Laser-Induced Fluorescence Study on Reactions of $C^+(^2P)$ and $C(^1D, ^1S)$ with Alcohols Leading to $CH(X^2\Pi)$ Radicals at Thermal Energy

MASAHARU TSUJI, ICHIRO NAGANO, NOBUAKI NISHIYAMA,
HIROSHI SEKIYA and YUKIO NISHIMURA

*Research Institute of Industrial Science and Department of Molecular
Science and Technology, Kyushu University, Kasuga-shi, Fukuoka 816,
Japan*

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Thermal energy reactions of $C^+(^2P)$ and $C(^1D, ^1S)$ with CH_3OH , C_2H_5OH , $n-C_3H_7OH$ and $i-C_3H_7OH$ to give $CH(X^2\Pi)$ radicals have been investigated by observing laser-induced fluorescence (LIF) spectra of $CH(A-X)$ in a flowing afterglow. In the hydride ion abstraction by $C^+(^2P)$, only CH_3OH exhibited the $CH(A-X)$ LIF spectrum with a vibrational distribution of $1.0 : 0.62$ for $v'' = 0$ and 1 , respectively. On the other hand, the $CH(A-X)$ LIF spectra exclusively from $v'' = 0$ were observed in the reactions of $C(^1D, ^1S)$ with all alcohols studied. By isotopic substitution for CH_3OH it was shown that the $CH(X)$ radicals arise from the selective attack on the methyl site in the reactions of $C^+(^2P)$ and $C(^1D, ^1S)$ with methanol.

KEY WORDS: Laser fluorescence detection, formation of CH , ion-molecule reactions, flowing afterglow.

INTRODUCTION

Although rate constants for reactions of the $C^+(^2P)$ ground-state ion and the $C(^1D, ^1S)$ metastable atoms with various molecules have been determined at thermal energy,^{1–5} little information has been obtained

on internal energy distributions of products. We have recently used a flowing afterglow apparatus coupled with LIF detection to determine internal energy distributions of products in ground electronic states.^{6–10} In this paper, we report a flowing afterglow-LIF study on thermal energy reactions of $C^+(^2P)$ and $C(^1D, ^1S)$ with a series of aliphatic alcohols leading to $CH(X^2\Pi)$.

Hydride ion abstraction from methanol by $C^+(^2P)$ has recently attracted considerable interest, because the product CH_2OH^+ ion is an important precursor in the interstellar formation of formaldehyde, ethanol and dimethyl ether.¹¹ The rate constant for the hydride ion abstraction has been determined to be $1.2 \pm 0.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ in an ion-cyclotron-resonance study of Anicich *et al.*¹ and $5.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ in a selected-ion-flow-tube study of Adams and Smith.² Very recently, Curtis and Farrar¹² have studied the hydride ion abstraction dynamics by using a crossed-beam technique in the relative energy range of 1.2–2.8 eV. They found that the hydride ion abstraction occurs predominantly at the methyl position on the basis of an isotopic labelling experiment with CH_3OD . A barycentric polar flux contour map for the CH_2OH^+ production demonstrated that the hydride ion abstraction proceeds through a direct stripping reaction in which large impact parameter collisions lead to product formation. To our knowledge, such kinetic and dynamic studies have not been performed on hydride ion abstraction from other alcohols.

The reactions of $C(^3P, ^1D, ^1S)$ with alcohols have been studied by Skell and Harris¹³ in the condensed phase at near 77 K. They found that all aliphatic alcohols react with carbon atoms to undergo deoxygenation and insertion into every OH and CH bonds from the product analysis and isotopic labelling experiments. No work, however, has been done on these reaction systems in the gas phase.

