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Radical chain addition of iodo-perfluoroalkanes to ethylenic or acetylenic substrates. Comparison of rates of iodine atom transfer from C_4F_9I to σ-vinyl and σ-alkyl α-F alkyl radicals

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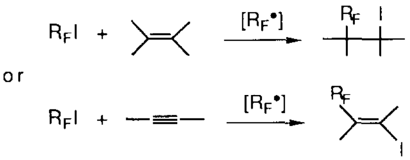
Abstract

Under electrochemical activation, the addition of C_4F_9I to ethylenic or acetylenic substrates proceeds via a radical chain involving addition of $C_4F_9^{\cdot}$ radicals to the multiple bond followed by iodine-atom transfer from C_4F_9I to the alkyl or vinyl α-F alkyl radical thus formed. Combined use of voltammetric and electrolytic techniques allows quantitative comparison of the reactivities of alkyl and vinyl radicals versus iodine-atom transfer from C_4F_9I.

Introduction

Controlled electrochemical reduction of iodo-perfluoroalkanes, R_FI, results in a source of perfluoroalkyl radicals [1, 2]. In the absence of reactive substrates, these may either combine to afford quantitative yields of dimer R_F–R_F, or may be further reduced at more negative potentials to yield the corresponding R_FH after protonation of the ensuing anion. In the presence of alkenes or alkynes, these radicals initiate a fast radical chain resulting in the overall addition of R_FI to the multiple bond (Scheme 1).



Scheme 1.

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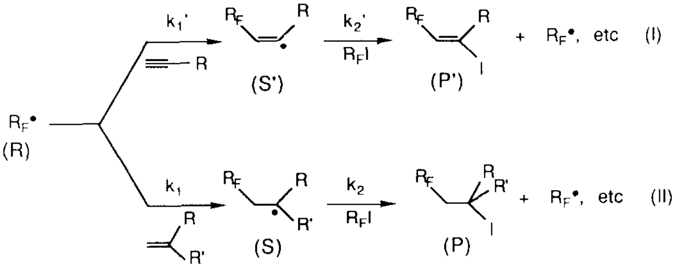
Electrochemical initiation: $R_FI + e^- \longrightarrow R_F^{\bullet} + I^-$
Propagation:



Scheme 2.

The mechanism of this radical-catalyzed addition has been shown [2a] to proceed via a sequence of two steps (see Scheme 2): (i) addition of $R_F^{\bullet}$ to the unsaturation, followed by (ii) iodine-atom abstraction from R_FI by the σ-carbon radical formed in step (i). This mechanism is akin to those shown to be involved in other radical-catalyzed syntheses [3–11], which have been reviewed recently by Curran [11c].

The termination steps of the chain reactions in Scheme 2 consist mainly of the dimerization (or possibly reduction) of the $R_F^{\bullet}$ radicals, as well as reduction of the σ-carbon radical S or S′ (Scheme 2). We have shown previously [2a] that cyclic voltammetric analysis of the electrochemical inducement of the chain reactions depicted in Scheme 2 allows the evaluation of the value of the ratio k_2/k_1 (or k'_2/k_1) of the rate constants of the two propagation steps of the chains. We wish to report here the result of such an analysis applied to a more extended series of ethylenic and acetylenic substrates.

Experimental

Cyclic voltammetry

Set-up and equipment

All experiments were performed in a three-electrode air-tight cell. The working electrode was a vitreous carbon disk (3-mm diameter) embedded in Teflon (Tacussel). The reference electrode consisted in an SCE (Tacussel) separated from the solution by a salt bridge containing a solution (DMF/TBAF, 0.05 M) identical to that in the cell. The potentiostat was computer-integrated (ESII, Sirius) and was designed and constructed by ESII in collaboration with the authors.

Procedures

DMF (16 ml) was introduced in the cell and 0.26 g NBu_4BF_4 (0.05 M) was added. An aliquot (3 ml) of this solution was withdrawn from the cell and introduced into the reference bridge. The solution was then degassed by nitrogen bubbling (10 min), the C_4F_9I and substrate introduced into the cell and kept under a continuous stream of nitrogen. Experiments were then conducted as previously described [2a].

Preparative electrolysis

Set-up and equipment

Two cells were used (cf. Table 2). Cell I consisted of two horizontal compartments separated by a glass fritt (P4 porosity); both compartments contained electrodes made from carbon cloth (Carbone Lorraine) of 28 cm^2 geometric surface area. The cathodic compartment was 65 ml in volume and the anodic compartment had a volume of 25 ml. Cell II was identical to that previously described in ref. 12.

