

## C<sub>2</sub>H<sub>2</sub>F<sub>4</sub> 이성질체의 탈플루오르화 수소반응에 있어서의 비교연구†

E. Tschuikow-Roux · K. R. Maltman · G. M. Millward\* · 鄭景薰\*\*

캐나다 Calgary 대학교 화학과

(1979. 3. 9 접수)

## Comparative Study of the Dehydrofluorination of the Structural Isomers of C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>†

E. Tschuikow-Roux, K. R. Maltman, G. E. Millward\* and K. H. Jung\*\*

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada

(Received March 9, 1979)

요 약. 1, 1, 2, 2-C<sub>2</sub>H<sub>2</sub>F<sub>4</sub> 와 1, 1, 1, 2-C<sub>2</sub>H<sub>2</sub>F<sub>4</sub> 의 아르곤가스와의 묽은 혼합물의 열분해반응을 충격관을 사용 1146 와 1232 °K 하 전체반사충격압력 3000 torr 근처에서 관찰하였다. 이들 조건하에서 반응은 주로 플루오르화수소의 분자제거반응을 보였다. α-탄소의 수소가 전부 플루오르로 치환된 이성질체는 다른 이성질체에 비하여 상당히 높은 활성화에너지를 나타내었으며 이는 이성질체간에 전하밀도의 차이에 기인한 것으로 추측된다.

반응속도 상수의 비는 다음식

$$\log(k_1/k_2) = -0.069 \pm 0.021 + (1388 \pm 113)/2.303RT$$

로 주어졌으며 이는 독립된 관측을 통해서 얻어진 값들과 좋은 일치를 보여 주었다.

**ABSTRACT.** The thermal decomposition of a dilute mixture of 1, 1, 2, 2-C<sub>2</sub>H<sub>2</sub>F<sub>4</sub> in argon has been investigated in a single-pulse shock tube between 1146 and 1232°K at total reflected shock pressures of about 3000 torr. Under these conditions the reaction proceeds exclusively by the molecular elimination of hydrogen fluoride. It has been found that the asymmetric isomer with the fully fluorinated α-carbon requires the higher activation energy which may be attributed to the difference in atomic charge densities between isomers.

The rate constant ratio is given by

$$\log(k_1/k_2) = -0.069 \pm 0.021 + (1388 \pm 113)/2.303RT$$

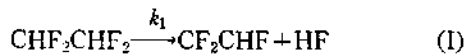
in good agreement with previous independent studies.

†Work supported by the National Research Council of Canada.

\*Postdoctoral Fellow 1970~71. Present address: Department of Chemistry, Cornell University, Ithaca, New York, U. S. A.

\*\*Present Address: Department of Chemistry, Korea Advanced Institute of Science, Seoul, Korea

The principal mode of the thermal decomposition of fluoroethanes<sup>1-3</sup> has been shown to involve the molecular elimination of hydrogen fluoride. In the case of the structural isomers of tetrafluoroethane identical products are obtained



Previous independent studies<sup>2,3</sup> of these compounds have shown that at temperatures above 1300 °K the decompositions were complicated by radical reactions resulting from C-C bond scission. Nevertheless, it was possible to extract the rate constants  $k_1$  and  $k_2$ ,

$$k_1(\text{sec}^{-1}) = 10^{13.3 \pm 0.4} \exp[-(69,400 \pm 3,100) / RT] \quad (1)$$

$$k_2(\text{sec}^{-1}) = 10^{13.42 \pm 0.28} \exp[-(70,700 \pm 1,700) / RT] \quad (2)$$

Although both activation energies are within experimental error of each other, it was tentatively concluded<sup>4</sup> that the change could be ascribed to the difference in atomic charge densities between the isomers. Since this observation has interesting theoretical implications it was thought desirable to examine the relative rates in more detail.

The present work is an extension of the previous studies and involves the decomposition of a binary mixture of the C<sub>2</sub>H<sub>2</sub>F<sub>4</sub> isomers using the single pulse shock tube (SPST) technique. The reactions were studied at very low conversion over the relatively narrow temperature range of 1146 to 1232 °K where the decomposition was free from radical reactions. The present results substantiate the conclusions drawn in the two independent studies.

