CO_2 Transverse Excitation Laser Induced Photochemical Enrichment of Carbon Isotopes

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Summary CO_2 transverse excitation laser photolysis of mixtures of Cl_2CF_2 with O_2, NO, and $Me_2C{=}CH_2$ is isotopically selective for carbon and experimental evidence indicates that the reaction may involve a laser produced difluorocarbene intermediate.

TABLE

System	Reactants (mmol taken), β_u[a]	Irradiation time/h	Principal products (mmol recovered), β[a]
I	Cl_2CF_2(0·112), 24; O_2(0·40)	6	COF_2(0·099), 0·221[b], $(ClCF_2)_2$(0·002), 0·32[c], Cl_2(0·107)
II	Cl_2CF_2(0·112), 7·2; NO(0·334)	4	C_2F_4(0·021), 0·126,[d] COF_2(0·052), 0·76,[b] ClCFO(0·0049), NOCl,[e] $(ClCF_2)_2$[e]
III	Cl_2CF_2(0·112), 4·1; $Me_2C{=}CH_2$ (0·336)	5	C_2F_4(0·03), 0·379[d] + complex array of other products.
IV	Cl_2CF_2(0·112); HCl(0·224)	4	HCF_2Cl(0·010) β,[e] $(ClCF_2)_2$(0·023) β,[e] Cl_2(0·0648)

[a] The enrichment factor β is defined as R/R_0 where R_0 is the normal $^{13}C/^{12}C$ isotope ratio and R is the isotope ratio after photolysis (*cf.* ref. 2). β_u determined for unconsumed Cl_2CF_2. R_0 values determined from measurements at quoted m/e positions are: CO_2(0·0116) Cl_2CF_2 (0·0105), $(ClCF_2)_2$ (0·0107), C_2F_4 (0·0108). [b] Determined as CO_2 at m/e 44,45. [c] Determined at m/e 135,136. [d] Determined at m/e 100,101. [e] Not determined.

SEVERAL groups have previously reported on the CO_2 laser photolysis of gaseous Cl_2CF_2.[1,2] In one case,[2] carbon isotopic perturbations were noted in samples subjected to high energy pulses from a CO_2 transverse excitation (TE) laser. We have studied the CO_2 TE laser photolyses of Cl_2CF_2 with several reagents and have observed substantial carbon isotope enrichments. Evidence for the participation of a reactive intermediate, difluorocarbene is presented.

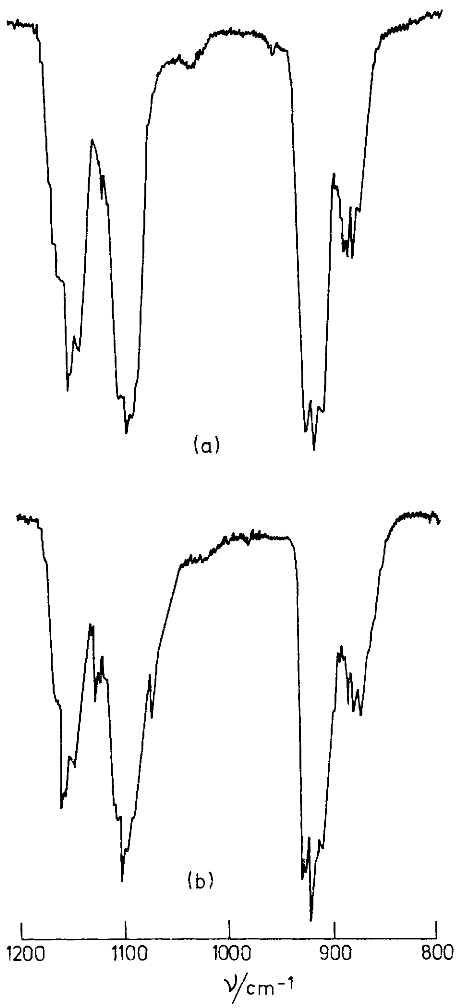

FIGURE. I.r. spectra at pressures of *ca.* 10 Torr (1333 Pa). Path length of 5 cm. (a) Cl_2CF_2 prior to laser photolysis. (b) Cl_2CF_2 recovered after laser photolysis in the presence of O_2.

The typical reaction mixtures (described in the Table) were contained in a 1 l stainless steel cell fitted with NaCl windows and photolysed with focussed 929 cm^{-1} P(36) radiation from a CO_2 TE laser (300 ns wide, 0·20 J/pulse at 2 p.p.s.).

Chlorine was removed by treatment of the crude reaction mixtures with Hg at 25 °C. Residual gases were subjected to g.l.c. (10 m, 20% squalane on firebrick). COF_2-containing mixtures were passed over uncoated firebrick to effect a quantitative $COF_2 \rightarrow CO_2$ conversion, in order to avoid this same conversion by firebrick support within the g.l.c. column. Separated components were identified by i.r. and isotope ratios were determined by mass spectroscopy with typical standard deviations of $< 3\%$. Estimates of the halogenocarbon product recoveries were made from g.l.c. peak area measurements, assuming equivalent TC detector response for all compounds. Other, generally less volatile materials, in amounts too small for identification, were noted in all of these reactions.

The enrichment factors (β) for the products of system I indicate depletion in ^{13}C while the analysis of unconsumed Cl_2CF_2 indicate its ^{13}C content (measured at m/e 101,102) to have changed from an initial 1% to 20% ($\beta_u = 24$). This alteration in ^{13}C content is sufficient for the i.r. spectrum of the recovered material to show two new bands at 1131 and 1077 cm^{-1} (Figure). Experiments performed under similar conditions using the R(18) (1077 cm^{-1}) line of the TE laser resulted in recovered Cl_2CF_2 which was depleted in ^{13}C giving $\beta_u = 0{\cdot}75$. Thus the results of the isotopically selective reactions support the assignment of the 1077 and 929 cm^{-1} absorptions to ^{13}C and ^{12}C species of the Cl_2CF_2, respectively. For systems II and III unconsumed Cl_2CF_2 enriched in ^{13}C ($\beta_u = 7{\cdot}2$ and 4·1, respectively) was recovered.

The reaction of thermally produced $:CF_2$ with O_2 is reported to give COF_2.[3] Tetrafluoroethylene has also been reported as a product from reactions which involve $:CF_2$.[4] The appearance of ^{12}C enriched COF_2 from system I and ^{12}C enriched C_2F_4 from systems II and III constitutes evidence for the laser induced, isotopically selective formation of difluorocarbene ($:CF_2$). Difluorocarbene is also implicated in the formation of HCF_2Cl from reactions with HCl (system IV).[3] Tetrafluoroethylene is not observed in the HCl and O_2 systems. This may be due in part to a reaction between Cl_2 and C_2F_4. In independent experiments we have found that Cl_2 (0·8 Torr) and C_2F_4(4 Torr) undergo reaction in the dark, at 25 °C, in the stainless steel cell to yield $(ClCF_2)_2$ (85% of the Cl_2 consumed in 4 h). Moreover, when Cl_2CF_2 is irradiated in the presence of NO or an olefin, both of which readily react with chlorine, then C_2F_4 is observed among the reaction products. Lyman and

Rockwood[2] also have observed C_2F_4 from the laser photodissociation of Cl_2CF_2.

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