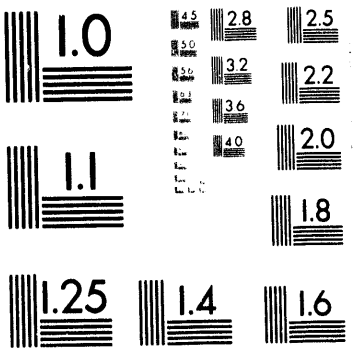
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by

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Keywords: Rate constants, Shock tubes, Chlorocarbon dissociations

ABSTRACT

Because of needs for understanding the chemical kinetic mechanism in chlorocarbon molecule incineration, we have recently completed studies on the thermal decompositions of $COCl_2$, CH_3Cl, CH_2Cl_2, CCl_4, and CF_3Cl. The shock tube technique combined with atomic resonance absorption spectrometry (ARAS), as applied to Cl atoms, has been used to obtain absolute rate data for these reactions. In all cases, the decompositions are nearly in the second-order regime. Theoretical calculations, using the Troe formalism, have been performed. In these calculations, both the threshold energies for decomposition, E_0, and the energy transferred per down collision, ΔE_{down}, are varied parametrically for best fitting to the data. The latter quantity determines the collisional deactivation efficiency factor, β_c.

INTRODUCTION

This article discusses thermal decomposition results obtained with the shock tube technique for five chlorocarbon molecules. One motivation is to supply thermal rate data for understanding the chemical destruction mechanisms in incinerators for this important class of compounds. The atomic resonance absorption spectrometric (ARAS) method is used to monitor the production of Cl atoms as they form during the decompositions. The reactions studied are:

$$COCl_2 \ (+ Kr) \rightarrow COCl + Cl \ (+ Kr), \qquad (1a)$$

$$\rightarrow CO + Cl_2 \ (+ Kr), \qquad (1b)$$

$$CH_3Cl \ (+ Ar) \rightarrow CH_3 + Cl \ (+ Ar), \qquad (2)$$

$$CH_2Cl_2 \ (+ Kr) \rightarrow CH_2Cl + Cl \ (+ Kr), \qquad (3a)$$

$$\rightarrow CHCl + HCl \ (+ Kr), \qquad (3b)$$

$$CCl_4 \ (+ Ar) \rightarrow CCl_3 + Cl \ (+ Ar), \qquad (4)$$

$$CF_3Cl \ (+ Kr) \rightarrow CF_3 + Cl \ (+ Kr). \qquad (5)$$

We have attempted to rationalize the results on these reactions with Troe type theoretical fits that are based on C—Cl bond strengths and the average energy transferred per down collision.[1-3] The results of these comparative theoretical calculations are discussed.

EXPERIMENTAL

The shock tube methods that are used in the present studies are traditional[4] and have been described in detail previously.[5-9] Therefore, only a brief description will be given here. Experiments in both incident and reflected shock waves have been carried out on these systems. In both instances, corrections for non-ideal shock wave behavior have been applied.[10] The tube has an optical path length of 9.94 cm, and the resonance radiation from a Cl-atom resonance lamp traverses the tube at a distance of 67 or 6 cm from the endplate for incident or reflected shock wave experiments, respectively.

In order to use the method, it was necessary to measure the curve-of-growth for Cl atoms. In experiments on CH_3Cl,[6] the curve-of-growth was determined; however, the results were slightly perturbed by secondary chemistry. We have checked the curve-of-growth by carrying out additional experiments with CF_3Cl where no such complications are present.[9] The results are shown in Fig. 1 where they are compared to the dashed line determined previously.[5,6] This result demonstrates that the perturbing secondary chemistry in the CH_3Cl case was adequately being described because the present agrees with the earlier result within experimental error. The line shown in the figure can be expressed in modified Beer's law form as:

$$-\ln(I/I_0) \equiv (ABS) = \sigma\ell[Cl]^{\alpha} = 4.41 \times 10^{-9}\,[Cl]^{0.581} \qquad (6)$$

when [Cl] is expressed in molecules cm^{-3}. Hence any value of $(ABS)_t$ can be converted into $[Cl]_t$ thereby giving a Cl-atom concentration profile for any experiment.

RESULTS

The thermal decomposition results were obtained at three loading pressures in either incident or reflected shock wave experiments. Bimolecular rate constant values, k/[M], were determined in each instance. The data were then plotted in Arrhenius form as shown in Figs. 2 to 7. Essentially no pressure effects could be documented in any of the cases within experimental error suggesting that the decompositions were near to the low pressure values. We then performed linear least squares analysis on the entire data base for each reactant. The results are given as equations (7) to (13) in units of cm^3 $molecule^{-1}$ s^{-1}.

