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RATE CONSTANT FOR THE REACTION OF ATOMIC CHLORINE WITH FORMALDEHYDE FROM 200 TO 500K

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ABSTRACT

The absolute rate constant for the reaction of atomic chlorine with formaldehyde has been measured from 200 to 500K using the flash photolysis - resonance fluoresence technique. The results were independent of substantial variations in [H_2CO], total pressure (Ar) and flash intensity (i.e., initial [$C\ell$]). The rate constant was shown to be invariant with temperature, the best representation for this temperature range being $k_1 = (7.48 \pm 0.50) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} where the error is one standard deviation. This result is compared with the only previous determination of k_1 which was a relative value obtained at 298K. The rate constant is theoretically discussed and the potential importance of the reaction in stratospheric chemistry is considered.

INTRODUCTION

Accurate and direct measurements of the reaction of Cℓ atoms with hydrogenous species are of great current interest due to the possible modification of the earth's stratospheric ozone layer by chlorofluoromethane release[1,2]. Rate constants for the reactions of Cℓ atoms with the stratospheric species CH_4, H_2, and H_2O_2, have recently been reported from this laboratory[3-5]. Though formaldehyde, H_2CO, has not yet been identified as a stratospheric species, a preliminary determination of the rate constant for the reaction

$$C\ell + H_2CO \rightarrow H\,C\ell + HCO, \qquad (1)$$

together with a one dimensional stratospheric modeling calculation, has indicated that reaction (1) should be considered in the chemical modeling of the stratosphere[6]. The argument for the inclusion of reaction (1) follows from the highly probable assumption that methyl radicals produced by the reactions

$$C\ell + CH_4 \rightarrow H\,C\ell + CH_3 \qquad (2)$$

$$OH + CH_4 \rightarrow H_2O + CH_3 \qquad (3)$$

$$O(^1D) + CH_4 \rightarrow OH + CH_3 \qquad (4)$$

will subsequently yield H_2CO through oxidation. The formaldehyde will likely be formed in a one to one correspondence with the methane destroyed in reactions (2) - (4). Detailed consideration of the rate of reaction (1) from the work of Niki, et al.[7] and the preliminary

work from this laboratory[6] shows that the rate constant is ~ 1600 times larger than that for reaction (2) at 40 km where T = 250K. Thus, mixing ratios for H_2CO in the range of a few tenths of a part per billion can compete effectively with CH_4 for Cℓ atoms. Consideration of the rate of methane destruction (and H_2CO formation) in a model calculation shows that such levels are obtainable. Furthermore, inclusion of reaction (1) indicates a decreased sensitivity for long term ozone perturbation by odd chlorine from the currently accepted value of 20% down to 18.5%.[6]

The only previous determination of the rate constant for reaction (1) is by Niki, et al[7] who determined the rate constant relative to $C\ell + C_2H_6$ at T = 298K. They report a value of $k_1^{298K} = (7.8 \pm 0.6) \times 10^{-11}$ (2σ) cm^3 $molecule^{-1}$ s^{-1}. This study reports the details of our preliminary study and extends the determination from 200 to 500K. Thus, the stratospheric temperature regime is well overlapped.

EXPERIMENTAL

The flash photolysis-resonance fluorescence apparatus (FP-RF)[8] and its application to hydrogen abstraction reactions by atomic chlorine[3-5] have been described previously so only those details specific to the present study will be given here. $C\ell$ atoms were generated by the flash photolysis of $CC\ell_4$ at initial concentration levels ranging from (1-5) x 10^{11} to (1-5) x 10^{10} atoms cm^3. In all of the present work, the photolysis wavelengths were determined by the absorption coefficient of $CC\ell_4$ above λ = 105 nm (LiF cut-off). Because of the relatively large source molecule concentration, $[CC\ell_4]$, compared to reactant, $[H_2CO]$, the possibility of significant competitive formaldehyle photolysis was negligibly small.

As in previous studies chlorine atom resonance radiation was obtained from a microwave electrodeless discharge in 0.5 torr of 0.1% $C\ell_2$ in He. The resonantly scattered fluorescent photons were detected at right angles to both the photolyzing and resonance light sources through a BaF_2 filter ($\lambda \geq 135$ nm), and they were recorded in repetitive flashes by a multichannel analyzer operating in the multiscaling mode.

