RADICAL ADDITIONS TO FLUOROOLEFINS: EXPERIMENTAL EVIDENCE FOR A FREE-RADICAL CHAIN MECHANISM IN THE PHOTO-INITIATED ADDITION OF ALCOHOLS TO FLUOROOLEFINS*

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Dedicated to Professor Milan Kratochvil on the occasion of his 70th birthday

Photo-initiated addition of 2-propanol to two fluoroolefinic compounds, i.e. methyl 2,4,4,5,6,6-hexafluoro-3-oxa-2-(trifluoromethyl)hex-5-enoate (*IV*) containing perfluoroallyloxy group and 8,9-dichloro-1,1,2,4,4,5,7,7,8,9,9-undecafluoro-3,6-dioxa-5-(trifluoromethyl)dodec-1-ene (*V*) containing trifluorovinyloxy group were used to verify a free-radical chain mechanism by means of quantum yield measurements based on substrate-decay kinetic. UV-Light energy (254 nm) was transferred to the reaction system via triplet-excited acetone. Quantum yields Φ of the addition products (*X*, *XI*) reached values 68 and 42, respectively, and thus confirmed the chain mechanism. The olefinic compounds *IV* and *V* were synthesized on the basis of the reaction of 2,3-dichloro-2,3,3-trifluoropropanoyl fluoride (*I*) with hexafluoropropene-1,2-oxide. The photoaddition of 2-propanol to both olefins took place with complete regioselectivity.

Free-radical addition reactions of alkanols with olefinic compounds belong to important synthetic methods. Such processes are described for several alkenes[1–5], fluoroalkenes[6–10], unsaturated carboxylic acids and their functional derivatives[3,4,11–13], unsaturated fluoro-carboxylic acids and their derivatives[14] and perfluorinated unsaturated ethers[15]. In general, a free-radical chain mechanism has generally been assumed for these examples, however, without strong verification.

In this paper we report a direct evidence of a free-radical chain mechanism for the photo-initiated addition of alcohols to two kinds of fluoroolefins, i.e. perfluoroallyloxy-

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type (*IV*) and trifluorovinyloxy-type (*V*). 2-Propanol was chosen as the representative of alkanols because it can be easily transformed to nucleophilic dimethylketyl radical[16] (2-hydroxy-2-propanyl, *VII*) by its reaction with triplet-excited acetone. In this arrangement, the light-energy transfer in the initiation step and the formation of reactive radicals were independent on the olefin present. It is well known that nucleophilic radicals are easily added[17,18] to double bonds with reduced π electron density; typical examples are α,β-unsaturated carboxylic acids and their functional derivatives and highly fluorinated olefins[19]. We have also verified that the hydroxyalkanyl radical $\bullet CH(OH)CH_3$ generated both photochemically and by dibenzoyl peroxide was added with the same regioselectivity to fluorinated propene[20]. According to these facts we used in this study higher-boiling fluoroolefins with terminal double bond that do not telomerize[7,21] in the presence of radical.

RESULTS AND DISCUSSION

The synthesis of olefinic compounds *IV* and *V* was based on the caesium fluoride-catalyzed reaction of acid fluoride *I* with hexafluoropropene-1,2-oxide that gave a mixture of telomeric acid fluorides[22] *IIa* – *IId*. To obtain higher yields of lower telomers, the earlier described procedure[22] was modified. The two products of this ionic telomerization, i.e. the 1:1- (*IIa*) and 1:2-telomers (*IIb*) were transformed to the targeted olefin models *IV* and *V*, respectively, in two steps (Scheme 1): in the preparation of olefin *IV*, the acid fluoride *IIa* was converted to the corresponding methyl ester *III* which was dehalogenated by zinc as a one-pot reaction to afford the olefinic compound *IV*, i.e. 2,4,5,6,6-hexafluoro-3-oxa-2-(trifluoromethyl)hex-5-enoate in the yield of 70%. In the preparation of olefin *V*, i.e. 8,9-dichloro-1,1,2,4,4,5,7,7,8,9,9-undecafluoro-3,6-dioxa-5-(trifluoromethyl)dodec-1-ene, acid fluoride *IIb* was hydrolyzed with aqueous sodium hydrogen carbonate to the corresponding sodium salt *IIe* which was pyrolyzed at 340 – 360 °C to give the olefin *V* in the preparative yield of 60 – 70% (Scheme 1).

