yield, bp 99–100 °C.

^{19}F nmr ($CDCl_3$): δ2.0 (CF, d, J_{CF_3-CH}=5.6 Hz). ^{1}H nmr ($CDCl_3$): δ4.43 (CH, q), 4.67 (OH), 5.33–6.10 (CH=CH_2).

Phenylation of 1, 1, 1-Trifluoro-3-buten-2-ol. A mixture of 1, 1, 1-trifluoro-3-buten-2-ol (1.26 g, 10 mmol), iodobenzene (2.04 g, 10 mmol), triethylamine (1. 313 g, 13 mmol), 3.3 m*l* of acetonitrile and palladium acetate (0.0067 g, 0.03 mmol) was refluxed for 10 hrs under nitrogen atmosphere. The reaction mixture was cooled to 20° C, diluted with 30 m*l* of water and extracted with diethyl ether. The ether layer was washed three times with water, then dried over sodium sulfate. Solvent removal and distillation gave 1.1 g of 1, 1, 1-trifluoro-4-phenyl-2-butanone (8, bp 57–59° C/2 mmHg) and 0.62 g of (E)-1,1,1-trifluoro-4-phenyl-3-buten-2-ol (7, bp 76–77° C/1 mmHg). The total yield of phenylation was 85%.

1, 1, 1-Trifluoro-4-phenyl-2-butanone (8): ^{19}F nmr (CDC_3): δ0.83 (CF_3, s). ^{1}H nmr ($CDCl_3$): δ3.0 ($-CH_2CH_2-$, s), 7.3 (Ar-H)

(*E*)-1,1,1-Trifluoro-4-phenyl-3-buten-2-ol (7):
^{19}F nmr ($CDCl_3$): δ0.5 (CF_3, *d*, J_{CF_3-CH}=6 Hz). ^{1}H nmr (CDC l): δ2.98 (OH), 4.57 (CH, *d*, *1*, $J_{CH-CH=}$=7.2 Hz), 6.16 (CH=, *d*,*d*,$J_{CH=CH(trans)}$=16.5 Hz), 6.83(=CH, d), 7.36(Ar-H).

1, 1, 1-Trifluoro-4-penten-2-ol (*9*). A 100 ml 4-neck flask containing zinc powder (1.50 g, 23 mmol), manganese chloride (2.90 g, 23 mmol) and tetrahydrofuran (30 m*l*) was equipped with dry-ice condenser, thermometer, gas inlet tube and dropping funnel. After ultrasonic irradiation for 10 min, allyl bromide (2.30 g, 20 mmol) was added slowly and α, α, α-trifluoroacetaldehyde (1.96 g, 20 mmol) was bubbled into the above flask under the ultrasonic irradiation. After irradiating for 2 hrs, the reaction mixture was poured into 2% aq HCl solution and worked up as described previously. Distillation gave 1, 1, 1-trifluoro-4-penten-2-ol in a yield of 80 %, bp 100–101 °C

^{19}F nmr ($CDCl_3$): δ2.0 (CF_3, *d*). ^{1}H nmr ($CDCl_3$): δ2.43 (CH_2), 3.9 (CH), 4.1 (OH), 5.16 (=CH_2), 5.73 (CH=)

Phenylation of 1,1,1-Trifluoro-4-penten-2-ol. 1,1,1-Trifluoro-4-penten-2-ol (1.39 g, 10 mmol) was used in the above phenylation, and worked up as discribed previously. Distillation gave only one product, (*E*)-1,1,1-trifluoro-5-phenyl-4-buten-2-ol (10), in 80 % yield, bp 92°C/2 mmHg.

^{19}H nmr ($CDCl_3$): δ1.16 (CF_3, *d*) ^{1}H nmr ($CDCl_3$): δ2.5 (CH_2, *d*, *d*), 3.34 (OH), 3.9 (CH, *t*, *q*), 6.13 (CH=, *d*, *t*, $J_{CH=CH(trans)}$=15.7 Hz, $J_{CH_2-CH=}$=7.5 Hz), 6.50 (=CH, *d*, $J_{CH=CH}$=15.7 Hz), 7.14 (Ar-H).

References

(1) B. Filler, "Organofluorine Chemicals and their Industrial Applications," Ed, by R. E. Banks, Soc. Chem. Ind., London, 1979, P. 154.