EXPERIMENTAL

The flowing afterglow-LIF apparatus used in the present study was identical to that employed for studying the $C(^3P) + NO$, N_2O reactions leading to $CN(X^2\Sigma^+)$ ⁸ and the $C^+(^2P) + \text{hydrocarbon}$ reactions leading to $CH(X^2\Pi)$ ¹⁰ except for the installation of an ion-collector grid (nickel 20 mesh) before a reaction zone. The ground-state $C^+(^2P)$ ions were generated through the dissociative charge-transfer reaction:

On the other hand, the C(¹D,¹S) metastable atoms were prepared through a microwave discharge of Ar/CO mixture or through the following dissociative excitation involving radiative cascade from upper electronic states:

The presence of C(¹D) in the reaction zone was confirmed by observing the CH(A—X) LIF spectrum from the C(¹D) + H₂ reaction.^{7,14,15} Although no direct information could be obtained on the presence of C(¹S) in the reaction zone, it must be involved in the flow system on the basis of the fact that a weak C(¹P→¹S:248 nm) atomic line resulting from reaction (2) appears around a CO gas inlet. Reactions by C⁺(²P) and C(¹D,¹S) were distinguished using an ion-collector grid placed between the first entry port of CO and the second one of sample gas. We found that one grid to which a negative potential of 40–80 eV was applied with respect to the stainless-steel reaction cell sufficiently removed ionic active species without a great reduction of concentrations of active species. The pressure in the reaction zone was 0.6–1.4 Torr for He, 5–70 mTorr for CO and 5–10 mTorr for sample gases. CH₃OD (CEA: the stated isotopic purity >99%) was taken without further purification.

A tunable N₂ laser pumped dye laser (Molelectron UV22–DL14P) was used to detect LIF spectra of CH(A—X). The laser was tuned to the Δv = 0 sequence in the 425–435 nm region and the resulting LIF signal was monitored through an interference filter. A cut-off filter was employed to record the total LIF signal from which the relative vibrational distribution of CH(X) was determined. LIF signals of a Hamamatsu Photonics R955 photomultiplier were fed to a boxcar integrator (NF Circuit Block Co.: BX–531) for signal averaging. The boxcar output was recorded on a chart recorder.

RESULTS AND DISCUSSION

In Table 1 is represented the energetics for the formation of CH(X) by reactions of C⁺(²P) and C(³P, ¹D, ¹S) with five aliphatic alcohols studied here. Thermochemical and spectroscopic data listed in Refs. 16–20

Table 1 Thermodynamics for CH(X²Π) formation in the reactions of C⁺(²P) and C(³P, ¹D, ¹S) with alcohols.

Reactant ^a	ΔH (eV)			
	C ⁺ (² P)	C(³ P)	C(¹ D)	C(¹ S)
CH ₃ OH	-3.06	0.47	-0.80	-2.22
CH ₃ OH	-1.72	0.89	-0.38	-1.80
CH ₃ OD	-3.05	0.60	-0.66	-2.08
CH ₃ OD	-1.83	0.78	-0.48	-1.90
CH ₃ CH ₂ OH	-3.3 ^b	0.8 ^c	-0.5 ^c	-1.9 ^c
CH ₃ CH ₂ OH	-3.95	0.36	-0.90	-2.32
CH ₃ CH ₂ OH	-1.31	0.85	-0.42	-1.84
CH ₃ CH ₂ CH ₂ OH	-3.2 ^d	0.7 ^e	-0.5 ^e	-1.9 ^e
CH ₃ CH ₂ CH ₂ OH	-3.9 ^f	0.6 ^g	-0.7 ^g	-2.1 ^g
CH ₃ CH ₂ CH ₂ OH	-4.00	0.6 ^h	-0.7 ^h	-2.1 ^h
CH ₃ CH ₂ CH ₂ OH	-1.31	0.76	-0.51	-1.93
CH ₃ CH(OH)CH ₃	-3.2 ⁱ	0.7 ^j	-0.5 ^j	-1.9 ^j
CH ₃ CH(OH)CH ₃	-4.50	0.19	-1.07	-2.49
CH ₃ CH(OH)CH ₃	-1.26	0.80	-0.46	-1.88

