A Molecular Source of $CF_2(\tilde{X})$ at Room Temperature

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In the molecular system of F_2 and C_3O_2 a fast formation of $CF_2(\tilde{X})$ was detected directly via LIF. The $CF_2(\tilde{X})$ production mechanism could be a single step process but also however a chain reaction via F atoms.

The $CF_2(\tilde{X})$ radical is of importance in several systems like stratospheric photo-chemistry [1] and in plasma etching [2]. The difluorocarbene is an interesting molecule due to its singlet electronic ground state and low reactivity.

The sources for CF_2 at high temperatures e.g. in shock tube experiments are the decomposition of C_2F_4. Also at low temperatures in flow reactors the pyrolysis e.g. of $CF_3H \rightarrow CF_2 + HF$ $(T = 1370\ \text{K})$ is used as a $CF_2(\tilde{X})$ source. Other possibilities to produce $CF_2(\tilde{X})$ are photodissociation of precursor molecules like CF_2Cl_2 [3], or the IR-multiphonon dissociation of CF_2HCl [1], or the radiofrequency discharge [4, 5], or microwave discharge of CF_2Br_2 [6].

All these methods have the disadvantage that other active species are formed, which can influence the kinetic system and create problems, in particular since the reactivity of $CF_2(\tilde{X})$ is low.

In this communication a new CF_2 source is described, which circumvents these problems. The reaction

$$F_2 + C_3O_2 \rightarrow \text{products} \qquad (1)$$

was studied in an isothermal flow reactor with laser induced fluorescence (LIF) detection. The LIF device consisting of a tunable dye laser (Lambda Physik LPD) pumped by the third harmonic of a Nd: YAG laser (Spectra Physics GCR3) was used as described in detail in [7].

The C_3O_2 was produced in the reaction of bis(trimethylsilyl)malonate ($C_9H_{20}O_4Si_2 > 98\%$ Fluka) with P_4O_{10} (purum Fluka) and cleaned by trap-to-trap distillation [8]. The F_2 which was applied as a He/F_2 mixture (5% F_2/He) (purity $He > 99.9999\%$) had a purity of $F_2 \geq 99.9\%$.

The molecular reaction $F_2 + C_3O_2$ was studied at a temperature of $T = 298$ K and in the pressure range $3 \leq p/\text{mbar} \leq 10$ using He as the main carrier gas. The production of $CF_2(\tilde{X})$ was observed directly by LIF. The typical $CF_2(\tilde{A}-\tilde{X})$ excitation spectrum in the wavelength range $260 \leq \lambda/\text{nm} \leq 262.5$ was observed.

The concentration of C_3O_2 was in the range $4 \leq [C_3O_2]_0 \cdot 10^{-12}\ \text{mol cm}^{-3} \leq 20$ and the F_2 in the range $2 \leq [F_2]_0 \cdot 10^{-10}/\text{mol cm}^{-3} \leq 10$. The reaction of F_2 molecules with C_3O_2 molecules is fast and produces $CF_2(\tilde{X})$. Large amounts of $CF_2(\tilde{X})$ were obtained even at very short reaction times in the order of ms.

The reaction

$$C_3O_2(\tilde{X}) + F_2(X) \rightarrow CF_2(\tilde{X}) + 2\,CO(X), \qquad (2).$$

which could be responsible for the $CF_2(\tilde{X})$ production, is exothermic with $\Delta_R H = -334\ \text{kJ/mol}$.

This radical source has three advantages over former ways to produce $CF_2(\tilde{X})$:

(i) large amounts of $CF_2(\tilde{X})$ can be produced,
(ii) no further reactive species are present in the system,
(iii) an absolute calibration of $[CF_2(\tilde{X})]$ is possible since both reactants are stable, can be calibrated without difficulties, and can be applied in large excess; either $[C_3O_2] \gg [F_2]_0$ or $[C_3O_2]_0 \ll [F_2]$.

Further kinetic studies to determine k_1, $k_1(T)$ and the reaction mechanism of this interesting molecular reaction are under way.

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