CW CO_2 LASER DRIVEN OXIDATION OF SOME PERHALOGENOCYCLOALKENES

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The title reaction of hexafluorocyclobutene, 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene and decafluorocyclohexene studied at total pressure 13·3 and 16 kPa yield oxalyl halides COX.COX ($X = F$, Cl) and C_2F_4 that undergo consecutive reactions to COF_2, CO and X_2. The oxidation of decafluorocyclohexene is preceded by retro-Diels–Alder decomposition affording hexafluorocyclobutene and C_2F_4. Two alternative mechanisms for the oxidation of the cyclobutenes are presented, one involving a novel cleavage of intermediary bicyclic dioxetanes. The decomposition of oxalyl fluoride into COF_2 and CO is favored over its oxidation.

Oxygenation reactions using triplet molecular oxygen are attracting renewed research interest[1–3]. The gas-phase oxidation of perhaloolefins with molecular triplet $^3O_2$ oxygen is a complex reaction involving carbenes and it is sensitive to reactor material[4,5]. Previous investigations by us have shown that truly gas-phase oxidation of acyclic perhaloolefins carried out as a cw CO_2 laser-photosensitized (SF_6) reaction proceeds via intermediary dioxetane to form two carbonyl halides[6,7]. In this paper we report a cw CO_2 laser photosensitized oxidation of perhalogenocycloalkenes, i.e. hexafluorocyclobutene (HFCB), 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (DCCB), and decafluorocyclohexene (DFCH) and show that this reaction can be explained as taking place via a novel cleavage of intermediary dioxetanes.

EXPERIMENTAL

The oxidation of HFCB, DCCB and DFCH, the operation of a cw CO_2 laser and monitoring the reaction progress by IR spectroscopy were carried out as reported elsewhere[6,7]. The reaction mixtures of perhalogenocycloalkene (5·3 kPa), SF_6 (2·7 or 5·3 kPa) and O_2 (5·3 kPa) were irradiated with unfocussed or slightly focussed laser beam of the output ranging from 10 to 14 W. Reaction products were identified by means of their characteristic infrared absorptions[8,9] and mass-spectral fragmentation patterns[10]. The quantities of the reaction products were measured by IR spectroscopy using absorption bands at 1 945 (COF_2), 1 870 (COF.COF), 1 100 (COFCl), 1 416 (HFCB), 1 335 or 1 290 (C_2F_4), 850 ($COCl_2$), 760 and 1 870 (COCl.COCl) and 2 160 (CO) cm^{-1}. The amounts of HFCB, C_2F_4 and CFCl : CFCl were also checked by GC/MS conducted on a Shimadzu QP 1000 quadrupole spectrometer (20 and 70 eV ionizing voltage) equipped with a 1·2 m long column packed with Porapak P. The depletion of HFCB, DCCB and DFCH was followed by using their i.r. analytical bands at 1 416 cm^{-1} ($\varepsilon =$ $=$ 0·0177 kPa cm^{-1}), 1 370 cm^{-1} ($\varepsilon =$ 0·125 kPa^{-1} cm^{-1}) and 1 095 cm^{-1} ($\varepsilon =$ 0·0056 kPa . . cm^{-1}).

Relative reactivities of HFCB, $Cl_2C{=}CF_2$ and CFCl=CFCl in the oxidation were ascertained by the technique[7], where depletion of the olefins in mixtures HFCB–$Cl_2C{=}CF_2$–O_2–SF_6 and HFCB–CFCl=CFCl–O_2–SF_6 (all 2·7 kPa) upon the irradiation with the laser output 10 W were monitored by using analytical absorption bands at 1 416 (HFCB), 885 (CFCl : CFCl), and 1 320 (CF_2 : CCl_2) cm^{-1}.

1,2-Dichlorodifluoroethene and 1,1-dichlorodifluoroethene were prepared according to the reported procedures[7]. HFCB (ref.[11]) and DCCB (ref.[12]), both glc purity, were obtained by thermal cyclization of hexafluoro-1,3-butadiene and 2,3-dichloro-1,1,3,3-tetrafluorobutadiene. Oxalyl fluoride was prepared after the procedure[13] and purified as reported[14]. DFCH (PCR Research Chemicals, Inc.), sulfur hexafluoride (Fluka, purum) and oxygen (Technoplyn, better than 99·5 per cent purity) were commercial samples.

