CONTINUOUS WAVE CO_2 LASER DRIVEN OXIDATION OF 2-BUTENE AND 2-OCTAFLUOROBUTENE

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Dedicated to late Academician Eduard Hála.

CW CO_2 laser induced reactions of 2-butene and 2-octafluorobutene with molecular ground state $^3O_2$ oxygen in the presence of sulfur hexafluoride afford products that can be rationalized by means of the earlier proposed mechanism involving transient dioxetane and its cleavage into carbonyl compounds.

Laser induced chemistry continues to attract much attention, more studies being directed to chemical reactions driven by short pulses of radiation. Chemistry using continuous-wave lasers represents only lesser part of the reserach field, but has a significant potential for inducing novel reacton pathways in the gas-phase[1].

One of the gas phase reactions that change dramatically their course upon the laser inducement is the oxidation of perhaloolefins with ground state molecular oxygen. Normal oxidation of these compounds in hot-wall reactors is sensitive to reactor material, proceeds via multitude of reaction steps involving carbenes and is of complex nature[2,3]. Conversely to this, continuous-wave CO_2 laser photosensitized (SF_6) oxidation of tetrafluoroethene with $^3O_2$ proceeds under wall-less conditions via an intermediary dioxetane to yield solely carbonyl fluoride[4,5]. Such a mechanism involving a non-concerted addition of $^3O_2$ to double bond, and an intermediary formation of dioxetane that further decomposes into two carbonyl halides has also been postulated (Scheme 1, ref.[6]) in the laser-powered oxidation of unsymmetrical $ClF : CF_2$, $CF_3CF : CF_2$, $Cl_2C : CF_2$ and $ClFC : CFCl$ compounds.
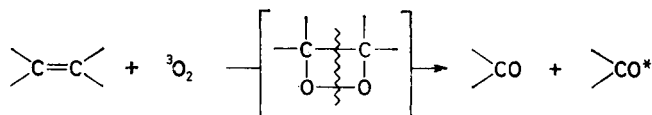
SCHEME 1

The postulated dioxetane mechanism gets support from the time-resolved emission spectra of the TEA CO_2 laser oxidation of tetrafluoroethene with molecular oxygen and represents a faster reaction compared to the oxidation of transiently formed difluorocarbene[7].

Herein we wish to report on the continuous-wave CO_2 laser photosensitized (SF_6) reaction of 2-butene and 2-octafluorobutene with ground state molecular oxygen. We show that not only perfluorinated but also perhydrogenated olefin react with oxygen in a specific way and that both reaction progresses can be explained by the earlier proposed[4-6] dioxetane mechanism.

EXPERIMENTAL

The oxidation of 2-butene and 2-octafluorobutene was carried out by irradiation of olefin–O_2– SF_6 mixtures in stainless steel cells of 3·6 inner diameter and 1·4 or 10·5 cm path lengths fitted with a valve and NaCl windows. The mixtures were prepared by using standard vacuum-line technique. A cw CO_2 laser operated at the $P(20)$ line of the $00^01 \rightarrow 10^00$ transition (944·19 cm^{-1}), the wavelength was checked by a 16-A model spectrum analyser (Optical Eng. Co.) and the output measured with a power meter (Physical Institute, Prague). The laser beam was unfocussed with a diameter restricted to 2 cm. The mixtures 2-C_4H_8 (2·4 kPa)–O_2 (5·3 kPa)–SF_6 (2·7 kPa) in the 10·5 cm long cell and 2-C_4F_8 (2 kPa)–O_2 (2·7—5·3 kPa)–SF_6 (0·7 kPa) in the 1·4 cm long cell were irradiated at measured intervals and the progress in the oxidation was monitored by scanning the i.r. spectra at 600—4 000 cm^{-1} on a Perkin–Elmer-model 621 i.r. spectrometer. Both the depletion of olefins (2-C_4H_8 at 1 400 cm^{-1}, 2-C_4F_8 at 890 and 1 280 cm^{-1}) and the increase in concentration of the products of the oxidation, (methane (1 300 cm^{-1}), carbon monoxide (2 160 cm^{-1}), carbonyl fluoride (1 945 cm^{-1}), trifluoroacetyl fluoride (1 890 cm^{-1}), acetylaldehyde (1 740 cm^{-1}) and tetrafluoroethene (1 190 cm^{-1}), were followed by means of characteristic absorption bands of these compounds. The absorption coefficients were ascertained by measuring the spectra of pure samples. The identification of the reaction products was also performed with a QP 1 000 GC-MS Shimadzu spectrometer.

2-Octafluorobutene (PCR), 2-butene, sulfur hexafluoride (both Fluka) and oxygen (Technoplyn) were commercial samples.

RESULTS AND DISCUSSION

2-Butene and 2-octafluorobutene are representatives of perfluorinated and perhydrogenated olefins whose mechanisms of conventional oxidation significantly differ. The results on their laser photosensitized oxidation are therefore presented separately.

