An Evaluation of the Kinetic Parameters for the Reaction of Trifluoromethyl Radicals with CH_3Cl in the Gas Phase in the Temperature Range from 416 to 636 K

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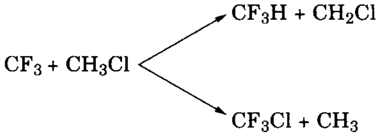
Abstract

The hydrogen and chlorine atom abstraction reactions from CH_3Cl by CF_3 radicals produced by the photolysis of hexafluoroacetone (HFA) and CF_3I were studied relative to the recombination of CF_3 radicals:

(3)

(4)



$$CF_3 + CH_3Cl \rightarrow CF_3H + CH_2Cl \quad (3)$$

$$CF_3 + CH_3Cl \rightarrow CF_3Cl + CH_3 \quad (4)$$

The Arrhenius parameters obtained in the temperature range 416 to 578 K are:

$$\text{Log } k_3/k_2^{1/2}[\text{cm}^{3/2}\ \text{mol}^{-1/2}\ \text{s}^{-1/2}] = (5.39 + 0.10) - (10490 + 150)/\theta$$

$$\text{Log } k_4/k_2^{1/2}[\text{cm}^{3/2}\ \text{mol}^{-1/2}\ \text{s}^{-1/2}] = (4.52 + 0.11) - (13370 + 250)/\theta$$

where $\theta = 2,303.RT$ cal mol^{-1} and k_2 is the recombination rate constant for the CF_3 radicals.

The factors that influence the transfer processes of chlorine and hydrogen are analyzed in a series of reactions of halomethanes with CF_3 and CH_3 radicals.

Introduction

Atmospheric pollution problems due to the incorporation of freons into the high atmosphere and of active haloalkanes into the troposphere produce the need to undertake systematic kinetic studies in order to understand the factors that influence in the reactivity of these species with the free radicals present in the different layers of the atmosphere. Kinetic studies on this series of compounds and the interpretation of the factors that govern the dynamics of these abstraction reactions will undoubtedly contribute to improve the predictive capacity for controlling the evolution of contamination. Hence, the abstraction reaction of an atom from a substrate by atoms or free radicals has been widely studied, especially the hydrogen atom transfer reactions.

With the haloalkanes, halogen, and hydrogen atom abstraction processes occur with different rates [1]. Thus, when the number of hydrogen atoms in the molecule increases the analytical difficulties to evaluate the rate of

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the halogen atom transfer increase. This situation has led in some cases to estimate the values of the kinetic parameters for this type of reactions. The only values calculated, for example, for the hydrogen and halogen atom transfer of the halomethanes, CH_3X (X = F, Cl, Br, I) by the CF_3 radical are those obtained by Whittle et al. [1(a),2]. Thus, the values of the activation energy obtained by Whittle for the halogen atoms transfer reaction from CH_3Cl by CF_3 radical is only a rough estimation; whereas with CH_3Br, Whittle obtained two values for the activation energy, one at low pressure (25 torr) and another at high pressure (180 torr). In the iodine atom transfer reaction from CH_3I by CF_3 radical several products were observed from secondary reactions. Also, Whittle et al. [1(a)] measured the hydrogen atom abstraction reaction from CH_4 by CF_3 radicals obtaining an activation energy (Ea (H) = 11.2 Kcal/mol) that he reevaluated later [3] as Ea (H) = 12.5 Kcal/mol. So, it should be pointed out the scattering of values and their uncertainties from the analytical difficulties that arise in these systems to determine the kinetic parameters by the conventional competitive method.

On account of all the above stated, we thought of interest to measure the transfer reactions of the H and Cl atoms from CH_3Cl by CF_3 radicals in order to obtain the kinetic parameters for these reaction channels and to analyze reactivity correlations as a continuation of our previous work about the abstraction reactions of Cl atoms by CF_3 radicals from chlorofluoromethanes [4].

