On the Gas-Phase Thermal Reaction between Perfluoroacetone and Propene

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The gas-phase thermal reaction between perfluoroacetone and propene has been studied in a quartz vessel in the temperature range 448–687°K. It is shown to be a homogeneous reaction, forming a product, $CH_2{=}CHCH_2C(CF_3)_2OH$, whose rate of formation equals $k\ [(CF_3)_2CO][C_3H_6]$, where

$$k = T^{1/2}(10^{4.90\pm0.10})10^{-(19{,}000\pm200)/4.6T}\ M^{-1}\ \mathrm{sec}^{-1}$$

where the limits are for one standard deviation. The Arrhenius parameters indicate that the reaction must be a cooperative process, since the E_a is much too low for a stepwise reaction path. The preexponential factor is some 10^5 lower than the collison rate, also consistent with the large steric demand of a cooperative reaction.

Introduction

In a recent paper, Urry, *et al.*,[1] have made an extensive study of the reaction between perfluoroacetone and olefins in the liquid phase, a type of reaction first reported by England.[2] Terminal olefins were found to be more reactive than nonterminal olefins. Adelman[3] in another study in the liquid phase noted that electron-donating groups on the carbon atom of the olefin linkage increased the reactivity. He postulated that the reaction occurred *via* a zwitterion intermediate. He supported his thesis by showing that ion-catalyzed polymerization occurred in the presence of the reacting system. It has also been postulated that a six-member cyclic intermediate is involved.[4]

The studies in the liquid phase were not designed to permit an elucidation of kinetic factors. If conditions for a homogeneous reaction could be established, a gas-phase kinetics study would permit an evaluation of the kinetic factors, as well as order of the reaction with respect to each of the reactants. Since the dielectric constant in the gas phase is so low, the mechanism would be restricted to nonionic paths. For all these reasons, a study of the gas-phase reaction was undertaken.

Apparatus and Procedure

The pyrolyses were carried out in a quartz cylindrical vessel of 45.7 cm^3 capacity with a surface:volume ratio (s/v) of 1.6 cm^{-1}. To determine the effect of surface, a similar vessel was packed with shell quartz tubing whose axes were parallel to the axis of the vessel, increasing the s/v to 7.6 cm^{-1}. The pyrolyzed mixture (less than 2% reacted) was transferred to a gas chromatography apparatus and analyzed. The product was trapped, followed by mass spectrometer analysis. It was identified as $CH_2{=}CHCH_2C(CF_3)_2OH$ by its mass spectrum and its appearance time in the gas chromatographic analysis. An authentic sample was used for comparison.[5] The sample was also used to calibrate the gc peak areas as moles.

In separate experiments it was shown that perfluoroacetone did not react with ethylene in the temperature and pressure range of this research. In another experiment, it was shown that the concentration of $CH_2{=}CHCH_2C(CF_3)_2OH$ formed in the reaction did not appreciably react with perfluoroacetone under the experimental conditions of this work. In order to generate the minimal sufficient product for accurate measurement of the gas chromatography peak, the reaction was run at variable times, from 1 hr at the lowest temperature to 3 min at the highest temperature.

Results and Discussion

The only product found in the gc analysis is $(CH_3)_2C(OH)CH_2CH{=}CH_2$. Data for the Arrhenius plot are shown in Table I, and the Arrhenius plot with the statistical best straight line placed through the points is shown in Figure 1. The tabulated results show clearly that the rate of reaction is homogeneous and first order with respect to concentration of both the reactants.

The specific rate constant calculated from the best straight line as seen in Figure 1 equals $T^{1/2}(10^{4.90\pm0.10}) \times 10^{-(19{,}000\pm200)/4.6T}$.

The zwitterion structure of the intermediate proposed by Adelman

$$(CF_3)_2C(O^-)(CH_2C^+HCH_3)$$

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[1] W. H. Urry, J. H. Y. Niu, and L. G. Lunsted, *J. Org. Chem.*, **33**, 2302 (1968).

[2] D. E. England, *J. Amer. Chem. Soc.*, **83**, 2205 (1961).

[3] R. L. Adelman, *J. Org. Chem.*, **33**, 1400 (1968).

[4] (a) H. R. Davis, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961; (b) I. L. Krunyants and B. L. Dyatin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 329 (1966).

[5] Kindly furnished by Dr. J. H. Y. Niu.

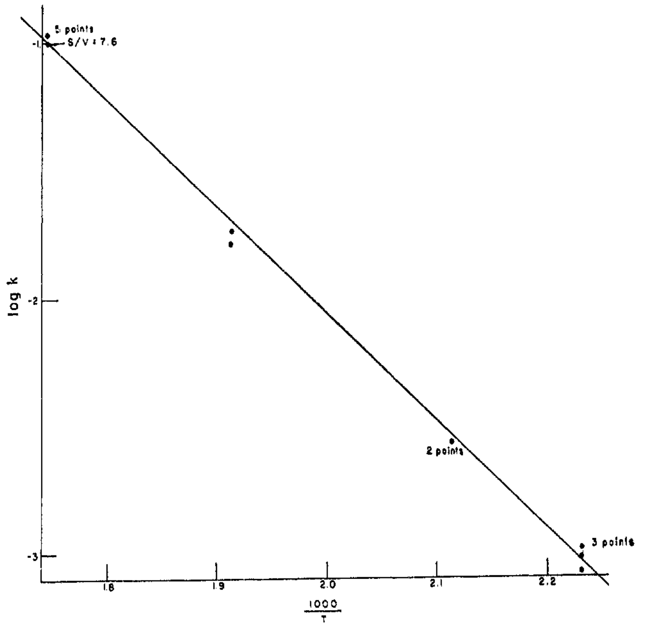


Figure 1. Arrhenius plot for the reaction between propene and perfluoroacetone.

Table I: Rate Data for Thermal Reaction of Perfluoropropene with Perfluoroacetone. (Surface/Volume of Reaction Vessel = 1.6 Except As Noted)

T,°K	Mol/l. × 10^3 C_3H_6	CF_3COCF_3	Rate of formation of $CH_2 = CHCH_2$-$C(CF_3)_2OH$ mol/l. sec × 10^8	Log k, l. mol^{-1} sec^{-1}
448	3.58	3.58	1.21	−3.023
448	3.58	3.58	1.07	−3.077
448	3.58	3.58	1.21	−3.023
448	3.58	3.58	1.30	−2.995
448	3.58	3.58	1.30	−2.994
473	1.69	1.69	0.79	−2.559
473	3.39	3.39	3.13	−2.564
523	1.53	1.53	3.90	−1.78
523	3.07	3.07	17.20	−1.74
573	1.40	1.40	19.90	−0.993
573	2.79	1.40	42.90	−0.959
573	1.05	1.05	11.60	−0.978
573	2.10	2.10	47.10	−0.973
573[a]	1.40	1.40	19.50	−1.005

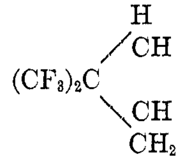
[a] S/V = 7.6.

would require many electron volts for charge separation in the gas phase. Also, such an intermediate would have a very strong drive to form an oxetane contrary to the experimental results.

A stepwise mechanism involving a biradical intermediate

$$(CF_3)_2C(O\cdot)(CH_2C\cdot HCH_3)$$

would be endothermic by at least 50 kcal/mol. The experimental E_a of just over 19 kcal/mol rules out both the above intermediates and suggests a cooperative mechanism with a six-membered cyclic intermediate



as consistent with the experimental order of the reaction and the E_a, as well as the unusually low preexponential factor reflecting the high steric demands of such a reaction path.