RESULTS AND DISCUSSION

Hexafluorocyclobutene

The cw CO_2 laser photosensitized oxidation of HFCB affords COF_2, COF.COF, C_2F_4, and CO. Mass balance indicates also formation of fluorine. Considering the mechanism of a stepwise $^3O_2$ addition across the double bond of perhaloolefins[6,7], the reaction products and their distribution along the reaction progress (Fig.1) suggest that the oxidation is consistent with Scheme 1, where intermediary dioxetane undergoes cleavage into COF.COF and C_2F_4, the former being decomposed into COF_2 and CO, and the latter being oxidized[6] into COF_2. The Scheme 1 is supported

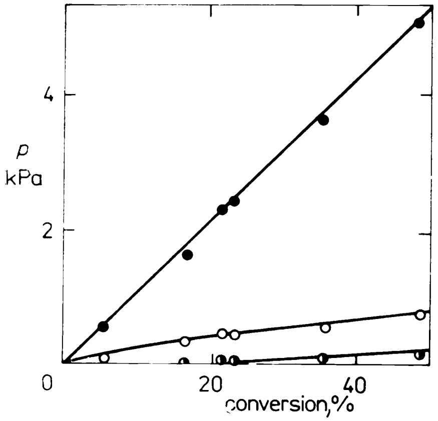
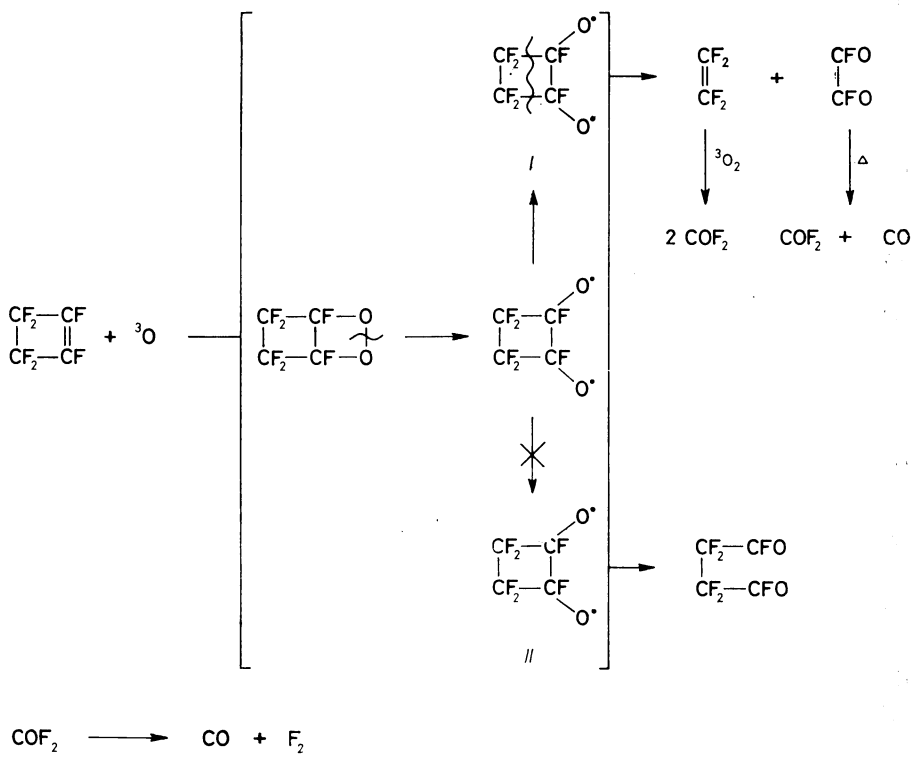