(2) G. A. Boswell, Jr. and W. C. Ripka, "Organic Reactions," **21**, 1 (1974).

(3) W. R. Hasek, W. C. Smith, V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960).

(4) J. Chapman, R. L. McGinty, *Chem. Abstr.*, **53**, 10035c. (1956).

(5) V. C. R. McLoughlin and J. Throwers, *Tetrahedron*, **25**, 5921 (1969).

(6) Y. Kobayashi and I. Kumadaki, *Tetrahedron Lett.*, 4071 (1979).

(7) (a) T. Kitazume and N. Ishikawa, *Chem. Lett.*, 1679,(1981); (b) T. Kitazume and N. Ishikawa, *Chem. Lett.*, 137, (1982); (c) T. Kitazume and N. Ishikawa, *Chem. Lett.*, 1453, (1982).

(8) N. Ishikawa, M. G. Koh, T. Kitazume and S. K. Choi, *J. Fluorine Chem.*, in press.

(9) F. Sato, H. Watanabe, Y. Tanaka, and M. Sato, *J. Chem. Soc., Commun.*, 1126, (1982).

(10) J. B. Melpolder and R. F. Heck, *J. Org. Chem.*, **40**, 1083 (1975).

(11) R. F. Heck, "Organic Reactions," **27**, 345 (1982).

(12) J. B. Melpolder and R. F. Heck, *J. Org. Chem.*, **41**, 265 (1976).

(13) K. V. Werner, *J. Organomet. Chem.*, **136**, 385 (1977).

Arrhenius Parameters for the Thermal Decomposition of Trichloroethylene

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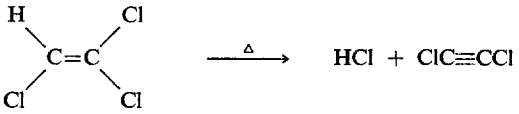
A thermal decomposition of trichloroethylene was studied in the temperature range of 440~460°C by using the conventional static system. In order to investigate the pressure dependence of reaction and to eliminate free radical process, propylene was used as the bath gas. The pressure range investigated was 10~900 Torr. The decomposition was the unimolecular dehydrochlorination and the reaction products were hydrogen chloride and dichloroacetylene.



Results were interpreted in terms of the Ric-Ramsperger-Kassel-Marcus (RRKM) unimolecular rate theory and the Arrhenius parameters were determined from fall-off behaviors. The Arrhenius parameters are found to be log A=13.8±0.2 sec^{-1} and E=56.6±0.7 kcal/mole, respectively.

Introduction

Thermal decomposition reactions of alkyl halides have been studied for a long time [1,2].

The mechanisms of the thermal decompositions of ethyl chlorides have been elucidated [3-5]. It has been pointed out that ethyl chlorides undergo thermal decompositions to the corresponding olefin or chloroolefin and hydrogen chloride by two easily distinguishable homogeneous mechanisms. The first of these, the radical chain mechanism undoubtedly involves the participitation of chlorine atoms in one or two propagation steps of the reaction. The second is the unimolecular elimination mechanism.

Ethylene halides are also known to decompose by both the radical chain mechanism and the unimolecular elimination[6-10].

Gas-phase pyrolyses of both the *cis* and *trans* isomer of 1,2-dichloroethylene were reported. These compounds decomposed to give hydrogen chloride and monochloroacetylene, the kinetics of both dehydrochlorinations being identical. Free radical chains played an important part in the overall reaction, but in the presence of the inhibitors, propylene, *n*-hexane and *n*-pentane, there was a residual reaction which had been identified as a unimolecular process with rate constant $10^{12.56}$ exp(−52,700/RT) sec^{-1} [6,7]. Zabel studied the thermal gas-phase decomposition of vinyl chloride behind shock waves over the temperature range of 1350°∼1900° K. The decomposition proceeded via unimolecular elimination of hydrogen chloride with the rate constant, $10^{14.0}\times\exp(-69{,}300/RT)$ sec^{-1} [8]. Zabel also investigated the thermal decomposition of trichloroethylene (TCE) and tetrachloroethylene highly diluted with argon from 1450° to 1900 °K and at the pressures from 2 to 175 atm behind reflected shock waves where TCE as well as tetrachloroethylene dissociated by Cl atom abstraction rather than by the unimolecular elimination [9]. TCE was also reported to decompose in the temperature range of 385∼445° C in the static system. The final products were hydrogen chloride and hexachlorobenzene. Hexachlorobenzene was the product of polymerization of dichloroacetylene which was the initial product of decomposition of TCE by the molecular elimination and the radical chain reaction. The chain reaction was inhibited relatively weakly by one of the reaction products and strongly by propylene and *n*-hexane [10].