When the solution of the individual olefins *IV* and *V* in the mixture 2-propanol–acetone was irradiated with monochromatic UV light (254 nm), only one addition product was found in the reaction mixture (*X* and *XI*, respectively). It can be concluded that the photo-addition of 2-propanol to the terminal double bond of both substrates *IV* and *V* took place with complete regioselectivity (with respect to the accuracy of analytical methods used, potential regioisomers could be formed in relative amount below 2%).

For the discussed photo-initiated addition, the system of assumed elementary reactions is depicted in Scheme 2. The incident UV light (254 nm) is totally absorbed by acetone that acts as a sensitizer during the whole course of the reaction. Due to the ratio of both extinction coefficients and concentrations, the other products of the reaction system cannot absorb any portion of the light. In the initiation step, triplet-excited acetone is formed (*VI*) with a high quantum yield[16] ($\varphi_{isc} = 0.9$). This short-lived species

reacts with a molecule of 2-propanol to give a couple of ketyl radicals (2-hydroxy-2-propanyl) *VII* with a quantum yield[23] $\varphi = 0.9$. The ketyl radical *VII* starts propagation step by the formation of adduct-radicals *VIII* and *IX*, respectively, that in turn react with 2-propanol to form addition products *X* and *XI*, respectively, under regeneration of the ketyl radical *VII*.

$$CF_2Cl-CFCl-\underset{\underset{F}{|}}{C}=O \quad + \quad CF_3-CF\overset{\diagdown O \diagup}{-\!\!\!-\!\!\!-}CF_2$$

$$I$$

$$CF_2Cl-CFCl-CF_2-O\underset{\underset{CF_3}{|}}{\left(CF-CF_2-O\right)_n}\underset{\underset{CF_3}{|}}{CF}-\underset{\underset{F}{|}}{C}=O$$

$$IIa - IId \qquad \begin{aligned} &IIa, \; n = 0 \\ &IIb, \; n = 1 \\ &IIc, \; n = 2 \\ &IId, \; n = 3 \end{aligned}$$

$$IIa \longrightarrow CF_2Cl-CFCl-CF_2-O-\underset{\underset{CF_3}{|}}{CF}-\underset{\underset{OCH_3}{|}}{C}=O \longrightarrow CF_2=CF-CF_2-O-\underset{\underset{CF_3}{|}}{CF}-\underset{\underset{OCH_3}{|}}{C}=O$$

$$III \qquad\qquad\qquad\qquad IV$$

$$IIb \longrightarrow CF_2Cl-CFCl-CF_2-O-\underset{\underset{CF_3}{|}}{CF}-CF_2-O-\underset{\underset{CF_3}{|}}{CF}-\underset{\underset{ONa}{|}}{C}=O$$

$$IIe$$

$$CF_2Cl-CFCl-CF_2-O-\underset{\underset{CF_3}{|}}{CF}-CF_2-O-CF=CF_2$$

$$V$$

Scheme 1

In formulae *IV*, *VIII*, *X* : $R_F = CH_3OOC-CF(CF_3)-O-CF_2$

In formulae *V*, *IX*, *XI* : $R_F = CF_2Cl-CFCl-CF_2-O-CF(CF_3)-CF_2-O$

SCHEME 2

FIG. 1
Time dependence of the substrate *IV* conversion in the photoaddition of 2-propanol

FIG. 2
Time dependence of the substrate *V* conversion in the photoaddition of 2-propanol

The quantum yields of the addition reaction, that can indicate a chain reaction, were calculated on the basis of kinetic measurements: the decrease of the olefin concentration in the irradiated reaction mixture was monitored by GC and calculated using the external standard. The time profiles of the reaction of 2-propanol with both olefins are shown in Fig. 1 (for olefin *IV*) and Fig. 2 (for olefin *V*). The initial linear parts of the curves correspond to a pseudo-zero-order kinetics and this linear dependence was used for the calculation of total quantum yields Φ.

The total quantum yields Φ of the reactions, that were simply calculated from the relation $\Phi = \Delta c/\Delta t$, where c is concentration of the olefin and t is time, reached value of 68 for the reaction of olefin *IV* and value of 42 for the reaction of olefin *V*. These high quantum yield values unequivocally confirm a free-radical chain mechanism for the additions. Kinetic chain length of the additions (kcl) is obtained by the division of total quantum yield Φ by the product of ε_{isc} and φ, i.e. kcl = $\Phi/2(\varepsilon_{isc}\varphi) = \Phi/0.81$ that gives values 42 (for *IV*) and 26 (for *V*), respectively. Our values of the mean kinetic chain length are relatively low in comparison with the published values for another photo-initiated chain reactions[6]. One of the reasons may be low substrate concentration in the reaction mixture (ca 10^{-2} mol l^{-1}). This can cause that the hydrogen abstraction from 2-propanol can successfully compete with the recombination of ketyl radical, i.e. process that results in chain termination.

