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Relative Rate Constants for the Reactions of CF_3OF with Olefins in Solution

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The addition reactions of CF_3OF to chloro fluoro olefins have been studied *in solution at low temperature* (−78, −105 °C), and their relative rate constants have been determined using the kinetic approach of competition reactions. The reactivity and regio- and stereoselectivity are consistent with a free radical chain-propagating reaction in which the alkenes are attacked by the $CF_3O^\bullet$ radical generated by homolitic cleavage of the O−F bond in the CF_3OF molecule.

Introduction

The reactions of hypofluorites with alkenes have been treated in several publications[1-5] and patents.[6,7] These works, however, were generally executed for preparative purposes due to the fact that fluoroalkenyl and fluoroalkyl ethers have high synthetic value as monomers for polymerizations as well as for their useful physical properties.

The reactivity of CF_3OF with some alkenes has been studied by Johri and DesMarteau.[8] The reaction products found were most readily accounted for on the basis of a free-radical reaction mechanism, which would account for the observed reactivity, regioselectivity, and low stereoselectivity.

The kinetic studies of the gas-phase thermal addition of CF_3OF to the double bond of the hexafluoropropene,[9] perfluorobut-2-ene,[10] 1,1-dichlorodifluoroethene,[11] and trichloroethene[12] showed that these reactions have the following basic steps in common: the generation of radical $CF_3O^\bullet$ in the bimolecular process between CF_3OF and alkene E, the formation of a radical $CF_3O(E)^\bullet$ by addition of $CF_3O^\bullet$ to the alkene, and the abstraction of the fluorine atom from CF_3OF by the radical $CF_3O(E)\bullet$ accompanied by a simultaneous generation of another radical $CF_3O^\bullet$.

To date, no kinetic data are available regarding the addition of CF_3OF to olefins in solution and at low temperatures.

Results and Discussion

According to the free radical mechanism postulated in the previously reported kinetic studies,[9-12] the addition of CF_3OF is initiated with the generation of radical $CF_3O^\bullet$ in the bimolecular process between CF_3OF and alkene E (eq 1):

$$CF_3OF + E \xrightarrow{k_1} F(E)^\bullet + CF_3O^\bullet \tag{1}$$

The propagation steps consist of the formation of an alkyl radical intermediate by addition of $CF_3O^\bullet$ to the alkene (eq 2) and the abstraction of the fluorine atom from CF_3OF by the adduct radical generated in eq 2 accompained by a simultaneous generation of another radical $CF_3O^\bullet$ (eq 3):

$$CF_3O^\bullet + E \xrightarrow{k_2} CF_3O(E)^\bullet \tag{2}$$

$$CF_3O(E)^\bullet + CF_3OF \xrightarrow{k_3} CF_3O(E)F + CF_3O^\bullet \tag{3}$$

The chain-terminating step is a recombination of radicals (eq 4):

$$R^\bullet + R^\bullet \xrightarrow{k_4} R{-}R \tag{4}$$

Considering the simultaneous reaction of two different olefins, A and B, with the radical $CF_3O^\bullet$ mostly generated in step 3 of the addition process of CF_3OF to A and B, it will obviously result in more rapid consumption of the more reactive of the two. The rate constants k_{3A} and k_{3B} can be considered to be similar and independent of radical stucture. This supposition is supported by the similar values of the rate constants for the abstraction of fluorine atom from CF_3OF by $CF_3^\bullet$,[13] $C_2H_5^\bullet$,[14] and $CF_3O(CF_2CCl_2)^\bullet$[11] in the gas phase. The O−F bond energy in CF_3OF is quite weak, about 45 kcal/mol,[15] so that the abstraction of F by an alkyl free radical is quite exothermic with low activation energy. It has been demonstrated[12,14] that the fluorine abstraction reaction is both fast and clean, providing the assurance that CF_3OF has great potential as a free-radical scavenger, even in reaction systems with other rapid reaction pathways available to the radicals.

The lack of formation of $CF_3O(E)OCF_3$ excludes the possibility of an aspecific $CF_3O^\bullet$ or $F^\bullet$ radical transfer in the propagation step 3. The lack of formation of F(E)F in all the experimental runs indicates that k_3 is consider-

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ably higher than k_1 independent of the nature of the reacting radical and more probably close to diffusion control.

The lack of CF_3OOCF_3, which is easily formed by recombination of radical $CF_3O^•$,[16] shows that the addition of $CF_3O^•$ to the double bond is considerably faster than any other reaction of $CF_3O^•$.[12,15,17-20] Recently we have also proved by EPR studies[5] that only radicals deriving from reaction 2 are detectable at steady-state concentration during the reaction of CF_3OF with the dimers of hexafluoropropene in the liquid phase.