^a The source of H⁻ or H to give CH(X) is in bold face type. ^b Estimated assuming D(CH₃CH₂OH⁺) = D(C₂H₆⁺), where H⁻ abstracted by C⁺(²P) is in bold face type. ^c Estimated assuming D(CH₃CH₂OH) = D(C₂H₆). ^d Estimated assuming D(CH₃CH₂CH₂OH⁺) = D(CH₃CH₂CH₃⁺). ^e Estimated assuming D(CH₃CH₂CH₂OH) = D(CH₃CH₂CH₃). ^f Estimated assuming D(CH₃CH₂CH₂OH⁺) = D(CH₃CH₂CH₃⁺). ^g Estimated assuming D(CH₃CH₂CH₂OH) = D(CH₃CH₂CH₃). ^h Estimated assuming D(CH₃CH₂CH₂OH) = D(CH₃CH₂CH₃). ⁱ Estimated assuming D(CH₃CH(OH)CH₃⁺) = D(CH₃CH₂CH₃⁺). ^j Estimated assuming D(CH₃CH(OH)CH₃) = D(CH₃CH₂CH₃).

were used for the calculation. It is clear from Table 1 that the formation of the CH(X) radicals is energetically accessible for all reactions by C⁺(²P) and C(¹D, ¹S), however, it is not allowed through the reactions by the ground-state C(³P) atoms. Both C—H and O—H bonds can be sources of H⁻ and H. The reactions are considerably more exothermic if the former bond is the sources of H⁻ and H. Since excitation energies of the emitting A²Δ, B²Σ⁻ and C²Σ⁺ states of CH radicals from the ground state are 2.9, 3.2 and 3.9 eV, respectively, some of these excited states can be produced in the H⁻ abstraction reactions: the available energies of the H⁻ abstraction reactions are given by ⟨E_{avail}⟩ = ΔH₀^o + 3RT (0.077 eV at 300 K). When CH(A—X, B—X, C—X) chemiluminescence was surveyed by using a flowing afterglow apparatus reported previously,^{21,22} no emission was detected. On the basis of this fact the formation of the excited CH

radicals is an unfavourable product channel and the possibility of the $CH(X)$ production through a radiative cascade from upper electronic states is ruled out.

Figure 1(a) shows a typical LIF spectrum obtained from the $C^+(^2P)$, $C(^1D, ^1S) + CH_3OH$ reactions in the He flow. The spectrum consists of the strong (0,0) band and the weak (1,1) and (2,2) bands. The rotational line assignment was made from Gerö's tables.²³ When the $C^+(^2P)$ ions are removed from the reaction zone using the ion collector grid, the intensity of LIF signal becomes weak and the (1,1) and (2,2) bands disappear as shown in Figure 1(b). A similar LIF spectrum is observed from the $C(^1D, ^1S) + CH_3OH$ reaction in the Ar flow (Figure 1(c)). Since the signal to noise ratio of Figure 1(c) is better than that of Figure 1(b) because of higher concentration of $C(^1D, ^1S)$ and weaker

Figure 1 Laser-induced fluorescence spectra of $CH(A^2\Delta-X^2\Pi)$ resulting from (a) the $C^+(^2P)$, $C(^1D, ^1S) + CH_3OH$ reaction in the He flow, (b) the $C(^1D, ^1S) + CH_3OH$ reaction in the He flow, and (c) the $C(^1D, ^1S) + CH_3OH$ reaction in the Ar flow. Weak rotational lines marked with • in (a) are due to the (1,1) transition.

background light in the Ar flow, the absence of vibrationally excited bands is more clearly demonstrated. These spectral observations show that CH(X) radicals for $v'' = 0-2$ are produced in the $C^+(^2P) + CH_3OH$ reaction, while only the vibrational ground state is formed in the $C(^1D, ^1S) + CH_3OH$ reaction.

