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An Evaluation of the Kinetic Data for Hydrogen Abstraction from Germanes in the Gas Phase by CF_3 and C_2F_5 Radicals

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After the review of kinetic data for reaction of hydrogen abstraction from germanoorganic compounds by trifluoromethyl and pentafluoroethyl radicals in the gas phase it was possible to determine the relative kinetic reactivity of the two radicals under consideration. The contributing factors are the thermochemical effects of the investigated reactions, steric hindrance derived mainly from the size of substrate molecules and the polar interaction between the polarized germane molecules and the radicals of different electrophilicity. The polar effects occurring in these radical reactions contribute primarily to the activation energy, but they have no significant contribution to the pre-exponential factor.

Key words: trifluoromethyl radicals, pentafluoroethyl radicals, hydrogen abstraction, radical reactions, germanoorganic compounds

The depletion of stratospheric ozone, due to chlorofluorocarbons (CFCs), has encouraged attempts to develop alternative compounds, less toxic to the environment. Of the substitutes believed to be acceptable for those chemical applications, where CFCs were used previously, hydrofluorocarbons (HFCs) have been given particular attention. Even though there is evidence to suggest that the presence of HFCs creates no serious threat in terms of stratospheric ozone depletion [1], the mechanisms that govern the degradation of these compounds in the troposphere are still far from being fully understood. A number of laboratory investigations have aimed at determining the products released in the atmospheric photooxidation of the HFCs. Among the main products obtained during the decomposition of the HFCs are the CF_3 and C_2F_5 radicals [2]. Reactions of CF_3 radical with O_2, HO_2, NO and NO_2 are considered to be of special importance for the complex chemistry of the polluted atmosphere. Kinetics of the formation of several fluorine-containing compounds has been studied both experimentally and theoretically [3–14]. There also are various airborne compounds, such as metalloorganics, coming from anthropogenic emissions, which induce reactions of the CF_3 and C_2F_5 radicals. Therefore, it seems necessary to undertake systematic kinetic studies in order to understand the factors that may affect the reactivity of these radicals. The hydrogen abstraction reactions by CF_3 and C_2F_5 radicals are of interest from both theoretical and experimental points of view. Results of the quantum mechanical *ab initio* calculations allow to gain some insight into molecular properties of reactants and provide the starting points for computational methods of the reaction rate theory. The rate constants derived theoretically, at the different level of theory, allow the realistic description of the kinetics of a wide class of hydrogen abstraction reactions [14–20]. However, theoretical analysis of the reaction kinetics is strongly limited by molecular dimensions of the reaction system. Therefore, experimental measurements are still a major source of the kinetic informations, which are necessary to describe the kinetic behaviour of the large and heavy-atoms containing the reaction systems. The results of kinetic studies of the CF_3 and C_2F_5 radicals with series of compounds, as well as the interpretation of the factors that govern the dynamics of these reactions, will undoubtedly help to improve the predictive capacity for controlling the development of the contamination.

The present paper gathers and reviews the results of kinetic investigations on hydrogen abstraction by CF_3 and C_2F_5 radicals from germanoorganic compounds in the gas phase. All these studies were carried out at the Department of Physical Chemistry, Wrocław University of Medicine. Such review makes it possible to gain a better understanding of how the reactivity of the two radicals toward the investigated group of compounds is influenced. Only with such data in hand, can one analyse the factors that affect the relative reactivity of the two radicals differing in electrophilicity.

METHODS

Free radical sources. In the kinetic investigations of the reactions of CF_3 and C_2F_5 radicals use was made of the photolysis of hexafluoroacetone and pentafluoropropionic acid anhydride as sources of these radicals. The support for the convenience of this method when studying the elementary reactions of the two radicals is given by the results reported by other investigators [21–24].