On the basis of these considerations we can reasonably conclude that a direct measure of the relative reactivity of A with respect to B is the ratio of reaction rate constants k_{2A}/k_{2B}. The presence of the simple addition products deriving from reactions 2 and 3 as the unique reaction products led to a simplification of the analysis and treatment of the experimental data. Determination of the reactivity ratio is accomplished by measuring the amount of A and B reacted (or $CF_3O(A)F$ and $CF_3O(B)F$ formed) in a competition reaction in which known amounts of the two olefins are present at the beginning of the reaction. If the amounts of A and B at the beginning of the reaction are the same, the steady-state treatment leads, for small conversions, to the simple expression (5)

$$\frac{[CF_3O(B)F]_f}{[CF_3O(A)F]_f} = \frac{k_{2B}}{k_{2A}} \tag{5}$$

where the subscript f refer to the amounts of the two products present at the end of the reaction.

If the study is concerned with the rates of addition to the ends of an unsymmetric olefin, $C_X{=}C_Y$, the product ratio is the orientation ratio, symbolized Or (eq 6) where

$$Or = \frac{[CF_3O(C_X-C_Y)F]_f}{[CF_3O(C_Y-C_X)F]_f} = \frac{k_{2X}}{k_{2Y}} \tag{6}$$

$CF_3O(C_X-C_Y)F$ and $CF_3O(C_Y-C_X)F$ represent the two regioisomers formed and k_{2X} and k_{2Y} the addition rate constants to the two ends of the olefin.

In our experiments the overall conversion of the reacting olefins was kept around 8%. In order to avoid telomerization processes, the concentration of olefins in solution ($CFCl_3$ as the solvent) was kept very low. The reactions were carried out at two different temperatures (−78 and −105 °C) because of the different boiling points of the olefins. Nevertheless, no differences in the ratios have been observed when the reaction was carried out at the two different temperatures for the same olefinic mixture. The relative addition rates (relative to 1,2-dichloro-1,2 difluoroethylene, ClFC=CFCl) together with the orientation ratios are reported in Table 1.

The radical chains seem to be quite long since the analysis of the reaction products showed in all experiments only traces (<2%) of the possible termination products.

The electrophilic character of the $CF_3O^•$ radical is pointed out, taking into consideration the relative rate constants and the orientation ratio values for the addition to $CH_2{=}CHF$, $CH_2{=}CF_2$, and $CHF{=}CF_2$. The trend of these values is in agreement with the data previously reported by Tedder and co-workers for the strongly electrophilic $CF_3^•$ radical.[21] In fact, for both radicals $CF_3O^•$ and $CF_3^•$ the overall addition rate decreases by decreasing the electron density of the olefin through the progressive increasing of the number of fluorine atoms on the double bond.

Table 1. Relative Rate Constants, Orientation Ratios, and Reaction Temperatures for the Addition of CF_3OF to Alkenes in Solution

compd (α, β)	$K/K_{dde}{}^a$	$2K_\alpha/K_{dde}{}^a$	$2K_\beta/K_{dde}{}^a$	Or = K_α/K_β	T (°C)
$H_2C{=}CHF$	1.9	3.1	0.7	4.4	−105
$H_2C{=}CF_2$	1.7	3.1	0.3	10.3	−105
$FHC{=}CF_2$	1.3	1.8	0.8	2.3	−105
$ClHC{=}CHCl_{(cis)}$	1.5	1.5	1.5	1.0	−78
$ClHC{=}CHCl_{(trans)}$	1.2	1.2	1.2	1.0	−78
$ClHC{=}CCl_2$	1.15	2.2	0.2	11.0	−78
$ClFC{=}CFCl$	1.0	1.0	1.0	1.0	−78
$F_2C{=}CFCl$	1.03	1.4	0.3	4.7	−78
$Cl_2C{=}CCl_2$	0.23	0.23	0.23	1.0	−78

[a] $K_{dde} = K_{1,2\text{-dichloro-}1,2\text{-difluoroethylene}}$.

If we compare the relative addition rates of $CF_3O^•$ to *cis*- and *trans*-1,2-dichloroethylene it is also evident how the polarity of the alkene may play an important role in this type of reactions. While for 1,2-dichloro-1,2-difluoroethylene no differences have been observed in the reactivity of the stereoisomers, for 1,2-dichloroethylene the cis isomer is more reactive than the trans isomer. In this case for both 1,2-dichloroethylene isomers the steric hindrance, which inhibits the CF_3O radical approaching the reaction site, and the intermediate adduct radical, deriving from eq 2, are the same, but the more polar cis isomer is more reactive.

