### RADICAL REACTIONS OF ETHYL ORTHOFORMATE

# WITH 3,3,3-TRIFLUOROPROPENE

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The radical addition of ethyl orthoformate (EOF) to 1-hexene proceeds with the formation of carbonate adduct (Ia) according to a scheme involving rearrangement of intermediate radicals (A) with subsequent fragmentation of the rearranged radicals (B) [1] (Scheme 1).

Scheme 1  
HC(OEt)<sub>8</sub> 
$$\xrightarrow{k_{CH}} \dot{C}(OEt)_3 \rightarrow (EtO)_2CO$$
  
 $\xrightarrow{k_{CH_2}} HC(OEt)_2O\dot{C}HMe \xrightarrow{k_f} HCOOEt$   
HC(OEt)\_2O\dot{C}HMe + RCH=CH<sub>2</sub>  $\xrightarrow{k_{Pf}} HC(OEt)_2OCH(Me)CH_2\dot{C}HR$   
(Aa, b)  
A  $\xrightarrow{1,5-H} \dot{C}(OEt)_2OCH(Me)CH_2CH_2R$   
(B)  
A + HC(OEt)\_3  $\rightarrow \times \rightarrow HC(OEt)_2OCH(Me)CH_2CH_2R$   
(IIa, b)  
B  $\xrightarrow{-Et} EtOC(O)OCH(Me)CH_2CH_2R$   
(I a, b)  
R=C\_4H\_9 (a), CF\_3 (b).

For the reaction with 1-hexene,  $k^{a}_{CH}/k^{a}_{CH_{2}} = 1.4$  and  $k_{f}^{a}/k_{pr}^{a} = 0.8$  mole/liter.

The use of 3,3,3-trifluoropropene (TFP) as the monomer in the reaction with EOF holds interest both relative to elucidation of the nature of this reaction and to the study of the effect of the polarity of the substituent at the double bond on the relative kinetics of the reaction.

In the case of TFP, an electron-withdrawing  $CF_3$  substituent is located on the double bond such that radical (Ab) (see Scheme 1) has marked electrophilicity (radical Aa is relatively nucleophilic); the  $CF_3$  group may have a significant effect on the reactivity of the double bond in the addition step.

The reaction of EOF with TFP was carried out in the presence of tert-butyl peroxide (TBP) at 140°C. The major reaction product containing a  $CF_3$  group is carbonate adduct (Ib). In addition, gas-liquid chromatography with authentic samples revealed diethyl carbonate and ethyl formate formed as a result of the homolytic decomposition of EOF (see Scheme 1). Preparative gas-liquid chromatography gave three products which were eluted after adduct (Ib). <sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C NMR spectroscopy showed that these products contained several TFP molecules and EOF fragments (Et and MeCHO) but are not carbonate telomers of asymmetric ortho esters such as (IIb). The formation of ortho esters such as (IIb) might be expected if radical A (R = CF<sub>3</sub>) participates in the chain transfer step with hydrogen atom abstraction in addition to rearrangement. The <sup>13</sup>C NMR spectrum lacks signals for carbon atoms of OC(0)0 or C(OR)<sub>3</sub> functional groups.

The formation of carbonate (Ib) in the case of TFP is described by the above scheme. The lack of compounds such as (IIb) indicates that radical A largely isomerizes with 1,5 hydrogen transfer.

