INTERNATIONAL JOURNAL OF CHEMICAL KINETICS, VOL. IV, 541–545 (1972)

Pyrolysis of 4,4-Bisperfluoromethylbutene-1,4 01 in the Gas Phase

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Abstract

Pyrolysis of $(CF_3)_2C(OH)CH_2CH{=}CH_2$, the reverse of the reaction between perfluoroacetone and propene, has been studied in the gas phase between 475° and 598°K. Even at 573°K, the unimolecular reaction rate constant appears to be in its pressure-independent region at 20.0 torr pressure. In a quartz vessel, the decomposition is homogeneous. The specific unimolecular rate constant is

$$k = T^{1/2}10^{[(10.3 \pm 0.10) - (\frac{40300 \pm 300}{4.575T})]}\ \mathrm{sec}^{-1}$$

where the limits are for one standard deviation. Combining these results with the previously reported results on the reverse reaction, the equilibrium constant for the reaction

$$C_3H_6 + CF_3COCF_3 \rightleftharpoons (CF_3)_2C(OH)CH_2CH{=}CH_2$$

is

$$K_p = 10^{[(1/4.576)(-34.0 \pm 1.0) + (\frac{18700 \pm 400}{T})]}\ \mathrm{atm}^{-1}$$

It is noteworthy that in the temperature range of the study of the forward reaction (448° to 573°K), the percentage of back reaction in the times of the experiments varies from less than 0.1 to 1.5. Using group additivities and the above ΔH^0, ΔH_f^0 of $(CF_3)_2CO$ is calculated to be −325.2 kcal/mole at 600°K and the average C—C bond is 42.0 kcal/mole.

1. Introduction

The unimolecular transfer reaction where an H atom is transferred in a cooperative process has been reported for *cis*-1,3-dienes [1]. Here, a 1,5-H-atom shift occurs via a six-membered complex, and there is no change in the number of molecules involved in the reaction.

There are many reports of unimolecular transfer of H atom in a six-membered complex where the number of molecules increases during the course of the reaction. Pyrolysis of organic esters results in the acid and an olefin [2]. Pyrolysis of organic carbonates, except for dimethyl carbonate, gives rise to one mole each of alcohol, olefin, and carbon dioxide [3]. In both types of pyrolysis involving more than one mole of product per mole of reactant, there is no evidence of back reaction. The pyrolysis of $CH_3CH(OH)CH_2CH{=}CH_2$ is very analogous to the reaction reported in this paper [4].

In this paper, a unimolecular six-membered complex hydrogen transfer is reported from an alcohol, $(CF_3)_2C(OH)CH_2CH{=}CH_2$. The reverse reaction has previously been reported [5].[1]

2. Apparatus and Procedure

The reactions were carried out in a cylindrical quartz reaction vessel of 45.7 cc set inside an oven. To determine the effect of surface, a similar vessel was packed with quartz shell tubing, increasing the S/V from 1.6 cm^{-1} to 7.6 cm^{-1} and a volume of 26.8 cc. On completion of the pyrolysis, all the products and reactants were frozen into a sample flask held at liquid N_2 temperature and then transferred to a gas chromatography unit. Since the reaction gives rise to C_3H_6 and perfluoroacetone, it was decided that C_3H_6 was a convenient compound to monitor the kinetics of the decomposition of the parent. An 8 ft × 3/16 in. copper tube filled with 26.6% Carbowax 400 on Chromabsorb P was employed since it could resolve propene from perfluoroacetone when the temperature was programmed from liquid N_2 to 100°C. The column was calibrated with C_3H_6 so that all the results were expressed in micromoles.

The data were analyzed and the results plotted via a computer program designed by Dr. R. H. Knipe of these laboratories.

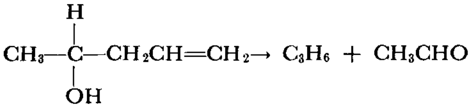
3. Results and Discussion

The results are shown in Table I together with the calculated unimolecular specific rate constants. Since limited vapor pressure of the parent compound made even moderate pressure runs inconvenient, the pressure insensitivity of the rate constant was checked by a mix which contained over 30 times as much pressure of Xe as of the reactant. Within the analytical limits of reproducibility, the rate constants were unaffected by the presence of the inert gas, actually being some 10% lower. Increase in S/V from 1.6 cm^{-1} to 7.6 cm^{-1} has little, if any, effect on the rate once the vessels are conditioned by one or two prior exposures to the parent compound.

The pertinent results are shown in Table I, and the corresponding Arrhenius plot, in Figure 1, with the calculated best fit line. From the slope and intercept,

$$k = T^{1/2}10^{\left[(10.3\pm0.1) - \frac{(40.3\pm.3)\times10^3}{4.57T}\right]}\ \text{sec.}^{-1}$$

where the limits are for one standard deviation. The $\Delta S^{\neq}$ is -8.3 gibbs/mole, which is consistent with the analogous reaction [4]



$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CH_2CH{=}CH_2 \rightarrow C_3H_6 + CH_3CHO$$

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[1] The author wishes to thank Dr. S. W. Benson for his comments on reference [5] which led to this problem.

