Atmospheric degradation of halogenated alcohols and aldehydes: A possible source of halogenated carboxylic acids

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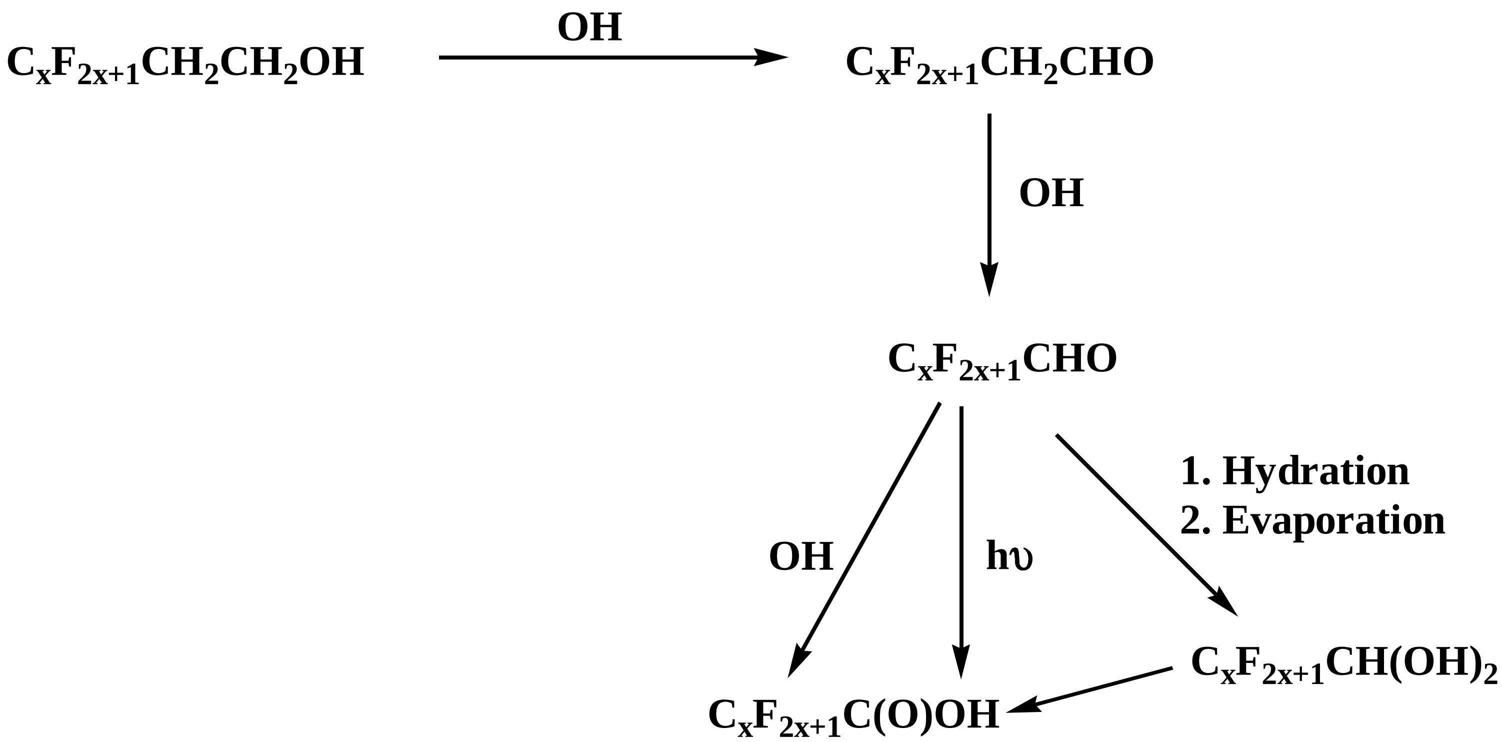
Atmospheric sources of halogenated organic compounds

- Hydrofluorocarbons, (e.g. CF_3CH_3)
- Hydrochlorofluorocarbons, (e.g. $CFCl_2CH_3$)
- Hydrochlorocarbons, (e.g. CCl_3CH_3, $CHCl{=}CCl_2$)
- Fluoroalcohols, (e.g. $C_xF_{2x+1}CH_2CH_2OH$, $C_xF_{2x+1}CH_2OH$)
- Chloroalcohols, (e.g. CCl_3CH_2OH)

$$\mathbf{CX_3CHO \longrightarrow CX_3C(O)OH}$$

$$\mathbf{CX_3CFO \longrightarrow CX_3C(O)OH}$$

Atmospheric fate of fluoroalcohols and aldehydes



Kinetics of the reactions of OH radicals and Cl atoms with halogenated alcohols and aldehydes

$$\dot{O}H / \dot{C}l \quad + \quad RCH_2OH \longrightarrow H_2O / HCl \quad + \quad R\dot{C}HOH$$

$$\dot{O}H / \dot{C}l \quad + \quad RCHO \longrightarrow H_2O / HCl \quad + \quad R\dot{C}(O)$$

Kinetic data for the reaction of OH and Cl with halogenated alcohols

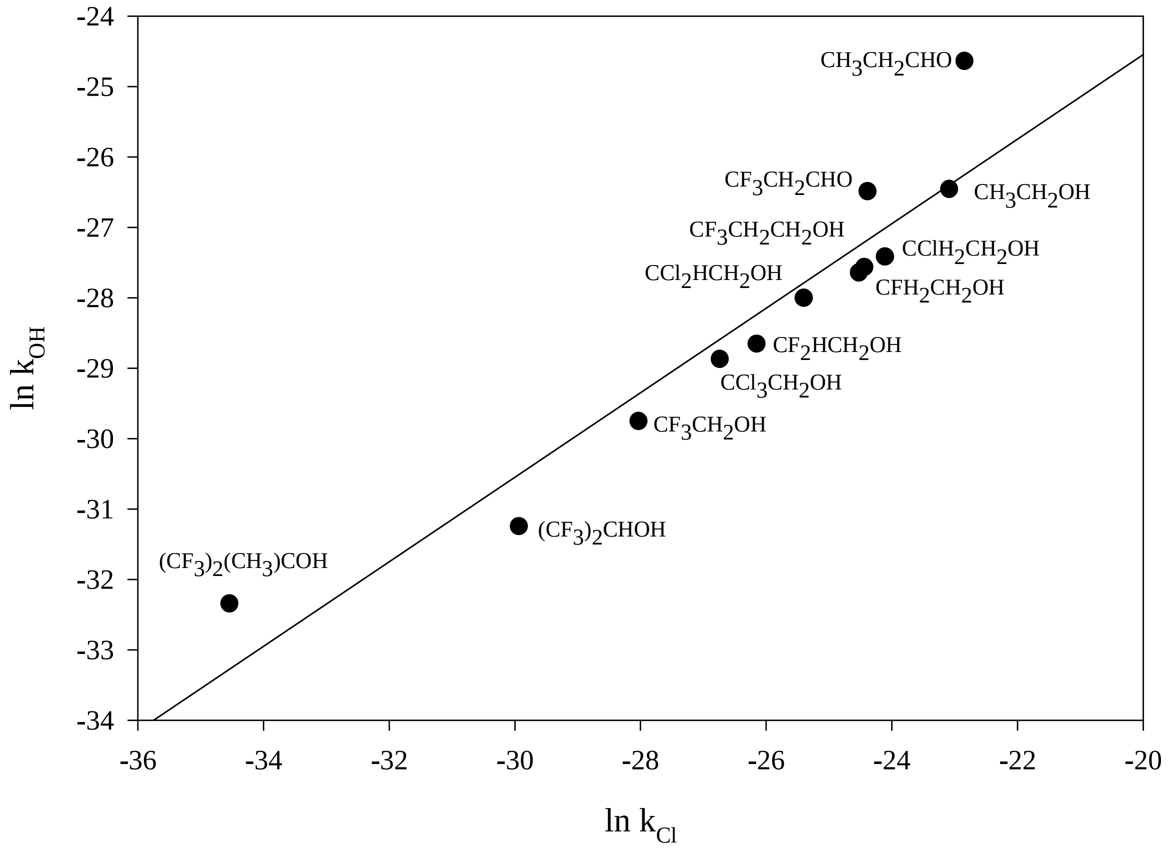
Substrate	10^{13} k_{OH} cm^3 $molecule^{-1}$ s^{-1}	10^{12} k_{Cl} cm^3 $molecule^{-1}$ s^{-1}
$CH_3CH_2CH_3$	11	61
CH_3CH_2OH	32	96
CFH_2CH_2OH	11	22
CF_2HCH_2OH	2.9	2.7
CF_3CH_2OH	1.0	0.64
$C_xF_{2x+1}CH_2OH$	1.0	0.65
$CF_3CH_2CH_2OH$	6.9-9.0	16-22
$C_xF_{2x+1}CH_2CH_2OH$	11	16
$(CH_3)_3CH$	21	18
$(CH_3)_2CHOH$	51	57
$(CF_3)_2CHOH$	0.26	0.009
$CF_3CH(OH)_2$	1.2 – 1.6	0.60 – 0.77
$(CF_3)_3COH$	< 0.002	< 0.00005
$CClH_2CH_2OH$	13	32
CCl_2HCH_2OH	6.9	9.3
CCl_3CH_2OH	3.0	3.5
$CCl_3CH(OH)_2$	5.5	7.3

