A PROCESS FOR CONVERSION OF HALON 1211

Richard Tran, Eric M. Kennedy and Bogdan Z. Dlugogorski
The University of Newcastle

ABSTRACT

The nonoxidative gas phase reaction of Halon 1211 ($CBrClF_2$) with methane was studied using a tubular plug flow alumina reactor at atmospheric pressure, over the temperature range of 673-1073 K and residence times between 0.1 and $1.3s$. With an equimolar intake concentration of $CBrClF_2$ and CH_4, the conversion of both species increase with temperature and residence times. Complete halon conversion was achieved at 1073 K for all residence times considered. The initial products of the reaction are predominated by $CHClF_2$ and CH_3Br, which is replaced by $C_2H_2F_2$ at higher temperatures. Minor species such as C_2H_3F, CHF_3, C_2F_4, $CHBrF_2$, and C_2HBrF_2 were also detected. The formation of $CHClF_2$, C_2F_4, $CHBrF_2$, and C_2HClF_2 was observed to maximize at a specific residence time. and the formation of soot was detected above 943 K. The reaction was found to follow second-order kinetics with a global constant, k:

$$k_{global} = 9.41 \times 10^{10} \, (L \, mol^{-1} s^{-1}) \times exp(-154.04 \, kJ \, mol^{-1} / RT).$$

INTRODUCTION

Concern over the contribution of bromine and chlorine to the stratospheric ozone depletion has given rise to a number of international regulations about the productions and uses of Halon 1211 ($CBrClF_2$), Halon 1301 ($CBrF_3$), CFCs. and other ozone-depleting substances (ODS). These compounds contain bromine and chlorine, and have atmospheric lifetimes long enough to be transported into the stratosphere, where they are dissociated by short-wave UV light. The dissociation process causes the release of bromine and chlorine atoms, which catalytically involve in the destruction of ozone. It is estimated that one molecule of chlorine can degrade over 100,000 molecules of ozone molecules before being removed from the stratosphere, and that a bromine atom is 40-100 times as effective as a chlorine atom in destroying ozone [1, 2].

Although halons are widely used fire-suppression and explosion-protection agents, they have high ozone-depletion potentials. Thus, their productions have been halted in industrialized countries, and their uses are being curtailed by the Montreal Protocol. First introduced in 1987, and amended four times. the Protocol is an international treaty developed to reduce and eventually to eliminate the emissions of anthropogenic ozone-depleting substances.

Most gases regulated by the Protocol have decreased remarkably in their emission rate; however, emissions of Halon 1211 have remained rather constant [3, 4]. Indeed, Halon 1211 is still approved for use, but only for mission-critical applications such as flight-line, landcraft, and aviation fire protection or rescue operations. This fact suggests that Halon 1211 emissions will continue, in spite of efforts to ban its production and limit its use as well as the development and wide availability of Halon 1211 alternatives [5]. With its current emission rate, Halon 1211 poses a more significant ozone destruction than any other halocarbon [6]; thus, treatment to reduce the growing stockpiles of this halon would make a considerable difference in stratospheric ozone protection.

In recent years, pyrolysis in an atmosphere of hydrogen. i.e., thermal hydrodehalogenation (THD) has proven to be a promising halon treatment process, where halons are reacted with hydrogen at high temperature. de Lijser et al. [7] have studied the THD of Halon 1211 ($CBrClF_2$), and found that the conversion of $CBrClF_2$ starts at 673 K, with the relatively weak $CClF_2$-Br bond

homolytically broken, followed by hydrogenation to yield $CHClF_2$. At higher temperatures, other products such as $CHBrF_2$ and CH_2F_2 emerge. At temperatures above 873 **K,** where complete conversion of halon is achieved, and methane production increases significantly with temperature [7].

Li et al. [8] also performed the THD of Halon 1301 at atmospheric pressure. It was found that hydrogen increases the conversion level of Halon 1301, and that the conversion level of both Halon 1301 and H_2 increases with temperature and residence time. Similar to de Lijser's analysis, the initiation reaction of the Li et al. study also involves the rupture of CF_3-Br (C-Br) bond, which generates the hydrogenation reaction of CF_3 radical with H_2 to produce CHF_3 and a hydrogen radical. Subsequently, debromination occurs when $CBrF_3$ is reacted with H radical, resulting in the formation of CF_3 radical and HBr. This result is also in agreement with the shock tube study of the reaction of CF_3Br with H_2 by Hidaka et al. [9], and the decomposition of CCl_2F-$CClF_2$ in H_2 by Ritter [10].