TCE, the reactant of this work, is supposed to be decomposed by the following two mechanisms.

$$TCE \longrightarrow HCl + C_2Cl_2 \quad (1)$$

$$\longrightarrow Cl + C_2HCl_2 \quad (2)$$

Reaction path (1) is the unimolecular dehydrochlorination reaction and reaction path (2) is the chlorine atom abstraction reaction, which is considered to be the initiation step of the radical chain reaction. In the respect of the entropy of activation, reaction path (2) is more favorable than reaction path (1) [11]. That is, the Arrhenius *A* factor of reaction path (2) is larger than that of reaction path (1). But the activation energy of reaction path (2) appears to be as large as the C_d–Cl bond dissociation energy so that the activation energy of reaction path (2) is expected to be much larger than that of reaction path (1). The rate constant of reaction path (2) measured by the shock tube method was shown to be $10^{15.8}$ exp(−84,000/*RT*) sec^{-1} [9]. This rate constant estimated to be $10^{-9}\sim10^{-10}$ sec^{-1} in the temperature range of this experiment, 400∼460° C. If the chain reaction is inhibited by the radical scavenger like propylene, the rate constants of these orders cannot be observed in the conventional static system and can be ignored. Consequently, the rate constants measured in the presence of the radical scavenger are regarded as the rate constants of the unimolecular elimination reaction.

In this work, the rate constants of the unimolecular elimination reaction were measured by quenching the radical chain reaction with propylene, which was used as the bath gas as well as the radical scavenger. The pressure dependence of the rate constants was observed and the experimental data were compared with the expected values of the Rice-Ramsperger-Kassel-Marcus (RRKM) unimolecular rate theory. The Arrhenius parameters were determined from the fall-off behaviors of the rate constants.

Experimental

Material. TCE, was obtained from Merck, 99.5% stated minimum purity, was purified by freeze-pump-thaw technique until no detectable impurities by gas chromatography (GC). TCE has mp −84.8° C, bp 86.7° C and vapor pressure of ca. 60 Torr at 20 °C.

Reaction mixtures of TCE in propylene, matheson, C. P. grade, 99.0% stated minimum purity, or argon were used after several freeze-pump-thaw cycles with liquid nitrogen. There were no impurities detectable by GC before reactions.

Reaction System. The reaction system is the conventional static system and the reactor is made of 57 mm O. D. cylindrical quartz vessel and 286 cc of its volume. The pressure of the reactor was read by a electronic pressure transducer, Validyne, Model CD 223. The reactor was seasoned by coating its wall with KCl and repeating preexperimental runs several times for homogeneous wall condition before the measurement. The temperature of the reactor was controlled within ± 0.5 °C by using the furnace (Fisher, Model 1012) with the feed-back temperature controller (Hanna) and the voltage transformer (Sanya). The temperatures were read by the digital temperature convertor (Omega, Model 2176A) using with the chromel-alumel thermocouple, Omega.

The reaction was monitored by GC (Yanaco, Model G180) and the rate constants were measured by analyzing the quantity of TCE as a funtion of the reaction times. The GC detector was the flame ionization detector (FID) and Ar or He was used as the carrier gas. The flow rates of carrier gas, hydrogen and air were 22 ml/min, 30 ml/min and 1050 ml/min, respectively. The columns used were PORAPAK Q (1.5 m) and FFAP (1.5 m) with 170 °C of the oven temperature.

Identification of the reaction products was done by comparing the GC retention times of the products with those of the authentic samples and observing these products.

The first order rate constant was obtained from the slope

of the plot of ln [TCE] *vs.* the reaction time.

$$\ln [TCE]_t = \ln [TCE]_0 - kt$$

where $[TCE]_t$ and $[TCE]_0$ denote the concentrations of TCE at $t=t$ and $t=0$, respectively. Rate constants were obtained from the plots and its correlation coefficient is larger than 0.98. Correction of the system pressure due to the injection of the reactant into GC was made and the decrease of the system pressure was 1.7% in the temperature range of 440~460°C.