Kinetic data for the reaction of OH and Cl with halogenated aldehydes

Aldehyde	**10^{12} k_{OH} cm^3 $molecule^{-1}$ s^{-1}**	**$10^{12}k_{Cl}$ cm^3 $molecule^{-1}$ s^{-1}**
CH_3CHO	14	57
CF_2HCHO	1.6	5.6
CF_3CHO	0.52	2.3
$C_xF_{2x+1}CHO$	0.60	2.0
CH_3CH_2CHO	20	120
CF_3CH_2CHO	3.0	22
CCl_3CHO	1.1	6.5

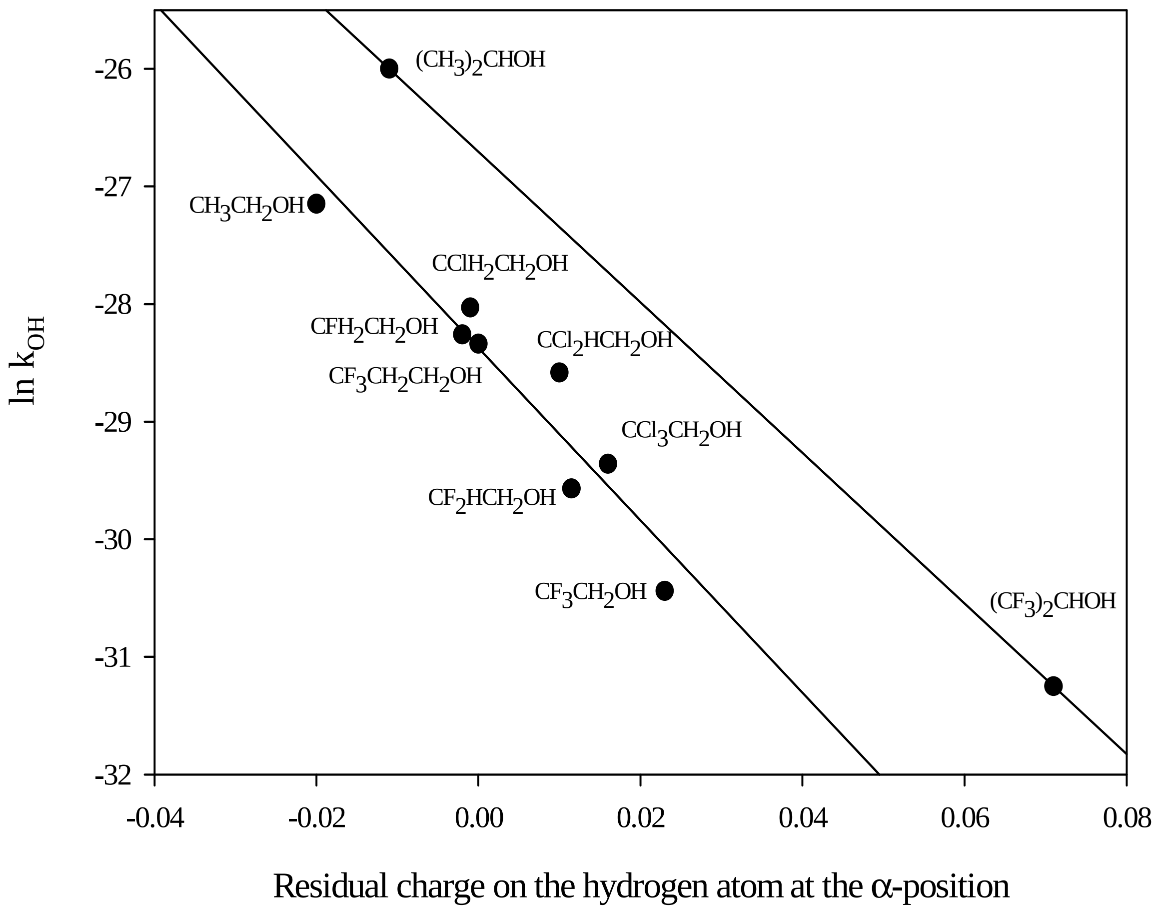
Reactivity of haloalcohols and haloaldehydes