We have examined the hydrodehalogenation of Halon 1301 with methane both experimentally and computationally [11]. These studies showed that methane substantially increases the conversion level of $CBrF_3$, resulting in a range of hydrofluorocarbon products.

In a continuing effort to convert restricted halons to products of economic value, as well as, to gather more information concerning the decomposition kinetics and mechanisms of $CBrClF_2$, the gas phase reaction of Halon 1211 at elevated temperatures, using methane as a hydrogen source was studied. Methane is available at relatively low cost in natural gas, and is an excellent hydrogen source since one molecule of methane can offer up to four hydrogen atoms per reacting halon molecule [11].

EXPERIMENTAL

The experimental apparatus used in these studies is shown schematically (Figure 1) and has been described elsewhere [11]. Since quartz tubes are easily degraded by fluorides at high temperature [10], a high punty (99.99%) alumina tube (inner diameter: 0.68 cm) was chosen as the reactor. A three-zone electrically heated furnace, surrounding the alumina plug plow reactor, was used to ensure an isothermal environment (within 5 K) throughout the reactor [11]. The temperature was measured by sheathed type K thermocouple probes placed axially in the reactor tube.

$CBrClF_2$ with a purity of 99.4%, CH_4 (99.97% purity) and N_2 (BOC Gases, 99.999% purity) were metered using calibrated electronic mass flow controllers. The reactor exit was directed through a liquid trap operated at 273 **K,** then through a caustic scrubber (0.1 M NaOH) to collect acid products: HBr, HCl and HF, at room temperature (293 **K).**

The remaining gas stream flowed directly to an online MTI micro gas chromatograph (M200H GC) equipped with dual thermal conductivity detectors. Products were quantified using a 5A molecular sieve column operated at $50\,^\circ C$, and a poraplot U column operated at $110\,^\circ C$. These columns used helium as a carrier gas and had the same sample time, injection time and run time, which were 20 s, 50 ms and 160 s respectively.
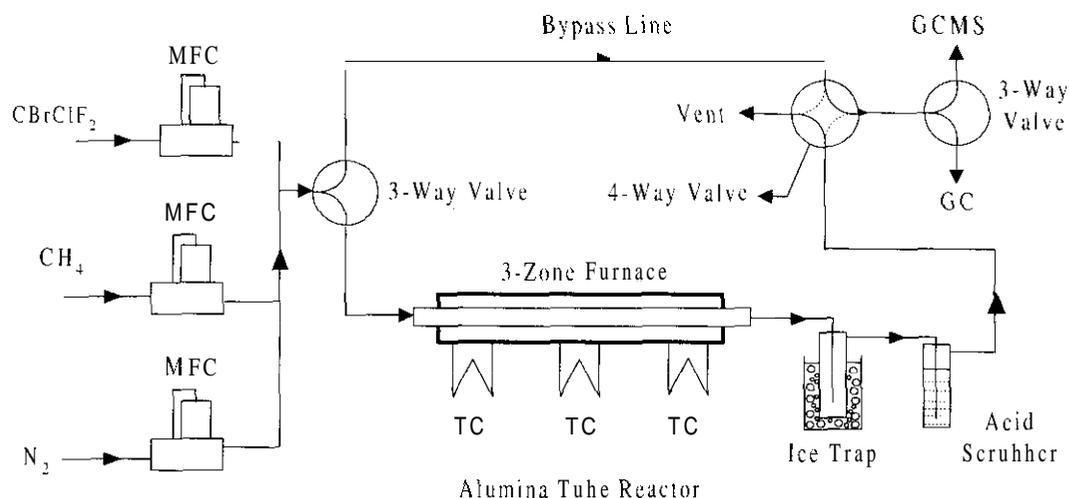
Figure 1. Schematic of the experimental facility.

For product identification, the gas chromatograph-mass spectrometer (GCMS-QP5000, Shimadzu) equipped with an AT-Q column (30 m by 0.32 mm) was used, having a temperature range of 60–230°C and ultra high purity helium (BOC Gases, 99.999% purity) as a carrier gas. The composition of the feed was analyzed using the bypass line.