Preliminary experiments with the ternary mixtures consisting of formaldehyde, carbon tetrachloride, and Ar, showed that small levels of formaldehyde had to be routinely measured due to the very fast reaction with chlorine atoms. We therefore elected to first prepare a fairly concentrated primary mixture of H_2CO in Ar, and then subsequently prepare the secondary reaction mixtures by dilution techniques. Such

a procedure increases the systematic error since two additional accurate pressure measurements are necessary to determine the formaldehyde concentration. However, the decrease in accuracy is not serious, the total uncertainty in concentration being $\sim \pm 3\%$.

It is well known that H_2CO tends to polymerize in the gaseous state, and initial values of the rate constant at T = 298K tended to be uniformly lower than that reported here by $\sim 30\%$. Flow rate variation through the reaction cell showed that formaldehyde was lost in the reaction cell below a critical flow rate; however, above that flow rate the decay constants scaled linearly with the calculated concentration. The derived rate constants, even though they were highly consistent, were still lower than the value reported here. Subsequent preliminary experiments starting with several different primary mixtures gave higher values for the rate constant leveling off asymptotically to the reported value. Clearly, the initially obtained low rate constant values were due to initial loss of the formaldehyde in storage, and with subsequent exposure, the storage vessel walls eventually became pre-treated, with subsequent stabilization of the homogeneous mixtures to the concentration level determined from the pressure measurements. Only when this condition was reached (as shown by invariance of the rate constant in repeat determinations) were the kinetic experiments carried out. Substantial variations in flash energy (i.e.; initial [Cl]), [H_2CO], and pressure showed no additional complications due to secondary reactions or other initial primary photolysis products.

The observed pseudo-first-order $C\ell$ atom decay plots were strictly linear. The decay constants from such plots are composite consisting of contributions from reaction (1) and diffusion of $C\ell$ atoms from the viewing zone. Therefore, experiments were carried out with no formaldehyde present under exactly similar conditions in order to measure the diffusional contribution. These contributions were less than 10% for most of the experiments reported here. However, for some experiments at 500K, the contributions were as high as 35% of the total decay constant.

Argon (Matheson, 99.9995%) and helium (Airco, 99.9999%) were used,without further purification. Chlorine (Matheson, 99.5%) was further purified by bulb-to-bulb distillation at 195K, the middle third being retained. $CC\ell_4$ (Matheson, Coleman, and Bell, 99%) was subjected to bulb-to-bulb distillation at 233K, and the middle third was retained. Formaldehyde was prepared from paraformaldehyde[9] by heating at 383K. The liquid N_2 trapped monomer was then bulb-to-bulb distilled at 193K with retention of the middle third. The sample was thoroughly outgassed at 113K in order to remove CO_2 and was stored at liquid N_2 temperature. Mass spectral analysis showed the sample to be 99.7% pure, the only measurable impurity being H_2O.

RESULTS

All of the reported experiments were carried out under pseudo-first-order conditions with $[H_2CO] \gg [C\ell]$. Then the decay of $[C\ell]$ is represented by

$$\ell n\ [C\ell] = -\ k_{observed}\ t + \ell n\ [C\ell]_0 \qquad (5)$$

with the pseudo-first-order decay constant given by

$$k_{observed} = k_1\ [H_2CO]_0 + k_d. \qquad (6)$$

k_1 is the bimolecular rate constant for reaction (1), and k_d is the first-order rate constant for $C\ell$ atom diffusion from the viewing zone. $k_{observed}$ is obtained by linear least squares methods from plots of the logarithm of accumulated counts against time. Accumulated counts are proportional to $[C\ell]$. Typical results at 200K are shown in Fig. 1. Similar experiments are performed with $[H_2CO] = 0$ in order to obtain k_d at each condition of the kinetic experiments. Then a knowledge of k_d and $[H_2CO]_0$ with eq. (6) allows the determination of k_1. The results at 200, 298, and 500K are shown in Table I over substantial changes in flash energy, $[H_2CO]$, and pressure. The errors are one standard deviation values as determined from repeat determinations at the indicated experimental condition. The results show that k_1 has no temperature dependence for $200 \leq T \leq 500K$. The best representation for this temperature range is $k_1 = (7.48 \pm 0.50) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} where the error is the mean of the standard deviations from the determinations at each temperature in Table I.