Photolysis of hexafluoroacetone. The photolysis of hexafluoroacetone [22] in the gas phase, carried out over the temperature range 298–573 K with wavelengths ranging between 250–340 nm, is governed by the following mechanism:

$$CF_3COCF_3 + h\nu \rightarrow CF_3COCF_3^* \quad (1), \qquad CF_3COCF_3^* \rightarrow CF_3 + CF_3CO \quad (2),$$

$$CF_3CO \rightarrow CF_3 + CO \quad (3), \qquad CF_3 + CF_3 \rightarrow C_2F_6 \quad (4),$$

and occurs in the presence of the vibrationally and electronically excited $CF_3COCF_3^*$ molecule in a singlet state of a comparatively long half-time, approximately 10^{-8} s. Trifluoroacetyl radicals decompose at a fast rate (3). The final products of the photolysis of hexafluoroacetone are carbon oxide and hexafluoroethane, which form in the reaction of CF_3 radical recombination (4) characterized by the rate constant $k = 10^{13.36}$ cm^3 mol^{-1} s^{-1} and a zero-point activation energy [25]. Above 573 K, CF_3COCF_3 undergoes a thermal decomposition, yielding the same final products [26]. The quantum yield with which the photolysis products are formed approaches unity, decreasing slightly with increasing pressure. The decrease in the quantum yield with the increase of pressure of the substrate and inert gases provides evidence ascribing a certain importance to the collision deactivation of the vibrating state of the excited hexafluoroacetone molecule.

Photolysis of pentafluoropropionacidic anhydride. This photolysis process [23] in the gas phase is carried out between 293–480 K with wavelengths varying from 200–300 nm, according to the following mechanism:

$$(C_2F_5CO)_2O + h\nu \rightarrow (C_2F_5CO)_2O^* \quad (5), \quad (C_2F_5CO)_2O^* \rightarrow C_2F_5CO + C_2F_5CO_2 \quad (6),$$

$$C_2F_5CO_2 \rightarrow C_2F_5 + CO_2 \quad (7), \quad C_2F_5CO \rightarrow C_2F_5 + CO \ (8), \ C_2F_5 + C_2F_5 \rightarrow n\text{-}C_4F_{10} \quad (9),$$

in the presence of the vibrationally and electronically excited $(C_2F_5CO)_2O^*$ molecule in a singlet state. The unstable intermediate products, C_2F_5CO and $C_2F_5CO_2$, undergo decomposition (7), (8) to form C_2F_5 radicals. The final products of the photolysis of pentafluoropropionacidic anhydride are carbon dioxide, carbon oxide and decafluoro-n-butane, which are formed in the recombination (9) of the C_2F_5 radicals at a rate constant $k = 10^{13.40}$ cm^3 mol^{-1} s^{-1} and a zero-point activation energy [21]. Above 500 K, the pentafluoropropionacidic anhydride is subject to thermal decomposition, yielding the same final products [27]. The quantum yield, with which the photolysis products are formed, depends neither on the wavelengths range, 254–265 nm, nor on the initial pressure of the substrate [28].

RESULTS AND DISCUSSION

Kinetic interpretation of the photolysis of hexafluoroacetone and pentafluoropropionacidic anhydride in the presence of germanoorganic compounds. The photolysis of hexafluoroacetone in the presence of germanoorganic compounds (RH) yields trifluoromethane, hexafluoroethane and carbon oxide according to the following scheme:

$$CF_3COCF_3 + h\nu \rightarrow 2CF_3 + CO \quad (10), \qquad CF_3 + RH \rightarrow CF_3H + R \quad (11),$$

$$CF_3 + CF_3 \rightarrow C_2F_6 \quad (12).$$

The CF_3 radicals that form in (10) take part in the abstraction of hydrogen atoms from the germanoorganic compounds (11) and in the simultaneous reaction of radicals recombination (12). Under the experimental conditions applied, no products of the reaction of chlorine atom abstraction by CF_3 radicals from the investigated chlorine derivatives of the germanoorganic compounds have been detected. If reactions

(11) and (12) are the only sources of the CF_3H and C_2F_6 products, then the following equation is satisfied:

$$k_{CF_3H}/k^{1/2}_{C_2F_6} = R_{CF_3H}/(R^{1/2}_{C_2F_6}[RH]) \qquad (13)$$

where k denotes the appropriate rate constants, R stands for the rates of products formation, and [RH] is the initial concentration of the germanoorganic compounds.