Experimental

All experiments and procedures were performed as previously reported [4]. CF_3I and hexafluoroacetone (HFA) were used as radical sources. The photolytic reaction was initiated using a high pressure mercury lamp (Osram HBO 500W) and a Corning Pyrex glass plate 7740 was used to remove wavelengths lower than 300 nm. The mixtures were heated and irradiated in a cylindrical quartz cell, 190 cm^3 volume, placed in a horizontal electric metal-block furnace. After photolysis, the total content of the cell was collected at 77 K and analyzed by gas chromatography using a KONIK chromatograph equipped with a flame ionization detector. The products were separated on a 2.5 m column filled with Porapak T(H-Merck, 100–120 Mesh). Products identification was made by comparison of the retention times with authentic samples and confirmed by IR spectroscopy.

CF_3I, HFA, and CH_3Cl (PCR Research Chem) were trap-to-trap distilled under vacuum in order to ensure the removal of impurities. The middle fractions were retained and stored at 77 K.

The HFA (pressure range between 20 and 50 torr) was photolyzed in the presence of CH_3Cl (15 to 50 torr) in the 416 to 636 K temperature range, whereas the CF_3I (25 to 60 torr) was photolyzed with CH_3Cl (20 to 60 torr) between 445 and 558 K. The conversions, calculated from the yield of CF_3H were kept below 3% to reduce the influence of possible secondary reactions. Besides, when the pressure of CH_3Cl was 100 torr, no changes in the rate constants for the hydrogen and halogen transfer reaction were observed.

Results and Discussion

When the CF_3 radicals are generated by the photolysis of HFA the main reactions are:

$$\mathrm{CF_3COCF_3 + h\nu \longrightarrow 2CF_3 + CO} \tag{1}$$

$$\mathrm{CF_3 + CF_3 \longrightarrow C_2F_6} \tag{2}$$

If CH_3Cl is added, both reactions, the abstraction of H and Cl atoms, can take place:

$$\mathrm{CF_3 + CH_3Cl} \begin{array}{ll} \nearrow \mathrm{CF_3H + CH_2Cl} & (3) \\ \searrow \mathrm{CF_3Cl + CH_3} & (4) \end{array}$$

When the CF_3 radicals are generated by the photolysis of CF_3I the following reactions are relevant in addition to reaction (2):

$$\mathrm{CF_3I + h\nu \longrightarrow CF_3 + I} \tag{5}$$

$$\mathrm{I + I + M \longrightarrow I_2 + M} \tag{6}$$

Also, some reactions with iodine participation such as the following can be taken into account:

$$\mathrm{R + I_2 \longrightarrow RI + I} \tag{7}$$

$$\mathrm{R + I \longrightarrow RI} \tag{8}$$

$$\mathrm{R' + RI \longrightarrow R'I + R} \tag{9}$$

where R and $R' = CF_3$, CH_2Cl, and CH_3 radicals.

It is well known [5] that the participation of iodine atoms in the hydrogen abstraction reactions decreases the influence of secondary reactions on the formation of extra CF_3H. However, there would be other probable reactions that would contribute to the formation of extra CF_3H [6] such as:

$$\mathrm{I + CH_3Cl \longrightarrow IH + CH_2Cl} \tag{10}$$

$$\mathrm{CF_3 + IH \longrightarrow CF_3H + I} \tag{11}$$

In view of the photolysis conditions in which the runs are performed (conversions lower than 3% at temperatures lower than 578 K), the participation of the iodine atom has been neglected because no significant differences were found using $(CF_3)_2CO$ as a radical source. Therefore, the validity of the kinetic equations studied would still hold.

In this way and if CF_3H and CF_3Cl are formed only from reactions (3) and (4), then the resulting rate expressions are:

$$k_3/k_2^{1/2} = R_{\mathrm{CF_3H}}/R_{\mathrm{C_2F_6}}^{1/2}[\mathrm{CH_3Cl}] \tag{12}$$

$$k_4/k_2^{1/2} = R_{\mathrm{CF_3Cl}}/R_{\mathrm{C_2F_6}}^{1/2}[\mathrm{CH_3Cl}] \tag{13}$$

$$k_3/k_4 = R_{\mathrm{CF_3H}}/R_{\mathrm{CF_3Cl}} \tag{14}$$

with k = rate constant and R = rate of formation.