The experiments were carried out using a modified SPST, the design and operation of which has been described previously.<sup>4,5</sup> The

samples of tetrafluoroethane were kindly supplied by the Du Pont de Nemours Co., the trifluoroethylene was obtained from Peninsular Chemresearch and the argon diluent was Matheson research grade. All gases had a purity of greater than 99.9 %. A dilute reaction mixture of 1 % C<sub>2</sub>H<sub>2</sub>F<sub>4</sub> in argon and precisely known relative composition  $[\text{CHF}_2\text{CHF}_2]_0 / [\text{CH}_2\text{FCF}_3]_0 = 1.735$  was prepared and allowed to mix thoroughly before use. Following each shock a sample of the fully mixed gases was withdrawn from the tube and subjected to gc analysis. Separation of product and reactants was achieved using a 12 ft silica gel column held isothermally at 150 °C with helium as a carrier gas at a flow rate of 30 cm<sup>3</sup>min<sup>-1</sup>. The conversion of each reactant ranged from 0.38 to 1.25 %. The reflected shock wave parameters were calculated from measured incident and reflected shock wave velocities.<sup>6</sup>

For simplicity we set  $A = [\text{CHF}_2\text{CHF}_2]$ ,  $B = [\text{CF}_3\text{CH}_2\text{F}]$ ,  $C = [\text{CF}_2\text{CHF}]$ , then  $A_0$  and  $B_0$  refer to initial concentrations. From the first-order rate law governing the depletion of  $A$  we obtain, at once

$$k_1 = (1/t) \ln(A_0/A) \quad (3)$$

and an analogous expression holds for  $k_2$ . The ratio of rate constants,  $k_1/k_2$ , is therefore

$$k_1/k_2 = \frac{\ln(A_0/A)}{\ln(B_0/B)} \quad (4)$$

The direct application of eq. (5) in the light of our method of product analysis requires gas-dynamic and PVT-computations to evaluate the ratios  $A_0/A$  and  $B_0/B$ , and has the disadvantage of being inaccurate for small conversions. A better procedure is to express  $k_1/k_2$  in terms of measured ratios:  $R_1 = B/A$ ,  $R_2 = C/A$ . Thus from the exact rate constant difference relation

$$t(k_1 - k_2) = \ln[(A_0/B_0)(B/A)] \quad (5)$$

and the theoretical carbon mass balance equation

$$\begin{aligned} C &= (A_0 - A) + (B_0 - B) \\ &= A(e^{k_1 t} - 1) + B(e^{k_2 t} - 1) \end{aligned} \quad (6)$$

we obtain the rate constant ratio

$$\frac{k_1}{k_2} = 1 + \frac{\ln W}{\ln Q} \quad (7)$$

where

$$\begin{aligned} W &= (A_0/B_0)R_1 \\ Q &= (1 + R_1 + R_2)/R_1[1 + (A_0/B_0)] \end{aligned}$$

and  $A_0/B_0 = 1.735$  is the initial composition of the mixture. It should be noted that the errors involved in the calculation of the reaction dwell time,  $t$ , cancel identically in eq. (7), while the errors associated with the finite cooling rate of the rarefaction fan are minimal in view of the proximity of the temperature coefficients for  $k_1$  and  $k_2$ . The results are listed in Table 1 and the temperature dependence of the ratio  $(k_1/k_2)$  is plotted in Fig. 1.

The scatter of the points is due to the sensitivity of the rate constant ratio at low conversions. However, further evidence that  $k_1 > k_2$  is given by the rate constant difference, *cf.* eq. 5 and Table 1, which is positive over the whole

Table 1. Experimental resultsa.

$T_s$ (°K)	$R_1^b$	$10^3 R_2^c$	$k_1/k_2$
1146	0.5773	5.963	1.559
1150	0.5793	19.334	1.565
1163	0.5769	3.835	1.559
1184	0.5773	6.536	1.540
1192	0.5781	11.946	1.535
1207	0.5776	8.678	1.525
1208	0.5774	7.296	1.518
1220	0.5781	12.497	1.504
1232	0.5778	9.992	1.501

<sup>a</sup> Mixture composition: 1%  $C_2H_2F_4$  in Ar;

$[CHF_2CHF_2]_0/[CF_3CH_2F]_0 = 1.735$ .