The photolysis of pentafluoropropionacidic anhydride in the presence of germanoorganic compounds (RH) leads to the formation of pentafluoroethane, decafluoro-n-butane, carbon dioxide and carbon oxide. For these processes, the following scheme was proposed to describe the formation of the identified products:

$$(C_2F_5CO)_2O + h\nu \rightarrow 2\ C_2F_5 + CO_2 + CO\ (14),\quad C_2F_5 + RH \rightarrow C_2F_5H + R \qquad (15),$$

$$C_2F_5 + C_2F_5 \rightarrow n\text{-}C_4F_{10} \qquad (16).$$

Like CF_3 radicals, the C_2F_5 radicals formed in the reaction (14) participate both in the hydrogen abstraction from the germanoorganic compounds (RH) and in the simultaneous reaction of recombination. Under the experimental conditions applied, no products of the chlorine atom abstraction by C_2F_5 from the investigated chlorine derivatives of the germanoorganic compounds have been detected. If the C_2F_5 radicals obtained *via* reaction (14) are converted exclusively in reactions (15) and (16), then the following equation is satisfied:

$$k_{C_2F_5H}/k^{1/2}_{C_4F_{10}} = R_{C_2F_5H}/(R^{1/2}_{C_4F_{10}}[RH]) \qquad (17).$$

With the experimental results for the thermal stability of germanes, as well as with the reported data on the stability of hexafluoroacetone and pentafluoropropionacidic anhydride [26,27], it was possible to establish the temperature range for the kinetic investigations of the elementary radical reactions of hydrogen abstraction.

Arrhenius parameters. ***Reactions of the CF_3 radical.*** The value of term $k_{CF_3H}/k^{1/2}_{C_2F_6}$ incorporated in (13) was determined by kinetic experiments and related to temperature to satisfy the Arrhenius plot. The absolute parameter values of the Arrhenius equation for the reactions considered have been calculated by the last square method, on the basis of the known [25] rate constant for the recombination of the CF_3 radicals ($k = 10^{13.36}$ cm^3 mol^{-1} s^{-1}; $E = 0$) and have been listed in Table 1.

Table 1. Arrhenius parameters for the reaction of hydrogen abstraction from germanes by trifluoromethyl radicals.

Compound	Temperature ΔT range [K]	E [kJ mol^{-1}]	log A [cm^3 mol^{-1} s^{-1}]	log $k_{400\,K}$ [cm^3 mol^{-1} s^{-1}]	Ref.
$HGeCl_3$	302–360	26.4 ± 0.1	12.25 ± 0.06	8.80	11
CH_3GeCl_3	349–561	33.2 ± 0.3	12.08 ± 0.04	7.75	12
$(CH_3)_2GeCl_2$	344–570	31.6 ± 0.1	11.26 ± 0.03	7.13	this study
$(CH_3)_3GeCl$	344–552	30.4 ± 0.1	11.38 ± 0.03	7.41	this study
$(CH_3)_4Ge$	323–473	28.2 ± 0.6	11.55 ± 0.09	7.84	12
$(C_2H_5)_4Ge$	323–563	21.7 ± 0.2	11.95 ± 0.02	9.12	12

Reactions of the C_2F_5 radical. With the results of kinetic experiments it was possible to establish the value of the term $k_{C_2F_5H}/k^{1/2}_{C_4F_{10}}$ in (17) as a function of temperature so as to satisfy the Arrhenius plot. The absolute parameter values of the Arrhenius equation for the reactions of interest have been calculated by the least-square method, making use of the known [21] rate constant for the recombination of the C_2F_5 ($k = 10^{13.40}$ cm^3 mol^{-1} s^{-1}; E = 0), and have collected in Table 2.

Table 2. Arrhenius parameters for the reaction of hydrogen abstraction from germanes compounds by pentafluoroethyl radicals.