Results and Discussion

Hydrogen chloride, dichloroacetylene and terachloroethylene were identified from the analyses of the gas-phase products of pyrolysis of TCE. Tetrachloroethylene was identified by mass spectrum and the GC retention time comparing that of authentic sample (Aldrich, 99.0% stated minimum purity). Hydrogen chloride, which can not be detected by FID, was identified by IR spectrum that shows the spectrum near 2989 cm^{-1} with the charateristic R and P branches [12]. Dichloroacetylene was identified by mas spectrum. Production of chloride molecule could not be found on the mass spectrum at all. Hexachlorobenzene identified in ref. 10 did not appear on the chromatogram because of boiling point, 223~224° C and was not identified by other method.

For a long time, propylene has been used as the collision partner of the thermal decomposition reaction to retard the radical chain mechanisms[6,10,13~17]. Propylene itself is known to decompose to hydrogen atom and allyl radical with the rate constant of $k=1.1\times10^{13}\exp(-72{,}000/RT)$ sec^{-1} ([18]). As this rate constant is given by the order of 10^{-9} sec^{-1} at 450° C, the thermal decomposition of propylene itself is negligible.

Figure 1 shows the first order rate constants for the pyrolysis of the mixtures of TCE in propylene with the different initial concentrations of TCE at 460°C. That the reaction mixtures with the different initial concentrations of the reactant give the same first order rate constants indicates that the rate is the first order and the radical chain mechanism is completely quenched. From the fact that tetrachloroethylene was not produced in the pyrolysis of the mixture of TCE in propylene, it is noted that tetrachloroethylene is the product of the radical chain reaction.

The rate constants of the unimolecular reaction, particularly that of small molecule with a few oscillators show the strong pressure dependence. These fall-off behaviors of the rate constants are related to the Arrhenius parameters. The pressure dependence of the rate constants can be calculated by the RRKM theory and the Arrhenius parameters may also be determined from the RRKM.

In this study, the Arrhenius parameters were determined from the fall-off behaviors of the rate constants. At 440, 450 and 460° C, the rate constants of the unimolecular dehydrochlorination of TCE were measured and the pressure dependence of the rate constants was observed at each temperature in the pressure range of 10~900 Torr. The rate contants were obtained from the reaction mixture of TCE/propylene=0.01.

The sum of quantum states and the partition function of

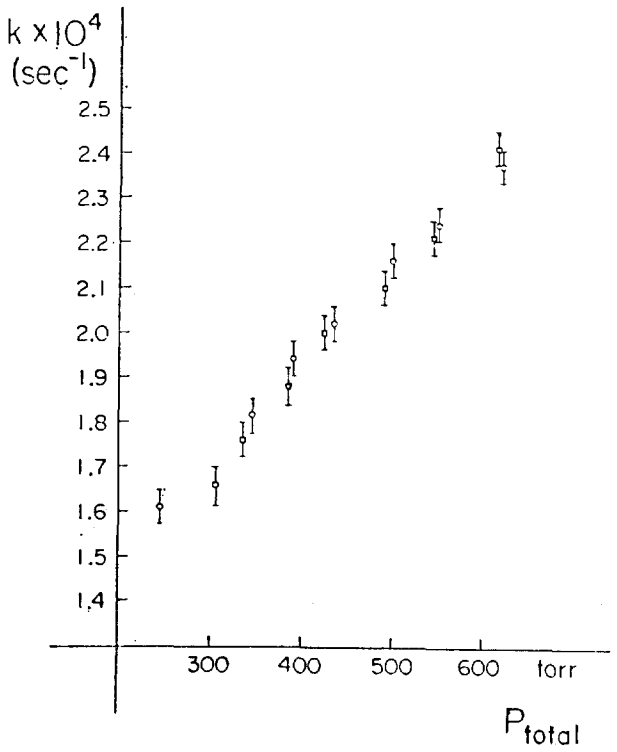


Figure 1. k_{uni} *vs.* P_{total} for the decomposition of TCE at 460 °C. □ : TCE/propylene=0.03; ● : TCE/propylene=0.01.

the activated complex are required in the calculation of $k_a(E)$ and mass, moment of inertia and the vibrational frequencies of the activated complex are needed to calculate the sum of states and the partition function. These values are related to the entropy of molecule, which determines the A factor of the reaction. The A factors of many reactions are well-known and it is possible to predict them very accurately[11]. On the basis of the known A factors of the molecular eliminations, high pressure activation energy, E_a and the deactivation efficiency β can be determined by the RRKM calculation[19,20]

Three parameters-the collision deactivation efficiency, the A factor and the critical energy have strong influence on the fall-off behaviors of the rate constants in the RRKM calculation while other parameters-the collision diameters and the well depths of Lennard-Jones potential of the reactant and the 3rd body have only trivial effects on the fall-off behaviors.