2-Octafluorobutene

The cw CO_2 laser powered oxidation of 2-octafluorobutene yields carbonyl fluoride, trifluoroacetyl fluoride and tetrafluoroethene. Only traces of tetrafluorosilane and carbon monoxide were observed as well. Normal thermal oxidation of 2-octafluoro-

butene in the gas-phase has not been studied and the laser powered reaction can thus be compared to only Hg-sensitized oxidation[8] which yields trifluoroacetyl fluoride as a primary and trifluoromethyl fluoroformate as a secondary product./We note that in the laser powered reaction the relative quantities of all compounds are not affected with reaction progress. Typical progress of the oxidation, seen in Fig. 1, is consistent with the simple reaction scheme (Eqs (A) and (B))

$$CF_3CF : CFCF_3 + {}^3O_2 \rightarrow 2\,CF_3CFO, \qquad (A)$$

$$CF_3CFO \rightarrow COF_2 + 1/2\,C_2F_4 \qquad (B)$$
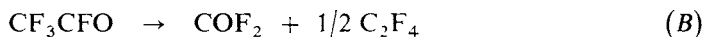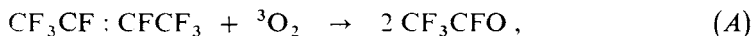
which is quite in line with our previous observations on the laser photosensitized oxidation of other perhaloolefins[4−7]. We can assume that the laser driven oxidation of 2-octafluorobutene proceeds via transient dioxetane that cleaves into two molecules of trifluoroacetyl fluoride. The formation of carbonyl fluoride and tetrafluoroethene can be explained by the decomposition of energized trifluoroacetyl fluoride into these compounds, since such a reaction in the presence of SF_6 and upon the CO_2 laser irradiation was earlier observed[9]. The absence of other products as poly-
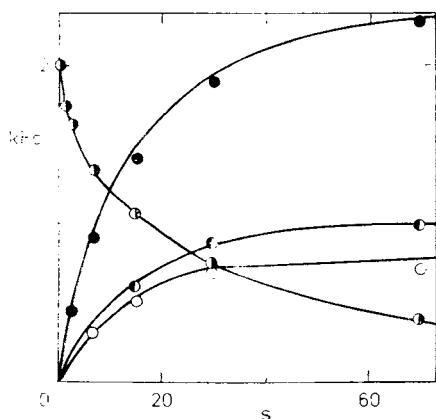
Fig. 1

The reaction progress of the laser powered (20 W) oxidation of 2-octafluorobutene with $CF_3CF : CFCF_3$ (2 kPa)–O_2 (5·3 kPa)–SF_6 (0·7 kPa) mixture. The compounds designated are $CF_3CF : CFCF_3$ (◑), COF_2 (●), CF_3COF (◯), and C_2F_4 (◐)

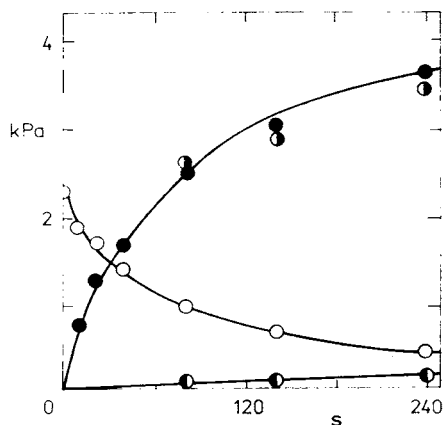Fig. 2

The reaction progress of the laser powered (20 W) oxidation of 2-butene with $CH_3CH : CHCH_3$ (2·4 kPa)–O_2 (5·3 kPa)–SF_6 (2·7 kPa) mixture. The compounds designated are $CH_3CH : CHCH_3$ (◯), CH_4 (●), CO (◑) and CH_3CHO (◐)

(oxyfluoromethylene) compounds or those arising from carbene species so typical for surface-assisted oxidation of tetrafluoroethene or hexafluoropropene (see e.g. refs[10,11]) is supportive of this interpretation.

2-Butene

The oxidation of alkenes by $^3O_2$ molecular oxygen is termed autoxidation which is best explained as a free-radical chain reaction involving attack of the initiating radical at either allylic hydrogen (abstraction) or double bond (addition). Such an oxidation of 2-butene is reported[12-14] to lead to variety of products as hydrocarbons (CH_4, C_2H_6, C_2H_2) methanol, aldehydes, acetic acid, carbon dioxide, ketones and epoxybutanes. During the induction period acetaldehyde is the main product and thereafter large quantities of other products are formed as well, methane and carbon monoxide being subsequently consumed[14]. It can be assumed that he oxidation of acetaldehyde that acts as the degenerate branching agent is important and masks the initial butene oxidation. Of a few mechanisms proposed[12-17], none can adequately treat all the data obtained with several research groups. Moreover, it can be surmised that the gas-phase oxidation can proceed via heterogeneous routes[14], which may also be suggested on the basis of the very well-known metal catalysis of this reaction. The last facts spurred our examination of the cw CO_2 laser photosensitized (SF_6) oxidation of 2-butene, since the laser technique obviates heterogeneous stages.

The laser powered homogeneous oxidation of 2-butene yields, surprisingly, only methane and carbon monoxide along with very little amounts of acetaldehyde and traces of ethene and ethine. Interestingly and conversely to the normal reaction, methane and carbon monoxide are not consumed during the reaction progress, but they steadily increase. Typical reaction progress is seen in Fig. 2. Acetaldehyde is known[18] to undergo thermal decomposition into CO and CH_4 and the results thus seem to be consistent with the very simple scheme (Eqs (C) and (D))

$$CH_3CH : CHCH_3 + {}^3O_2 \rightarrow 2\,CH_3CHO \qquad (C)$$

$$CH_3CHO \rightarrow CH_4 + CO \qquad (D)$$
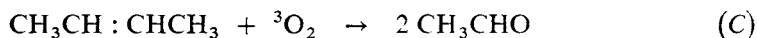
which can indicate that a non-concerted addition of molecular oxygen across the double bond and further intermediary dioxetane cleavage into two carbonyl compounds are operative, similarly as was postulated by us previously with the oxidation of alkenes without hydrogen. The reaction itself deserves more detailed examination which can answer whether this quite novel and unique reaction mechanism really operates and whether it is a consequence of the elimination of hot-wall assistance.

More study related to different hydrogenated olefins is in progress.

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Translated by the author (J.P.)