Reaction (1a): $k/[Kr] = 7.24 \times 10^{-8} \exp(-30594\ K/T)$ (7)

Reaction (1b): $k/[Kr] = 7.60 \times 10^{-9} \exp(-30594\ K/T)$ (8)

Reaction (2): $k/[Ar] = 1.09 \times 10^{-8} \exp(-29325\ K/T)$ (9)

Reaction (3a): $k/[Kr] = 6.64 \times 10^{-9} \exp(-28404\ K/T)$ (10)

Reaction (3b): $k/[Kr] = 2.26 \times 10^{-8} \exp(-29007\ K/T)$ (11)

Reaction (4): $k/[Ar] = 1.19 \times 10^{-7} \exp(-25050\ K/T)$ (12)

Reaction (5): $k/[Kr] = 1.73 \times 10^{-7} \exp(-33837\ K/T)$ (13)

DISCUSSION

We have used the semi-empirical form of Troe theory[1-3] to calculate theoretical rate constants for these reactions. Since there are no potential energy surface calculations for the present cases, as described earlier,[6] the best choice of transition states are the Lennard-Jones (LJ) complexes where the LJ-distance between the combining species is taken to be the reaction coordinate, and all rotational degrees of freedom in each of the combining species are considered to be free. Using conventional transition state theory, this model will always give, as the high pressure limit for the recombination of the two species making up the complex, the collision rate constant with electronic degeneracy factors included. Hence,

$$k_{-1LJ} = (g^{\ddagger}/g_1 g_2)\, \sigma_{12}^2 \Omega(2,2)^* \,(8\pi kT/\mu)^{1/2} \exp(\varepsilon_{12}/kT). \qquad (14)$$

With $g^{\ddagger} = 1$, $g_1 = g_{radical} = 2$, and $g_2 = g_{Cl} = 2\,(2 + \exp(-hc(882.36\ cm^{-1})/kT))$, equation (14) has been evaluated for the various back reactions. The value for the high pressure dissociation rate constants are then calculated as $k_{\infty} = k_{-1LJ}K$ where equilibrium constants, K, have been directly calculated from molecular constants.

The theory of Troe and coworkers[1-3] has then been used to calculate the limiting low pressure rate constants, k_{sc}^{o}, which are functions of the various threshold energies, E_o. These values for k_{∞} and k_{sc}^{o}, along with the LJ model for the transition states and values for the collisional deactivation efficiency factor, β_c, can then be used to calculate values for S_K, B_K, F_{cent}, and finally, k/[M] = $k_{\infty}F_{LH}F(P_r)$ where F_{LH} is the Lindemann-Hinshelwood factor, $P_r/(1+P_r)$, and $F(P_r)$ is the broadening factor, a function of reduced pressure, $P_r = \beta_c k_{sc}^{o}[M]/k_{\infty}$. The parameter, ΔE_{down}, determines β_c. In all of the present calculations, we parametrically vary both E_o and ΔE_{down}. The final fitted theoretical results are compared to the data in Figs. 2-7.

For $COCl_2$, parametric calculations were carried out with E_o between 65.4 and 77.5 kcal $mole^{-1}$ and with respective ΔE_{down} values between 420 and 4897 cm^{-1}.[5] Mutual values, (75.5, 2553), (75.0, 2169), (74.5, 1714), or (73.75, 1574), can explain the data shown in Fig. 2; however, the best overall fit is with the third set. This threshold value implies a heat of formation for COCl that is consistent with new thermochemical data[11] within experimental error. Similar parametric calculations were carried out for CH_3Cl, again yielding a range of acceptable values which are: (81.3, 866), (80.3, 761), (79.3, 638), (78.3, 560), or (77.3, 490). The calculation for the middle set is shown in Fig. 3. Using the heat of formation for CH_3Cl given in the JANAF tables,[12] the