Figure 1



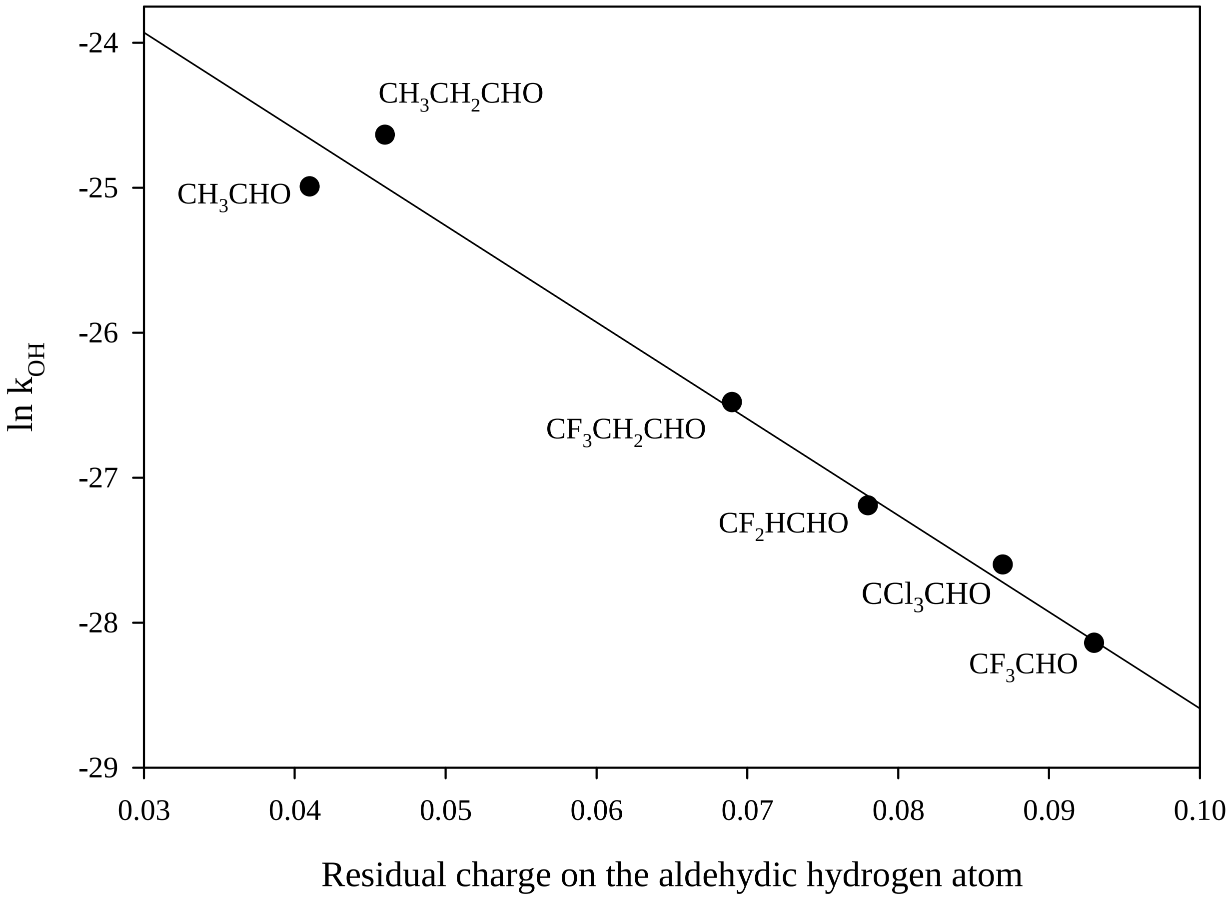
Reactivity of haloalcohols and haloaldehydes - continued

Figure 2



Reactivity of aldehydes

Figure 3



Electrophilic nature of OH radicals and Cl atoms

$\dot{O}H\ (\dot{C}l) \quad + \quad CH_3\dot{C}(O)H^{\delta+} \longrightarrow CH_3\dot{C}(O) \quad + \quad H_2O\ (HCl)$

$\dot{O}H\ (\dot{C}l) \quad + \quad CF_3C(O)H^{\delta++} \longrightarrow CF_3\dot{C}(O) \quad + \quad H_2O\ (HCl)$

$k\ (OH(Cl) + CH_3C(O)H) \quad > \quad k\ (OH(Cl) \quad + \quad CF_3C(O)H)$

$\longrightarrow$

$H_3CC(O)- - - -H- - - - - - - - - -OH\ (Cl)$

$\longleftarrow$

$F_3CC(O)- -H- - - - - - - - - - - - -OH\ (Cl)$

$\dot{C}H_3 \quad + \quad ^{\delta+}HCl \longrightarrow \dot{C}l \quad + \quad CH_4$

$\dot{C}H_3 \quad + \quad H\text{-}H \longrightarrow \dot{H} \quad + \quad CH_4$

$k\ (CH_3 \ + \ HCl) \quad > \quad k\ (CH_3 \ + \ H\text{-}H)$

$\longleftarrow$

$Cl - - - -H - - - - - - - - - - - - -CH_3$

$H - - - - - - -H - - - - - - - - - - -CH_3$

Atmospheric lifetimes of fluoroalcohols and aldehydes for reaction with OH radicals

$C_xF_{2x+1}CH_2CH_2OH$	$\tau_{OH} \sim$ 11 days
$C_xF_{2x+1}CH_2OH$	$\tau_{OH} \sim$ 115 days
$C_xF_{2x+1}CH_2CHO$	$\tau_{OH} \sim$ 4 days
$C_xF_{2x+1}CHO$	$\tau_{OH} \sim$ 22 days
$CF_3CH(OH)_2$	$\tau_{OH} \sim$ 80 days

Oxidation of fluoroalcohols in air

$$OH + CF_3CH_2OH \xrightarrow{-H_2O} CF_3CHOH \xrightarrow[-HO_2]{O_2} CF_3CHO$$

$$OH + (CF_3)_2CHOH \xrightarrow{-H_2O} (CF_3)_2COH \xrightarrow[-HO_2]{O_2} (CF_3)_2CO$$

$$OH + CF_3CH_2CH_2OH \xrightarrow{-H_2O} CF_3CH_2CHOH \xrightarrow[-HO_2]{O_2} CF_3CH_2CHO$$

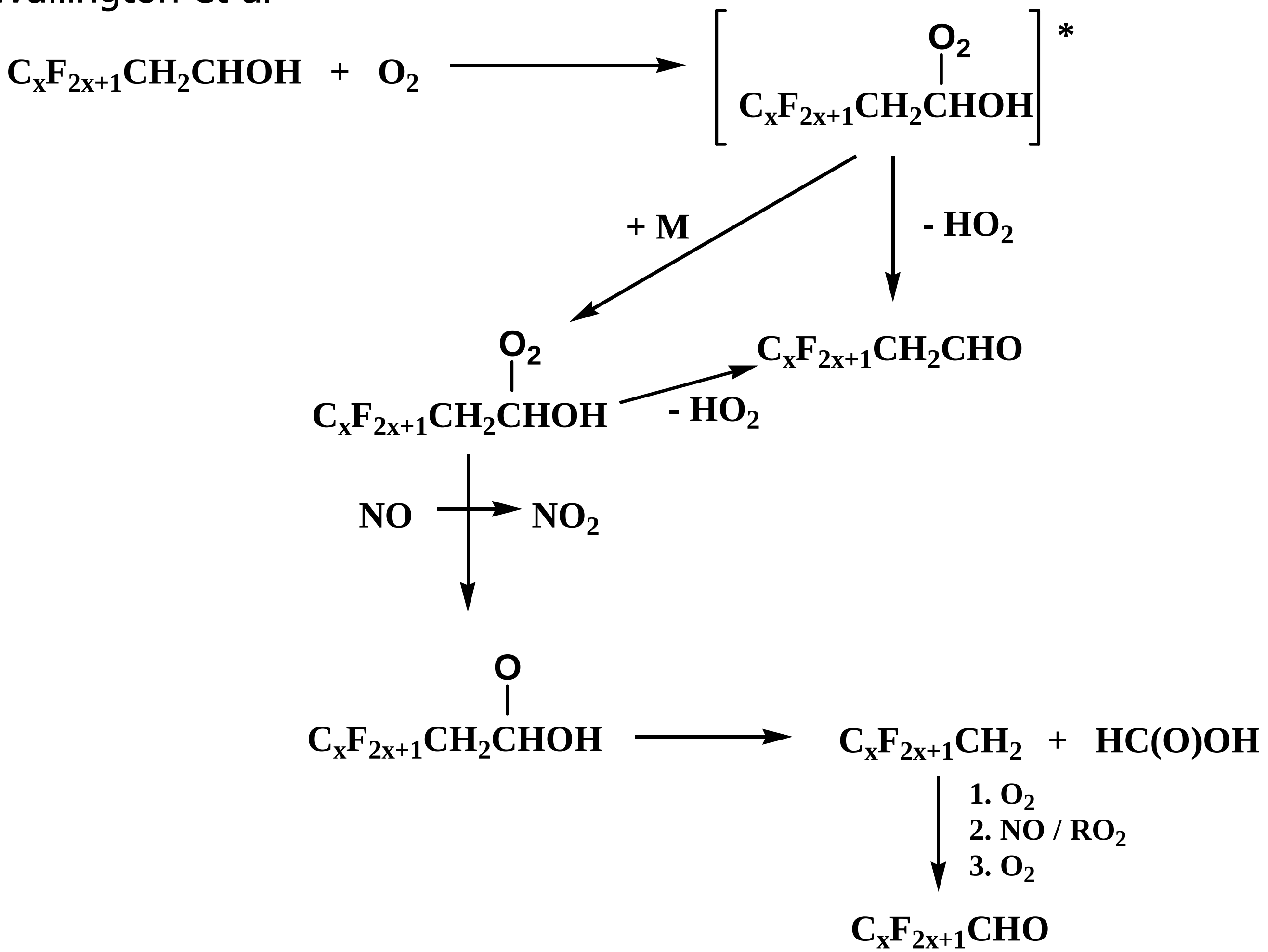
$$OH + CH_3C(CF_3)_2OH \xrightarrow{-H_2O} CH_2C(CF_3)_2OH \xrightarrow[\text{1. } O_2 \text{; 2. } NO / RO_2]{} OCH_2C(CF_3)_2OH$$