<sup>b</sup>  $R_1 = [CF_3CH_2F]/[CHF_2CHF_2]$

<sup>c</sup>  $R_2 = [CF_2CHF]/[CHF_2CHF_2]$

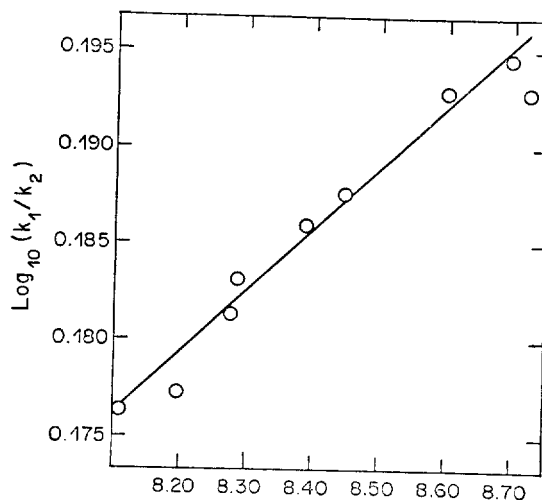


Fig. 1. The temperature dependence of the rate constant ratio  $(k_1/k_2)$ .

temperature range. A least squares analysis of the data gives

$$\begin{aligned} \log(k_1/k_2) &= -0.069 \pm 0.021 + (1388 \pm 113) \\ &\quad / 2.303 / 2.303RT \\ &= \log(A_1/A_2) - (E_1 - E_2) / 2.303RT \end{aligned}$$

where the error limits are standard deviations and the correlation coefficient is 0.978. Thus,  $(E_1 - E_2) = -1388$  cal and hence  $E_2 > E_1$ . This result is in excellent agreement with the previous findings<sup>4</sup> and supports the conclusion that the asymmetrized isomer with a fully fluorinated  $\alpha$ -carbon atom requires a higher activation energy for HF elimination. Also,  $\log(A_1/A_2) = -0.069$  and hence  $A_2 > A_1$ . This may be expected purely on the basis of reaction path degeneracy ( $g=4$  for  $CHF_2CHF_2$  and 6 for  $CF_3CH_2F$ ) which makes a positive contribution to the entropy of activation.

#### ACKNOWLEDGEMENT

We thank Dr. R. F. Hein of the Du Pont de Nemours Co. for the samples of 1, 1, 2, 2- $C_2H_2F_4$  and 1, 1, 1, 2- $C_2H_2F_4$ .

## REFERENCES

1. (a) E. Tschuikow-Roux, W. J. Quiring and J. M. Simmie, *J. Phys. Chem.*, **74**, 2449 (1970); (b) E. Tschuikow-Roux and W. J. Quiring, *ibid.*, **75**, 295 (1971); (c) G. E. Millward, R. Hartig and E. Tschuikow-Roux, *Chem. Commun.*, 465(1971); (d) E. Tschuikow-Roux, G. E. Millward and W. J. Quiring, *J. Phys. Chem.*, **75**, 3493 (1971); (e) P. Cadman, M. Day, A. W. Kirk and A. F. Trotman-Dickenson, *Chem. Commun.*, 203 (1970); (f) P. Cadman, M. Day and A. F. Trotman-Dickenson, *J. Chem. Soc., A*, 2498 (1970); (g) P. Cadman, M. Day and A. F. Trotman-Dickenson, *ibid.*, **A**, 1356 (1971); (h) M. Day and A. F. Trotman-Dickenson, *ibid.*, **A**, 233 (1969).
2. G. E. Millward, R. Hartig and E. Tschuikow-Roux, *J. Phys. Chem.*, **75**, 3195 (1971).
3. G. E. Millward and E. Tschuikow-Roux, *ibid.*, (in press).
4. E. Tschuikow-Roux, *Phys. Fluids*, **8**, 821 (1965).
5. J. M. Simmie, W. J. Quiring and E. Tschuikow-Roux, *J. Phys. Chem.*, **73**, 3830 (1969).