FIG. 1

The reaction progress of laser photosensitized (10 W) oxidation of HFCB with HFCB–O_2–SF_6 (all 5·3 kPa) mixture. Designated products are COF_2 (●), COF.COF (○), and C_2F_4 (◑)

by the observed decomposition of COF.COF into CO and COF_2. The laser photosensitized process (Fig. 2) is consistent with the stoichiometry

$$COF.COF \rightarrow COF_2 + CO$$

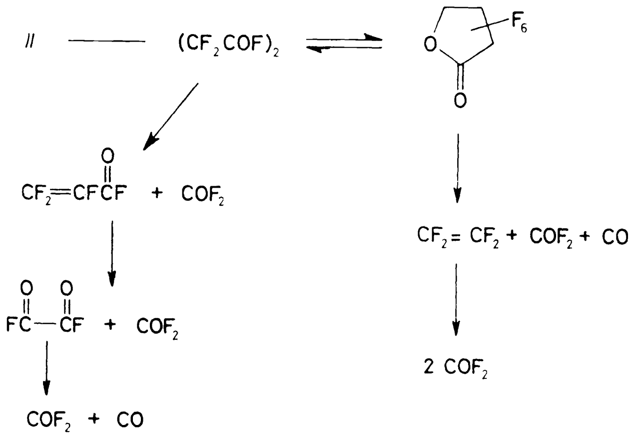


Scheme 1

and it occurs in the presence of oxygen. The reaction velocities (k_{total}) with mixtures COF.COF (5·3 kPa)–SF_6 (2·7 kPa) (13 W, unfocussed beam), COF.COF (5·3 kPa)–SF_6 (2·7 kPa) (13 W, slightly focussed beam), and COF. COF (5·3 kPa)–SF_6 (2·7 kPa)–O_2 (5·3 kPa) (13 W, slightly focussed beam) are very alike and are in the given order 0·23 s^{-1}, 0·50 s^{-1}, and 0·60 s^{-1}.

The yield of COF_2 along the reaction progress reveals that COF_2 undergoes further decomposition into CO and F_2 as was observed[15] under similar conditions. No occurrence of the products of the oxidation of COF.COF (CO_2 and $C_2O_4F_2$ ref.[14]) and of the reaction of fluorine with CO ($F_2C_2O_3$, CO_2, ref.[16]) shows that these reactions are insignificant. The oxidation of CO in the presence of halogen atoms[17] and COF_2 disproportionation[18] can be discarded on similar grounds.

To comment on the low probability of the pathway leading to $(CF_2COF)_2$ we mention that CF_3COF, which should be similarly stable under studied conditions as $(CF_2COF)_2$, is a major proucts of the laser photosensitized oxidation of $CF_3CF=$ $=CF_2$ (ref.[7]). The absence of $(CF_2COF)_2$ among the products of the oxidation of HFCB can thus suggest that intermediary dioxetane is not cleaved via strcture *I* so typical for acyclic dioxetanes[19,20]. We did not succeed to prepare pure $(CF_2COF)_2$ and were thus unable to verify whether thermal stabilities of $(CF_2COF)_2$ and CF_3COF are really very alike. Unequivocal evidence for the mechanism presented in Scheme 1 cannot thus be given, since the observed products can be also explained by reactions in Scheme 2.