$$OCH_2C(CF_3)_2OH \longrightarrow CH_2O + C(CF_3)_2OH$$

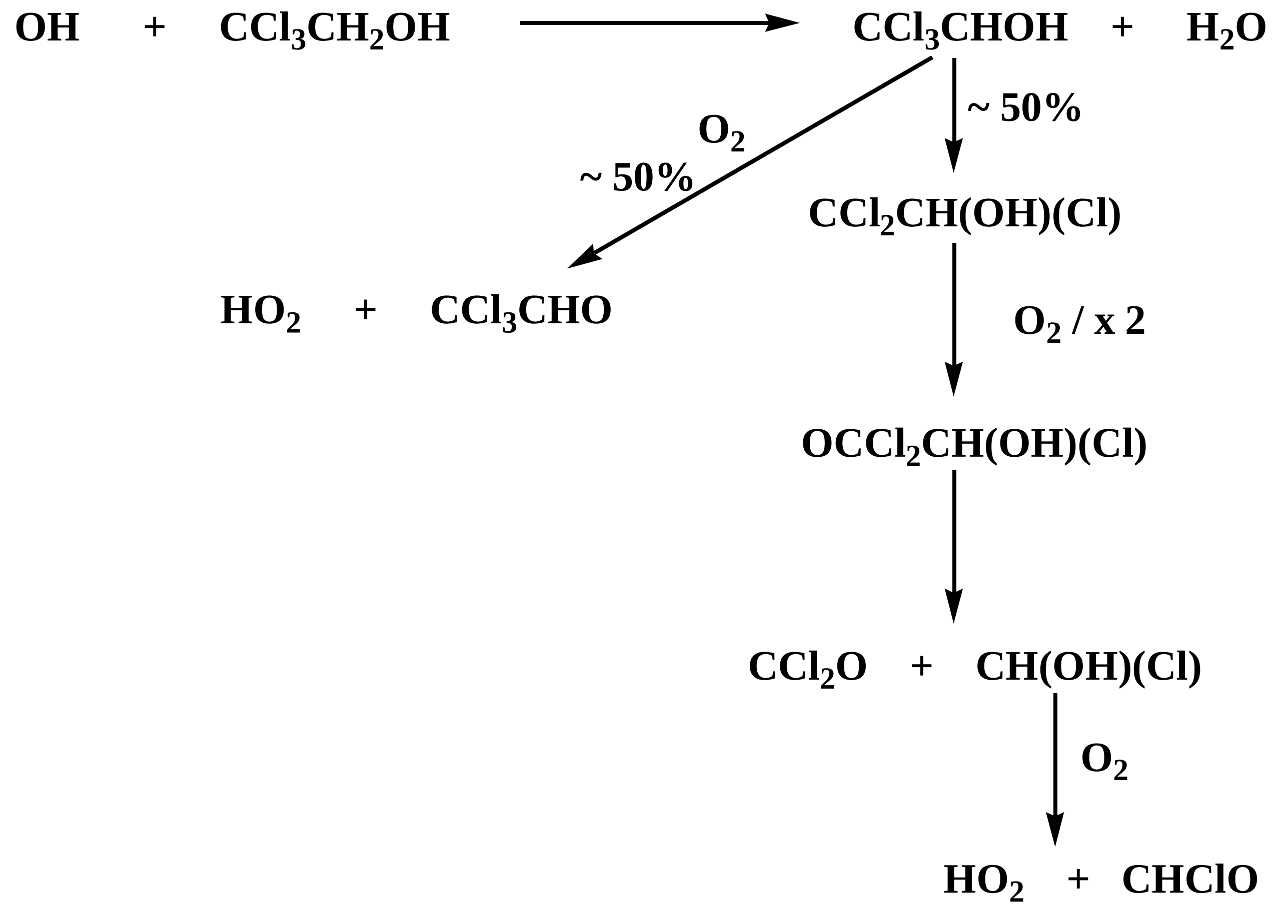
$$C(CF_3)_2OH \xrightarrow[-HO_2]{O_2} (CF_3)_2CO$$