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Charge, mmoles	Conversion,%		EOF an	av	Reaction product distri- bution, mole %			k <sup>b</sup> <sub>CH</sub> /	kb/kb
TFP EOF	TFP	EOF	TFP/ me.	[TFP	HCO₂Et	(EtO)2CO	(Ib)	<sup>k</sup> <sup>D</sup> CH <sub>2</sub>	"f "pr
$\begin{array}{ccccccc} 6,7 & 58,3 \\ 13,0 & 56,8 \\ 8,4 & 37,0 \\ 8,7 & 31,7 \\ 17,0 & 54,0 \\ 15,5 & 34,3 \\ 19,8 & 37,4 \\ 40,8 & 56,7 \\ 46,3 & 59,2 \\ 38,6 & 28,3 \end{array}$	2 6 10 8 8 11 13 11 16 15	$ \begin{array}{c c} 14\\17\\17\\14\\19\\22\\19\\18\\20\\27\\15\end{array} $	$\begin{array}{c} 0,12\\ 0,24\\ 0,24\\ 0,29\\ 0,33\\ 0,37\\ 0,47\\ 0,54\\ 0,75\\ 0,83\\ 1,36\\ \end{array}$	$\left \begin{array}{c} 0,43\\ 0,61\\ 0,76\\ 0,88\\ 0,78\\ 0,89\\ 1,38\\ 1,74\\ 1,82\\ 1,93\\ 3,32\\ \end{array}\right.$	$ \begin{array}{c} 35.9 \\ 37,1 \\ 30,2 \\ 34,4 \\ 36.0 \\ 36.9 \\ 30,8 \\ 26,5 \\ 26,9 \\ 25,7 \\ 16,8 \end{array} $	$58,5 \\ 55,6 \\ 61,7 \\ 55,1 \\ 54,7 \\ 54,5 \\ 55,6 \\ 57,2 \\ 56,4 \\ 58,6 \\ 63,5 \\ 8,5 \\ 63,5 \\ 8,6 \\ 63,5 \\ 8,6 \\ 63,5 \\ 8,6 \\ 63,5 \\ 8,6 \\ 63,5 \\ 8,6 \\ 63,5 \\ 8,6 \\ 63,5 \\ 8,6 \\ 8,5 \\ 8,6 \\ 8,5 \\ 8,6 \\ 8,5 \\ 8,6 \\ 8,5 \\ 8,6 \\ 8,5 \\ 8,6 \\ 8,5 \\ 8,6 \\ 8,5 \\ 8,6 \\ 8,5 \\ 8,6 \\ 8,5 \\ 8,6 \\ 8,5 \\ 8,6 \\ 8,5 $	5,6 7,3 8,1 10,5 9,3 9,6 13,6 16,3 16,7 15,7 19,7	1,4 1,3 1,6 1,3 1,2 1,3 1,3 1,4 1,3 1,4 1,7	2,8 3,1 2,8 2,9 3,0 3,3 3,4 2,8 2,9 3,2 2,8 2,2 8

TABLE 1. Addition of Ethyl Orthoformate (EOF) to Trifluoropropene (TFP) in the Presence of TBP at 140°C over 2 h



Fig. 1. Dependence of the concentration of adduct (I) on the monomer/EOF ratio for 1-hexene (a) and 3,3,3-trifluoropropene (b).

Carrying out the reaction in a broad range of TFP/EOF ratios and rigorously controlled conditions (Table 1) permitted us to determine the relativeconstants  $k_{CH}^{b}/k_{CH_{2}}^{b}$  and  $k_{f}^{b}/k_{pr}^{b}$ .

The results for the homolytic decomposition of EOF in the presence of TBP [2] indicate that  $C(OEt)_3$  and  $HC(OEt)_2OCHMe$  radicals largely react in accord with the scheme. Hence, for the reaction of EOF with TFP, we have

 $k_{\text{CH}}^{\text{b}}/k_{\text{CH}_2}^{\text{b}} = [(\text{EtO})_2\text{CO}]/[\text{HCO}_2\text{Et}] + [(\text{Ib})]$  $k_{\text{f}}^{\text{b}}/k_{\text{pr}}^{\text{b}} = [\text{HCO}_2\text{Et}]_1[\text{TFP}]/[(\text{Ib})]$ 

The mean values of the relative constants for the reaction of EOF with TFP are given in Table 1. The value  $k_{CH}^{b}/k_{CH_2}^{b} = 1.4$  is close to that obtained in the reaction of EOF with 1-hexene [1] and in the absence of monomer [3]. This finding indicates that the reactivity of EOF relative to the CH and CH<sub>2</sub> groups is only slightly sensitive to the polarity of the attacking radicals participating in chain transfer on EOF.