Cell I was employed in an attempt to avoid migration of fluorinated compounds from the catholyte (lower compartment) to the anolyte (upper compartment), a problem which occurred in cell II [2a, 12]. However under conditions which favoured formation of the dimer R_F–R_F, cell I could not be used due to progressive blocking of the electrode surface because of deposition of R_F–R_F. Cell II was therefore used in these circumstances since its vertical configuration and the smooth surface of the cathode avoided this problem.

The cells were controlled by a potentiostat–galvanostat (Tacussel PJT 35 V-24) operated at -1.33 V relative to SCE (cell I) or at 70 mA (cell II). Charge consumptions were determined using a coulometer (Tacussel IGSN).

Typical procedures

Electrolyses in cell II were performed as previously described [2a, 12]. Electrolyses in cell I were performed as follows: DMF (25 ml) was introduced into the cathodic compartment and 0.42 g (0.2 M) LiCl was added. An identical solution (25 ml) was introduced into the anodic compartment. C_4F_9I (6 ml) (12 g, 0.53 M) was then introduced into the cathodic compartment together with 18 ml (14.7 g, 2.6 M) of 2-methylbut-3-en-2-ol and 16 ml (13.9 g, 2.6 M) of 2-methylbut-3-yn-2-ol. The initial electrolysis current was 200 mA which decreased with time (70 mA after 2 h 45 min).

Radical initiation with azobisisobutyronitrile (AIBN) [5b]

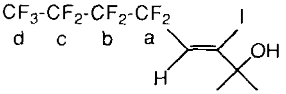
C_4F_9I (17.3 g, 0.05 M), 2-methylbut-3-en-2-ol (21.5 g), 2-methylbut-3-yn-2-ol (21 g) and AIBN (0.164 g) were reacted at 70 °C for 8 h. AIBN (2%) was added after 2 h and after 5 h. After 8 h the solution was analyzed and was shown to contain 3-iodo-2-methyl-4-perfluorobutylbut-4-en-2-ol (24%), 3-iodo-2-methyl-4-perfluorobutylbut-2-ol (42%) and unreacted C_4F_9I (34%).

Characterisation of the reaction products

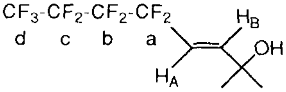
At the end of the electrolysis, 1 ml of catholyte was withdrawn and $C_6H_5CF_3$ added as an internal standard. The sample was then analyzed by means of ^{19}F NMR spectroscopy. The overall content of fluorinated derivatives in the cell was evaluated to be in the range 80–90% relative to the initial R_FI.

The remaining fraction of the catholyte was then extracted with excess water, the fluorinated derivatives were decanted, and the fluorine-containing phase washed with ether, dried over Na_2SO_4, filtered and evaporated under low pressure.

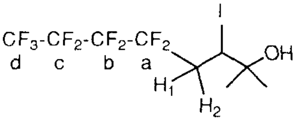
NMR spectral analyses of the reaction products were conducted with a 250 MHZ Bruker spectrometer. The chemical shifts reported below are in ppm relative to CF_3Cl_3 (^{19}F NMR) or TMS (^1H NMR).



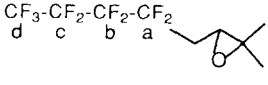
Solvent, CCl_4. ^1H NMR: δ 6.89 (t, 1H), J(FH) 15 Hz; 2.88 (s, 1H); 1.55 (s, 6H) ppm. ^{19}F NMR: δ (CF_2)a −109.1, b −124.1, c −126.1, d −81.5 ppm.



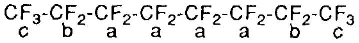
Solvent, CCl_4. ^1H NMR: δ AB (2H) [A from AB 5.92, B from AB 6.48, J(AB) 20 Hz, $J(FH_A)$ 13.5 Hz, $J(FH_B)$ 1.6 Hz]; 3.6 (s, 1H); 1.53 (s, 3H); 1.34 (s, 3H) ppm. ^{19}F NMR: δ (CF_2) a −111.5, b −125.1, c −126.1, d −81.5 pp.



Solvent, $CDCl_3$. ^1H NMR: δ 4.25 (dd, 1H), $J(HH_1)$ 1.9 Hz, $J(HH_2)$ 9.18 Hz; 3.1 (m, 1H); 2.75 (m, 1H); 1.44 (s, 3H); 1.47 (s, 3H); 1.8 (s, 1H) ppm. ^{19}F NMR: δ (CF_2) a AB [A from AB−116.93, B from AB−114.19, J(AB) 0.988 Hz, b −125, c −126, d −81.5 ppm.