Predicted relative molar response factors (RMR) were used to calculate the absolute amounts of each individual species identified by the GCMS. The RMR values were obtained using the following equation [12]:

$$RMR_i = \left[\frac{\sigma_i - \sigma_1}{\sigma_@ + \sigma_1} \right]^2 \left[\frac{M_i - M_1}{M_i + M_1} \right]^{0.50} \times 100 \tag{1}$$

where σ is collision diameter (Å), given by equation [13]:

$$\sigma = 110.2423 \, (T_c / P_c)^{1/3} \tag{2}$$

M is molecular weight, T_c is critical temperature (K), P_c is critical pressure (Pa) and the subscripts i, I, and @ refer to the species under consideration, the carrier gas, and benzene [14,15]. The factor of 100 (units/mol) represents the arbitrary response of benzene as an internal standard.

Experiments were performed at atmospheric pressures, over a range of temperatures (673–1073 K), each with a series of residence time (0.1–1.3 s). Residence time was altered either hy adjusting the gases flowrate or the reactor volume; thus, residence time is a function of temperature, flowrate and the volume of thermal zone.

RESULTS AND DISCUSSION

An equimolar concentration of $CBrClF_2$ and CH_4, diluted by N_2 was examined using the bypass line. The intake volumetric ratio of $N_2 : CBrClF_2 : CH_4$ was determined to be 10 : 1 : 1. Figures 2 and 3 show the resulting conversion of $CBrClF_2$ and CH_4, which began at about 773 K and increased rapidly over the temperature range of 823–973 K.
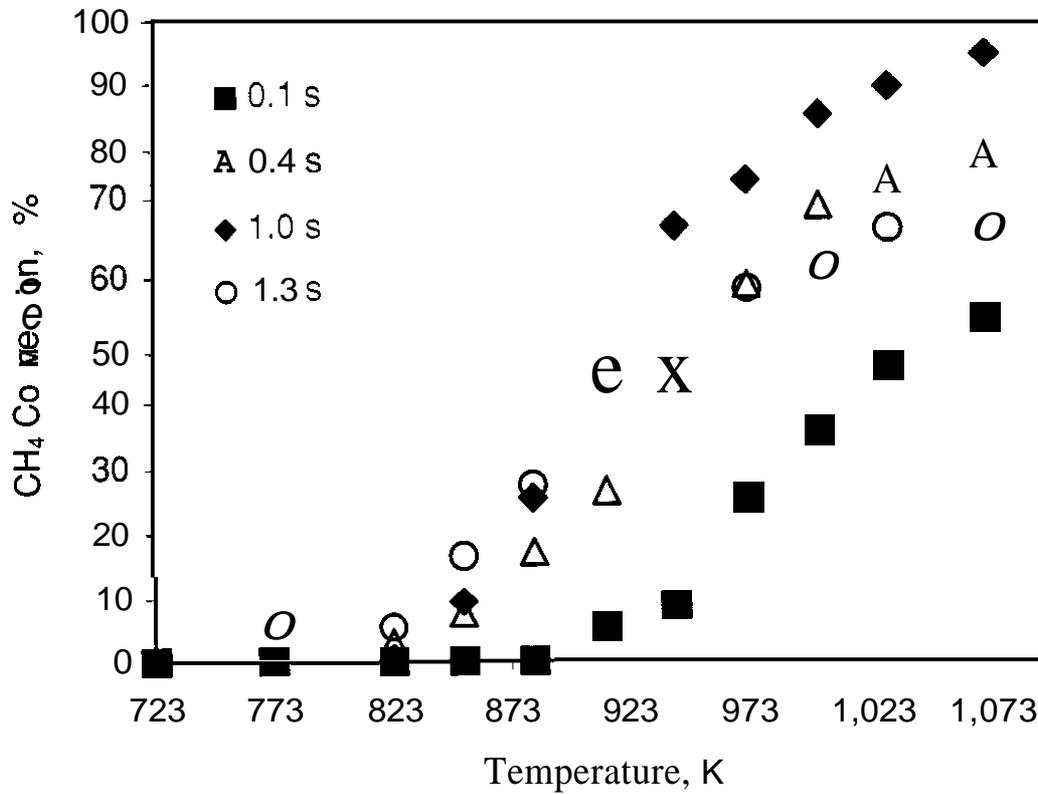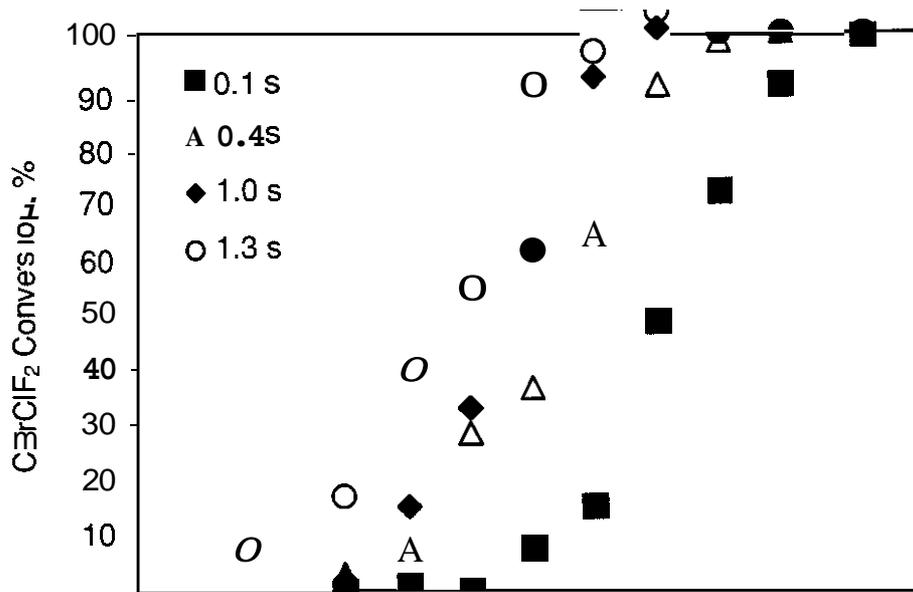
Figure **3.** CH$_4$ conversion as a function of temperature at different residence times.

