

Photolysis of CO₂ with 158 nm (F₂) Laser. Reactivity of O (¹D) with CH₄, CF₃H, and CF₃CH₃

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Electronically excited oxygen atom O (¹D), generated by photolysis of CO₂ with a 158 nm (F₂) laser, reacts with CH₄, CF₃H, and CF₃CH₃ to give corresponding vibrationally excited alcohols (ROH*) by insertion into the C-H bonds, which collapse to vibrationally relaxed alcohols or alkyl and hydroxy radical pairs depending on the stability and lifetime of ROH*.

Photolysis of CO₂ with vacuum-ultraviolet (VUV) lights between 120 and 167 nm has been demonstrated to give O (¹D) as a major primary photoproduct, together with O (³P) as a spin-forbidden product [the quantum yield for producing O (³P) = 0.06].¹⁻⁵ However, few photochemical reactions of CO₂ with hydrocarbons using VUV lights have been investigated until now.⁵ In this paper we report that O (¹D), generated by photolysis of CO₂ with a 158 nm (F₂) laser, undergoes insertion into the C-H bonds of CH₄ (**1a**), CF₃H (**1b**), and CF₃CH₃ (**1c**) to give corresponding vibrationally excited alcohols as an initial product, but not to produce alkyl and hydroxy radical pairs by abstraction of hydrogen atom.

Irradiation of **1a**/CO₂ = 1/1 mixtures (total pressure: 200 Torr, 1 Torr = 133.322 Pa) in a cylindrical reaction cell (20 mm inner diameter x 8 cm) with 158-nm laser pulses (40 mJ/pulse, 20 ns of FWHM, and 10 Hz) from an F₂ laser (Lambda Physik LPF 205) through a MgF₂ window (diameter: 2.5 cm) gave ethane (**2a**), methanol (**3a**), and propane as major products. The amounts of **2a** and propane increased approximately in proportion to the irradiation time; however, **3a** was unstable under the conditions above owing to its absorption of 158-nm light much stronger than CO₂. As shown in Fig. 1, **2a** was a predominant product, while irradiation of **1b**/CO₂ mixtures under the similar conditions gave carbonyl fluoride (COF₂, **4**) exclusively and hexafluoroethane (**2b**) was not produced at all. It has been considered that trifluoromethanol (CF₃OH) is incapable of existence because compounds with a fluorine atom in an α position to a hydroxy group would eliminate hydrogen fluoride easily.⁶ Therefore, production of **4** without forming **2b** shows that O (¹D) generated by photodissociation of CO₂ with a 158-nm laser pulse undergoes insertion into the C-H bond of **1b** to give vibrationally excited (hot) alcohol (**3b***) selectively, but not H abstraction to give CF₃• and •OH radicals. In the case of **1c**, 2,2,2-trifluoroethanol (**3c**) was produced predominantly, contrast to the reaction of **1a** with O (¹D): the amount of **3c** produced after 900 laser pulses increases linearly in the pressure range of **1c**