When HFA was used as the source of CF_3 radicals, the main products were C_2F_6, CF_3Cl, CF_3H, and CO, while with CF_3I the same halogenated products were obtained in addition to I_2. No reaction products were detected in the blank experiments when the CH_3Cl was photolyzed alone ($\lambda > 300$ nm) or when mixtures of HFA + CH_3Cl or CF_3I + CH_3Cl were left in the reaction vessel in the dark for periods similar or longer than those of the experiments. Also, no significant amounts of products, other than those already mentioned, were observed under the present experimental conditions and in the temperature range 416–578 K.

The plots of $R_{CF_3H}/R_{C_2F_6}^{1/2}$ and $R_{CF_3Cl}/R_{C_2F_6}^{1/2}$ vs. concentration of CH_3Cl (Figs. 1 and 2), at each temperature, show linear dependencies with zero intercepts. From the slopes of these plots, the experimental rate constants, $k_{exp.} = k_x/k_c^{1/2}$, were calculated. A least squares analysis of these results in the temperature range between 416 to 578 K shown in the Arrhenius plot (Fig. 1) yields the following expressions:

$$\log k_3/k_2^{1/2}[\text{cm}^{3/2}\ \text{mol}^{-1/2}\ \text{s}^{-1/2}] = (5.39 + 0.10) - (10490 + 150)/\theta$$

$$\log k_4/k_2^{1/2}[\text{cm}^{3/2}\ \text{mol}^{-1/2}\ \text{s}^{-1/2}] = (4.52 + 0.11) - (13370 + 250)/\theta$$

$$k_3/k_4 = (7.4 + 0.2)\exp[(2880 + 200)/RT]$$

where $\theta = 2.303.RT$ (kcal/mol) and the errors limits are one standard deviation. The kinetic parameters for the hydrogen atom abstraction satisfactorily agree with those obtained by Whittle [7], whereas the Ea for the abstraction reaction to the chlorine atom is lower than the estimated value of ≥17 kcal/mol [7], which seems to be high.

In Figure 3 is also observed a curvature at temperatures higher than 578 K suggesting that extra CF_3H and CF_3Cl is formed, so eqs. (7), (8), and (9) are no longer valid. A possible explanation of this curvature at high temperatures could be due that, both k_3 and k_4, increase, so that the rates of formation of the radicals CH_3 and specially CH_2Cl (which is favored over reaction (4)), increase their stationary concentrations.

The reactions of the CH_2Cl and CH_3 radicals obtained from reactions (3) and (4) could be the following:

(15) $CH_2Cl + CH_2Cl \longrightarrow CH_2ClCH_2Cl$

(16) $CH_2Cl + CF_3 \longrightarrow CH_2ClCF_3$

(17) $CH_2Cl + CH_3 \longrightarrow CH_2ClCH_3$

(18) $CF_3 + CH_3 \longrightarrow CF_3CH_3$

. . . .

(19) $CF_3 + CH_2ClCH_2Cl \longrightarrow CF_3H + CHClCH_2Cl$

(20) $CF_3 + CH_2ClCH_2Cl \longrightarrow CF_3Cl + CH_2CH_2Cl$

No attempt was made for the determination of any of the reactions products (15–20) because their retention times were either similar to those of the unreacted materials or too long to allow a good analysis. Nevertheless,

