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Photolysis of CO_2 with 158 nm (F_2) Laser. Reactivity of O (^1D) with CH_4, CF_3H, and CF_3CH_3

Masanobu KOJIMA,* Yuichi OJIMA,† Nobuaki NAKASHIMA,*,†† Yasukazu IZAWA,††
Toru AKANO,††† and Chiyoe YAMANAKA†
Faculty of Liberal Arts, Shinshu University, Asahi 3-1-1, Matsumoto, Nagano 390
†Institute for Laser Technology, Yamada-Oka, Suita, Osaka 565
††Institute of Laser Engineering, Osaka University, Yamada-Oka, Suita, Osaka 565
†††Technical Research Center, Kansai Electric Power Co. Ltd., Amagasaki, Hyogo 661

Electronically excited oxygen atom O (^1D), generated by photolysis of CO_2 with a 158 nm (F_2) laser, reacts with CH_4, CF_3H, and CF_3CH_3 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 CO_2 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 CO_2 with hydrocarbons using VUV lights have been investigated until now.$^{5)}$ In this paper we report that O (^1D), generated by photolysis of CO_2 with a 158 nm (F_2) laser, undergoes insertion into the C-H bonds of CH_4 (**1a**), CF_3H (**1b**), and CF_3CH_3 (**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**/CO_2 = 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 F_2 laser (Lambda Physik LPF 205) through a MgF_2 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 CO_2. As shown in Fig. 1, **2a** was a predominant product, while irradiation of **1b**/CO_2 mixtures under the similar conditions gave carbonyl fluoride (COF_2, **4**) exclusively and hexafluoroethane (**2b**) was not produced at all. It has been considered that trifluoromethanol (CF_3OH) 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 CO_2 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 CF_3• 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**

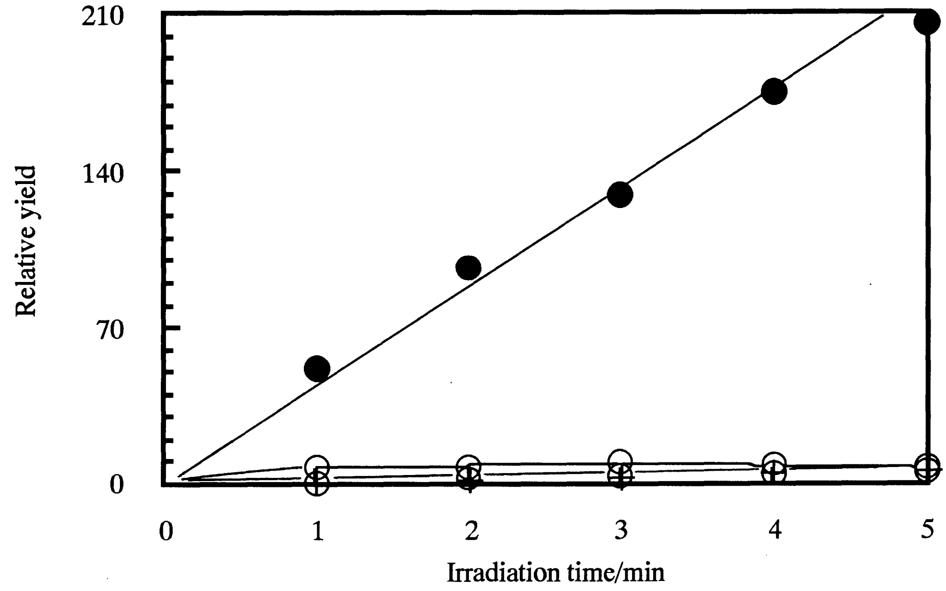


Fig. 1. Relative yields of **2a** (●), **3a** (○), and propane (⊕) vs. irradiation time.

between 30 and 900 Torr at the constant pressure (30 Torr) of CO_2 (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]