The olefin *V* and the addition products *X*, *XI* are new compounds, while the unsaturated ester *IV* was mentioned in patent literature[24]. The structures of all compounds *IV*, *V*, *X* and *XI* were confirmed by NMR spectra and elemental analyses. The NMR spectra of compounds *IV* and *V* contain signals of fluorine atoms in CF=CF$_2$ group, the spectra of addition products *X* and *XI* contain signals of CHF and C(CH$_3$)$_2$OH groups.

EXPERIMENTAL

The temperature data are uncorrected. GC analyses were performed on a Chrom 5 apparatus (Laboratorni pristroje Praha), conditions: FID, 3.8 m × 3 mm column packed with Silicone SE-301 oil (10% *w/w*) on Chromaton N-AW-DMCS (Lachema Brno), grading 0.1 – 0.125 mm; kinetic measurements were performed on GHF 18.3 apparatus (VEB Chromaton, Berlin), conditions: FID, 3 m × 4 mm column packed with Poly(propylene glycol adipate), (10% *w/w*) on Porolyth 20. Preparative GC was accomplished on a Chrom 3 apparatus (Laboratorni pristroje Praha), conditions: 3.5 m × 0.6 cm, packing as for Chrom 5. UV spectra were measured on Specord M40 apparatus (Zeiss Jena). NMR spectra (δ, ppm; J, Hz; ds = diastereoisomer) were taken on a Bruker 400 AM (FT, ^{19}F at 376 MHz) apparatus; CFCl$_3$ as the internal standard, solvent CDCl$_3$ except fluorinated telomers, which were measured in a 1 : 1 diethyl ether–tetrahydrofurane-d$_8$ mixture.

Chemicals: Anhydrous caesium fluoride (Fluka AG), tetraethylene glycol dimethyl ether (Fluka AG) were treated as described earlier[22], hexafluoropropene (Matheson) was used without further purification. Acetone and 2-propanol were purified by standard procedures and their fotochemical purity was checked by UV spectra. 2,3-Dichloro-2,3,3-trifluoropropanoyl fluoride (*I*) was prepared as described earlier[22].

Actinometric apparatus: A UV low-pressure mercury lamp HNU 6 (VEB Narva) with a parabolic reflector served as a source of light which passed through mechanical shutter, adjustable slits and 1 cm

thick layer of saturated water solution of nickel sulfate. Intensity of the monochromatic (254 nm) light that irradiated the reaction cell was measured using ferrioxalate actinometer[3,25,26] and it was of value $I_0 = (1.66 + 0.08) . 10^{-10}$ mol quanta per second (i.e. Einstein s^{-1}).

Ionic Telomerization of 2,3-Dichloro-2,3,3-trifluoropropanoyl Fluoride (*I*) with Hexafluoropropene-1,2-oxide. Acid Fluorides *IIa* – *IId*