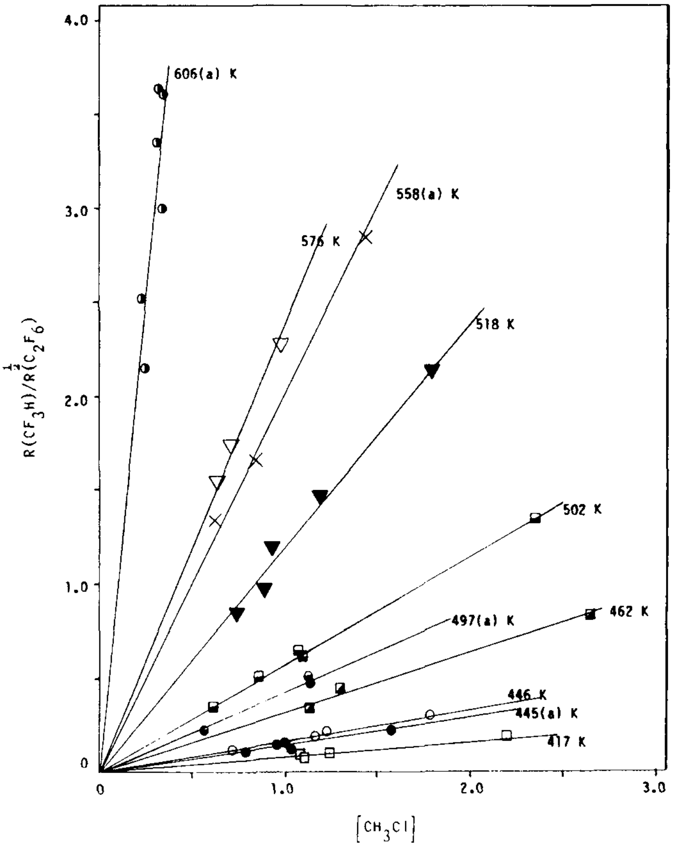

Figure 1. Plot of $R_{CF_3H}/R^{1/2}_{C_2F_6}$ (units of 10^5, mol$^{1/2}$ cm$^{3/2}$ s$^{1/2}$) vs. [CH_3Cl] (units of 10^6, mol/cm^3). (a) CF_3 radicals generated by photolysis of CF_3I.

some of these secondary processes would significantly occur at temperatures higher than 578 K and at conversions higher than 3% (as in the case of the temperatures measured at 606 and 636 K) due to the appearance of CF_3CH_3 and CH_2ClCH_2Cl among other reaction products which were not identified in the chromatographic runs. However, as in most experiments the conversion percentage was maintained below 3% (all experiments were made at temperatures lower than 578 K), the participation of these products in secondary reactions yielding extra CF_3H or CF_3Cl was completed discarded.

The kinetic parameters of transfer reactions are generally explained in terms of polar effects and enthalpy changes. As it is well known, data on reaction rates for halogen atom abstraction reactions are very scarce mainly due to the fact that the competitive transfer of the hydrogen atom in haloalkanes is the predominant reaction pathway. In the case of the halogen atom abstraction reaction with nucleophilic or electrophilic radicals, the polarizability of the halogen atom in the transition state would make the polar effects relatively more important than in the hydrogen atom abstraction reaction.

For the halogen atom abstraction by the CF_3 radical (Table I) the Ea decreases with the increase of the size of the halogen atom. Thus, a decrease

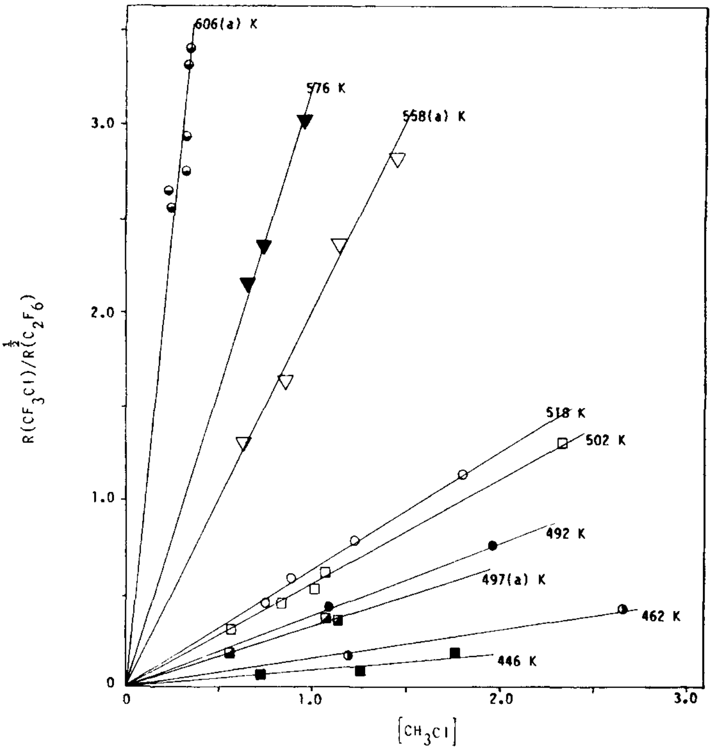

Figure 2. Plot of $R_{CF_3Cl}/R^{1/2}_{C_2F_6}$ (units of 10^7, mol$^{1/2}$ cm$^{3/2}$ s$^{1/2}$) vs. [CH_3Cl] (units of 10^6, mol/cm^3). (a) CF_3 radicals generated by photolysis of CF_3I.

