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Kinetics of gaseous fluorination of 1,1,1,2-tetrafluoroethane with elemental fluorine

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Abstract

The kinetics and temperature dependence of gaseous fluorination of 1,1,1,2-tetrafluoroethane (TFE) with elemental fluorine have been investigated between 105–148°C. Experiments were conducted in a stationary isothermic regime in copper tubes. Undiluted fluorine was used in a mixture with 1,1,1,2-TFE in concentration from 4% to 10% by volume. Explanations of observed mechanisms are suggested on the basis of the theory of chain reactions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 1,1,1,2-Tetrafluoroethane; Elemental fluorine; Chain reactions

1. Introduction

One of methods of production of pentafluoroethane (PFE) and hexafluoroethane (HFE) is the gaseous fluorination of 1,1,1,2-tetrafluoroethane (TFE) with elemental fluorine [1]. However, the literature on the kinetics of gaseous fluorination of fluoroalkanes is very limited [2], and the temperature dependence of these processes has not been studied. In devising a chemical reactor for these highly exothermic reactions, a knowledge of the magnitude of the activation energy is extremely important.

2. Experimental

The mixture of 1,1,1,2-TFE and fluorine without inert diluent was blown through a thermostatically controlled copper tube of internal diameter 2 mm. The temperature of the tube wall was varied from 105°C to 148°C. The time of stay of the mixture at a given temperature was varied by changing the tube length (1.2–15 m) as well as the flow rate (3–7 ml s^{-1}). Concentration of fluorine was taken from 4% to 10% by volume. The reacting gas mixtures, extracted at the output tube, were purified from unreactive fluorine by a lime absorber and then were analyzed using a gas chromatograph (catharometer, silica gel KSS-4 (0.25–0.5 mm) and vaseline oil, 6 m length and 3 mm internal diameter column, 50°C column temperature and 30 ml min^{-1} He flow).

From treatment of the experimental data and heat transfer calculations it was shown, that in all experiments a stationary isothermic regime takes place, the temperature over the tube axis exceeded that of the wall by not more than 4°C. In all experiments the gas flow in the tubes was laminar and a mode of ideal replacement was realized, as shown by calculation.

The greatest gas superheating takes place in the experiment for 1.2 m tube length, 7 ml s^{-1} flow rate, the concentration of fluorine 8.5% by volume and the temperature of the tube wall 148°C. The conversion of 1,1,1,2-TFE was 1.3%. The heat generation q in the tube is 1.5 W, the heat transfer coefficient $\alpha = \mathrm{Nu} \times \lambda \times d^{-1} = 3.66 \times 0.03 \times 0.002^{-1} = 57\ \mathrm{W\,m^{-2}\,K^{-1}}$, and the $\Delta T = T_w - T_g = q \times \alpha^{-1} \times S^{-1} = 3.5°\mathrm{C}$, where T_w is the temperature of the tube wall and T_g is the gas temperature on the tube axis. Before the experiments, the tube surface was passivated with fluorine, and we assumed that the wall was always the same. In all experiments the quantity of PFE was much more than HFE, therefore, HFE synthesis was not taken into account.

3. Results

It is believed that the reactions of gaseous fluorination of fluoroethanes with elemental fluorine are free radical in nature [3], and that the process of fluorination of 1,1,1,2-TFE in the gas phase

$$F_2 + C_2H_2F_4 \rightarrow C_2F_5 + HF, \quad \Delta H = -426\,\mathrm{kJ} \qquad (1)$$

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can be written as

$$F_2 \rightarrow 2F^{\bullet}, \quad \Delta H = 163\,\text{kJ}$$

$$C_2H_2F_4 + F^{\bullet} \rightarrow C_2HF_4^{\bullet} + HF, \quad \Delta H = -155\,\text{kJ},$$

$$C_2HF_4^{\bullet} + F_2 \rightarrow C_2HF_5 + F^{\bullet}, \quad \Delta H = -274\,\text{kJ} \qquad (2)$$

In the reaction mixture a stationary concentration of fluorine atoms $F^{\bullet}$, determined by the equilibrium fluorine dissociation at a given temperature, is established by analogy with the reaction of chlorination of a hydrogen [4]. Then, according to [5] the activation energy of the process (1) will be not less than half the energy of dissociation of a fluorine molecule, and will be not less than 82.5 kJ mol^{-1} with the order of the reaction for fluorine as 0.5. The treatment of experimental results was conducted on the basis of this hypothesis.

3.1. Chain generation and influence of the wall

In the first series of experiments the amount of conversion of 1,1,1,2-TFE to PFE was measured as a function of time. The results are presented in Fig. 1. The non-stationary part of the curve is caused by adsorption of fluorine atoms on the tube wall and shows that the wall is an inhibitor of the chain reaction in the form:

$$F^{\bullet} \rightarrow [F], \qquad [F] + F^{\bullet} \rightarrow F_2 \qquad (3)$$

where [F] is an adsorbed fluorine atom.