Oxidation of fluoroalcohols in air - continued

Wallington et al



Oxidation of chloroalcohols in air



Oxidation of chloroalkenes

$$OH + CHCl{=}CCl_2 \longrightarrow [CCl_2CH(OH)(Cl)]^*$$

$$[CCl_2CH(OH)(Cl)]^* \longrightarrow CCl_2CHO + HCl$$

$$CCl_2CHO \xrightarrow{O_2 \,/\, x\ 2} OCCl_2CHO$$

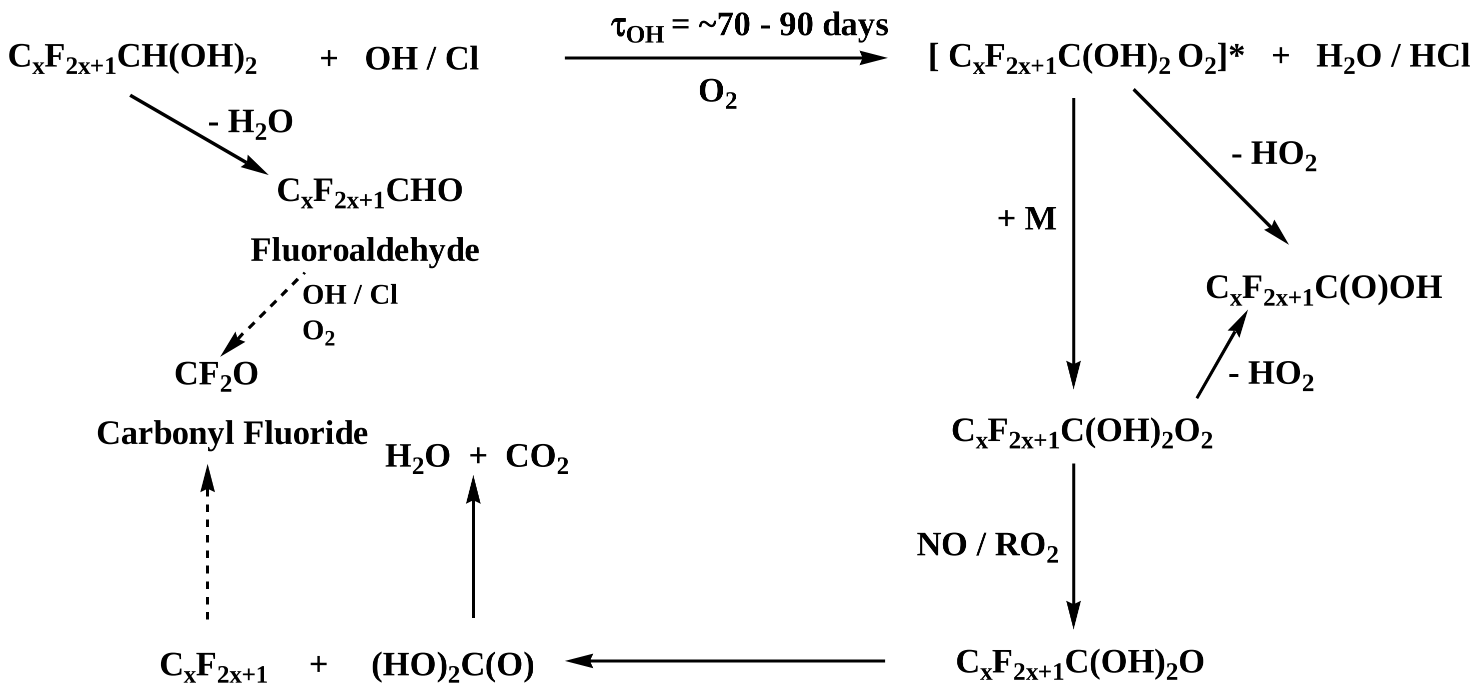
$$OCCl_2CHO \longrightarrow CCl_2O + HCO$$

$$HCO \xrightarrow{O_2} HO_2 + CO$$

Atmospheric degradation of halogenated aldehydes hydrates

$$C_xF_{2x+1}CHO + H_2O \rightleftharpoons C_xF_{2x+1}CH(OH)_2$$

$$pK_{298K} > 10^4$$



Product distribution studies on the radical initiated oxidation of haloaldehydes in air

$$OH / Cl + CX_3CHO \longrightarrow CX_3C(O) + H_2O / HCl$$

$$CX_3CH_2CHO \longrightarrow CX_3CH_2C(O) + H_2O / HCl$$

$$CX_3C(O) \longrightarrow CX_3 + CO$$

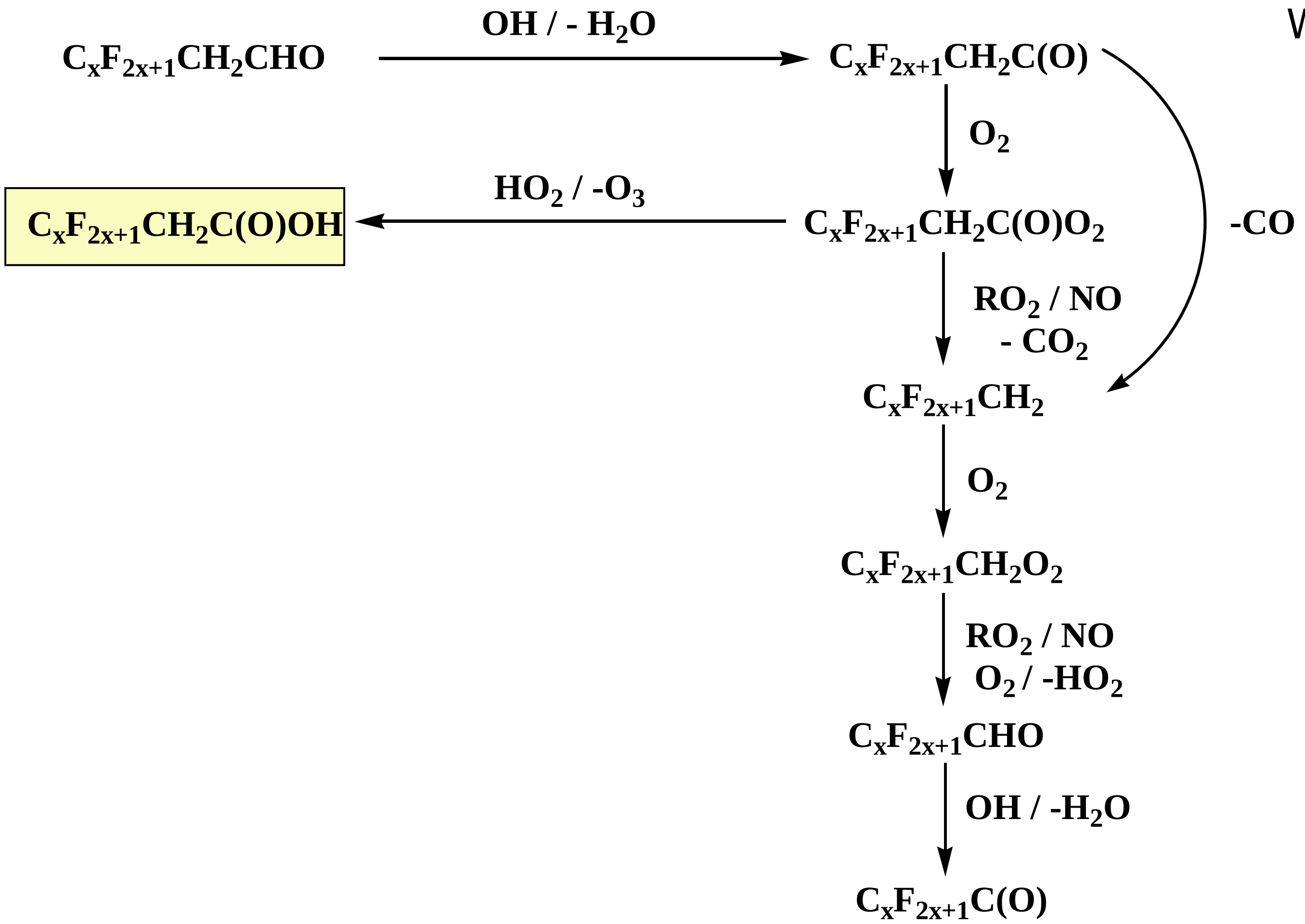
$$CX_3C(O) + O_2 \longrightarrow CX_3C(O)O_2$$