Reactant conversion increases with increasing temperature and longer residence times. Complete conversion of $CBrClF_2$ was observed at 1073 K for all residence times examined. At low temperatures, there was little difference between the conversion levels of $CBrClF_2$ and CH_4; however, at higher temperatures, the conversion of $CBrClF_2$ is clearly greater than that of CH_4. In figure 4 the conversion of CH_4 as a function of the conversion of $CBrClF_2$ throughout the examined range of temperatures and residence times has been correlated.

$$x_{CH_4} = 6.36 \exp (0.025 x_{CBrClF_2} \tag{3}$$

with x being the conversion of the specified species,

At a low conversion of $CBrClF_2$ (under 70%), the fractional conversion ratio of CH_4 is about 0.56 the conversion of $CBrClF_2$ (Figure 4). This observation could be explained through the ability of CH_4 hydrogen transfer and its competition among the product species to donate hydrogen containing species for secondary reaction. Less CH_4 is required to react with $CBrClF_2$ because more than one hydrogen atom per molecule of methane can be utilised, effectively allowing each individual molecule of CH_4 to donate more than one hydrogen for reaction. Furthennore, hydrogen donors [16] such as HCl and HBr compete with CH_4 to react with $CBrClF_2$, which effectively lead to a lower consumption of CH_4.
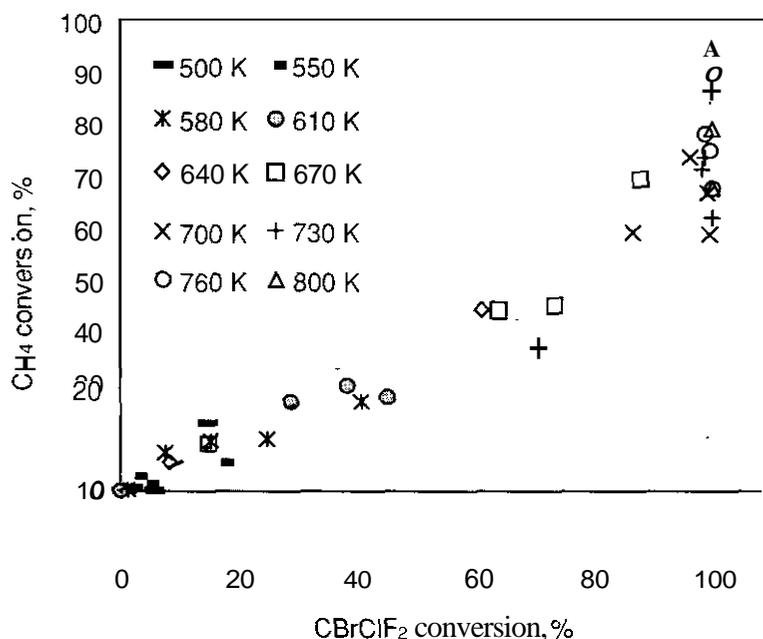

Figure 4. CH_4 conversion as a function of $CBrClF_2$ conversion for all temperatures (773-1033 K) and residence times (0.1-1.3 s).