DISCUSSION

The present value for $k_1 = (7.48 \pm 0.50) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for $200 \leq T \leq 500K$ can be compared to the recent value of Niki, et al.[7] These workers determined the rate constant relative to $C\ell + C_2H_6 \rightarrow HC\ell + C_2H_5$ by observing relative reactant destruction on photochlorination. The concentration detection technique was Fourier transform infrared spectroscopy and a room temperature value for k_1 of $(7.8 + 0.6) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} was obtained. Comparison with the present room temperature value shows exact agreement within combined experimental uncertainties.

A related reaction with which reaction (1) can be compared is the reaction of $C\ell$ with C_2H_6. This reaction has been directly studied by Manning and Kurylo (FP-RF)[10] and Lewis et al.[11] (discharge flow-resonance fluorescence) who report respective rate constants of $(7.29 \pm 1.23) \times 10^{-11} \exp(-61 \pm 44/T)$ and $8.1 \times 10^{-11} \exp(-126 \pm 33/T)$ cm^3 $molecule^{-1}$ s^{-1}. The reaction has been theoretically discussed by Johnston[12] who shows that little, if any, effect of a potential energy barrier should be expected since the reactant zero point energy exceeds the barrier height. This is born out by the two cited direct studies where only a minimal energy barrier is indicated.[10,11] With regard to the present reaction, the relationship noted by Johnston is even more in favor of no measurable energy barrier since the zero point energy of reactants is very much higher than the potential energy barrier. This can be easily seen within the framework of the BEBO

method[12] since the potential energy of activation is described in terms of single bond energies for R-H and HCℓ. Qualitatively, if the bond strength of R-H decreases, then the derived potential energy of activation will also decrease. Comparison of D^{o}_{CH} values for the series CH_4, C_2H_6, and H_2CO shows a decreasing trend from 103, 98, and 86 kcal/mole, respectively.[13,14]

It therefore appears that the rate constant for reaction (1) is totally determined by two factors, (1) the interaction rate constant and (2) the relative orientation of Cℓ and H_2CO. The interaction rate constant can be fairly accurately estimated from transport property data.[15,16] Judeikis and Wun have reported a value for the diffusion coefficient of Cℓ atoms in Ar of (0.26 ± 0.05) cm^2 s^{-1} at 1 atm and 295K.[17] Their value is consistent with Lennard-Jones parameters of $\sigma_{C\ell,Ar} = 2.89$Å and $\epsilon_{C\ell,Ar}/k = 119$K. With combining rules, $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ and $\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2}$, and Lennard-Jones parameters for Ar, the corresponding values for Cℓ atoms are $\sigma_{C\ell} = 2.34$Å and $\epsilon_{C\ell}/k = 119$K. Values for H_2CO are not available but are not expected to be much different than those for the isoelectronic molecule C_2H_4 (i.e.; $\sigma = 4.07$Å and $\epsilon/k = 230$K)[16]. Then the Lennard-Jones rate constant can be calculated as[15]

$$Z_{LJ} = \sigma_{12}^2\, \Omega^*(2,2)\, (8\pi kT/\mu)^{1/2} \qquad (7)$$

All quantities have their usual meanings, and $\Omega^*(2,2)$ is a tabulated integral.[16] The calculated values from $200 \leq T \leq 500$K range from 2.4 to 2.7×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Because of uncertainties in

potential parameters, the hard sphere values have also been calculated, and these range from 1.6 to 2.6 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1} over the same range of temperature. Comparison of the present value of k_1 (i.e., (7.48 $\pm$ 0.50) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}) with these estimates of thermalized collision rate constants suggests a value for the steric factor in the range of 0.3 - 0.5. We note that the most navie estimate of the steric factor would be 0.5. The point to this discussion is to indicate the simplicity of reaction (1) and to illustrate that the use of even the simplest theoretical formalism is sufficient to predict the rate constant within a factor of 1.7.