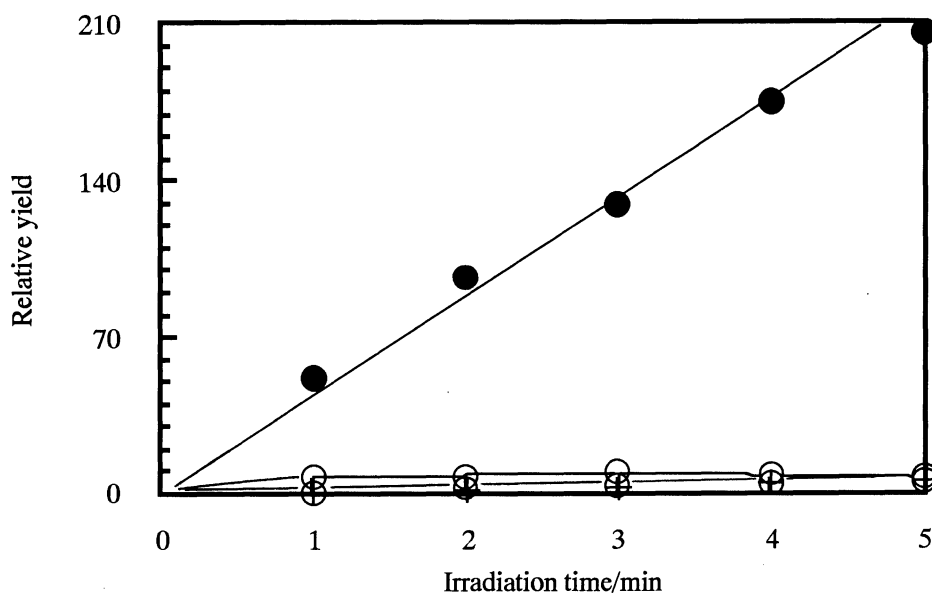


Fig. 1. Relative yields of **2a** (●), **3a** (○), and propane (⊕) vs. irradiation time.

between 30 and 900 Torr at the constant pressure (30 Torr) of CO₂ (Fig. 2). Under the conditions employed further decomposition of **3c** was negligible. Furthermore, at the initial pressure of **1c** less than 100 Torr, several unknown products were observed on GC analysis; however, their formation was suppressed at the initial pressure of **1c** higher than 200 Torr.⁷⁾

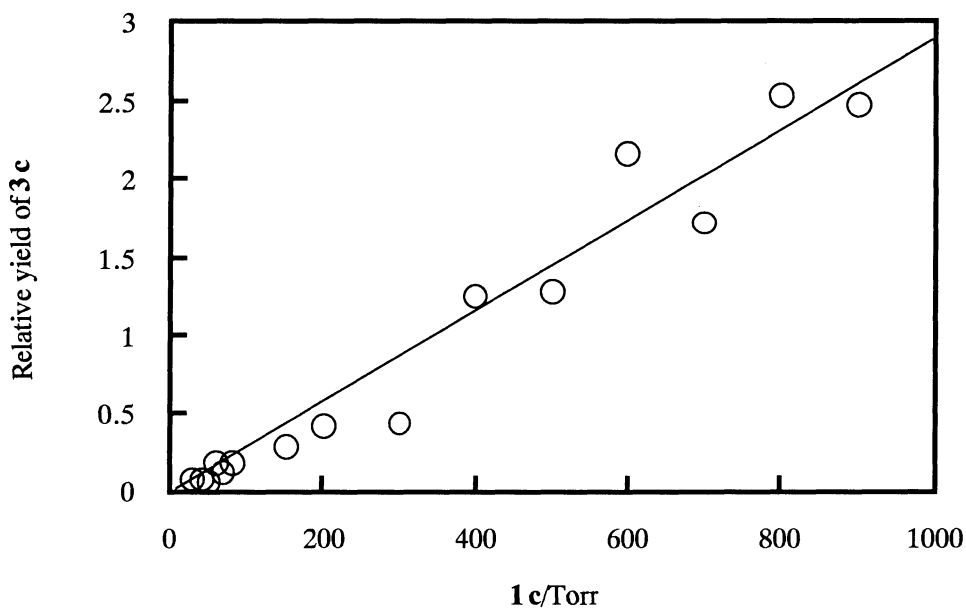
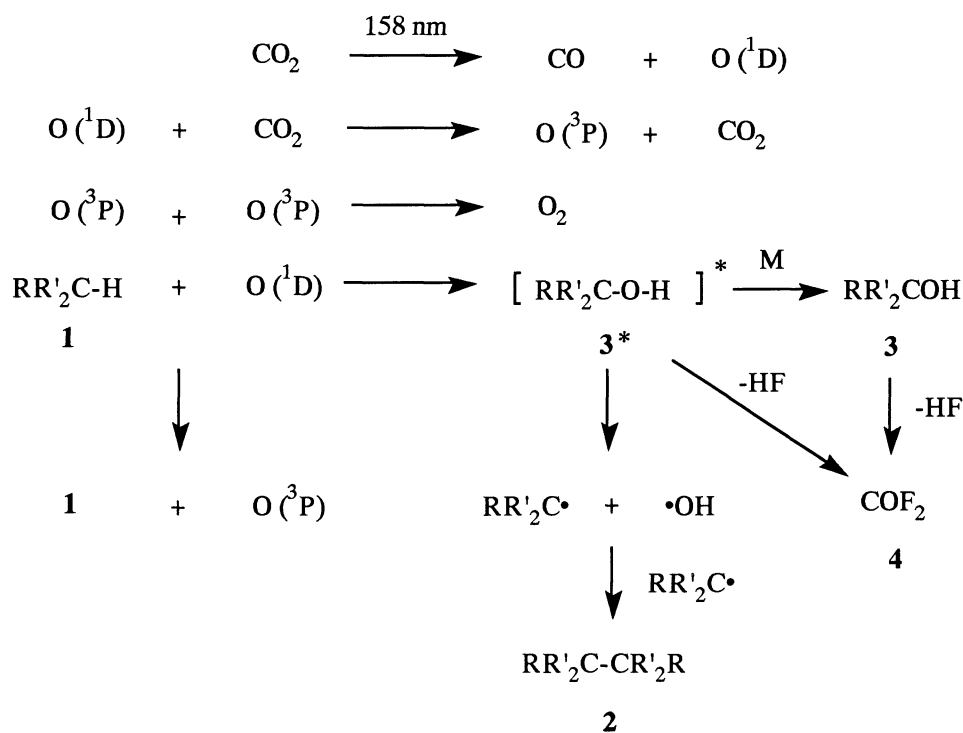