Figure 5 shows the effect of CH_4 in the conversion of $CBrClF_2$ at a residence time of 1.3 s. With an equimolar intake concentration of CH_4 and $CBrClF_2$, complete conversion of $CBrClF_2$ was obtained at 1003 K, whereas at the same temperature, only 70% conversion was achieved when CH_4 was not presented. Clearly, the addition of CH_4 enhances the conversion level of $CBrClF_2$ as was also observed during reaction of methane with Halon 1301.
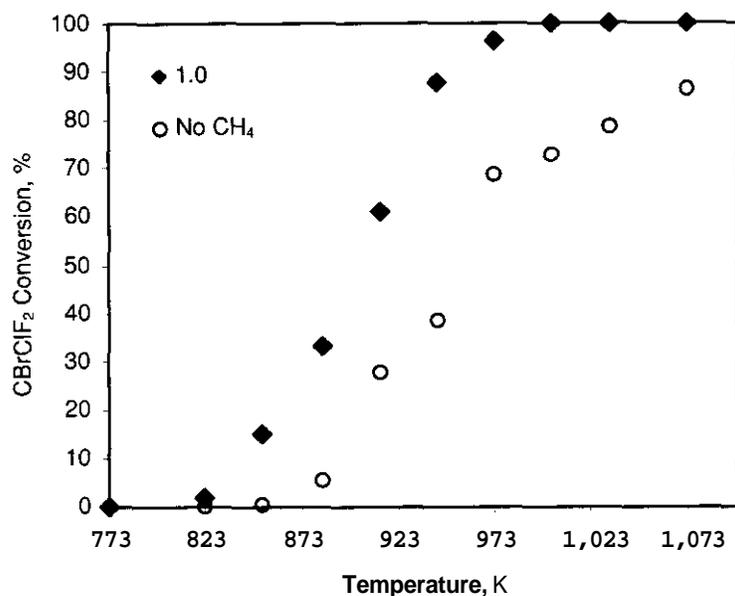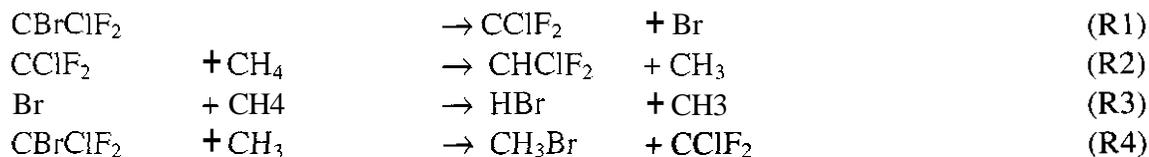
Figure 5. The effect of methane on the conversion of $CBrClF_2$ as a
function of temperature at a residence time of $\tau = 1.3$ s.

Among the many possible processes that a radical chain can be initiated, most studies suggest that (R1) represents the most important initiation step, at least at low temperatures. The relatively weak $CClF_2$ - Br bond is homolytically cleaved, producing two reactive radicals [17]. When these reactive radicals combine with a methane molecule via reaction (R2) and (R3), they abstract a hydrogen atom to produce $CHClF_2$, HBr and two methyl radicals. These methyl radical reacted further with $CBrClF_2$ in the propagation step to produce CH_3Br and generate a new $CClF_2$ radical. It is this step (R4) that is the main reaction pathway for the decomposition of $CBrClF_2$ at low temperature . If there is no methane molecule, (R2–R4) would not occur, resulting in a lower conversion of $CBrClF_2$.