Solvent, $CDCl_3$. ^1H NMR: δ 3 (t, 1H), J(HH) 5.9 Hz; 2.35 (td, 2H), J(HH) 5.9 Hz, J(HF) 25 Hz; 1.36 (s, 3H); 1.3 (s, 3H) ppm. ^{19}F NMR: δ (CF_2) a −113, b −124.8, c −126.6, d −81.5 ppm.



$\underset{c}{CF_3}\text{-}\underset{b}{CF_2}\text{-}\underset{a}{CF_2}\text{-}\underset{a}{CF_2}\text{-}\underset{a}{CF_2}\text{-}\underset{a}{CF_2}\text{-}\underset{b}{CF_2}\text{-}\underset{c}{CF_3}$

Solvent, $CDCl_3$. ^{19}F NMR: δ (CH_2) a −119, b −123.4, c −80 ppm.

Results and discussion

Table 1 presents the values of the ratios k_2/k_1 (or k'_2/k'_1) as obtained by application of voltammetric techniques [2a] to a series of ethylenic and acetylenic substrates. For all cases studied the iodine atom-transfer step is considerably faster than the addition of $R_F^{\bullet}$ to the unsaturated bond. This results in the steady-state concentration of the radical S (or S′) being considerably less than that of the $R_F^{\bullet}$ radicals. This explains why the main termination step consists of the dimerization of $R_F^{\bullet}$ radicals, while side-products originating from the coupling of S (or S′) radicals or from cross-coupling between $R_F^{\bullet}$ and S (or S′) radicals are not observed.

Examination of the results in Table 1 shows that the values for k'_2/k'_1 (addition to acetylenic substrates) exceed by at least one order of magnitude those of k_2/k_1 (addition to ethylenic substrates). On the other hand the rates of addition of $R_F^{\bullet}$ radicals to ethylenic or acetylenic substrates are expected to be comparable on the basis of the Hammond postulate, when the similar enthalpies of both reactions are taken into consideration.

Indeed the enthalpy difference between the two reactions can be evaluated from thermochemical calculations [13, 14] as: $\Delta(\Delta H^0) = \Delta H^0(\equiv) - \Delta H^0(=) \approx \Delta H_f^0(\equiv) - \Delta H_f^0(=) + 40$ kcal mol^{-1}.

Using $\Delta H_f^0(\equiv) \approx \Delta H_f^0(C_2H_2) = -55$ kcal mol^{-1} and $\Delta H_f^0(=) \approx \Delta H_f^0(C_2H_4) = -12.5$ kcal mol^{-1} [12], one obtains $\Delta(\Delta H^0) \approx -2.5$ kcal mol^{-1}. Note that such a value compares satisfactorily to that deduced from the estimated energy difference (-2 kcal mol^{-1}) between the 'second' bond of ethylene (≈ 58 kcal mol^{-1}) and the 'third' bond of acetylene (60 kcal mol^{-1}) [15]. Hence, considering that $k_1 \approx k'_1$, the results in Table 1 imply that $k'_2 \gg k_2$, which fall in line with the expected larger reactivity of σ-vinyl radicals as compared to σ-alkyl radicals. To validate this estimation quantitatively, one must determine k_1/k'_1 (or k_2/k'_2) independently. Values of k_1/k'_1 may

TABLE 1

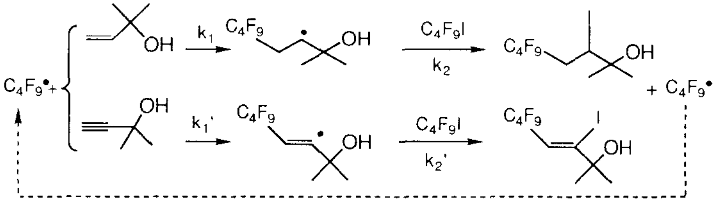
Values of the ratio k_2/k_1 (or, k_2'/k_1') for the propagation steps in Scheme 2, as determined by cyclic voltammetry [2] in dimethylformamide (DMF) with 0.05 M tetrabutylammonium tetrafluoroborate (TBAF), for perfluorobutyl radicals