Compound	Temperature ΔT range [K]	E [kJ mol^{-1}]	log A [cm^3 mol^{-1} s^{-1}]	log $k_{400\,K}$ [cm^3 mol^{-1} s^{-1}]	Ref.
$HGeCl_3$	310–358	23.1 ± 0.3	11.42 ± 0.04	8.40	this study
CH_3GeCl_3	351–455	29.4 ± 0.5	11.25 ± 0.07	7.41	12
$(CH_3)_2GeCl_2$	350–480	28.6 ± 0.6	10.56 ± 0.08	6.83	this study
$(CH_3)_3GeCl$	340–466	27.4 ± 0.3	10.72 ± 0.03	7.14	this study
$(CH_3)_4Ge$	342–481	25.5 ± 0.5	11.16 ± 0.06	7.83	15
$(C_2H_5)_4Ge$	328–457	21.2 ± 0.2	11.68 ± 0.03	8.91	15

The error intervals calculated for the two radicals by the statistical method do not include systematic errors.

From the analysis of the kinetic parameters for the investigated reactions of trifluoromethyl and pentafluoroethyl radicals (Tables 1 and 2) can be inferred that the preexponential factors log A are "typical" of this kind of hydrogen abstraction. The noticeably exothermic nature of the investigated reactions affects the comparatively low activation energy. The rate constants at 400 K characterize the kinetic reactivity of the radicals toward the germanoorganic compounds considered, a parameter which is influenced by the energy effects of the reaction, by steric factors and the polar effects between the substrate molecules.

The rate constants at 400 K (Tables 1 and 2) also show that hydrogen abstraction by the CF_3 and C_2F_5 radicals from trichlorogermane proceeds with a faster rate and with a lower activation energy than from methylchlorogermanes, which is in agreement with the thermochemical analysis of these processes. Assuming that the average dissociation energies are D_{298}(Ge-H) = 339.0 kJ mol^{-1} [31,32] and D_{298}(C-H) = 401.0 kJ mol^{-1} in methylchlorogermanes [33], we can see that the reactions of hydrogen abstraction from trichlorogermane are more exothermic than from methylchlorogermanes for both the radicals. Furthermore, radical reactions with methylchlorogermanes run with greater steric hindrance (due to a greater molecule size), and this is what explains the slightly lower values of the preexponential factors. The higher kinetic reactivity of the two radicals toward trichlorogermane results from the energy effects considered, and to a smaller extent from the contribution of the steric hindrance.

Analysis of the kinetic parameters for CF_3 radical (Table 1) and C_2F_5 radical (Table 2) reactions methylchlorogermanes points to the significant contribution of the polar effects to the reactivity of the electrophilic radicals to the polarized molecules of methylchlorogermanes. In terms of the number of methyl groups, the preexponential factors for the particular radical reactions do not considerably differ, except for the reaction with CH_3GeCl_3. The comparatively high A factor for the reactions of the two radicals with the most polarized CH_3GeCl_3 particle may have been influenced by the ionic nature [34,35] of the active complex concomitant with the presence of the polar Ge–Cl bond in its structure. The presence of the polar effects in the reactions of CF_3 and C_2F_5 with methylchlorogermanes is corroborated by the activation energies, which increase with the increasing number of substituted chlorine atoms, *i.e.* with the increasing polarity of the methylchlorogermane molecules. The highest activation energies are those of the CF_3 and C_2F_5 reactions with methylchlorogermane molecules, where the inducing effect of the chlorine atoms is the most distinct, thus, contributing to the decrease in the electron density on the abstracted hydrogen atoms and, consequently, inhibiting (in terms of energy) the attack of electrophilic radicals. When the number of substituted chlorine atoms in the methylchlorogermanes increases, the polar effect of the attracting interaction between the electrophilic radicals and the abstracted hydrogen atoms becomes weaken. The highest electron density on the hydrogen atoms in $(CH_3)_4Ge$ favours the attractive interactions between the CF_3 and C_2F_5 radicals and the abstracted hydrogen atoms, which is reflected in the lowest activation energy value for the reactions of these radicals with tetramethylgermane.

As expected, the CF_3 and C_2F_5 radical reactions with $(C_2H_5)_4Ge$ occur with a lower activation energy than that for the same radical reactions with $(CH_3)_4Ge$. This is due to the main attack of the radicals on the secondary hydrogen atom in particles of tetraethylgermanes.