$CBrClF_2$		$\rightarrow CClF_2$	$+ Br$	(R1)
$CClF_2$	$+ CH_4$	$\rightarrow CHClF_2$	$+ CH_3$	(R2)
Br	$+ CH4$	$\rightarrow HBr$	$+ CH3$	(R3)
$CBrClF_2$	$+ CH_3$	$\rightarrow CH_3Br$	$+ CClF_2$	(R4)

GLOBAL REACTION KINETICS

Using the measured conversion of $CBrClF_2$, the rate reaction order and the global reaction kinetics were determined. Equimolar intake concentrations of $CBrClF_2$ and CH4 were used. Under the experimental condition, reversible reaction was neglected and thus the reaction rate law depends only on the concentration of reactants. By selecting the two reactant species' initial concentrations to he in stoichiometric ratio, 1:1 the rate law can he written:

$$\text{Rate} = k\,[CBrClF_2]\, x\, [CH_4]\, y = k[CBrClF_2]\, n \qquad (4)$$

$$n = x + y \quad \text{(global reaction order)}$$

where k is the proportionality rate constant in terms of $L^{n-1}\, mol^{1-n}\, s^{-1}$, the concentration of $CBrClF_2$ and CH_4 is in $molL^{-1}$, and the rate of the reaction is in $mol\, L^{-1}\, s^{-1}$.

The global kinetics of the reaction were calculated using the ideal plug-flow equation and an assumed constant density system for simplicity. The experimental data of the global reaction was found to obey second-order kinetics. Figure 6 illustrates Arrhenius plots for a second order coupling reaction, x/(1-x) versus residence time. t. Using the rate constants determined hy Figure 6, an Arrhenius plots of natural log of rate constants versus $1/T$ were shown in Figure 7. The second-order global rate constant were estimated:

$$k_{global} = 9.41 \times 10^{10} \, (L^{1-n} \, mol^{-1} s^{-1}) \times \exp(-154.04 \, kJ \, mol^{-1} / RT) \tag{5}$$
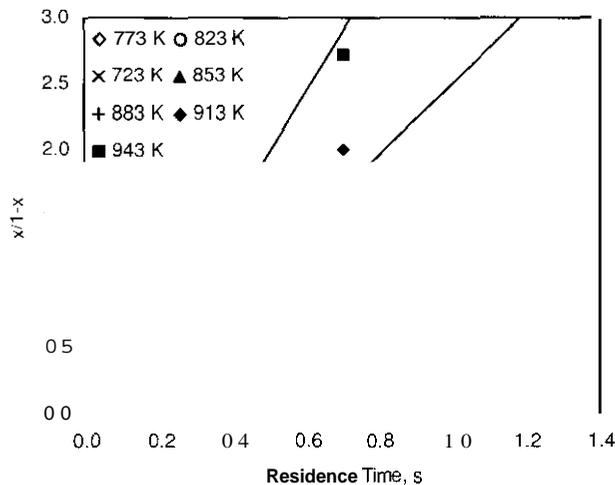
Figure 6. 2nd-order behavior for the coupling reaction of $CBrClF_2$ and CH_4 over the temperature range 673–1003 K. X represents fractional conversion of $CBrClF_2$.
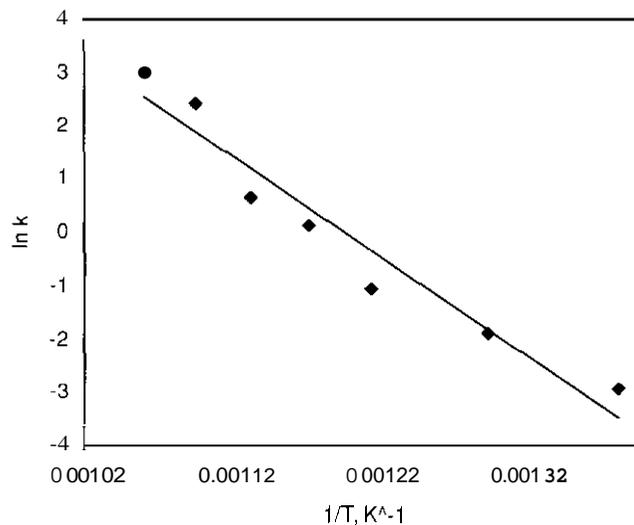
Figure 7. Arrhenius plot for 2nd-order reaction rate constant for the coupling reaction of $CBrClF_2$ and CH_4.