	Substrates	k_2/k_1 or k_2'/k_1'
1	$H{-}C{\equiv}C{-}C(CH_3)_2OH$	300
2	$H{-}C{\equiv}C{-}CHCH_3OH$	500
3	$H{-}C{\equiv}C{-}(CH_2)_3{-}CH_3$	250
4	$H_2C{=}CH{-}C(CH_3)_2OH$	15
5	$H_2C{=}CH{-}CH(CH_3)OH$	80
6	$H_2C{=}CH{-}CH_2{-}OH$	15
7	$H_2C{=}C(CH_3){-}CH_2{-}OH$	15
8	$H_2C{=}CH{-}O{-}C_4H_9$	55
9	$H{-}C{\equiv}C{-}C(CH_3)OH{-}CH{=}CH_2$	140
10	$H{-}C{\equiv}C{-}C(CH_3){=}CH{-}CH_2OH$	100

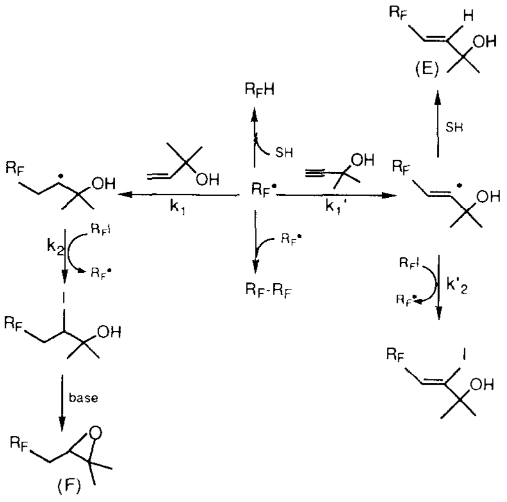
be determined by competitive experiments in which $R_F^{\bullet}$ radicals are exposed to an ethylenic and an acetylenic substrate.

Such competitive experiments are presented below. Thus a preparative electrolysis of C_4F_9I was performed in the presence of identical concentrations of substrates 1 and 4, both being in excess compared to C_4F_9I. Under such conditions, the experimental ratio of the yields of the addition products of R_FI to each (*vide infra*) is a direct measurement of k_1/k'_1, as shown in Scheme 3. This arises since the intermediate vinyl or alkyl radicals obey steady-state conditions because of the large values of k_2/k_1 or k'_2/k'_1.

Application of the above method yields $k_1/k'_1 = 1.75$ for the substrates in Scheme 3, when $C_4F_9^{\bullet}$ radicals are produced by the reduction of C_4F_9I at a carbon cloth electrode. To test for a possible alteration of such a result due to termination steps (*vide infra*), the same experiment was performed using azobisisobutyronitrile (AIBN) [5b] to initiate the reactions in Scheme 3. Thus, $k_1/k'_1 = 1.70$ was obtained, which is almost identical to that determined by electrolysis provided that the reduction products (see species E in Scheme 4) or further evolution products (see species F in Scheme 4) formed under the basic conditions prevailing in electrolysis are taken into account (cf. Table 2).



Scheme 3.



Scheme 4.

TABLE 2

Experimental results obtained

Substrate	Run No.	$[R_FI]$ (M)	$[R_FI]$: substrate ratio	Charge (F mol^{-1}) per R_FI consumed	Unconverted R_FI (%)	Product yields (%)[f]				Recovered (%)[f]	Cell[g]
						Iodide P or P′	Olefin	Epoxide	R_FH		
a	1	1	1:5	0.15	7	54[d]	16			77	I
(≡)	2	1	1:1	0.4	11	23[d]	43		6	83	I
	3	0.27	1:5	0.4	5		70		2	76	I
	4	0.27	1:1	0.8	14		53		11	78	I
b	5	1	1:5	0.2	18	49[e]		8		75	I
(=)	6	1	1:1	0.2	16	58[e]		6	6	86	I
	7	0.27	1:5	0.9	18	31[e]		20	14	83	I
	8	0.27	1:1	0.8	30	28[e]		20	11	89	I
c	9	5				R_F–R_F					II
	10	1				R_FH					II

[a] Substrate = 2-methylbut-3-yne-2-ol.

[b] Substrate = 2-methylbut-3-en-2-ol.

[c] Electrolysis in the absence of ethylenic or acetylenic substrate.

[d] Vinylic iodide P′ (see Scheme 2).

[e] Alkyl iodide P (see Scheme 2).

[f] Yields are given (in per cent) with respect to the initial C_4F_9I.