As indicated in the Introduction, reaction (1) is also important in the stratosphere.[6,7] H_2CO is thought to be produced in a one to one correspondence from the product methyl radicals in reactions (2) - (4). However, this assumption is clearly an oversimplication since initially the methyl radicals are destroyed by

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad [18-22] \tag{8}$$

and/or

$$CH_3 + O_2 \rightarrow H_2CO + OH \quad [21] \tag{9}$$

Baldwin and Golden[23] doubt the existence of reaction (9), and this ambiguity suggests the need for further study. If reaction (8) dominates then methyl peroxy radicals can be removed in the stratosphere by

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad [24-27] \tag{10}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \quad [27] \tag{11}$$

$$CH_3O_2 + NO_2\ (+M) \rightarrow CH_3O_2NO_2\ (+M). \tag{12}$$

Methoxy radical (CH_3O) oxidation possibly by O_2, HO_2, NO, or NO_2 can yield formaldehyde, but methanol (CH_3OH) may also result. By direct analogy with the reaction between HO_2 and NO_2 giving peroxy nitric acid,[28-30] we have also included reaction (12). This reaction is favorable since CH_3O_2 has a large number of degrees of freedom and the temperature is low. Thus, in the context of RRKM theory, the vibrationally hot adduct should have a long lifetime, and reaction (12) may be near its high pressure limit even stratospheric densities. The above scheme suggests the probability of several compounds which contain the methoxy group. We note that Cℓ atom reactions with such compounds would have similar rate constants as Cℓ + H_2CO. Lastly, the radicals produced from such reactions will likely yield H_2CO so that the noted decreased sensitivity to odd chlorine[6] may be as much as doubled.

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REFERENCES

1. F.S. Rowland and M.J. Molina, Rev. Geophys. Space Phys. 13, 1 (1975).
2. R.D. Hudson, Ed., "Chlorofluoromethanes and the Stratosphere", NASA Reference Publication 1010 (1977).
3. D.A. Whytock, J.H. Lee, J.V. Michael, W.A. Payne, and L.J. Stief, J. Chem. Phys. 66, 2690 (1977).
4. J.H. Lee, J.V. Michael, W.A. Payne, L.J. Stief, and D.A. Whytock, J. Chem. Soc. Faraday Trans. I 73, 1530 (1977).
5. J.V. Michael, D.A. Whytock, J.H. Lee, W.A. Payne, and L.J. Stief, J. Chem. Phys. 67, 3533 (1977).
6. L.J. Stief, J.V. Michael, W.A. Payne, D.F. Nava, D.M. Butler, and R.S. Stolarski, Geophys. Res. Letts., 5, 829 (1978); also NASA TM 79552, May 1978.
7. H. Niki, P.D. Maker, L.P. Breitenbach, and C.M. Savage, Chem. Phys. Letts. 57, 596 (1978).
8. R.B. Klemm and L.J. Stief, J. Chem. Phys. 61, 4900 (1974).
9. R. Spence and W. Wild, J. Chem. Soc. 338 (1935).
10. R.G. Manning and M.J. Kurylo, J. Phys. Chem. 81, 291 (1977).
11. R.S. Lewis, S.P. Sander, S.G. Wagner and R.T. Watson (manuscript in preparation, 1978).
12. H.S. Johnston, "Gas Phase Reaction Rate Theory", (Ronald, New York, 1966), p. 251.
13. NBS Special Publication 513 "Reaction Rate and Photochemical Data for Atmospheric Chemistry - 1977", R. F. Hampson, Jr. and D. Garvin, Eds., May 1978.