All results described below were obtained over the stationary part of the time dependence of 1,1,1,2-TFE conversion.

In order to verify the hypothesis (3) some experiments were conducted using a tube of internal diameter 4 mm, as shown in Fig. 2. The experimental dependence can be approximated by straight lines with a correlation coefficient not less than 0.95. The reaction rate increases with the tube diameter confirming the assumption of the inhibiting action of the wall.

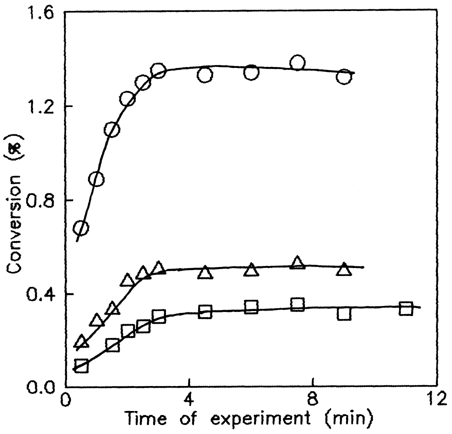

Fig. 1. Conversion of 1,1,1,2-TFE to PFE versus time for different process conditions: the temperature in the reaction zone $T = 119°C$, initial concentration of fluorine $C_{F_2} = 7.1$ vol.%, time of reaction $\tau = 0.87$ s (○); $T = 133°C$, $C_{F_2} = 7.6$ vol.%, $\tau = 0.45$ s (△); $T = 148°C$, $C_{F_2} = 8.5$ vol.%, τ=0.75 s (□).

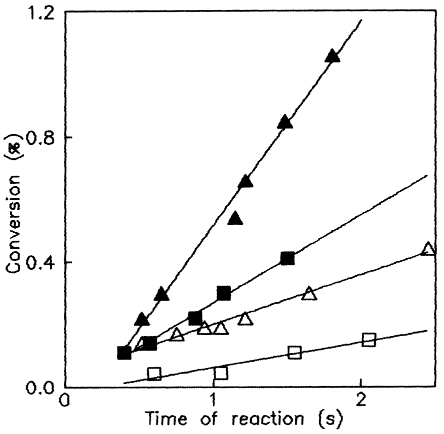

Fig. 2. Conversion of 1,1,1,2-TFE to PFE in tubes of internal diameter 2 mm and 4 mm versus time: the temperature in the reaction zone $T = 119°C$, initial concentration of fluorine $C_{F_2} = 4.1$ vol.%, tube diameter $d = 2$ mm (□); $T = 119°C$, $C_{F_2} = 4.5$ vol.%, $d = 4$ mm (△); $T = 148°C$, $C_{F_2} = 3.8$ vol.%, $d = 2$ mm (■); $T = 148°C$, $C_{F_2} = 4.0$ vol.%, $d = 4$ mm (▲).

Analysing the data in Figs. 1 and 2 it is possible to say that chain generation occurs in the gas phase after thermal dissociation of fluorine molecules to atoms. A heterogeneous breaking of the reaction chain takes place on the surface of the tube wall.

The overall reaction rate (Fig. 2) is proportional to the tube diameter, from which it follows, that under the conditions of the experiment, for heterogeneous chain breaking the adsorption of the fluorine atom on the surface is the limiting stage, rather than the diffuse flow, as in the processes of photochemical chlorination of hydrogen [5]. If the diffuse flow is the limiting stage, the rate of reaction should depend on the diameter to the second power [6].

3.2. Autocatalytic character of the reaction

A series of experiments were conducted at large fluorine conversions in a tube of 2 mm internal diameter. Results of these experiments are presented (Fig. 3). The experimental dependences indicate an autocatalytic (or a branched chain) character for the process and considering characteristic times of reaction (10–15 s) it is possible to deduce, that a degenerate branched chain process occurs [5].