CONCLUSION

For an equimolar intake concentrations of $CBrClF_2$ and CH_4, the conversion level of $CBrClF_2$ and CH_4 increases with increasing temperature and residence time. Throughout the temperature range studied, the conversion of CH4 is well below that of $CBrClF_2$. Complete conversion of $CBrClF_2$ was obtained at 1073 K for all residence times considered. The reaction (at low temperatures) obeys second-order kinetics, with a global activation energy of $154.4 kJ/mol$. For a given temperature, there exists an optimum residence time that maximizes the formation of $CHClF_2$, C_2F_4, $CHBrF_2$, and C_2HClF_2. These species are consumed at longer residence time.

ACKNOWLEDGMENT

REFERENCES

1. Garcia, R.R., and Solomon, S.A., "New Numerical Model of the Middle Atmosphere, 2, Ozone and Related Species," *J. Geophys. Res.,* 99(D6), 12,937-12,951, 1994.

2. Solomon, S., Wuebbles, D., Isaksen, I., Kiehl, J., Lal, M., Simon, P., and Sze, N.D., *Ozone Depletion Potentials, Global Warming Potentials, and Future Chlorine/Bromine Loading, in Scientific Assessment of Ozone Depletion:* 1994, Rep. 31, pp. 13.1-13.6, World Meteorol. Org. Global Ozone Res. and Monit. Proj., Geneva, 199.5.

3. Butler, J.H. et al., "Growth and Distribution of Halons in the Atmosphere," *J. Geophys. Res.,* 103, pp. 1503-1511, 1998.

4. Fraser, P.J. et al., "Southern Hemispheric Halon Trends (1978-1998) and Global Halon Emissions," *J. Geophys Res,* 104(D13):15985-15999, 1999.

5. *UNEP Technology and Economic Assessment Panel April 1998 Report,* United Nations Environment Programme, Nairobi, Kenya, 1998.

6. Montzka, S.A., Butler, J.H., Elkins, J.W., Thompson, T.M., Clarke, A.D., and Lock, L.T., "Present and Future Trends in the Atmospheric Burden of Ozone-Depleting Halogens," *Nature,* 398, pp. 690-694, 1999.

7. de Lijser, H.J.P., Louw, R., and Mulder, P., "Thermal Gas Phase Hydrodehalogenation of Bromochlorodifluoromethane," *Journal of the Chemical Society, Perkin Transaction II,* pp. 139-145, 1994.

8. Li, K., Kennedy, E.M., Behdad, M., and Dlugogorski, B.Z., "Experimental and Computational Studies on the Gas Phase Reaction of $CBrF_3$ with Hydrogen," *Environnzental Science and Technology* 35(4), 219, 2000.

9. Hidaka, Y., Nakamura, T., and Kawano, H., "CF_3Br-H_2 Reaction in Shock Waves," *Inter-national Journal of Chemical Kinetics,* 25, pp. 983-993, 1993.

10. Ritter, E.R., "Experimental Study on Freon 113 Decomposition Under Inert and Reducing Conditions," *Combustion Science and Technology,* 101, pp. 171-186, 1994.

11. Li, K., Kennedy, E.M., and Dlugogorski, B.Z., "Gas-Phase reaction of Halon 1301 ($CBrF_3$) with methane," *Industrial and Engineering Chemistry Research* 38(9), p. 334.5, 1999.

12. Height, M.J.. Kennedy, E.M., and Dlugogorski. B.Z., "TCD Relative Molar Response Factors for Halogenated Compounds," *J Chromatography A*. 841(2), **pp.** 187-195, 1999.

13. Tee, L.S., Gotch, S., and Stewart, W.E., *Ind. Eng. Chem. Fund.,* 5, p. 356, 1966.

14. Lide. D.R., and Kehiaian. H.V., *CRC Handbook of Chemistry urid Physics*, 79ed, CRC Press, Boca Raton, FL, 1998.

15. Yaws, C.L., *Handbook of Chemical Compound Data for Process Safety*, Gulf Publishing Co, Houston, TX. pp. 5-12, 1997.

16. Zumdahl, Steven S., *Chemical Principles*. 2ed., pp. 221-223, 1995,

17. Babushok, V., Noto, T., Burgess, D.R.F., Hamins, A., and Tsang. W., "Influence of CF_3I, CF_3Br, and CF_3H on the High-Temperature Combustion of Methane," *Conihustion and Flume*. 107, pp. 351-367, 1996.