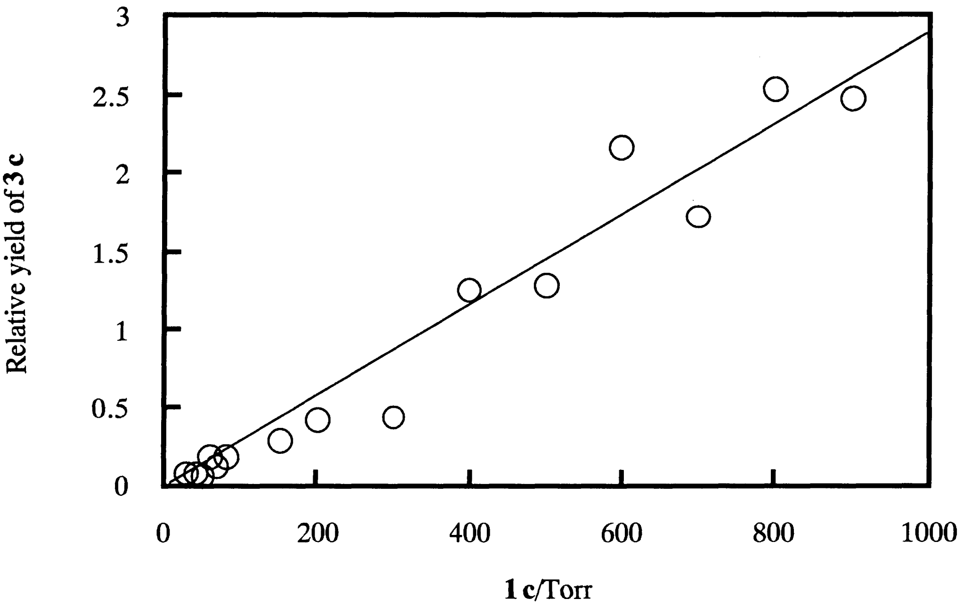
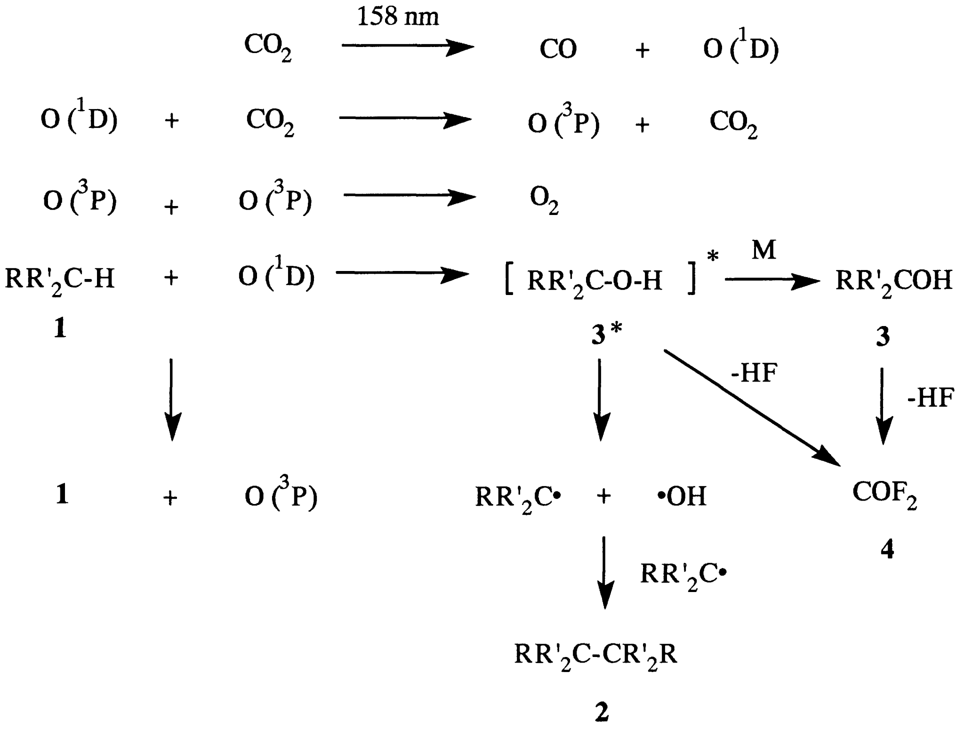


Fig. 2. Dependence of yield of **3c** produced after 900 laser pulses on the initial pressure of **1c**.

As showed in Scheme 1, it has been recognized that some amount of O (^{1}D) is quenched efficiently by CO_2 to generate O (^{3}P) under the conditions employed above.2) Recently, Warren et al. also reported that halogenated hydrocarbons can quench O (^{1}D) to O (^{3}P).8) However, O (^{3}P) 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 (^{3}P) would collapse to triplet oxygen molecule through the combination with another O (^{3}P).2) Based on the present results, it is reasonably elucidated that the primary reaction process of O (^{1}D) 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, τ (= $1/k_d$) = $h\rho^*/W$, 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, ≈1140 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 ($CH_3C_6F_5$, τ_F = 1300 ns) is 2.6 times as long as that of hot toluene (τ_H = 500 ns) with an internal energy of ≈630 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, ≈2900 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 ($CH_3CH_2OH^*$).

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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