General procedure was the same as published in the literature[22]. Acid fluoride *I* (76.5 g, 0.384 mol), hexafluorpropene-1,2-oxide (75.5 g, 0.455 mol), caesium fluoride (3.75 g, 24 mmol) and tetraethylene-glycol dimethyl ether (35 ml) gave crude mixture of products (125 g, 82.6% relatively to the fluoro-epoxide) that consisted (GLC, ^{19}F NMR) of acid fluorides: *IIa* (5,6-dichloro-2,4,4,5,6, 6-hexafluoro-3-oxa-2-trifluoromethylhexanoyl fluoride, 18 rel.%), *IIb* (8,9-dichloro-2,4,4,5,7,7,8,9,9-nonafluoro-3,6-dioxa-2,5-bis(trifluoromethyl)nonanoyl fluoride, 27 rel.%), *IIc* (11,12-dichloro-2,4,4,5,7,7,8,10,10,11,12,12-dodeca-fluoro-3,6,9-trioxa-2,5,8-tris(trifluoromethyl)dodecanoyl fluoride, 32 rel.%) and *IId* (14,15-dichloro-2,4,4,5,7,7,8,8,10,10,11,13,13,14,15,15-pentadecafluoro-3,6,9,12-tetraoxa-2,5,8,11-tetrakis(trifluoro-methyl)pentadecanoyl fluoride, 23 rel.%). By the rectification of the mixture, individual acid fluorides were obtained with the following preparative yields (purity 95 – 97% by GC: 200 °C, nitrogen 0.14 MPa): *IIa*, b.p. 160 – 162 °C, 13.82 g (9.9%); *IIb*, b.p. 58 – 59.5 °C/1.1 kPa, 27.9 g (22.9%) and *IIc*, b.p. 91 – 92.5 °C/1.1 kPa, 25.1 g (23.7%). ^{19}F NMR spectra: *IIa*: 24.6 q, 1 F (COF); −63.4 dq, 1 F (CClF$_2$); −64.5 dq, 1 F, $^2J_{FF} = 136$, $J_{FF} = 12$ (CClF$_2$); −74.1 ddm, 1 F, $J_{FF} = 49$ and 12 (CF$_2$O); −80.6 dm, 1 F, $J_{FF} = 143$ and 12 (CF$_2$O); −82.2 bs, 3 F (CF$_3$); −130.4 d, 1 F, $J_{FF} = 40$ (CClF); −132.6 m, 1 F, $J_{FF} = 8$ (CF). *IIb*: 26.3 s, 1 F (COF); −63.3 dm, 1 F (CClF$_2$); −64.6 dm, 1 F, $^2J_{FF} = 175$ (CClF$_2$); −75.1 m, 2 F (CF$_2$O); −78.4 dm, 1 F (CF$_2$O); −79.8 bs, 3 F (CF$_3$); −82.2 s, 3 F (CF$_3$); −85.1 ddm, 1 F (CF$_2$O); −130.4 bs, 1 F (CF); −132.3 bs, 1 F (CClF); −145.3 t, 1 F, $J_{FF} = 20$ (CF). *IIc*: 26.3 m, 1 F (COF); −63.68 dm, 1 F (CClF$_2$); −65.0 dm, 1 F, $^2J_{FF} = 174$ (CClF$_2$); −75.5 m, 2 F (CF$_2$O); −78.4 dm, 1 F (CF$_2$O, ds$_1$); −78.9 dm, 1 F (CF$_2$O, ds$_2$); −79.8 m, 3 F (CF$_3$); −80.1 m, 2 F (CF$_2$O); −82.2 s, 3 F, (CF$_3$); −85.0 dm, 1 F, $^2J_{FF} = 151$ (CF$_2$O, ds$_2$); −85.5 dm, 1 F, $^2J_{FF} = 151$ (CF$_2$O, ds$_1$); −130.7 s, 1 F (CF); −132.8 s, 1 F (CClF); −145.1 m, 1 F (CF).

Methyl 5,6-Dichloro-2,4,4,5,6,6-hexafluoro-3-oxa-2-(trifluoromethyl)hexanoate (*III*)

Acid fluoride *IIa* (4.96 g, 16.2 mmol) was added dropwise to methanol (5 ml) while stirring at 0 °C, the mixture was stirred for additional 30 min, then kept 30 min at the room temperature and finally refluxed for 30 min. The crude reaction mixture was washed with ice-water (10 ml), then with con-centrated solution of calcium chloride and finally with water (5 ml). The crude oily product *III* was dried with calcium chloride which was filtered off to afford the ester *III* in the yield of 3.88 g (76%). ^{1}H NMR spectrum: 3.99 s, (ds$_1$ 60 rel.%, CH$_3$); 4.00 s, (ds$_2$ 40 rel.%, CH$_3$). ^{19}F NMR spectrum: −63.8 dm, 1 F, $^2J_{FF} = 172$ (ds$_1$ + ds$_2$, CClF$_2$); −65.0 dm, 1 F (60 rel.%, ds$_1$, CClF$_2$); −65.1 dm, 1 F, $J_{FF} = 12$ (40 rel.%, ds$_2$, CClF$_2$); −73.9 dsext, 1 F, $^2J_{FF} = 143$, $J_{FF} = 10$ (40 rel.%, ds$_2$, CF$_2$O); −74.7 dsext, 1 F, $^2J_{FF} = 142$, $J_{FF} = 11$ (60 rel.%, ds$_1$, CF$_2$O); −80.84 dm, 1 F (ds$_1$, CF$_2$O); −81.5 dm, 1 F (ds$_2$, CF$_2$O) −82.6 s, 3 F (CF$_3$); −132.3 tm, 1 F, $J_{FF} = 24$ (CF); −133.2 m, 1 F (CClF).