Fig. 2. Dependence of yield of **3c** produced after 900 laser pulses on the initial pressure of **1c**.

As showed in Scheme 1, it has been recognized that some amount of $O(^1D)$ is quenched efficiently by CO_2 to generate $O(^3P)$ under the conditions employed above.²⁾ Recently, Warren et al. also reported that halogenated hydrocarbons can quench $O(^1D)$ to $O(^3P)$.⁸⁾ However, $O(^3P)$ does not undergo insertion to the C-H bond of **1** to give hot alcohol **3*** because of the triplet spin; therefore, most of $O(^3P)$ would collapse to triplet oxygen molecule through the combination with another $O(^3P)$.²⁾ Based on the present results, it is reasonably elucidated that the primary reaction process of $O(^1D)$ with fluorohydrocarbons (**1**) is insertion to the C-H bond of **1** (Scheme 1), but not H abstraction, to yield hot alcohols **3***, which relax to cold alcohols **3** releasing the excess vibrational energy by collision with hydrocarbons and CO_2 (M). If **3*** produced is not sufficiently stabilized by collision, **3*** readily decomposes to alkyl and hydroxy radicals, finally giving dimerization products **2** as reported in the cases of **1a** and other simple paraffins such as ethane and propane etc.⁹⁻¹⁷⁾

The lifetime of hot molecule (τ) is defined here as the inverse of the dissociation rate constant (k_d) of hot molecule at a fixed internal energy. The k_d is called a specific rate constant and can be estimated by an unimolecular reaction theory.¹⁸⁾ At a fixed energy, $\tau (= 1/k_d) = h\rho^*/W$, where h is Planck constant, ρ^* is the state density, and W is the sum of the reaction routes (or the open channels). Introduction of the C-F bonds which have low vibrational energies (CF stretching mode, $\approx 1140\text{ cm}^{-1}$) is expected to make the lifetimes of hot molecules longer, because ρ^* increases more greatly than W by effect of the low vibration modes of the C-F bonds. Actually, it has been demonstrated that the lifetime of hot fluorotoluene ($CH_3C_6F_5$, $\tau_F = 1300\text{ ns}$) is 2.6 times as long as that of hot toluene ($\tau_H = 500\text{ ns}$) with an internal energy of $\approx 630\text{ kJ/mol}$.¹⁹⁾ It is



Scheme 1. **1a**: $R=R'=H$; **1b**: $R=R'=F$; **1c**: $R=CF_3$, $R'=H$

consistent with the vibrational frequency of the C-F bond lower than that of the C-H bond (CH stretching mode, $\approx 2900\text{ cm}^{-1}$). It would be similarly elucidated by an increase of the state density ρ^* that the lifetimes of hot alcohols increase with the number of carbon atoms in paraffin molecules; for example, ca. 0.01 ns for the hot propyl alcohol and 4 ns for the hot neopentyl alcohol.⁸⁾ It is no doubt that **3c*** has a lifetime longer than **3a*** and hot ethanol ($\text{CH}_3\text{CH}_2\text{OH}^*$).

Further investigation concerning the substitution effect of a C-F for C-H bond on products and quantitative analysis is now in progress.

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