For the observed homogenous reaction an energetic branched chain could take place. It is believed that in the gaseous fluorination of hydrocarbons hydrogen fluoride can accumulate more than 60% of the reaction heat in the vibrationally excited molecule [7]. The energetic branching occurs as a result of formation of vibrationally excited molecules of hydrogen fluoride. For the given reacting system the following equation can be written

$$C_2H_2F_4 + F^{\bullet} \rightarrow C_2HF_4 + HF^{*}, \quad HF^{*} + F_2 \rightarrow HF + 2F^{\bullet} \qquad (4)$$

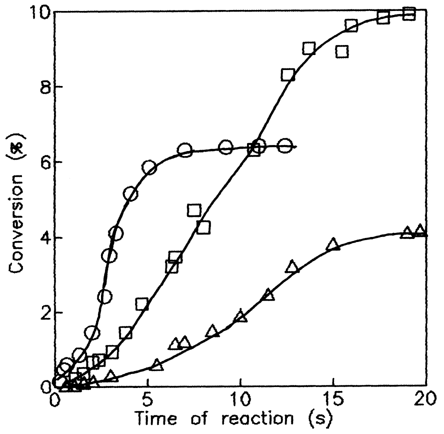

Fig. 3. Conversion of 1,1,1,2-TFE to PFE versus time: the temperature in the reaction zone $T = 119°C$, initial concentration of fluorine $C_{F_2} = 4.1$ vol.% (△); $T = 148°C$, $C_{F_2} = 6.4$ vol.% (□); $T = 105°C$, $C_{F_2} = 10.0$ vol.% (○).

where HF^* is a vibrationally excited molecule. It is necessary to add Eq. (4) to Eqs. (2) and (3).

3.3. Dependence of order of reaction on fluorine

To determine the order of reaction on fluorine, experiments were conducted in which the initial concentration of 1,1,1,2-TFE was much more than the amount of conversion of 1,1,1,2-TFE. Here, it is possible to neglect the influence of concentration of 1,1,1,2-TFE on the rate of reaction (zero-order reaction for 1,1,1,2-TFE).

The results of the experiments are shown in Fig. 4, all experiments were carried out in a tube of diameter of 2 mm. From Fig. 4, it can be seen that the time dependences of the conversion have a linear character. The calculations of reaction order on fluorine were carried out in accordance with the formula

$$n = \ln\left(W_1 W_2^{-1}\right)\left[\ln\left(f_1 f_2^{-1}\right)\right]^{-1}$$

where f_1,f_2 are initial fluorine concentrations and W_1, W_2 are rates of the reaction. In the calculations, the values of W_1, W_2 were used, as obtained at those temperatures. The order of the reaction obtained on fluorine is 0.8, which is a little more than $n = 0.5$, which should result from model (2). The discrepancy could be caused by the influence of processes (3) and (4) on the equilibrium concentration of the fluorine atoms.

3.4. Activation energy of reaction

From the experimental results, shown in Fig. 4 the activation energy and the pre-exponential factor of the reaction were calculated using the model

$$W = kf^n$$

where $n = 0.8$ and k is the rate constant of reaction (1).

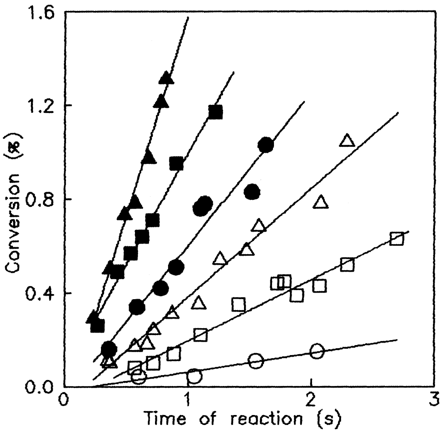

Fig. 4. Conversion of 1,1,1,2-TFE to PFE versus time: the temperature in the reaction zone $T = 119°C$, initial concentration of fluorine $C_{F_2} = 4.1$ vol.% (○); $T = 105°C$, $C_{F_2} = 6.3$ vol.% (□); $T = 119°C$, $C_{F_2} = 7.1$ vol.% (△); $T = 119°C$, $C_{F_2} = 9.7$ vol.% (●); $T = 133°C$, $C_{F_2} = 7.6$ vol.% (■); $T = 148°C$, $C_{F_2} = 8.5$ vol.% (▲).

The following results are obtained: $E = 50 \pm 10\ \mathrm{kJ\ mol^{-1}}$, $k_0 = (5.2 \pm 0.6) \times 10^{-5}\ \mathrm{s^{-1}}$. The values of activation energy for the reaction obtained are less than those in model (2), indicating once again the necessity of considering processes (3) and (4).

4. Conclusions

It has been shown, that the process of interaction of 1,1,1,2-TFE and fluorine in a copper tube between 105°C and 148°C has degenerate branched chain character. Thus, the action centres are formed in the gas phase by thermal dissociation of fluorine. Breaking of the reaction chain occurs on the wall, the limiting stage of breaking is the adsorption of fluorine atoms on the wall surface. It is likely, that chain branching occurs because of formation of vibrationally excited hydrogen fluoride molecules in the reaction. The activation energy ($50\ \mathrm{kJ\ mol^{-1}}$), the pre-exponential multiplier and the order of reaction dependence on fluorine (0.8) have been calculated for the reaction.

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