14. S.W. Benson, "Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters", (Wiley, New York, 1968).

15. S.C. Chan, J.T. Bryant, L.D. Spicer, and B.S. Rabinovitch, J. Phys. Chem. 74, 2058 (1970).

16. J.C. Hirschfelder, C.F. Curtiss, and R.B. Bird, "Molecular Theory of Gases and Liquids", (Wiley, New York, 1964).

17. H.S. Judeikis and M. Wun, J. Chem. Phys. 68, 4123 (1978).

18. H.E. van den Bergh and A.B. Callear, Trans. Faraday Soc. 67, 2017 (1971).

19. N. Basco, D.G.L. James, and F.C. James, Int. J. Chem. Kinet. 4, 129 (1972).

20. A.H. Laufer and A.M. Bass, Int. J. Chem. Kinet. 7, 639 (1975).

21. N. Washida and K.D. Bayes, Int. J. Chem. Kinet. 8, 777 (1976).

22. C.J. Hochanadel, J.A. Ghormley, J.W. Boyle, and P.J. Ogren, J. Phys. Chem. 81, 3 (1977).

23. A.C. Baldwin and D. Golden, Chem. Phys. letts. 55, 350 (1978).

24. C.T. Pate, B.J. Finlayson, and J.N. Pitts, Jr., J. Am. Chem. Soc. 96, 6554 (1974).

25. R. Simonaitis and J. Heicklen, J. Phys. Chem. 78, 2417 (1974).

26. R.A. Cox, R.G. Derwent, P.M. Holt, and J.A. Kerr, J. Chem. Soc. Faraday Trans. I 72, 2044 (1976).

27. K.L. Demerjian, J.A. Kerr, and J.G. Calvert, Adv. Environ. Sci. Tech. 4, 1 (1974).

28. R.A. Cox and R.G. Derwent, J. Photochem. 4, 139 (1975).

29. C.J. Howard, J. Chem. Phys. 67, 5258 (1977).

30. R. Simonaitis and J. Heicklen, Int. J. Chem. Kinet. 10, 67 (1978).

Table I. RATE DATA FOR THE FLASH PHOTOLYSIS-RESONANCE FLUORESCENCE STUDY OF THE REACTION Cl + H_2CO

T / K	$[H_2CO]$ / m Torr	$[CCl_4]$ / m Torr	[Ar] / Torr	Flash Energy / Joule	No. of Expts	k_{bi}[a] / $10^{-11}cm^3molecule^{-1}sec^{-1}$
200	0.11	13	25	20-81	4	7.44 ± 0.10
	0.15	13	25	23-81	4	7.72 ± 0.28
	0.23	25	50	20-81	4	6.97 ± 0.40
	0.29	25	50	20-95	4	8.02 ± 0.67
	0.34	38	75	20-81	4	7.04 ± 0.59
	0.44	38	75	20-95	4	7.77 ± 0.77
	0.46	50	100	20-81	3	7.49 ± 0.13
	0.59	50	100	36-81	3	7.72 ± 0.86
					30	7.52 ± 0.59[b]
298	0.18	13	25	20-81	4	7.52 ± 0.42
	0.20	13	25	56,81	2	7.10 ± 0.37
	0.23	17	25	20-68	4	7.46 ± 0.21
	0.35	25	50	20-81	4	7.48 ± 0.80
	0.39	25	50	20-81	4	7.17 ± 0.19
	0.47	34	50	20-81	3	8.03 ± 0.12
	0.53	38	75	20-81	4	7.65 ± 0.22
	0.59	38	75	20-81	4	7.17 ± 0.54
	0.70	52	75	20-68	3	7.73 ± 0.38
	0.70	50	100	20-81	4	7.68 ± 0.36
	0.78	50	100	20,36	2	7.21 ± 0.12
	0.94	69	100	20-127	4	7.24 ± 0.29
					42	7.46 ± 0.43[b]
500	0.29	13	25	56-95	3	7.28 ± 0.38
	0.47	25	50	36-127	3	7.52 ± 0.48
	0.59	25	50	95	1	6.95
	0.70	38	75	36-110	3	6.66 ± 0.08
	0.88	38	75	36-95	4	6.89 ± 0.38
	0.94	50	100	36-95	4	7.53 ± 0.35
	1.17	50	100	56-95	2	7.64 ± 0.08
					20	7.45 ± 0.48[b]

a. Error limit is the standard deviation.