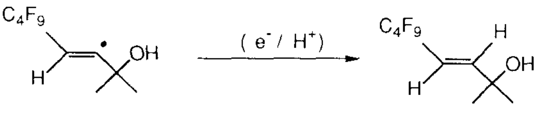
[g] See experimental section. Electrolysis conditions: (I) controlled potential electrolysis (−1.33 V versus SCE) at a carbon cloth (28 cm^2) cathode and anode, *in DMF, 0.2 M LiCl (catholyte:* 65 ml; anolyte: 25 ml); (II) galvanostatic electrolysis (70 mA) at a vitreous carbon disk (12 cm^2) cathode and anode, in DMF, 0.2 M LiCl (catholyte: 5 ml; anolyte: 2 ml).

To further assess the validity of the above experiments, electrolyses of C_4F_9I have been performed independently in the presence of various excesses of unsaturated compounds and at different concentrations of C_4F_9I. The results of the corresponding series of electrolyses are reported in Table 2, and are compared to the results of electrolyses performed in the absence of unsaturated substrates. In the latter case, (entries 9 and 10) the nature of the cathode was changed, a vitreous carbon disk being preferred to avoid blocking of the carbon cloth electrode by the insoluble dimer R_F–R_F [2].

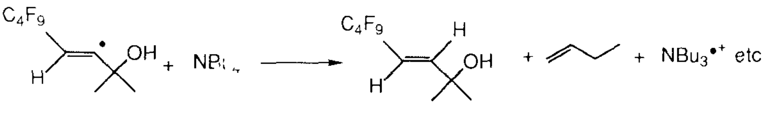
Table 2 shows that significant yields of addition products (P or P′) of R_FI to the unsaturated substrates are obtained provided that the concentrations of both the substrate and the perfluoroalkyl iodide are large (entries 1, 2, 5 and 6). This agrees with the low charge (0.15–0.4 F mol^{-1}) consumed during the corresponding electrolyses, since formation of the addition products P and P′ involves a zero charge consumption. Conversely, two series of by-products are obtained when the R_FI or substrate concentration are low. With the exception of R_FH, these by products correspond to the further evolution of the addition product (epoxide) or arise from the reduction of the transient vinyl or alkyl radical formed by addition of $R_F^{\bullet}$ to the unsaturated substrate. This reductive process may proceed either by direct reduction, as e.g. Scheme 5, or by H-atom transfer from the tetrabutylammonium ion [16] (Scheme 6).

It is noteworthy that this termination route appears to be ineffective in the case of ethylenic substrates. This observation again points to the larger stability of the transient alkyl radicals (S in Scheme 2) relative to vinylic radicals (S′ in Scheme 2). However, in the case of the ethylenic substrates the addition product P may react further under the basic conditions prevailing in the catholyte compartment during electrolysis. Thus deprotonation of the hydroxy group followed by intramolecular substitution of the iodide results in the formation of the epoxide (F in Scheme 4).

Based on the independent determination of k_2/k_1 and k'_2/k'_1 (Table 1, entries 4 and 1) on the one hand and of $k_1/k'_1 = 1.7$ on the other, one can determine $k'_2/k_2 = 11$ for the ratio of the rate constants of iodine-atom transfer from C_4F_9I to the vinylic and alkyl radicals as depicted in Scheme 3. Assuming similar activation entropies for iodine transfer to both radicals, this result



Scheme 5.



Scheme 6.

corresponds to an activation enthalpy difference of ca. -1.4 kcal mol^{-1}. Such a difference is reasonable in view of the difference between the bond dissociation energies of alkyl–iodine (54 kcal mol^{-1} [14]) and vinyl–iodine (66 kcal mol^{-1} [14]) bonds. Moreover, such a result suggests that the transition state for the iodine-atom transfer is an early transition state since $\Delta(\Delta H^{\#}) \approx 0.12\ \Delta(\Delta H^{0})$, in agreement with the Hammond postulate.

Conclusions

The present study has allowed us to determine the ratio of the rate constants k_2/k_1 (or k'_2/k'_1 respectively) for the propagation steps of the radical chain addition of C_4F_9I to ethylenic (or acetylenic, respectively) substrates. From competitive experiments $k'_2/k_2 = 11$ has been determined for the ratio of the rate constants for iodine-atom transfer to the correspondingly formed radicals. Such a result points to the larger reactivity of vinyl radicals in comparison to the corresponding alkyl radicals. This result is further confirmed by the observation of side-products resulting from the overall reduction of vinylic radicals during preparative electrolysis. Such side-products are not observed during the electro-initiated addition of R_FI to ethylenic substrates.

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