Table 1 shows the RRKM input data used in the reproducing the experimental results. Molecular data are the reported values [21]. Figure 2 shows the RRKM results and the rate constants of the dehydrochlorination of TCE at 440°C in the pressure range of 10~900 Torr. The solid line is the RRKM calculation and shows good agreement with the experimental data where the calculated Arrhenius parameters were $A=10^{13.8}$ sec^{-1}, E_a = 56.6 kcal/mole. The calculation results using the same parameters as those at Table 1 show good agreement with the experimental results at 450°C and 460°C (Figures 3, 4).

The dehydrochlorination reaction of TCE is one of the unimolecular reactions which proceed through four-center cyclic transition states. Calculation of the A factor requires

TABLE 1: Molecular Parameters for the RRKM Calculations of Trichloroethylene Decomposition

Vibrational frequencies (cm^{-1})		
Approx. character	Ground state	Activated complex
Stretchings		
CH	3080	2200
CC	1590	1850
CCl	930	960
CCl	840	900
CCl	630	reaction coordinate
Deformation		
CH	1240	1200
CH	780	750
skeletal	450	470
skeletal	380	420
skeletal	270	120
skeletal	210	250
skeletal	170	80

Pricipal moment of inertia [$(g \cdot cm^2)^3$]	
Ground State	Activated Complex
0.905×10^{-112}	1.055×10^{-112}

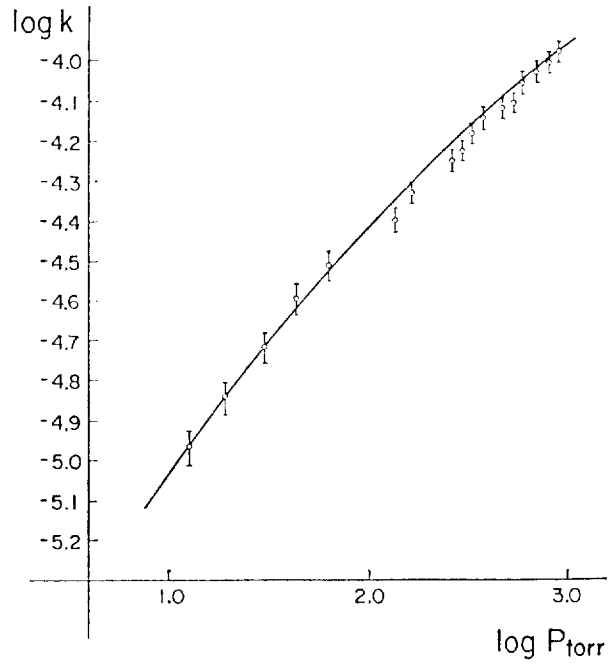


Figure 2. log k_{uni} *vs.* log P_{torr} for the decomposition of TCE at 440 °C: Solid line–The RRKM result.
$P_{torr}=P_{total}$ (TCE/propylene=0.01); E_a=56.6 kcal/mole, log A=13.8 sec^{-1}

the estimate of entropy of activation. The vast majority of the reactions with four-center cyclic activated complexes have shown the A factors of $10^{13.5\pm1.0}$ sec^{-1} [1,2,22]. The A factor determined in this work is in this range and is considered to be reasonable.

The reaction of vinyl chloride was observed with shock tube method by two groups[8,23]. The reported activation energies are 69.3 kcal/mole and 72.1 kcal/mole, respectively and the A factors are $10^{14.0}$ sec^{-1} and $10^{13.8}$ sec^{-1}, respectively.