of 10.1 kcal/mol in the Ea from CH_3Cl to CH_3I is accompanied by a decrease of 27.4 kcal/mol in the dissociation energy D(C—X) favoring the halogen abstraction, thus we can represent this as:

$$\overset{\delta-\ \delta+}{F_3C} \;\text{——}\; \overset{\delta-}{X} \;\text{——}\; \overset{\delta+}{CH_3}$$

The same considerations are observed for the halogen transfer from chlorofluoromethanes, CF_3X (X = Cl, Br, I), by the CH_3 radical, Table I, taking into account the data obtained by Sidebottom [8], where Ea and D(C—X) decrease with the increase of the halogen size in going from CF_3Cl to CF_3I. The electronegativity of the halogen atom decreases with the size of the atom, and it will be more polarizable by the inductive effect of CF_3 and the halogen (X) becomes relatively more positive decreasing its electronic density and favoring the abstraction reactions by the nucleophilic radical CH_3.

In the hydrogen atom transfer of the halomethanes, CH_3X (X = H, Cl, Br, I) by the CF_3 radical, Table I, the Ea decreases with the increase of the halogen size, whereas, the D(C—H) slightly increases. This could be due to a reduced repulsion between the CH_2X—H molecule and the CF_3 radical as a result of an increase of the electronic density on the hydrogen atom with the increase of the halogen size.

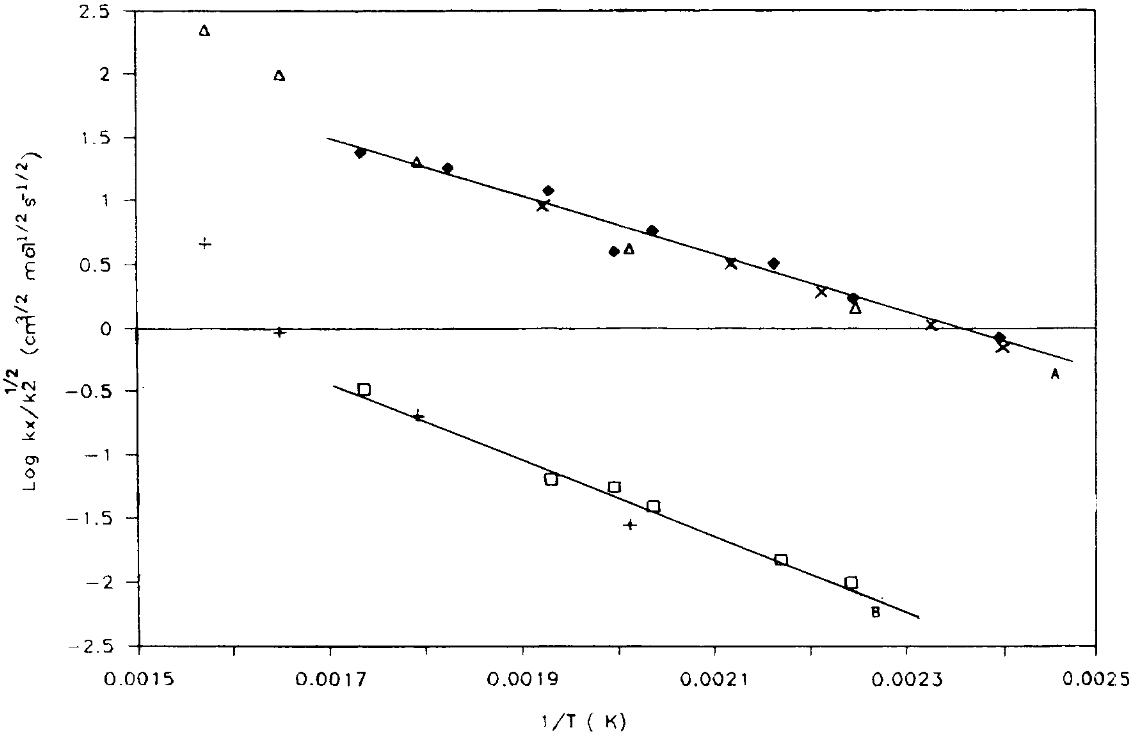

Figure 3. Arrhenius plot for the reaction CH_3Cl + CF_3 Curve A: Hydrogen abstraction reaction: △-with CF_3I; ◆-with HFA; and ×-Ref. 1. Curve B: Chlorine abstraction reaction: +-with CF_3I and □-with HFA.

