Ref. 9

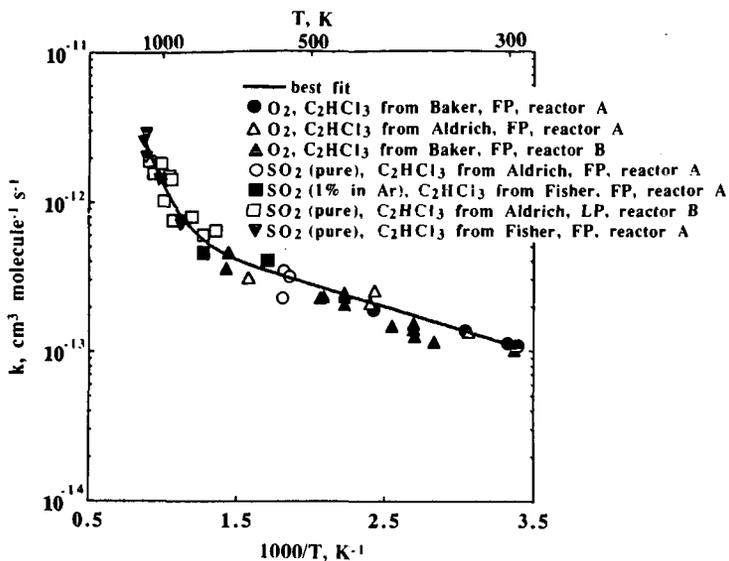


Figure 3. Summary of the rate coefficient measurements for the O + trichloro-ethylene reaction

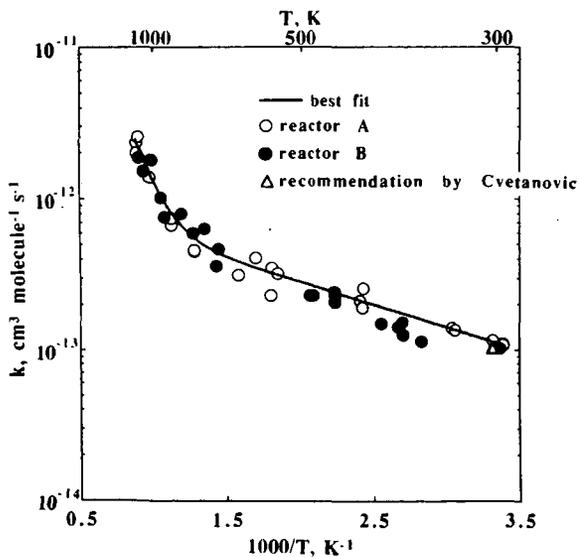


Figure 4. Rate coefficient measurements for the O + trichloro-ethylene reaction differentiated by the reactor

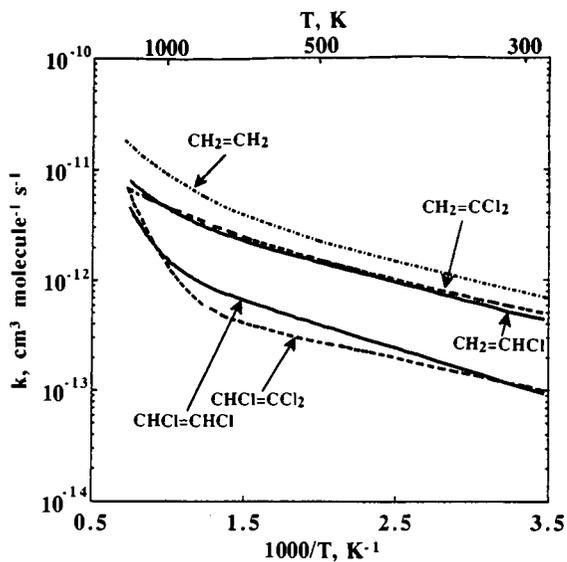


Figure 5. Comparison of ethylenic reactions

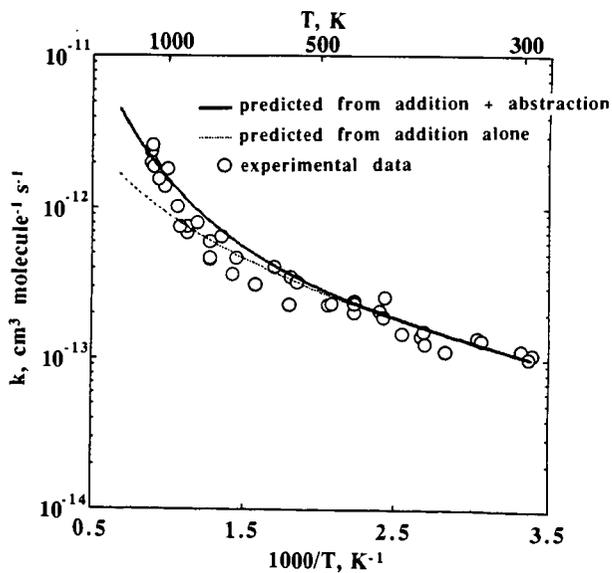


Figure 6. Comparison of the predicted and measured rate coefficients for the O + trichloro-ethylene reaction