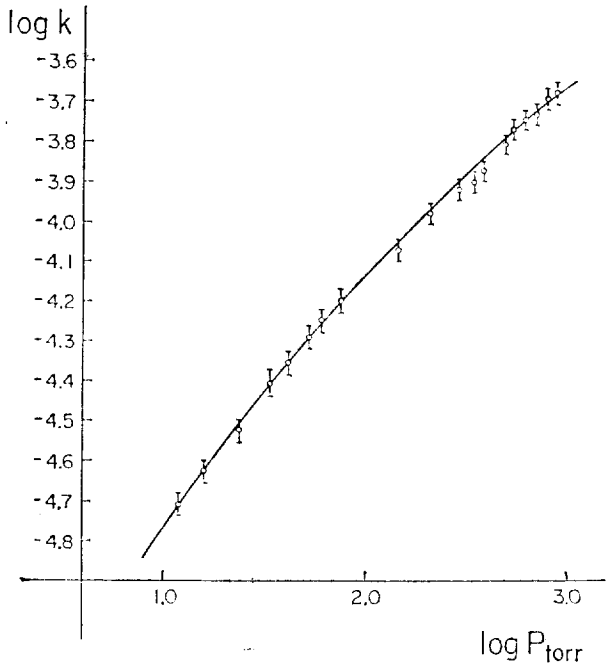


Figure 3. log k_{uni} *vs.* log P_{torr} for the decomposition of TCE at 450 °C. Solid line–the RRKM result
$P_{torr}=P_{total}$ (TCE/propylene=0.01); E_a=56.6 kcal/mole, log A=13.8 sec^{-1}.

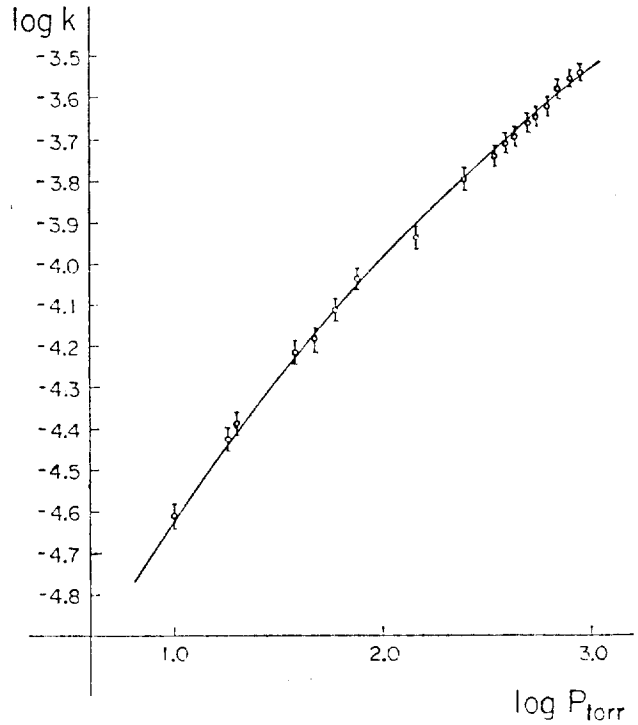


Figure 4. log k_{uni} *vs.* log P_{torr} for the decomposition of TCE at 460 °C. Solid line–the RRKM result.
$P_{torr}=P_{total}$ (TCE/propylene=0.01); E=56.6 kcal/mole, log A=13.8 sec^{-1}.

In these reports of the reaction of vinyl chloride, the rate constants were determined by monitoring of the reactant under the assumption that the observed reaction was the unimolecular elimination of hydrogen chloride. However, in the experiments with shock tube method, the reaction temperature is generally higher than 1000 °C. At these temperatures, TCE is

reported to decompose principally by chlorine atom abstraction[9]. Therefore, chlorine atom abstraction reaction of vinyl chloride will also be supposed to occur considerably and the observed reaction of vinyl chloride may contain chlorine atom abstraction reaction. Goodall and Howelett studied the unimolecular elimination of 1,2-dichloroethylene in the static system, which is also expected to show the activation energy similar to those of the unimolecular elimination of vinyl chloride and TCE[7]. Rate constant was reported to be $k = 10^{12.56} \exp(-52{,}700/RT)$ sec^{-1}, where the A factor seems to be estimated a little less than the real value. If the rate constant itself is accepted to be reliable and re-estimated with the new A factor, $10^{13.8}$ sec^{-1}, the activation energy will be 56.7 kcal/mole, which is in good agreement with that of this work.