The values found  $k_f^{b}/k_{pr}^{b} = 2.9$  moles/liter are significantly greater than the analogous value obtained for 1-hexene  $(k_f^{a}/k_{pr}^{a} = 0.8 \text{ mole/liter})$ . In both cases, the same radical,  $HC(OEt)_2OCHMe$  undergoes fragmentation and, hence,  $k_f^{a} = k_f^{b}$ . As a result, we find  $k_{pr}^{a}/k_{pr}^{b} = 2.9/0.8 = 3.6$ , i.e., the rate constant for the addition of  $HC(OEt)_2OCHMe$  to 1-hexene is 3.6 times greater than that for trifluoropropene. Apparently, the presence of the electron-with-drawing CF<sub>3</sub> group markedly reduces the reactivity of the double bond in TFP relative to 1-hexene. Hence, it is interesting to note that under similar reaction conditions, the concentration of the adduct in the reaction mixture in the case of (Ia) (R = C<sub>4</sub>H<sub>9</sub>) is only 15-20% higher than for (Ib) (R = CH<sub>3</sub>) (Fig. 1). We may assume that radical (Ab) (R = CF<sub>3</sub>) rearranges to a greater extent due to a favorable combination of polar factors relative to (Aa) (R = C<sub>4</sub>H<sub>9</sub>), in which the nucleophilic radical site attacks the nucleophilic EOF telogen in the intramolecular chain transfer step.

#### EXPERIMENTAL

The <sup>13</sup>C NMR spectra were taken on a Bruker WP-200 spectrometer at 22.635 MHz with CCl<sub>4</sub> as the internal standard; the chemical shifts were relative to TMS. The gas-liquid chroma-tographic analysis was carried out on an LKhM-8MD chromatograph using a  $3 \times 3000$  mm column packed with 15% SKTFT-50 on Chromaton N-AW. Preparative gas-liquid chromatography was carried out on a PAKhV chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 1200$  mm column packed with 15% SE-30 on Chromatograph using a  $9 \times 120$ 

Addition of Ethyl Orthoformate to 3,3,3-Trifluoropropene. a) Preparative runs were carried out in 20-ml stainless steel autoclaves. Air was eliminated from the reagents in the autoclave. Then, the reagents were heated for 2 h at 140°C with continuous rotation of the autoclave. The charge consisted of 8.5 g ethyl orthoformate, 0.4 g TBP, and 0.6 g trifluoropropene. The reaction mixture from six runs were combined and the starting reagents were distilled off. The residue was fractionated. Adduct (Ib) was isolated from the fraction distilling at 50-90°C (50 mm) (8 g) using preparative gas-liquid chromatography, np<sup>20</sup> 1.3671, d<sup>20</sup><sub>4</sub> 1.1902. Found: C 44.42; H 5.86%. Calculated for C  $_{8}H_{13}O_{3}F_{3}$ : C 44.91; H 6.10%. PMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm from TMS): 1.17 t (CH<sub>3</sub>CH<sub>2</sub>), 4.21 q (CH<sub>2</sub>O), 4.73-4.91 m (CH), 1.20 d (CH<sub>3</sub>CH), 1.71-1.88 m, 2.02-2.31 m (CH<sub>2</sub>). <sup>13</sup>C NMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm from TMS): 154.2 (OC(O)), 72.3 (CHO), 63.0 (CH<sub>2</sub>O), 126.7 q (CF<sub>3</sub>), 19.4 (CH<sub>3</sub>CH), 13.9 (CH<sub>3</sub>), 28.1, 29.8 (CH<sub>2</sub>). <sup>19</sup>F NMR spectrum: 8.43 t.

b) The analytical experiments were carried analogously in 10-ml autoclaves. The conditions and results of the gas-liquid chromatographic analysis are given in Table 1. The internal standard was the dimethyl ester of adipic acid. The reaction mixture contained 2-7% oligomers (depending on the TFP/EOF ratio).

# CONCLUSIONS

The radical reaction of 3,3,3-trifluoropropene with ethyl orthoformate largely leads to the formation of the adduct,  $EtOC(0)OCH(Me)CH_2CH_2CF_3$  due to rearrangement of the intermediate radicals with 1,5 hydrogen atom migration.

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### REACTION OF FLUORONITROACETIC ACID WITH HYDROCHLORIC ACID

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Heating difluoro- and fluorochloronitroacetic acids with hydrochloric acid leads to their decarboxylation and formation of difluorochloro- [1] and fluorodichloronitrosomethanes [2]. Halonitrocarboxylic acids containing a hydrogen at the  $\alpha$ -carbon do not undergo this reaction.

In the present work, we showed that the reaction of fluoronitroacetic acid with hydrochloric acid gives previously unreported fluorochloronitrosomethane (II).



The reaction was carried out at 70°C with distillation of product (II) into a trap cooled to -60°C. Nitrosomethane (II) is stable in inert solvents and in the gas phase and may be stored for a long period in ether without marked change. This compound dimerizes below -30°C

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