

A Molecular Source of $\text{CF}_2(\tilde{\text{X}})$ at Room Temperature

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In the molecular system of F_2 and C_3O_2 a fast formation of $\text{CF}_2(\tilde{\text{X}})$ was detected directly via LIF. The $\text{CF}_2(\tilde{\text{X}})$ production mechanism could be a single step process but also however a chain reaction via F atoms.

The $\text{CF}_2(\tilde{\text{X}})$ 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 $\text{CF}_3\text{H} \rightarrow \text{CF}_2 + \text{HF}$ ($T = 1370 \text{ K}$) is used as a $\text{CF}_2(\tilde{\text{X}})$ source. Other possibilities to produce $\text{CF}_2(\tilde{\text{X}})$ 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 $\text{CF}_2(\tilde{\text{X}})$ is low.

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



was studied in an isothermal flow reactor with laser induced fluorescence (LIF) detection. The LIF device

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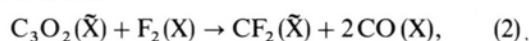
consisting of a tunable dye laser (Lambda Physik LPD) pumped by the third harmonic of a Nd: YAG laser (Spectra Physics GCR3) was used as described in detail in [7].

The C_3O_2 was produced in the reaction of bis(trimethylsilyl)malonate ($\text{C}_9\text{H}_{20}\text{O}_4\text{Si}_2 > 98\%$ 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 $\text{F}_2 \geq 99.9\%$.

The molecular reaction $\text{F}_2 + \text{C}_3\text{O}_2$ was studied at a temperature of $T = 298 \text{ K}$ and in the pressure range $3 \leq p/\text{mbar} \leq 10$ using He as the main carrier gas. The production of $\text{CF}_2(\tilde{\text{X}})$ was observed directly by LIF. The typical $\text{CF}_2(\tilde{\text{A}} - \tilde{\text{X}})$ 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 $4 \leq [\text{C}_3\text{O}_2]_0 \cdot 10^{-12} \text{ mol cm}^{-3} \leq 20$ and the F_2 in the range $2 \leq [\text{F}_2]_0 \cdot 10^{-10} / \text{mol cm}^{-3} \leq 10$. The reaction of F_2 molecules with C_3O_2 molecules is fast and produces $\text{CF}_2(\tilde{\text{X}})$. Large amounts of $\text{CF}_2(\tilde{\text{X}})$ were obtained even at very short reaction times in the order of ms.

The reaction



which could be responsible for the $\text{CF}_2(\tilde{\text{X}})$ production, is exothermic with $\Delta_R H = -334 \text{ kJ/mol}$.

This radical source has three advantages over former ways to produce $\text{CF}_2(\tilde{\text{X}})$:

- (i) large amounts of $\text{CF}_2(\tilde{\text{X}})$ can be produced,
- (ii) no further reactive species are present in the system,
- (iii) an absolute calibration of $[\text{CF}_2(\tilde{\text{X}})]$ is possible since both reactants are stable, can be calibrated without difficulties, and can be applied in large excess; either $[\text{C}_3\text{O}_2] \gg [\text{F}_2]_0$ or $[\text{C}_3\text{O}_2]_0 \ll [\text{F}_2]$.

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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