Interesting information is offered by the comparison of the kinetic parameters (Table 3) for the reactions of CF_3 and C_2F_5 with the molecules of germanoorganic compounds, where polar radicals differing considerably in electrophility are involved.

Table 3. Comparison of kinetic parameters for CF_3 and C_2F_5 radicals reactions with germanes.

Compound	$E_{CF_3} - E_{C_2F_5}$ [kJ mol^{-1}]	$A_{CF_3}/A_{C_2F_5}$	$k_{CF_3}/k_{C_2F_5}$ at 400 K
$HGeCl_3$	3.3	6.76	2.59
CH_3GeCl_3	3.8	6.76	2.19
$(CH_3)_2GeCl_2$	3.0	5.01	2.00
$(CH_3)_3GeCl$	4.9	4.57	1.86
$(CH_3)_4Ge$	2.7	2.45	1.02
$(C_2H_5)_4Ge$	0.5	1.86	1.62

The bond dissociation energies are $D_{298}(CF_3\text{-}H)$ = 441.0 kJ mol^{-1} [36] and $D_{298}(C_2F_5\text{-}H)$ = 424.0 kJ mol^{-1} [37], respectively. The differences in enthalpy between the reactions of the two radicals derive from the differences in the dissociation energy for the bonds that are formed and cleaved in the course of the reaction. Since the dissociation energy of bond cleavage is the same for the reactions of the two radicals with the same substrate, we can write:

$$\Delta H_{CF_3} - \Delta H_{C_2F_5} = D_{298}(C_2F_5\text{-}H) - D_{298}(CF_3\text{-}H) = -17 \text{ kJ mol}^{-1}.$$

The differences in the enthalpies of these processes seem to favour, in terms of energy, the reaction of atom abstraction by the CF_3 radicals, which should manifest in lower activation energies for these radicals in the reaction with germanes. However, as it can be seen from the data in Table 3, the radical reactions of hydrogen atom abstraction involve an activation energy, which is higher for CF_3 than for the more electrophilic C_2F_5 radicals with the same substrate. The differences in the activation energy between the two radicals ($E_{CF_3} - E_{C_2F_5}$) increase with the number of chlorine atoms substituted in the germane molecules, *i.e.* with the polarization of the molecule. It should also be expected that in the reactions of the CF_3 and C_2F_5 radicals with the non-polar molecules, $(CH_3)_4Ge$ and $(C_2H_5)_4Ge$, the E_{CF_3} will be lower than that of $E_{C_2F_5}$. In fact, $E_{CF_3} - E_{C_2F_5} > 0$, which, again, suggests poor polar interactions. Such strong polar effects, manifested in the inversion of activation energy, have been reported so far only for the reactions of CF_3 and C_2F_5 radicals with methylfluorosilanes [38] and for the reactions of CH_3 and CF_3 with halide hydrogens [39]. The reactions of C_2F_5 radicals run with a greater steric hindrance than do the reactions of the CF_3 radicals, which are smaller. The value of $A_{CF_3}/A_{C_2F_5}$, which is 6.76 for the reactions of these radicals with $HGeCl_3$ and CH_3GeCl_3, decreases with the decreasing number of chlorine atoms substituted in the germanes to the value of 1.86 for the reaction with $(C_2H_5)_4Ge$. It is interesting to note that the reactivity of the CF_3 radicals toward the compounds considered is higher than the reactivity of C_2F_5, and that the relative reactivity, $k_{CF_3}/k_{C_2F_5}$, increases with the increase in the polarity of molecules, although the polar effects, which affect the activation energy, suggest a reversal of reactivity. This indicates that the relative reactivity of the two radicals is also influenced by steric factors.

The discussion of the results from the kinetic studies of the reactions of the electrophilic radicals, CF_3 and C_2F_5, with germanes enables the following conclusion to be drawn: the polar effects occurring in these reactions contribute primarily to the activation energy and, in general, also to the kinetic reactivity, but no significant contribution of the polar effects has been observed with respect to the preexponential factor.

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