Methyl 2,4,4,5,6,6-Hexafluoro-3-oxa-2-(trifluoromethyl)hex-5-enoate (*IV*)

Acid fluoride *IIa* (15.3 g, 50 mmol) was added dropwise to stirred ice-cold methanol (20 ml) and stirring was continued for 3 h at room temperature. The reaction mixture was then cooled to 0 °C, zinc powder (9.8 g, 150 mmol) activated with acetic anhydride was added, the mixture was stirred for 3 h at room temperature and then 30 min at 50 – 55 °C (to the complete conversion of the hexa-noate *III*). After decantation (methanol, 10 ml), the crude solution was distilled (b.p. up to 40 °C/2.3 kPa),

distillate (31.4 g) was washed with ice-water and dried with magnesium sulfate. Distillation afforded the product *IV*, b.p. 42 – 43 °C/2.3 kPa, yield 9.03 g (70.2%), purity 96% (GC: E 301, 125 °C). ^{1}H NMR spectrum: 3.97 s, 3 H (ester group). ^{19}F NMR spectrum: −67.9 dm, 1 F (CF$_2$O); −73.7 dm, 1 F, $^2J_{FF}$ = 162 (CF$_2$O); −82.7 s, 3 F (CF$_3$); −91.7 ddt, 1 F, $^3J_{FF}$ = 38, $^4J_{FF}$ = 4 (=CF$_2$ *cis*); −104.5 dddd, 1 F, $^2J_{FF}$ = 51, $^3J_{FF}$ = 118, $^4J_{FF}$ = 23 and 19 (=CF$_2$ *trans*); −132.2 d, 1 F, J_{FF} = 19 (CF); −190.7 ddt, 1 F, $^3J_{FF}$ = 118, 38 and 15 (CF=). For C$_7$H$_3$F$_9$O$_3$ (306.2) calculated: 27.47% C, 0.98% H, 55.86% F; found: 27.20% C, 1.107% H, 55.80% F.

8,9-Dichloro-1,1,2,4,4,5,7,7,8,9,9-undecafluoro-3,6-dioxa-5-(trifluoromethyl)dodec-1-ene (*V*)

Acid fluoride *IIb* (24.14 g, 35 mmol) was neutralized by 1 M sodium hydrogen carbonate to yield sodium salt *IIe*, the solution was evaporated to dryness and then dried for 3 h at 100 °C/0.33 kPa. The flask was then connected to a trap (dry ice) and the salt *IIe* was pyrolyzed in a metal bath at 360 °C/1.3 kPa. The distillate (17.34 g) was washed with a solution of sodium hydrogen carbonate, then with water and dried with magnesium sulfate. The product *VI* was obtained by fraction distillation, b.p. 78 – 79 °C/1.2 kPa, yield 14.3 g (67%), purity 96% (GC: E 301, 140 °C). ^{19}F NMR spectrum: −63.8 dm, 1 F (CClF$_2$); −65.3 dm, 1 F, $^2J_{FF}$ = 172 (CClF$_2$); −75.2 dm, 1 F (CF$_2$O); −76.9 dm, 1 F, $^2J_{FF}$ = 146 (CF$_2$O); −80.5 m, 6 F (CF$_3$); −81.4 d, 2 F, $^2J_{FF}$ = 139 (CF$_2$O); −85.6 m, 2 F (CF$_2$O); −113.7 ddm, 1 F, J_{FF} = 67 (=CF$_2$ *cis*); −122.2 dd, 1 F, $^2J_{FF}$ = 84, $^2J_{FF}$ = 112 (=CF$_2$ *trans*); −133.2 dm, 1 F $^4J_{FF}$ = 6 (CClF); −136.1 dm, 1 F, $^2J_{FF}$ = 110, $^4J_{FF}$ = 6 (CF); −145.6 q, 1 F, J_{FF} = 23 (CF); −146 m, 1 F (CF=). For C$_{11}$Cl$_2$F$_{20}$O$_3$ (631.0) calculated: 20.94% C, 11.24% Cl, 60.22% F; found: 21.10% C, 11.50% Cl, 60.50% F.