$$CX_3CH_2C(O) \longrightarrow CX_3CH_2 + CO$$

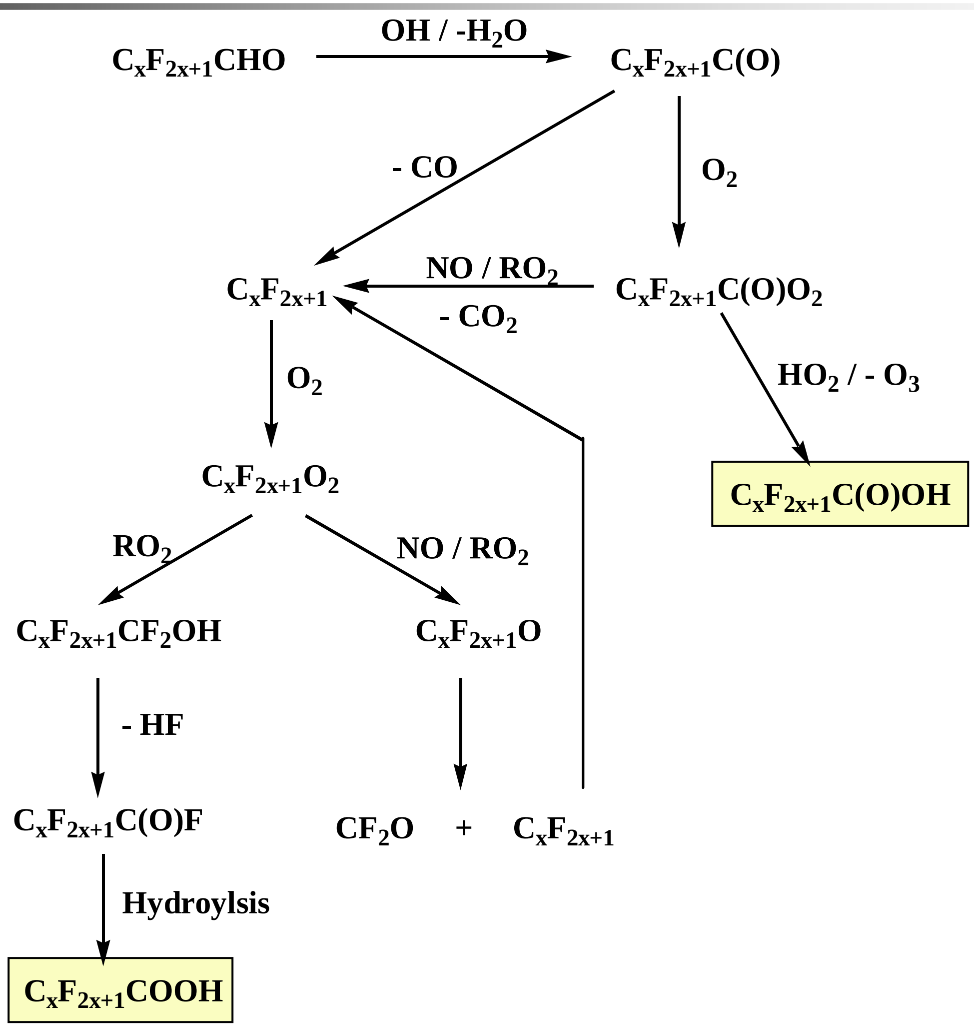
$$CX_3CH_2C(O) + O_2 \longrightarrow CX_3CH_2C(O)O_2$$

Oxidation of fluoroaldehydes

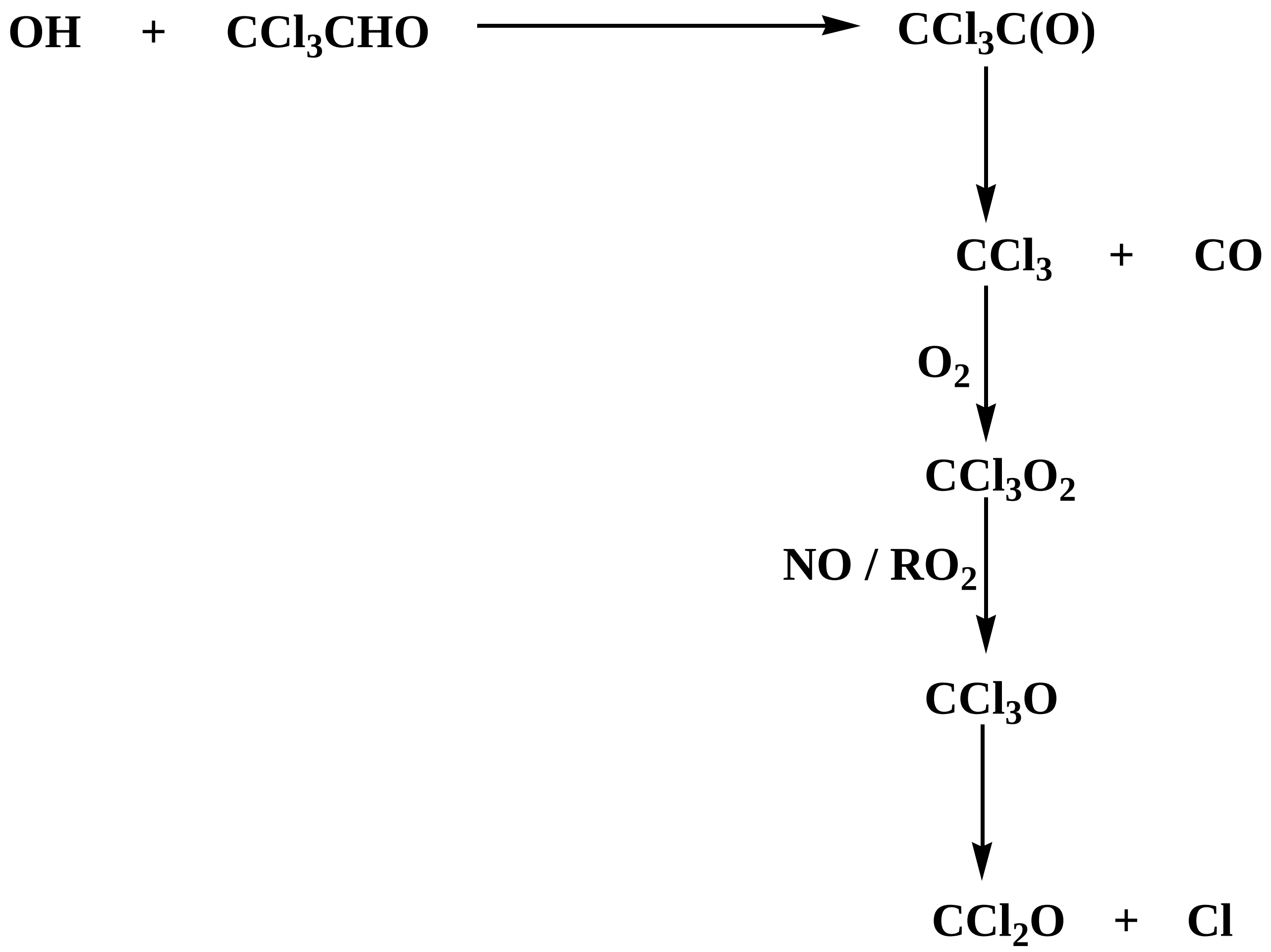
Wallington et al



Oxidation of fluoroaldehydes - continued



Oxidation of chloroaldehydes



Photolysis of halogenated aldehydes

$$C_xF_{2x+1}CHO \quad + \quad h\upsilon \longrightarrow \quad \text{Products}$$

$$CCl_3CHO \quad + \quad h\upsilon \longrightarrow \quad \text{Products}$$

Required :