SCHEME 2

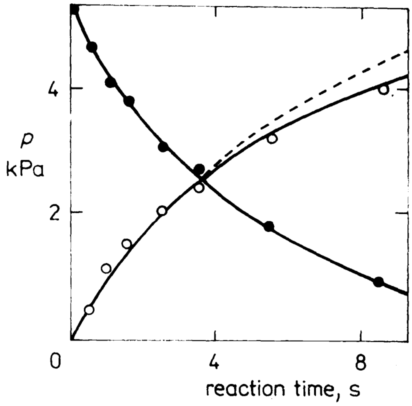


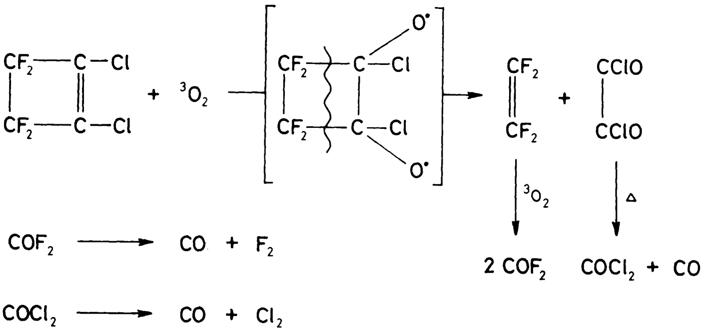
FIG. 2

The reaction progress of the laser photosensitized (10 W) decomposition of oxalyl fluoride with COF.COF (5·3 kPa)-O_2 (5·3 kPa)-SF_6 (5·3 kPa) mixture. The circles relate to COF.COF (●) and COF_2 (○). The dashed line corresponds to a quantitative conversion of COF.COF into COF_2

Reactivity of HFCB in the oxidation exceeds that of acyclic fluorinated olefins. The mean effective temperature[21] of the reacting olefin–SF_6–O_2 system (all 2·7 kPa, cell volume 140 cm^3, laser output 10 W) reaches 710 K (refs[6,7]). Regarding the reactivities of C_2F_4 and $CF_3CF : CF_2$ measured earlier[7], the observed total rate constant ratios $k_{HFCB} : k_{CFCl=CFCl} = 2{\cdot}13$ and $k_{HFCB} : k_{CF_2=CCl_2} = 1{\cdot}75$ (in 10 per cent error) show that HFCB react at $T = 717$ K with triplet oxygen about 1·9–2·1 times as rapidly as do C_2F_4 or $CF_3—CF{=}CF_2$.

1,2-*Dichloro*-3,3,4,4-*tetrafluorocyclobutene*

The cw CO_2 laser photosensitized oxidation of DCCB affords COF_2, C_2F_4, minor quantities of COCl.COCl, COFCl and $COCl_2$ and traces of SiF_4. The products and their amounts as the reaction progresses (Fig. 3) are in line with (Scheme 3), which is similar to Scheme 1 for HFCB.



SCHEME 3

Compared to the oxidation of HFCB, oxalyl halide COCl.COCl is produced in lower yields, which is apparently due to its easier decomposition into $COCl_2$ and CO. This, laser photosensitized decomposition of COCl.COCl was reported as occurring via molecular mechanism[22].

Decafluorocyclohexene

The cw CO_2 laser photosensitized oxidation of DFCH yields COF_2.COF.COF, CO, C_2F_4, HFCB and traces of SiF_4 and C_2H_6. For the interpretation of its reaction progress (Fig. 4), knowledge of the laser photosensitized decomposition of DFCH is useful.

The latter reaction of DFCH gives equal amounts of C_2F_4 and HFCB along with very small amounts of C_2F_6. These compounds were observed up to conversions almost 50 per cent with DFCH–SF_6 (both 5·3 kPa) mixture irradiated in 8·1 cm^3

cell with unfocussed beam (8 W output), or with DFCH–SF_6 (both 1 kPa) mixture irradiated in 100 cm^3 cell with focussed beam (12 W output). Hexafluoro-1,3-butadiene is, under the used conditions, transformed[7] into HFCB. The products thus prove that retro Diels–Alder reaction (RDA) of DFCH into C_2F_4 and nascent hexafluoro-1,3-butadiene occurs in our thermalized system, as it does under the conditions of the i.r. multiphoton-induced[23] and the pulsed laser sensitized (SF_6. ref.[24]) decomposition. Conventional thermal[25] decomposition of DFCH at 753 to 823 K produces perfluorinated 1-methylcyclopentene, 1,2-dimethylcyclopentene and mesitylene, while the UV irradiation in the presence of air affords[26,27] mainly perfluoromethylenecyclopentane. The difference between the products of the conventional and pulsed laser initiated process was taken as an evidence of a non-thermal nature of the latter due to a massive energy transfer between the sensitizer SF_6 and DFCH (ref.[24]). Our results show that RDA also ocuurs as a thermal reaction when heterogeneous, hot reactor effects are avoided. Similar reaction is in fact observed also under electron impact[28] when the major pathway for $C_6F_{10}^{\bullet +}$ is the extrusion of C_2F_4 to give $C_4F_6^{\bullet +}$.