Benson and coworkers have developed on the electrostatic model for the quantitative prediction of the activation energies of four-center addition reactions, the reverse reactions of the unimolecular elimination reactions, can be used to estimate the activation energy of the unimolecuar elimination [24~26]. In the case of vinyl chloride,

$$\text{vinyl chloride} \underset{E_r}{\overset{E_f}{\rightleftharpoons}} \text{acetylene} + \text{hydrogen chloride}$$

the electrostatic model estimates an activation energy $E_f = E_r + \Delta H_r = 36.4 + 23.7 = 60.1$ kcal/mole which is 9~12 kcal/mole less than the reported values. The enthalpy of reaction, ΔH_r, is calculated from the known heats of formation of acetylene (54.3 kcal/mole)[27], hydrogen chloride (-22.0 kcal/mole)[11] and vinyl chloride (8.6 kcal/mole)[27].

The unimolecular dehydrofluorination of vinyl fluoride was investigated with shock tube method by two groups and the activation energies are reported to be 81.4 kcal/mole and 70.8 kcal/mole [23,28]. The Benson's electrostatic model predicts the activation energy of this reaction will be 72.8 kcal/mole where the enthalpy of reaction is estimated from the known heats of formation of vinyl fluorde (-31.2kcal/mole) [29], hydrogen fluoride (-64.8kcal/mole) [11] and acetylene (54.3 kcal/mole) [27]. The calculated activation energy is similar to that of ref. 28 but is far from that of ref. 23.

In Benson's method, the activation energy of the unimolecular elimination reaction of TCE is calculated to be $(48 \pm 3 + \Delta)$ kcal/mole where Δ is the uncertainty of the heat of formation of dichloroacetylene and less than 13 kcal/mole [9,26]. Thus, the activation energy is estimated to be less than 61 kcal/mole. This adds the confidence to the activation energy determined in this work.

In the course of calculating the fall-off curves by RRKM calculations, the collision deactivation efficiency was determined to be 0.001. The collisional efficiency can be approximately calculated by the simple method [2,11]. At the transition pressure $P_{1/2}$ at which $k_{uni}/K_\infty = 1/2$, k_a is equal to $k_2 P_{1/2}$. By RRK theory, k_a is given by

$$k_a = A\left(\frac{E-E_0}{E}\right)^{s-1} = \beta Z P_{1/2}$$

where s is the number of the effective oscillators which can be calculated from the vibrational heat capacity at a given temperature. The heat capacities of TCE in the high temperature ranges are calculated by using Benson's group additivity Table [2]. TCE consists of the groups, $[C_d-(H)(Cl)]$ and $[C_d-(Cl)_2]$. Table 2 shows the heat capacities of TCE and each group in the temperature range of 300°-800°K. As the number of the effective oscillators is given by C_{vib}/R, $(s-1)$ is 8.1 and the vibrational energy at 450°C, $(E-E_0)$ is calculated to be 8.2 kcal/mole. Then, $\beta P_{1/2}$ is calculated to be 0.41. From the experimental results, the transition pressure is noted to be larger than 100 torr and the collisional efficiency is calculated to be less than 0.004. The transition pressure larger than 100 torr is feasible for six-atomic molecule like TCE [2]. The calculated collisional deactivation efficiency supports the validity of the value used in this work.

TABLE 2: Heat Capacities of TCE and Its Groups in the Temperature Range of 300-800° K

	group		TCE	
Temp. (°K)	$[C_d-(H)(Cl)]$	$[C_d-(Cl)_2]$	C_p*	C_{vib}**
300	7.9	11.4	19.3	11.3
400	9.2	12.5	21.7	13.7
500	10.3	13.3	23.6	15.6
600	11)2	13.9	25.1	17.1
800	12.3	14.6	26.9	18.9

All in cal/mole/K unit. * Heat capacity at constant pressure. ** Vibrational heat capacity.

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References

(1) A. Maccoll, *Chem. Rev.*, **69**, 33 (1969).
(2) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, London, 1972.
(3) D. H. R. Barton and P. F. Onyon, *J. Amer. Chem. Soc.*, **72**, 988 (1950).
(4) D. H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, 155 (1949).
(5) D. H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, 2033 (1951).
(6) A. M. Goodall and K. E. Howlett, *J. Chem. Soc.*, 2640 (1956).
(7) A. M. Goodall and K. E. Howlett, *J. Chem. Soc.*, 3092 (1956).
(8) F. Zabel, *Intl. J. Chem. Kinet.*, **9**, 651 (1977).
(9) F. Zabel, *Ber. Bunsenges. Phys. Chem.*, **78**, 232 (1974).
(10) A. M. Goodall and K. E. Howlett, *J. Chem. Soc.*, 2599 (1954).
(11) S. W. Benson, "Thermochemical Kinetics," 2nd Ed. John Wiley and Sons, New York, 1976.
(12) G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecule," 2nd Ed. van Nostr and Reinhold Co., New York, 1950.
(13) E. S. Corner and R. N. Pease, *J. Amer. Chem. Soc.*, **67**, 2267 (1945).