- Lifetimes
- Products

Photolysis of chloral under atmospheric conditions

Figure 4: Photolytic loss rate of chloral

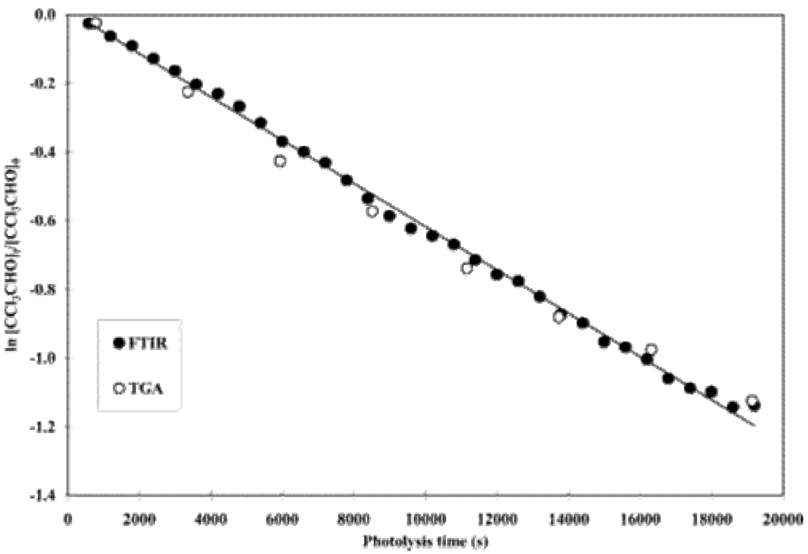
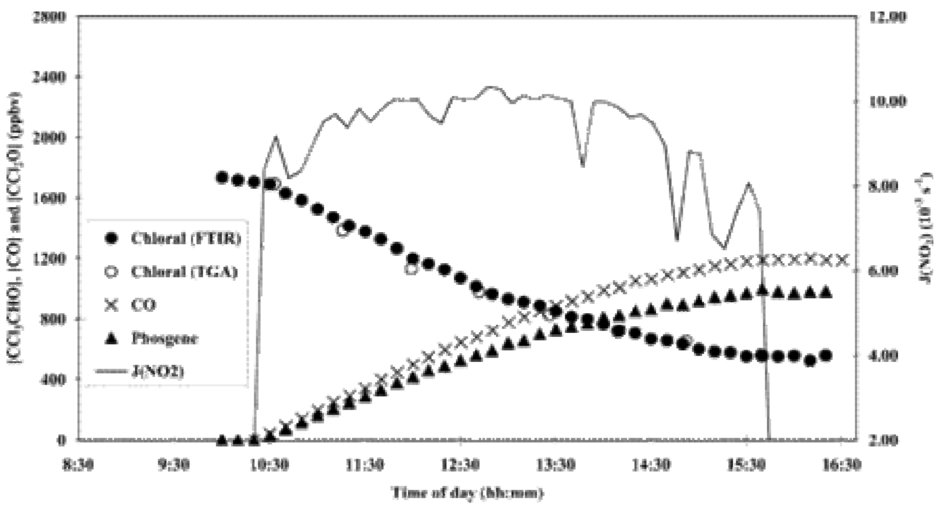


Figure 5: Concentration – time profiles



Photolysis of chloral under atmospheric conditions – continued

$CCl_3CHO + h\upsilon \longrightarrow$ products

$\longrightarrow$ loss by leakage

$\longrightarrow$ wall loss

$$k_{obs} = k_{phot} + k_{dil} = (7.1 \pm 0.1) \times 10^{-5}\ s^{-1}$$

$k_{dil} = (1.0 \pm 0.1) \times 10^{-5}\ s^{-1}$ $\quad \tau_{dil} = 28$ hours

$k_{phot} = (6.1 \pm 0.2) \times 10^{-5}\ s^{-1}$ $\quad \tau_{phot} = 4.6$ hours