The occurence of significant quantities of C_2F_4 and HFCB during the CO_2 laser photosensitized oxidation of DFCH proves that RDA of DFCH is important even in the presence of O_2. We can therefore assume that COF_2, COF.COF and CO are

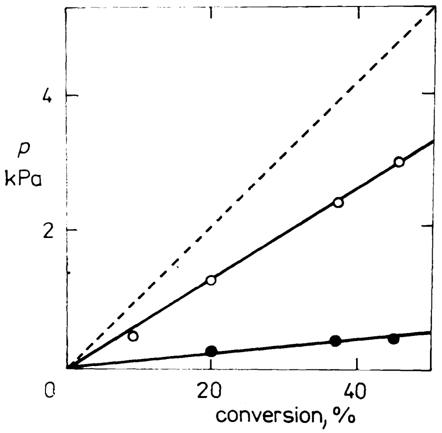


Fig. 3

The reaction progress of laser-photosensitized (15 W) oxidation of DCCB. The points relate to COF_2 (○) and COFCl (●)

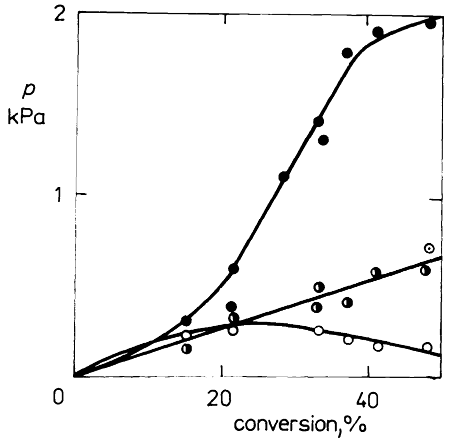
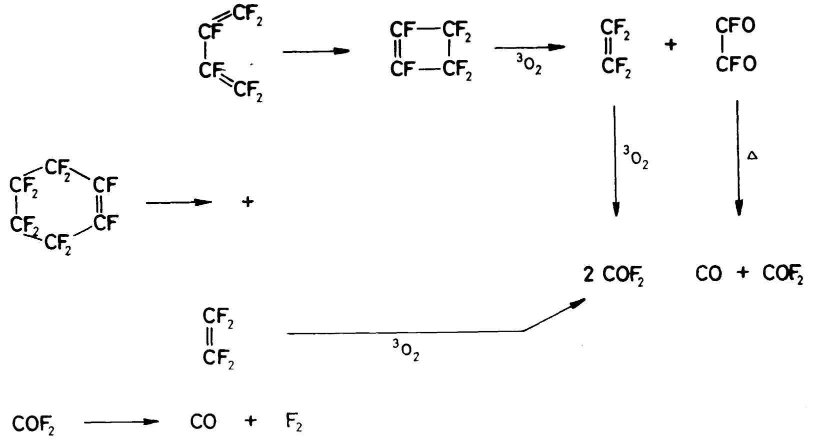


Fig. 4

The reaction progress of laser photosensitized (15 W) oxidation of DFCH with DFCH–O_2–SF_6 (all 5·3 kPa) mixtures. Designated products are COF_2 (●), COF.COF (○), C_2F_4 (⊙), and HFCB (◑)

formed by the reactions envisaged (Scheme 4) to take place during the oxidation of C_2F_4 (ref.[6]).



SCHEME 4

The gas-phase, truly homogeneous oxidation of perhalogenocycloalkenes appears to be a complex reaction. In the light of previous investigation of this oxidation of some acyclic haloalkenes[6,7] it seems probable that this reaction proceeds via cleavage of the CX—CF_2 (X = F, Cl) bonds of 1,2-dioxabicyclo[2,2,0]hexahalogenoalkane and represents a novel decomposition pathway for the class of [2,2,0]-hexanes that are known[29] to thermolyze via cyclohexene-1,4-diradical into dienes. Time resolved spectra of the oxidation of HFCB initiated with pulsed IR laser radiation together with theoretical treatment of this reaction might help to obtain more information and get here forwarded interpretation on firmer grounds.

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