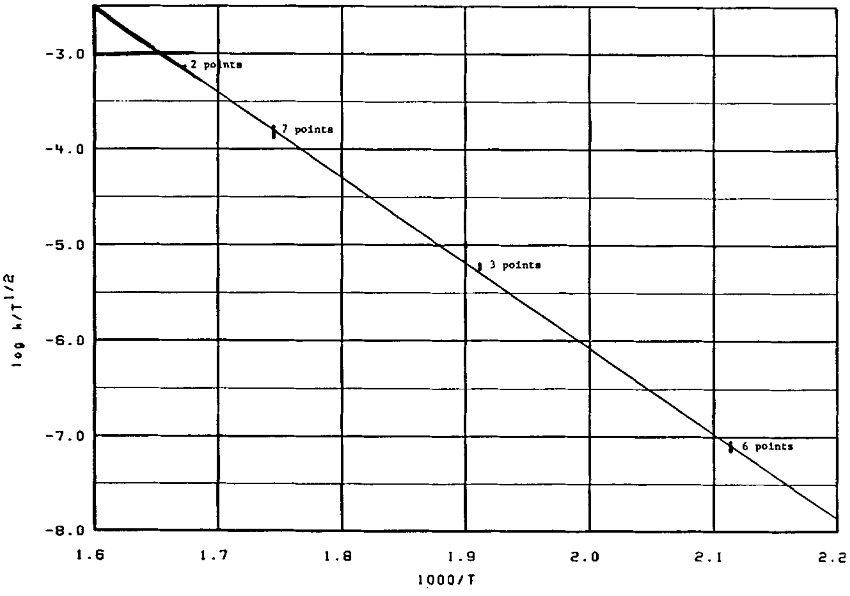
TABLE I. Pyrolysis data and calculated unimolecular specific rate constant *k* for $(CF_3)_2C(OH)CH_2CH{=}CH_2$.

Pressure,[a] torr	T, °C	Time, sec	C_3H_6, micromoles	k, sec^{-1}
25	325	60	1.67	9.32×10^{-4}
25	325	60	1.68	9.38×10^{-4}
20	300	120	.628	2.07×10^{-4}
21.9[b]	300	120	.615	1.85×10^{-4}
20	300	120	.566	1.86×10^{-4}
20	300	180	.797	1.76×10^{-4}
38	300	120	1.30	2.26×10^{-4}
20	300	120	.621	2.05×10^{-4}
20	300	120	.597	1.97×10^{-4}
20	250	900	.198	7.86×10^{-6}
20	250	300	.0723	8.61×10^{-6}
20	250	300	.0739	8.80×10^{-6}
20	200	3600	.0143	1.29×10^{-7}
20	200	7200	.0236	1.06×10^{-7}
20	200	7200	.0244	1.10×10^{-7}
20	200	7200	.0242	1.09×10^{-7}
20	200	3600	.0121	1.09×10^{-7}
38[c]	200	7200	.0295	1.19×10^{-7}

[a] $(CF_3)_2C(OH)CH_2CH{=}CH_2$.

[b] 690 torr Xe also present.

[c] S/V = 7.64 cm^{-1}. All other data S/V = 1.55 cm^{-1}.



Combining these results with the previously reported reverse reaction [5], the equilibrium constant

$$K_p = 10[^{(1/4.575)(-34.0\pm1.0)} + \frac{18700 \pm 400}{T}] \text{ atm}^{-1}$$

has been calculated.[2] ΔH^0 is seen to be -18.7 ± 1.0 kcal/mole and ΔS^0 is -34.0 ± 1.0 gibbs/mole.

The group additivity rules of Benson et al. [7] have been very successful in predicting $\Delta H_f{}^0$ and ΔS^0 for many molecules.

For the system studied in this report, the group values for C—$(F)_3$(CO) are not known. Using the known group additivity values for the product $(CF_3)_2C(OH)CH_2CH{=}CH_2$ and the experimental heat of reaction, the $\Delta H_f{}^0$ of $(CF_3)_2CO$ is calculated to be -325.2 ± 0.4 kcal/mole at 600°K. From this value, the $\Delta H_r{}^0$ of the reaction

$$(CF_3)_2CO \rightarrow 2CF_3 + CO + \Delta H_r{}^0$$

is 84.0 ± 0.4 kcal/mole CF_3COCF_3, so that the average bond strength of the C—C bonds is 42.0 ± 0.2 kcal at 600°K. For the similar reaction of acetone, the average C—C bond strength is 47.4 kcal at 600°K. Therefore, the average C—C bond strength is between 5.0 and 6.0 kcal less for the perfluoroacetone than for acetone. The mutual repulsion of the F atoms on the two CF_3 groups or the repulsion of the F and O of the carbonyl is probably the reason. At room temperature, the CH_3—CO bond is about 13.0 kcal, and the acetyl radical is moderately stable, while the CF_3CO is so unstable that very little evidence for its existence can be established. It is thus more likely that the mutual repulsion of the F and O atoms is responsible for the weakening of the C—C bond.

The entropy change of the perfluoroacetone–propene reaction was calculated by group additivity, assuming that the carbonyl has no effect on the CF_3 group. The calculated value of 35.8 gibbs/mole is in quite good agreement with the experimental value of 34.0 ± 1.0.

In reactions analogous to the one reported herein [8], e.g.,

$$CH_3CH(OH)CH_2CH{=}CH_2 \rightarrow C_3H_6 + CH_3CHO$$

the experimental and calculated log A factors are 11.93 and 11.9, respectively between 625° and 663°K [8]. This compares with the experimental value of 11.7 ± 0.1 for the reaction

$$(CF_3)_2C(OH)CH_2CH{=}CH_2 \rightarrow C_3H_6 + CF_3COCF_3$$

extrapolated to 645°K. Thus, the substitution of a CH_3 group by CF_3 has a small effect on the $\Delta S^{\neq}$ of the reaction.

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[2] ΔS° is calculated following the formulae for rate constants in reference [6]. ΔH^0 is calculated by converting the experimental K_c to K_p and substituting the above ΔS^0 into the expression $K_p = 10 \frac{1}{4.575}\left(-\frac{\Delta H^0}{T} + \Delta S^0\right)$.

Acknowledgement

The author appreciates the many helpful discussions with Dr. R. H. Knipe.

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Received August 19, 1971.
Revised April 20, 1972.