It was not possible to carry out the experiments with $CH_2{=}CH_2$ and $CF_2{=}CF_2$ because of the high vapour pressure of the two olefins even at low temperature.

Experimental Section

Materials. Alkenes were obtained from commercial source, and distilled prior to use. CF_3OF was prepared according to the literature method.[13]

Caution!! : appropriate precautions should be taken when handling hypofluorites. Under certain conditions, these compounds are capable of an energetic explosive decomposition.

General Methods. Volatile compounds were handled in a Pyrex glass or stainless steel vacuum system equipped with Druck PDCR 110/W differential pressure gauge (0−1000 mbar). Amounts of gaseous reactants and products were measured assuming ideal gas behavior. ^{19}F and ^1H NMR spectra were recorded on Varian 200 MHz and Varian 300 MHz instruments, using $CFCl_3$ as internal reference and $CDCl_3$ as solvent.

General Procedure for Competition Experiments. The apparatus used to carry out the experiments is shown in Figure 1.

The solvent $CFCl_3$ (50 mmol), ClFC=CFCl (3 mmol), and the olefin for comparison (3 mmol) were condensed from the vacuum line into a 25 mL glass reactor **4** at −196 °C. The system was degassed through several freeze-thaw cycles under vacuum. The temperature of the reactor was held constant by means of the thermostatic bath (reaction temperatures are reported in Table 1).

The reaction mixture was kept under magnetic stirring and CF_3OF (0.5 mmol) slowly added in a semicontinuous way by opening valve **5**. During the addition, the CF_3OF pressure (15 mbar) over the solution was kept constant by means of the

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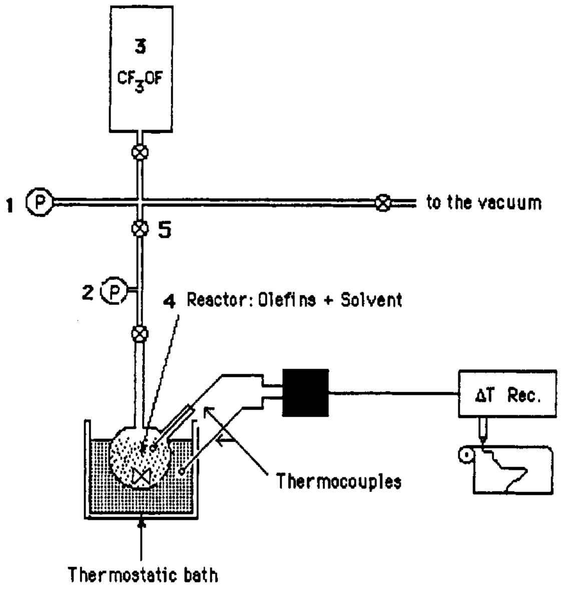

1,2 pressure gauges ; 3 CF_3OF reservoir ; 4 reactor ; 5 regulator valve

Figure 1.

pressure gauge **2**, while the temperature inside the reactor was been controlled by a thermocouple.

Reaction products were identified by ^1H- and ^{19}F-NMR. The samples for the NMR analysis were prepared using two different methods: (1) When the starting compounds and the products were high boiling the samples were prepared by transferring a portion of the liquid phase in the NMR tube, (2) When the starting compounds or the products were low boiling the whole reaction mixture was transferred, by vacuum line, into a 2 L vessel, being careful that no high boiling point or polimeric material remained in the reactor. The mixture was then allowed to expand inside the vessel, and when the mixture was totally in the gas phase a portion of this homogenized phase was transferred to the vacuum line and totally condensed into an air tight NMR tube.

NMR data (references). Reaction with $CH_2{=}CHF$: ($CF_3OCH_2CHF_2$);[8] ($CF_3OCHFCH_2F$)[8].

Reaction with $CH_2{=}CF_2$: ($CF_3OCH_2CF_3$);[8] ($CF_3OCF_2CH_2F$)[8].

Reaction with $CHF{=}CF2$: ($CF_3OCHFCF_3$);[22] ($CF_3OCF_2CHF_2$)[22].

Reaction with $ClHC{=}CHCl$: (*erythro* $CF_3OCHClCHClF$);[8] (*threo* $CF_3OCHClCHClF$).[8]

Reaction with $ClHC{=}CCl_2$: ($CF_3OCHClCCl_2F$);[23] (CF_3OCCl_2CHClF).[23]

Reaction with $ClFC{=}CFCl$: ($CF_3OCClFCClF_2$).[24]

Reaction with $CF_2{=}CFCl$: ($CF_3OCF_2CClF_2$);[25] ($CF_3OCClFCF_3$).[25]

Reaction with $Cl_2C{=}CCl_2$: ($CF_3OCCl_2CCl_2F$).[26]

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