implied E_o value would be 82.32 kcal mole^{-1}. Since the heats of formation of Cl and CH_3 are not in doubt, the present results would suggest a (-3.0 ± 2.0) kcal mole^{-1} modification to (-15.1 ± 2.0) kcal mole^{-1} for the heat of formation of CH_3Cl at 0 K. It should be pointed out that the large ΔE_{down} value of 1600 cm^{-1}, reported earlier,[6] is mostly due to the fact that E_o was fixed at the JANAF value of 82.32 kcal mole^{-1}. Two thermal decomposition processes have to be considered in the thermal decomposition of CH_2Cl_2.[7] The one that gives Cl atoms is about one-third of the molecular elimination process. We have carried out parametric calculations on both processes. The Cl-atom process can be fitted with mutual values, (81.25, 560), (78.25, 394), and (75.25, 268) with the middle set being only slightly superior at all pressures. The best set for the molecular elimination process is (73.0, 630). These two best fits are shown in Figs. 4 and 5. Our conclusion is that the heat of formation for CH_2Cl at 0 K is (28.5 ± 3.0) kcal mole^{-1}, and this agrees with a recent evaluation.[13] Several Troe calculations have been carried out for CCl_4 using only the ARAS data from this laboratory.[8] Mutual values, (68.7, 1329), (67.7, 1049), (66.7, 735), (65.7, 560), or (64.7, 428), bracket the acceptable sets of fits. The lines shown in Fig. 6 are calculated from the middle set. Hence, the implied value for E_o is (66.7 ± 2.0) kcal mole^{-1}, and this agrees with a recent thermochemical determination for the heat of formation of CCl_3, 16.7 kcal mole^{-1}.[14] Lastly, the acceptable parametric fits for the CF_3Cl experiments[9] are: (87.0, 1049), (86.0, 857), (84.8, 700), or (84.0, 595). The best fit is with the second set implying that E_o = (86.0 ± 2.0) kcal mole^{-1}, and this calculation is shown in Fig. 7. This suggests that the heat of formation for CF_3Cl at 0 K is (-1.2 ± 2.0) kcal mole^{-1} lower than the JANAF value[12] at (-169.2 ± 2.0) kcal mole^{-1}. Therefore, the present value agrees with JANAF within experimental error. The findings from the theoretical calculations are summarized in Table 1.

In four out of the five cases, the thermochemical conclusions from the present analysis are in agreement with earlier thermochemical data. The only exception is CH_3Cl where a downward modification of 3.0 kcal mole^{-1} in the heat of formation would be more compatible with our results. Stronger thermochemical conclusions from the present results are simply not possible because, in each case, there are a number of acceptable fits spanning a range of threshold energies. In principal, this range could be narrowed if the temperature range were substantially expanded; however, with the present ARAS technique, a large increase in the temperature range is not possible. We point out that even if the temperature range was much greater, there is a strong coupling between E_o and ΔE_{down} (i. e., they are strongly correlated). Hence, an uncertain knowledge in either parameter creates a significant uncertainty in the other quantity. Troe and coworkers have given a rationale for understanding the behavior of the collisional deactivation efficiency factor, β_c, in terms of the energy loss per collision with bath gas molecules. These factors decrease with increasing temperature thereby supplying a reason for the usual observation that apparent experimental activation energies are always lower than the bond strengths of the bond being broken in a dissociation. This is a significant advance in understanding; however, it is still true that there is really no first principles theory for *a priori* calculation of these quantities.[15] Trends in β_c's (or in the ΔE_{down} values that determine them) might be discovered if the thermochemistry is known perfectly. This may be the case in hydrocarbon chemistry; however, there are still uncertainties in the chlorocarbon thermodynamic functions. We believe that this is a partial explanation for the unrelated values for ΔE_{down} in Table 1. With this state of affairs, continuing experimental studies on this type of molecule are absolutely necessary if the thermal rate behavior is desired for any reason. Theoretical calculations alone will not be predictive and therefore will not be helpful.

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Table 1. **Theoretical Results**

Reaction	ΔE_{down}/cm^{-1}	E_0/kcal mole^{-1}	Comments	Ref.
$COCl_2$ (+ Kr) → COCl + Cl (+ Kr)	1714	74.5±1.0	75.6 implied by	11,12
CH_3Cl (+ Ar) → CH_3 + Cl (+ Ar)	638	79.3±2.0	compared to 82.3	12
CH_2Cl_2 (+ Kr) → CH_2Cl + Cl (+ Kr)	394	78.25±3.0	79.0 implied by	12,13
→ CHCl + HCl (+ Kr)	630	73.0±3.0	79 or 70.1, from	12or13
CCl_4 (+ Ar) → CCl_3 + Cl (+ Ar)	735	66.7±2.0	67.7 implied by	12,14
CF_3Cl (+ Kr) → CF_3 + Cl (+ Kr)	857	86.0±2.0	compared to84.8	12

