REACTION OF CHLOROFLUOROCARBENE WITH WITH CYCLOPENTADIENE

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Previously we had found a high-temperature method for the preparation of fluorobenzene, which consisted in the joint pyrolysis of cyclopentadiene and a source of either difluorocarbene or chlorofluorocarbene in the gas phase in a flow system [1]. The advantage of the discovered method over other methods [2-4] for the synthesis of aryl fluorides is the ready availability of the starting reactants, the efficiency and simplicity of both the process itself and the apparatus, and the fact that it is of practical interest. However, the kinetics and mechanism of this process have not been studied. In the present paper we report the results of studying the reaction of cycloepentadiene with chlorofluorocarbene, generated by the pyrolysis of dichlorofluoromethane.

According to the data in [5], the high-temperature transformations of dichlorofluoromethane proceed along the following main directions.

CHCl₂F $\stackrel{k_1}{\underset{k_{-1}}{\leftarrow}}$ CClF + HCl CClF + CClF $\stackrel{k_2}{\rightarrow}$ CClF = CClF

According to [1], fluorobenzene is formed in the presence of cyclopentadiene by the scheme:



In the range $550-670^{\circ}$ the process proceeds in the same manner in platinum and quartz reactors, which testifies to its homogeneity. For most of the experiments the material balance in carbon and fluorine is found to be in the range 90-100% (based on identified products), and decreases somewhat in carbon with increase in the contact time at 670° due to partial decomposition of the cyclopentadiene (Fig. 1); here the formation of tarry products in the heating zoning is observed.

The principal reaction products are fluorobenzene, hydrogen chloride, and 1,2-dichloro-1,2-difluoroethylene, in which connection the yield of $C_{\rm g}H_{5}F$ reaches 90-100%. The absence of noticeable amounts of other compounds testifies to the fact that side reactions are not present, and confirms the fact that the limiting step of the reaction (3) is the addition of CC1F to the cyclopentadiene. Two 6-chloro-6-fluorobicyclo[3.1.0]-2-hexene isomers should be formed as the result of the addition.



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Fig. 1. Calculated kinetic curves and experimental points for consumption of $CHCl_2F$ (1) and cyclopentadiene (2), and accumulation of C_6H_5F (3) and CClF = CClF (4), at various temperatures (in the graphs the CClF = CClF concentration is increased 100 times).

According to the known rules for the retention of orbital symmetry [6], only the cleavage of the endohalogen atom can be accompanied by an expansion of the five-membered ring; consequently, the formation of fluorobenzene from the endo-chlorine, and of chlorobenzene from the endo-fluoride, could be expected. However, recent nonempirical calculations disclosed that in synchronous processes of halogen cleavage and cyclopropylallylic transformation the difference in the activation energies of the allowed and forbidden (according to Woodward-Hoffman) processes does not exceed 10 kcal/mole [7]. Since this value is noticeably smaller than the difference in the energies of the C - F and C - Cl bonds (40-50 kcal/mole), while the isomeric chlorofluorobicyclo[3.1.0]-2-hexenes are formed as the result of the exceedingly exothermic addition of CClF, the endo-fluoride in our case evidently also undergoes cleavage of the Cl atom with the subsequent formation of fluorobenzene. A similar rule was also observed previously in the reaction for the ring expansion of the chlorofluorocarbene adduct to 2,3-dihydrofuran [8].

The process for the preparation of fluorobenzene [reactions (1)-(3)] is described by the following system of differential equations.

$$\frac{d \,(\mathrm{CHCl}_2\mathrm{F}]}{d\tau} = -k_1 \,[\mathrm{CHCl}_2\mathrm{F}] + k_{-1} \,[\mathrm{CClF}] \,[\mathrm{HCl}]$$

$$-\frac{d \,\left[\swarrow \right]}{d\tau} = \frac{d \,[\mathrm{C}_{\mathrm{e}}\mathrm{H}_3\mathrm{F}]}{d\tau} = k_3 \,[\mathrm{CClF}] \,\left[\swarrow \right]$$

$$\frac{d \,[\mathrm{CClF}=\mathrm{CClF}]}{d\tau} = k_2 \,[\mathrm{CClF}]^2$$

$$\frac{d \,[\mathrm{CClF}]}{d\tau} = k_1 \,[\mathrm{CHCl}_2\mathrm{F}] - k_{-1} \,[\mathrm{CClF}] \,[\mathrm{HCl}] - k_3 \,[\mathrm{CClF}] \,\left[\swarrow \right] - 2k_2 \,[\mathrm{CClF}]^2$$

$$[\mathrm{HCl}] = \,[\mathrm{CHCl}_2\mathrm{F}]_0 + \left[\swarrow \right]_0 - [\mathrm{CHCl}_2\mathrm{F}] - \left[\swarrow \right]$$

The constant k_3 was determined by the method of sorting for each point, starting with the minimization condition

$$\sum_{i=1}^n (\mathcal{C}_i^e - \mathcal{C}_i^c)^2,$$

where C_i^e and C_i^c are, respectively, the experimentally found and calculated concentrations of the reaction products. The following expression was obtained by the method of least squares.

$$k_{3} = 10^{9,32\pm0,15} \exp\left(-\frac{5078\pm620}{RT}
ight)$$
 liter/mole.sec.

As can be seen from Fig. 1, the calculated kinetic curves based on Eqs. (1)-(V), using the values of k_1 , k_{-1} , k_2 [5], and k_3 found by us here and previously, show satisfactory agreement with the experimental points.

EXPERIMENTAL METHOD

The starting mixtures were prepared by diluting dichlorofluoromethane and cyclopentadiene with nitrogen in a dry gas meter, connected to a U-shaped mercury manometer. The experiments were run under the conditions of the stream method described in [5]. The gas mixture was analyzed chromato-graphically in a Tswett-1 instrument equipped with a flame-ionization detector (column length 1 m, packed with 10% dibutyl phthalate deposited on INZ-600 brick, 0.25-0.50 mm, 60°, carrier gas H₂, 2.5 liter/h).

The Runge-Kutta equation [9] was used for the numerical integration of the system of Eqs. (I)-(V), with an automatic selection of the spacing on an Nairy-2 electronic computer.

CONCLUSIONS

1. The kinetics of the gas-phase reaction of chlorofluorocarbene with cyclopentadiene, leading to the formation of fluorobenzene, was studied and the rate constant was determined.

2. The value of the a tivation energy for the reactions of carbenes, containing multiple bonds, was experimentally determined for the first time on the example of the reaction of CCIF with cyclopentadiene.

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