Methyl 2,4,4,5,6,6-Hexafluoro-7-hydroxy-7-methyl-3-oxa-2-(trifluoromethyl)nonanoate (*X*)

Solutions from runs of photoreactions of hexenoate *IV* with 2-propanol were collected from reaction cells and concentrated by rectifying off 2-propanol. The residue (ca 3 ml) was diluted with 1,1,2-trichlorotrifluoroethane (CFC-113, 25 ml), washed twice with water and dried with magnesium sulfate. CFC-113 was distilled off, then removed under the reduced pressure and the residue was distilled twice. Product *X* was obtained as a fraction of b.p. 140 – 142 °C/2 kPa, yield 0.43 g, purity 96% (GC: Reoplex 400, 200 °C). ^{1}H NMR spectrum: 1.36 s, 3 H (CH$_3$); 1.40 s, 3 H (CH$_3$); 2.65 bs, 1 H (OH); 3.98 s, 3 H (COOCH$_3$); 6.1 m, 1 H, $^2J_{FF}$ = 46.8 (CHF). ^{19}F NMR spectrum: −72.8 dm, 1 F (CF$_2$O, ds$_1$); −73.8 dm, 1 F, $^2J_{FF}$ = 166 (CF$_2$O, ds$_1$); −80.5 dm, 1 F (CF$_2$O, ds$_2$); −81.0 dm, 1 F, $^2J_{FF}$ = 149 (CF$_2$O); −82.7 s, 3 F (CF$_3$); −123.6 ddm, 1 F (CF$_2$); −127.3 dm, 1 F, $^2J_{FF}$ = 270 (CF$_2$); −131.9 d, 1 F, J_{FF} = 19 (CF); −205.7 dm, 1 F, $^2J_{FF}$ = 47 (CHF). For C$_{10}$H$_{11}$F$_9$O$_4$ (366.2) calculated: 32.80% C, 3.03% H, 46.69% F; found: 32.90% C, 3.21% H, 47.10% F.

13,14-Dichloro-3,3,4,6,6,7,9,9,10,12,12,13,14,14-tetradecafluoro-2-methyl-5,8,11-trioxa-7,10-bis(trifluoromethyl)tetradecan-2-ol (*XI*)

Crude compound *XI* was obtained in the same way as the compound *X*. The final distillation afforded compound *XI* as a fraction of b.p. 153 – 157 °C/2.1 kPa, yield 0.56 g, purity 94% (GC as for *X*). ^{1}H NMR spectrum: 1.42 s, 6 H (2 CH$_3$); 2.64 bs, 1 H (OH); 6.55 ddd, 1 H, $^2J_{HF}$ = 52.4 (CHF). ^{19}F NMR spectrum: −63.9 dm, 1 F (CF$_2$Cl); −65.2 dm, 1 F, $^2J_{FF}$ = 173 (CF$_2$Cl); −76.2 m, 2 F (CF$_2$O); −80.4 m, 6 F (2 CF$_3$); −81.2 m, 2 F (CF$_2$O); −84.1 m, 1 F (CF$_2$O); −85.9 m, 1 F (CF$_2$O); −125.3 dm, 1 F (CF$_2$); −131.5 dm, 1 F, $^2J_{FF}$ = 270 (CF$_2$); −133 m, 1 F (CClF); −140.8 d, 1 F, $^2J_{FF}$ = 42 (CHF). For C$_{14}$H$_8$Cl$_2$F$_{20}$O$_4$ (691.1) calculated: 24.33% C, 1.17% H, 10.26% Cl, 54.98% F; found: 24.60% C, 1.52% H, 10.10% Cl, 54.10% F.

Kinetic Measurements

Concentrations of the sensitizer (acetone) and the substrates (compounds *IV* and *V*) in 2-propanol were calculated on the basis of molar extinction coefficients ε_{254} at wavelength 254 nm that have the following values (l mol cm^{-1}): acetone, $\varepsilon_{254} = 14$, compound *IV*, $\varepsilon_{254} = 1.0$, compound *V*, $\varepsilon_{254} = 0.2$; concentrations (mol l^{-1}): for mixture acetone–compound *IV*, 0.5 and 0.05, respectively (reaction solution A), for mixture acetone–compound *V*, 0.1 and 0.05, respectively (reaction solution B). Reaction solution (10 ml) in a quartz cell sealed with a rubber septum was 20 min deoxygenated with argon at −40 °C. The cell was then placed in the photochemical housing at the same conditions as for light intensity measurements (i.e. set up of shutters, spinbar revolutions). For each period a new solution was used. The conversion of the substrate was checked by GC ("adipate", 300 cm, 150 °C) using method of external standard. The external standard used was solution of methylcyclohexane (0.05 mol l^{-1}) in 2-propanol which was mixed with the irradiated solution in ratio 1 : 1. Kinetic curves are shown in Fig. 1 (substrate *IV*) and Fig. 2 (substrate *V*). Quantum yields were calculated from the initial linear parts of kinetic dependences as shown in Figs 1 and 2.

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