(14) F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci. U. S. A.*, **38**, 937 (1952).
(15) T. Fujimoto, F. M. Wang and B. S. Rabinovitch, *Canad. J. Chem.*, **50**, 3251 (1972).
(16) K. A. Holbrook and R. A. Scott, *J. Chem. Soc. Faraday Trans.*, **71**, 1849 (1975).
(17) D. C. Tardy and B. S. Rabinovitch, *Chem. Rev.*, **77**, 1849 (1977).
(18) M. Szwarc, *J. Chem. Phys.*, **17**, 284 (1949).
(19) D. M. Golden, C. N. Spokes and S. W. Benson, *Angew. Chem. Intl. Edit.*, **12**, 434 (1973).
(20) K. Y. Choo, D. M. Golden and S. W. Benson, *Intl. J. Chem. Kinet.*, **7**, 713 (1975).
(21) G. Allen and H. J. Bernstein, *Canad. J. Chem.*, **32**, 1044 (1954).
(22) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967).
(23) P. Cadman and W. J. Engelbrecht, *Chem. Comm.*, 453 (1970).
(24) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1967).
(25) S. W. Benson and G. R. Haugen, *J. Amer. Chem. Soc.*, **87**, 4036 (1965).
(26) S. W. Benson and G. R. Haugen, *J. Phys. Chem.*, **70**, 3336 (1966).
(27) J. D. Cox and G. Pilcher, "Thermochemistry of organic and organometallic compounds," Academic Press, London, 1970.
(28) J. M. Simmie and W. J. Quiring and E. Tschukow-Roux, *J. Phys. Chem.*, **74**, 992 (1970).
(29) M. Kh. Karapet'yants and M. L. Karapet'yants, "Thermodynamic constants of inorganic and organic compounds," Ann Arbor–Humphrey Science Publisher, Ann Arbor, 1970.

Kinetics of Reactions Between Substituted Benzyl Chlorides and Anilines in MeOH-MeCN Mixtures

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Kinetic studies of nucleophilic substitution reactions of *para*-substituted benzylchlorides with anilines were conducted in a range of MeOH–MeCN mixtures at 55.1 °C. Hammett ρ_C, ρ_N values and Brönsted β values were determined, in other to examine the transition state variations caused by changes in nucleophiles, substituents and solvents properties (π^* and α). Applications of potential energy surface (PES) and quantum mechanical (QM) models of transition state characterization lead us to conclude that the reaction proceeds *via* the dissociative S_N2 mechanism.

Introduction

Although benzylation of tertiary amines (Menschutkin reaction[1]) were widely studied as one of the best examples of solvent effects on reaction rates, the reaction with primary amines has not been investigated to the same extent. Moreover nucleophilic substitution reaction of benzylchloride attracted considerable interest with special regards to the detailed transition state (TS) analysis.[2,3] Hill *et al.*[3a] and Ballistreri *et al.*[2a-b] reported that electron-donating substituent, *e.g.*, *p*-OCH_3 on the benzene ring promotes S_N1 nature while electron-withdrawing group, *e.g.*, *p*-NO_2 increases e_N2 character of the reaction.

Recently reacting bond rules[4] in a form of More O'Ferrall[5]–Jencks[6] type plot have been applied to interpretation of TS variation accompanying substituent and medium changes. Harris *et al.*[3d] used the More O'Ferrall plot for predicting TS variation in the nucleophilic substitution of benzyl compounds. Lee *et al.*[7] also applied the potential energy surface (PES) model to the characterization of TS in the S_N2 reactions of benzoyl and benzenesulfonyl halides. It has been demonstrated that the PES model predicts TS variation correctly in most cases but it fails to account for TS variation due to leaving group changes.[2d]

This difficulty has been overcome by Shaik[8] *et al.*, using a simple quantum mechanical (QM) model of TS characterization.

Solvatochromic equation, (1), developed by Taft[9] has