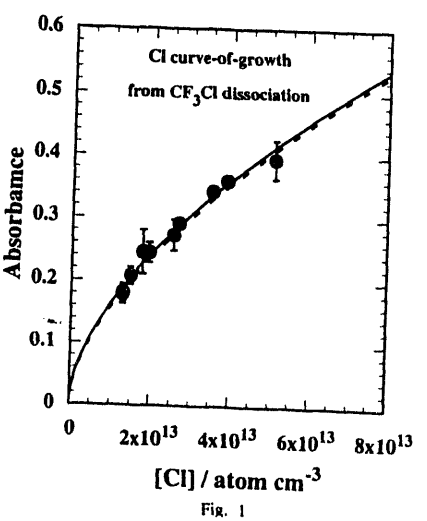
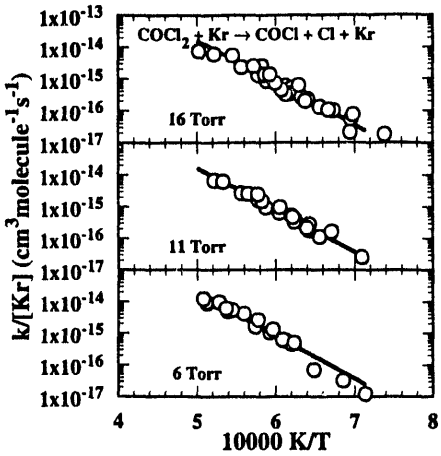


Fig. 1



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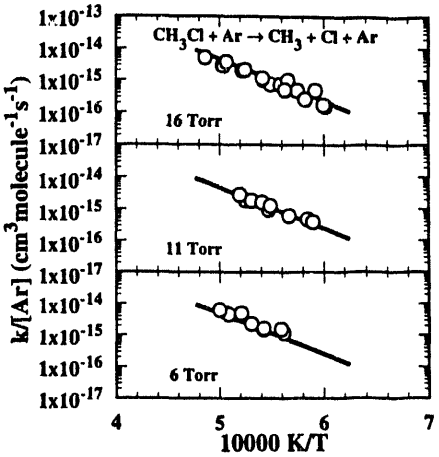

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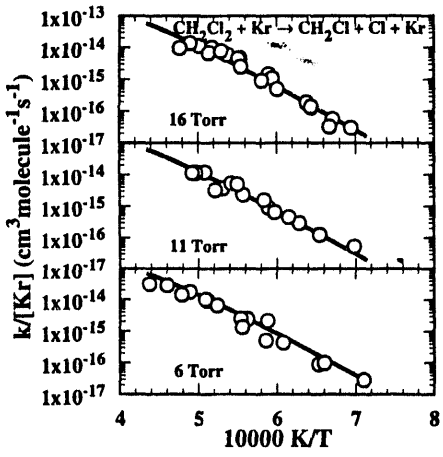

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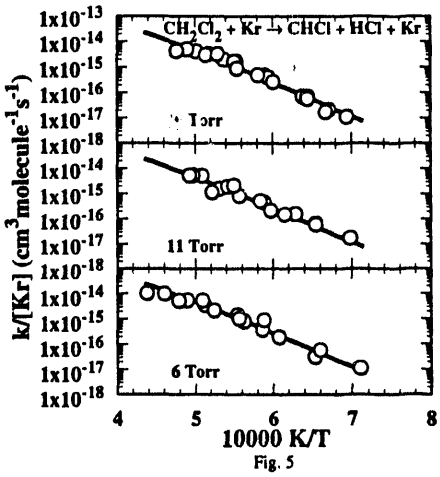

Fig. 5

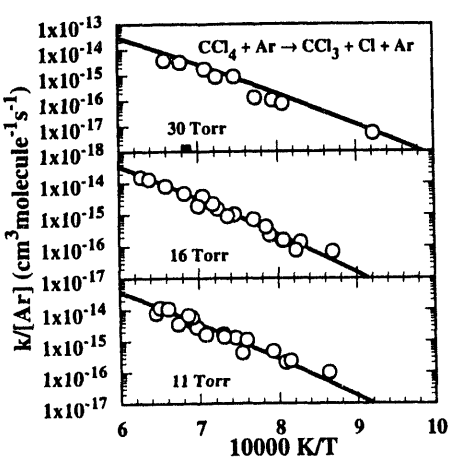

Fig. 6

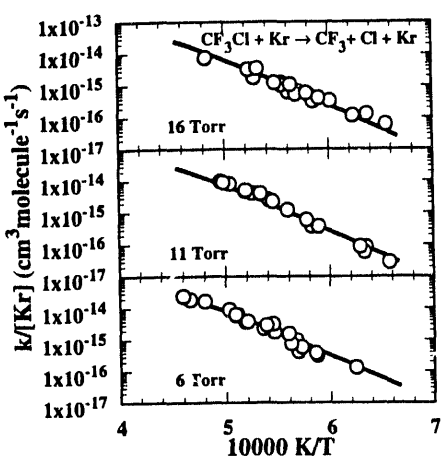

Fig. 7

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