$$\Phi_{phot} = 1.0 \pm 0.1$$

Photolysis of chloral under atmospheric conditions – continued

$$CCl_3CHO + h\upsilon \longrightarrow CCl_3 + HC(O)$$

$$\longrightarrow CCl_2CHO + Cl$$

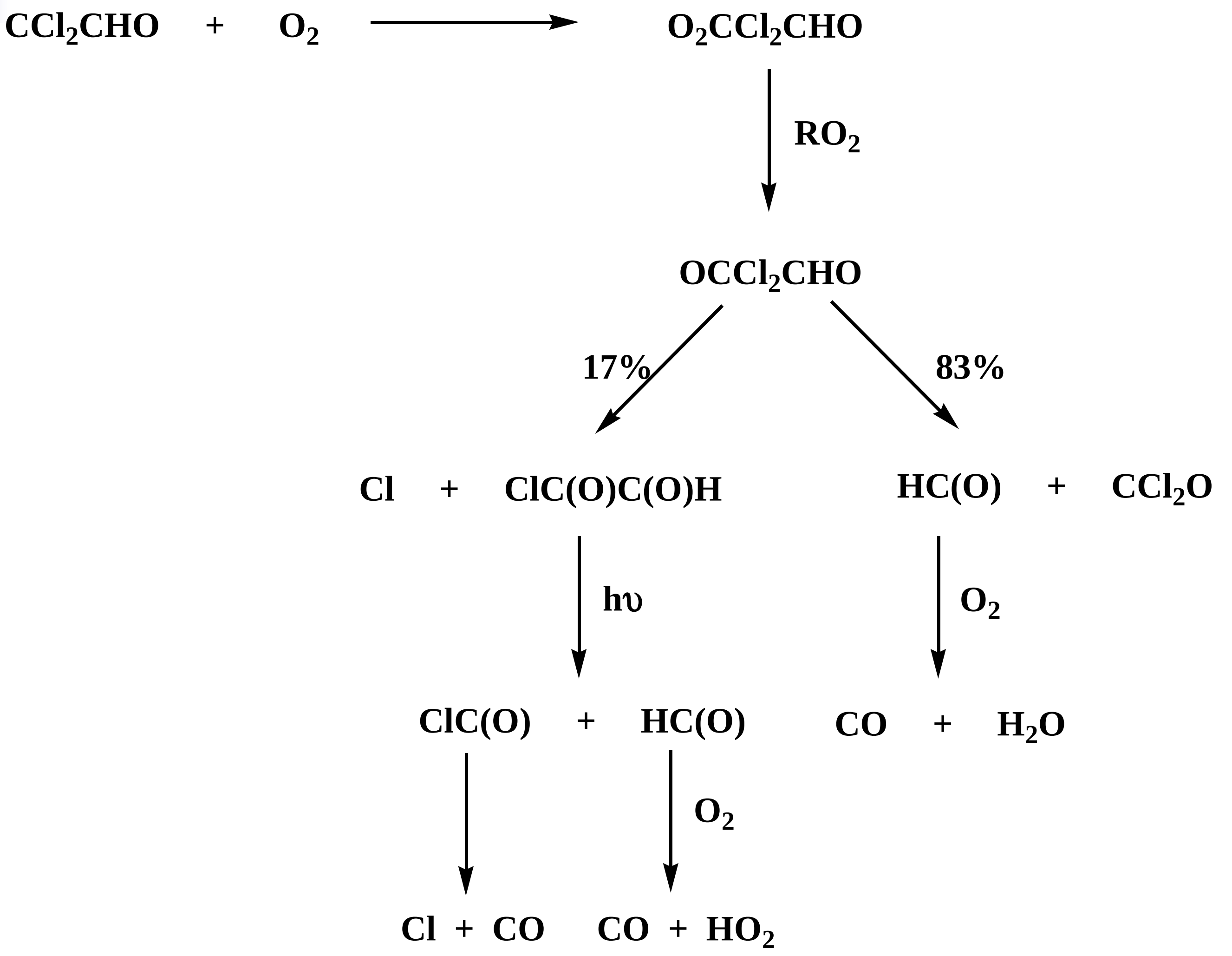
$$\longrightarrow CCl_3H + CO$$

$$\longrightarrow CCl_3C(O) + H$$

$\phi_{Cl} = 1.3 \pm 0.3$ $\lambda = 308nm$

Talukdar et al, J.Phys. Chem. A 2001, 105, 5188-5196

Photolysis of chloral under atmospheric conditions - continued



Photolysis of fluoroaldehydes

Wallington et al

CF_3CHO $\Phi_{(308nm)} = 0.17$
C_4F_9CHO $\Phi_{(308nm)} = 0.08$
CF_3CH_2CHO $\Phi_{(308nm)} = 0.04$

CF_3CHO $\tau_{phot} \sim 6$ days (~17days)
C_4F_9CHO $\tau_{phot} \sim 2$ days (~ 6 days)
CF_3CH_2CHO $\tau_{phot} \sim 13$ days (~ 35 days)

Kelly et al

CF_3CHO $\Phi_{(sunlight)} < 0.02$
CF_3CH_2CHO $\Phi_{(sunlight)} < 0.04$

Compare with:

Moortgat et al

CH_3CHO $\Phi_{(308nm)} = 0.33$
CH_3CHO $\Phi_{(sunlight)} = 0.06$

Photolysis of fluoroaldehydes - continued

Kelly et al.

CF_3CHO	CF_3CH_2CHO
$k_{obs} = k_{phot} + k_{dil} = (7.7 \pm 0.5) \times 10^{-6}\ s^{-1}$	$k_{obs} = k_{phot} + k_{dil} = (7.5 \pm 0.3) \times 10^{-6}\ s^{-1}$
$k_{dil} = (7.5 \pm 0.3) \times 10^{-6}\ s^{-1}$	$k_{dil} = (5.2 \pm 0.2) \times 10^{-6}\ s^{-1}$
$k_{phot} < 1 \times 10^{-6}\ s^{-1}$	$k_{phot} < 2.8 \times 10^{-6}\ s^{-1}$
$\Phi_{phot} < 0.02$	$\Phi_{phot} < 0.04$
τ_{phot} > 10 days	τ_{phot} > 4 days

Photolysis of C_3F_7CHO and C_4F_9CHO at EUPHORE

C_3H_7CHO

$k_{obs} = (1.8 \pm 0.2) \times 10^{-5}\ s^{-1}$
$k_{leak} = (0.5 \pm 0.1) \times 10^{-5}\ s^{-1}$

$k_{phot} = (1.3 \pm 0.6) \times 10^{-5}\ s^{-1}$

$\Phi_{phot} \sim 0.02$ $\tau_{phot} = 21 \pm 10$ hours

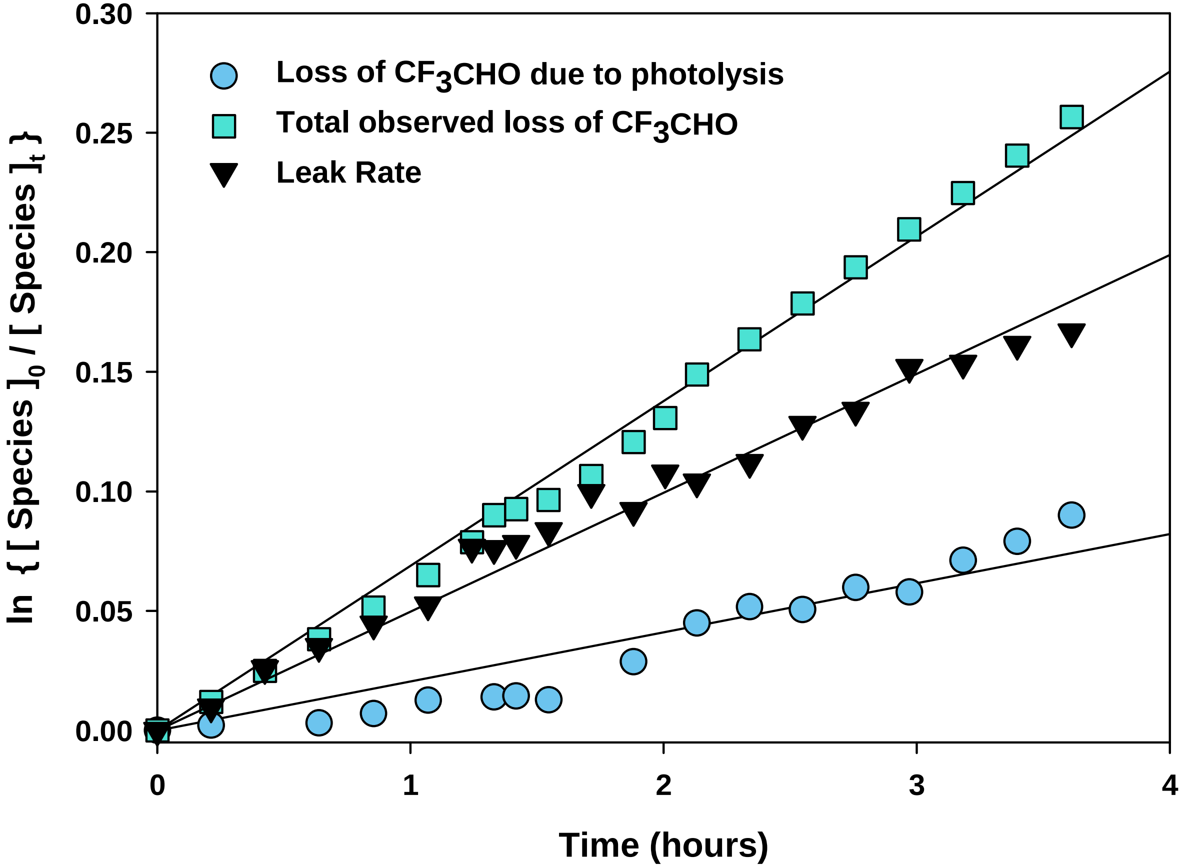
C_4H_9CHO

$k_{obs} = (3.3 \pm 0.6) \times 10^{-5}\ s^{-1}$
$k_{leak} = (1.5 \pm 0.3) \times 10^{-5}\ s^{-1}$

$k_{phot} = (1.8 \pm 0.6) \times 10^{-5}\ s^{-1}$

$\Phi_{phot} \sim 0.03$ $\tau_{phot} = 15 \pm 7$ hours

Photolysis of CF_3CHO performed at EUPHORE



Total observed loss of CF_3CHO = $(2.0 \pm 0.1) \times 10^{-5}\ s^{-1}$

Leak Rate = $(1.3 \pm 0.1) \times 10^{-5}\ s^{-1}$

Loss of CF_3CHO due to photolysis = $(0.65 \pm 0.20) \times 10^{-5}\ s^{-1}$

τ_{phot} ~ 2 days

Atmospheric fate of fluoroaldehydes