b. Average k_1 at that temperature

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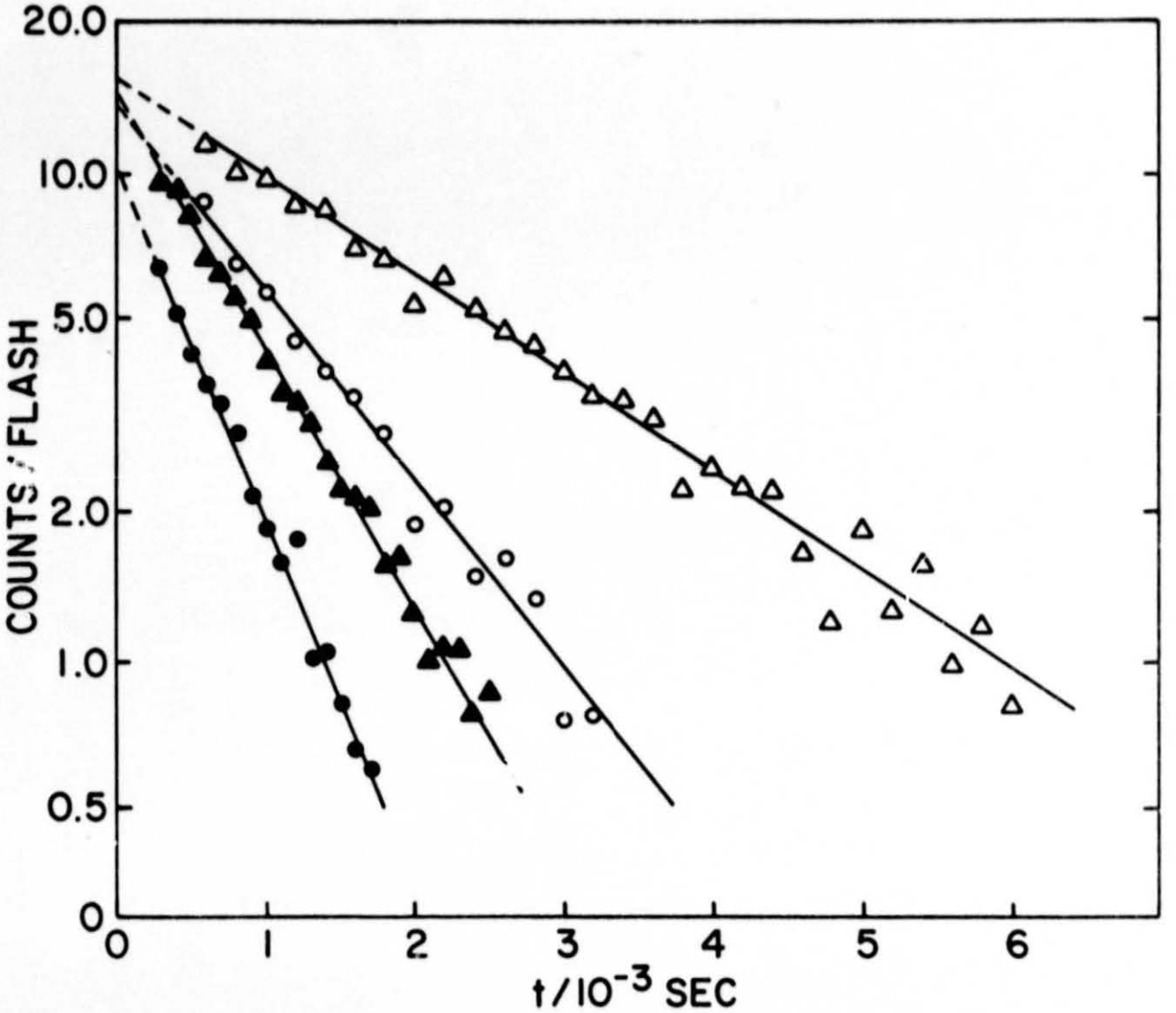
FIGURE CAPTION

Fig. 1: Typical first-order plots for the reaction, $Cl + H_2CO \rightarrow HCl + HCO$ at 200K. The lines are determined from a linear least squares analysis of the data, and errors in decay constants are one standard deviation. Δ - $P_T = 25$ torr, $P_{CCl_4} = 12.5$ mtorr, $P_{H_2CO} = 0.11$ mtorr, flash energy = 56J, and $k_{observed} = 463 \pm 14 s^{-1}$; ○ - $P_T = 50$ torr, $P_{CCl_4} = 25$ mtorr, $P_{H_2CO} = 0.23$ mtorr, flash energy = 56J, and $k_{observed} = 881 \pm 53\ s^{-1}$; ▲ - $P_T = 75$ torr, $P_{CCl_4} = 37.5$ mtorr, $P_{H_2CO} = 0.34$ mtorr, flash energy = 56J, and $k_{observed} = 1215 \pm 39\ s^{-1}$; ● - $P_T = 100$ torr, $P_{CCl_4} = 50$ mtorr, $P_{H_2CO} = 0.46$ mtorr, flash energy = 36J, and $k_{observed} = 1678 \pm 56\ s^{-1}$.

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