A different situation is observed for the hydrogen atom abstraction from halomethanes by CH_3 radical (Table I). In this serie there are some uncertain values, one is the corresponding to CH_3Br (Ea(H) = 10.1 kcal/mol), obtained by Steacie et al. [9], because he had problems with the experiments as there was always an extras CH_4 [10]. The corresponding value to CH_3I reported by Benson et al. (Ea(H) = 13.7 kcal/mol) is an estimation only, on basis of the values obtained by Steacie et al. [9]; then it was recalculated by Kerr and Personage (Ea(H) = 12.3 kcal/mol) [11]. The Ea apparently increases with the increase of the halogen size and the D(C—H). This variation could be due to the increase of the polar repulsive effect with the CH_3 radical because of an increase of the electronic density on the hydrogen atom, and also an increase of the steric effect in the halomethane [12], for the increase of the halogen size. So in this way the reactivity for the nucleophilic radical CH_3 decrease along this serie.

Also, it should be noted for the hydrogen atom abstraction reactions that the Ea is always lower with the electrophilic radical CF_3 than with the nucleophilic radical CH_3. This can be due, as suggested by Tedder [12,13] to the fact that in the transition state the repulsion between the molecule formed and the new radical produced is more important than the repulsion effects between the attacking radical and the substrate.

Several methods [14] have attempted to develop relationships or correlations to predict the Ea of transfer reactions in general and do not applicable

TABLE I. Activation energies for the hydrogen and chlorine atom abstraction reactions from halomethanes by CF_3 and CH_3 radicals.

	CF_3[d]				CH_3[d]					
	Ea(H)	Ref.	Ea(X)	Ref.	Ea(H)	Ref.	Ea(X)	Ref.	D(C — H)[a,d]	D(C — X)[a,d]
CH_4	11.2	[1,16]	—		14.6	[17]	—		105.1	—
	12.5	[3]								
CH_3F	11.2	[2]	—		8.7	[9]	—		100.0	—
					11.4	[11,18a]				
CH_3Br	10.4	[1]	8.3	[1]	10.1	[9]	—		102.0	70.9
CH_3I	7.5	[1]	3.3	[1]	13.7	[15]	—		103.0	57.2
					12.3	[11]				
CH_3Cl	10.6	[1]	13.4[c]		9.4	[9]	—		101.0	84.6
	10.5[c]				11.6	[10]				
CH_2Cl_2	7.6	[7]	11.8	[7]	7.2	[9]	—		98.0	80.1
	6.3	[16]	12.0	[7]	9.0	[10]				
$CHCl_3$	6.6	[7]	11.0	[19]	5.8	[9]	—		96.0	77.6
					6.7	[10]				
CCl_4	—		10.4	[7,20]	—		9.9	[23]	—	70.0
							10.1	[10]		
$CFCl_3$	—		14.9	[4]	—		10.7	[8]	—	74
CF_2Cl_2	—		16.9	[4]	—		11.3	[8]	—	76
CF_3Cl	—		—		—		11.8	[8]	—	85.9[b]
CF_3H	—		—		10.4	[18b]	—		106.7	—
					12.0	[11]				
CF_3Br	—		—		—		9.3	[8]	—	70.6
CF_3I	—		—		—		4.3	[8]	—	55.0

[a] Ref. [21].
[b] Ref. [22].
[c] This work.
[d] Ea and D(C — X) in kcal/mol.

