# Gas Phase Fluorination of $CO_2$ by $SF_6$

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*Summary* Quantitative fluorination of $CO_2$ to $CF_2O$ is achieved by laser induced breakdown in $SF_6$–$CO_2$ mixtures.

FORMATION of carbonyl fluoride, $CF_2O$, from CO or $CO_2$ requires extreme conditions and is achieved with relatively low yields. The high temperature reaction of $SF_4$ with

$CO_2$ gives only 10% of $CF_2O$ with $CF_4$ being the main carbon-bearing product.[1] Better yields (*ca.* 45%) of $CF_2O$ are obtained during the electrolysis of carbon monoxide in liquid hydrofluoric acid, HF.[2] Other products in this method are $CF_4$ (26%), $CF_3OF$ (5%), and $CO_2$ (23%).

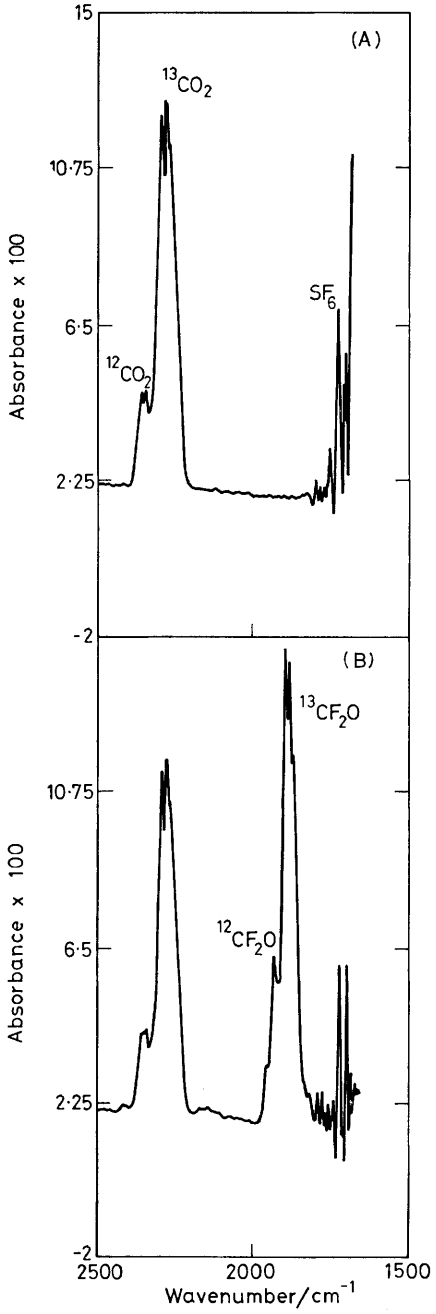


FIGURE. I.r. spectral traces in the ν(CO) region of a $CO_2$–$SF_6$ mixture. (A) Before irradiation. (B) After a small fraction of the $CO_2$ has reacted.

Direct fluorination of $CO_2$ gives $CF_2(OF)_2$ as the dominant product.[3] We report here a laser-based process which quantitatively converts $CO_2$ into $CF_2O$ with no detectable carbon-bearing side products. The method involves plasma breakdown in $CO_2$–$SF_6$ mixtures at pressures in the 10—50 Torr range. The only other products detected were $SO_2F_2$, and $SiF_4$ which is presumably formed by interaction with the glass walls of the cell used. The overall equation of reaction can be written as in equation (1) but we have not

$$SF_6 + 2CO_2 \rightarrow 2CF_2O + SO_2F_2 \quad (1)$$

determined a formal stoicheiometry.

All irradiations were performed with a line-tunable TEA $CO_2$-laser (Lumonics Research Limited model 103) using the P(20) line of the 10·6 μm band which is very strongly absorbed by $SF_6$. The mixture was contained in a 10 cm long, 2·4 cm diameter cell with the beam focussed at the centre of the cell by a 7·5 cm focal length germanium lens. The beam was apertured to 1·4 cm, incident pulse energies were 4—6 J at a repetition rate of 0·7 Hz.

Analysis of the reaction mixture was achieved by i.r. spectroscopy on a Digilab FTS-11 Fourier Transform spectrometer equipped with a mercury–cadmium telluride detector. Interferograms were collected with an optical retardation of 0·25 cm$^{-1}$ apodized with a triangular function and transformed to yield a resolution of 4 cm$^{-1}$. Spectra of the products were isolated by subtracting the spectrum of the starting material from the irradiated mixture, and intensities were calibrated with known samples.

In a typical experiment $CO_2$ (3·8 Torr) and $SF_6$ (4 Torr) were introduced into the i.r. cell and after four freeze–pump–thaw cycles, the gas mixture was irradiated. After 10 pulses (all giving rise to plasma breakdown resulting in total absorption of the incident energy) 93·5% of the $SF_6$ was decomposed and only traces of $CO_2$ were still present. Similar behaviour was noted for higher pressure mixtures although as the pressure was increased more pulses were necessary, for example at 10 Torr of $SF_6$ and 10 Torr of $CO_2$, 200 pulses were required to decompose all the $SF_6$. Prolonged irradiation after the $SF_6$ is decomposed leads to a steady (slow) decline in the $CF_2O$ content with an apparent regrowth in the $CO_2$. Within the precision of our experiments, the $CO_2$ is quantitatively transformed into $CF_2O$ but to achieve this it is necessary to have an excess (>2 : 1) of $SF_6$ to obviate the laser-induced back reaction.

The integrity of the method is shown by the data in the Figure. Figure (A) shows the spectrum before irradiation where $CO_2$ (90% $^{13}C$) and $SF_6$ are mixed. Figure (B) shows the composition of the mixture after a small fraction of the $CO_2$ has reacted. The isotopic composition of the $CF_2O$ product exactly matches the initial composition of the $CO_2$ substrate.

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[1] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, 1960, **82**, 543.
[2] T. Nagase, H. Baba, and T. Abe, Jap. Patent 7,026,611, 1970.
[3] R. L. Cauble and G. H. Cady, *J. Am. Chem. Soc.*, 1967, **89**, 1962; F. A. Hohorst and J. M. Shreeve, *ibid.*, p. 1809.