only to related series. The difficulty of all these methods is in the scarcity of complementary data (such as electronic affinities, vibrational frequencies, polarizabilities, etc.) necessary to solve the proposed equations. The Evans-Polanyi relation is applicable quite well in homologous series of strongly related compounds it is known that there are many exceptions to this equation, so its generalization is difficult. For the halogen and hydrogen abstraction reactions by CF_3 and CH_3 radicals, it can be observed in Table I, for the halomethanes and for chloromethanes and chlorofluoromethanes, that in general the Ea(H, Cl) increase with the increase of D(C—Cl) or D(C—H). Therefore, these experimental results suggest that the Evans-Polanyi equation could be applied reasonably well. In Figure 4 are plotted the Ea vs. the halogen or hydrogen atom transfer reaction by CH_3 and CF_3 radicals. The differences in the different experimental values of Ea and D(C — X) and their uncertainties must also be considered, since it is difficult to evaluate correctly if the Evans-Polanyi equation is applicable in some series. Thus, the chlorine atom abstraction in the reaction $CH_3 + CF_3Cl$ (Ea(Cl) = 11.8 kcal/mol) [8], which is common to the series (Fig. 4), (F)$CH_3 + CF_nCl_{4-n}$ and (D)$CH_3 + CF_3X$ (X = Cl, Br, and I) seems to have a rather low Ea value. For this reason it is not possible to state that the series (D) has a lineal behavior of the E.P. equation whereas in the series (F) it is possible to observe a lineal behavior of the E.P. equation.

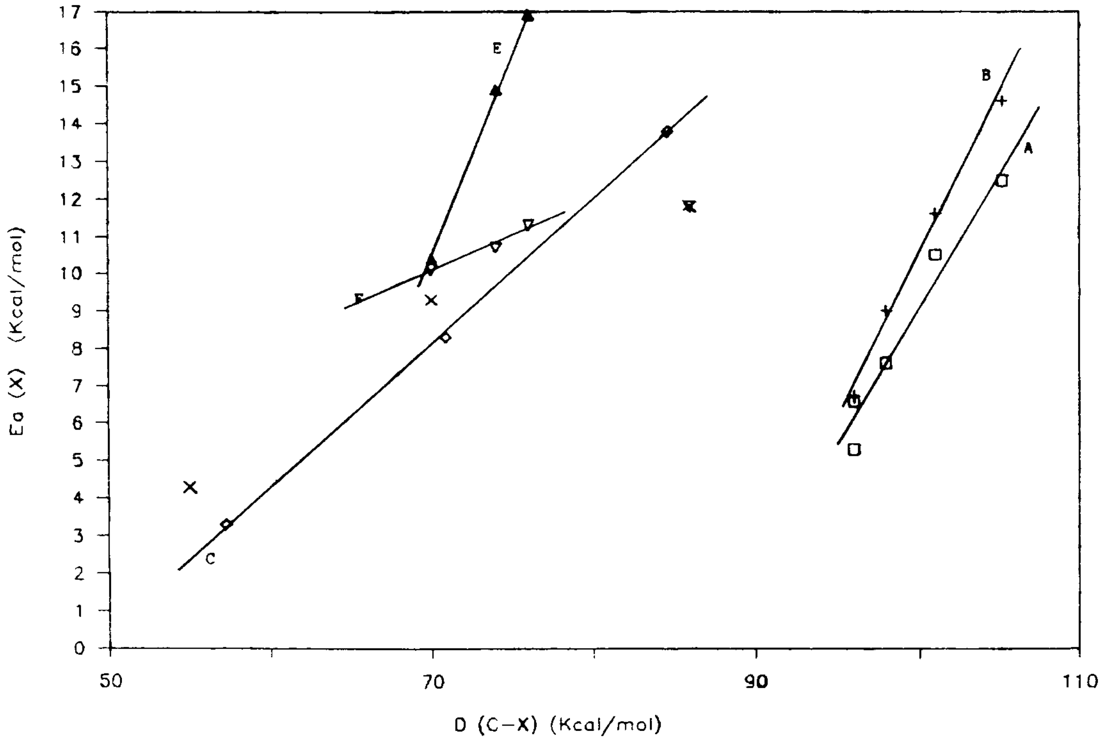

Figure 4. Evans-Polanyi plot for the hydrogen and chlorine abstraction reactions by CF_3 and CH_3 radicals (1). A: □-CF_3 + $C\underline{H}_nCl_{4-n}$; B: +-CH_3 + $C\underline{H}_nCl_{4-n}$; C: ◇-CF_3 + $CH_3\underline{X}$; D: ×-CH_3 + $CF_3\underline{X}$; E: ▲-CF_3 + $CF_n\underline{C}l_{4-n}$; and F: ▽-CH_3 + $CF_n\underline{C}l_{4-n}$. (1) Where the abstracted atom is underlined.

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