In order to determine whether the product CH(X) radicals arise from the attack on the methyl site or the hydroxyl one, LIF spectra of CH(A—X) and CD(A—X) from CH_3OD were observed. The only CH(A—X) LIF spectrum was detected in the reactions of both $C^+(^2P)$ and $C(^1D, ^1S)$ with CH_3OD , indicating that more stable CH_2OD^+ cations and CH_2OD radicals are produced exclusively by the attack on the methyl site. The present observation that the hydride ion abstraction by $C^+(^2P)$ at thermal energy occurs at carbon position is consistent with the crossed-beam result of Curtis and Farrar at higher collisional energies of 1.2–2.8 eV,¹² where the primary product was CH_2OD^+ cations and only a trace signal of CH_3O^+ cations was detected. The site selectivity in the attack on methanol by $C(^1D, ^1S)$ is similar to the reaction of $O(^3P)$ which involves abstraction of a hydrogen atom of the methyl group only.²⁵ However, it is in marked contrast to the reactions of $O(^1D)$ ²⁶ and $CH_2(\tilde{a}^1A_1)$,²⁷ which show a preference for attack on hydroxyl site. Although the higher reactivity of isoelectronic $O(^1D)$ and $CH_2(a^1A_1)$ at the hydroxyl site of methanol has been interpreted in terms of relative electron density on the target hydrogen in the electrophilic attack,²⁶ the opposite site selectivity for $C(^1D, ^1S)$ implies that other factors (e.g. stability of production) dominate the reaction.

The rotational distribution of CH(X) is thermalized at about 300 K, indicating rotational relaxation by collisions with He, CO and CH_3OH is complete during the time between formation and detection. The vibrational population ratio between the $v'' = 0$ and $v'' = 1$ levels was determined by the same manner as that described previously.¹⁰ The N_1/N_0 ratio in the $C^+(^2P) + CH_3OH$ reaction was estimated by subtracting the band intensity of CH(A—X) LIF due to $C(^1D, ^1S) + CH_3OH$ (e.g. Figure 1(b)) from that due to $C^+(^2P)$, $C(^1D, ^1S) + CH_3OH$ (e.g. Figure 1(a)). Although the N_1/N_0 ratio was invariant over the He pressure range of 0.8–1.3 Torr and the CH_3OH pressure range of 2–10 mTorr, it was sensitive to the CO gas pressure. It was difficult to examine directly the dependence of the N_1/N_2 ratio on the CO gas pressure because He active species ($He(2^3S)$, He^+ , and He_2^+)

are not completely quenched by CO and directly react with CH_3OH to yield $CH(X)$ radicals at low CO pressures below about 10 mTorr. Therefore, the correction for vibrational relaxation by CO was made by reference with the variation of the N_1/N_0 ratio in the $C(^3P) + HI$ reaction,⁹ $C(^3P)$ atoms being produced through the $Ar(^3P_{0,2}) + CO$ reaction. The nascent N_1/N_0 ratio was found to be 0.62 ± 0.05 . This ratio is smaller than a value of 0.84 predicted from a statistical prior distribution based on a three body model in which CH_2OH^+ ions are treated as an atom²⁷ and a value of 0.70 based on an extended three body model in which three rotational degrees of freedom are included.²⁷ If the reaction dynamics of the hydride ion abstraction are governed by kinematics associated with the $H + L-H'$ mass combination (H = heavy, L = light), a large fraction of the available energy is expected to be released as a vibrational energy of $CH(X)$.²⁸ In such a case, much higher vibrational excitation of $CH(X)$ is predicted based on a large available energy deduced from Table 1. The low vibrational excitation of $CH(X)$ suggests that the dynamic factor associated with potential energy surfaces is more important than the kinematic factor in the present system. It also implies that most of the available energy is deposited into the internal energy of CH_2OH^+ and relative kinetic energies of products. The release of a large fractional energy to the internal energy of CH_2OH^+ , not to CH vibration, may be explained by the fact that the abstraction process is sufficiently short that the residual alkoxy radical cation does not relax before the products separate and the radical cation stabilization energy is converted into internal motion of CH_2OH^+ .

In similar LIF measurements on larger aliphatic alcohols, no $CH(A-X)$ LIF spectra was observed from the hydride ion abstraction from C_2H_5OH , $C_2H_5CH_2OH$, and $(CH_3)_2CHOH$ by $C^+(^2P)$, indicating that the H^- abstraction is an unfavorable product channel for these larger alcohols. Although rate constants and product branching ratios have not been measured for the reactions of $C^+(^2P)$ with these larger alcohols, by analogy with the known reaction for CH_3OH ,^{1,2} the formation of parent cations by charge-transfer and that of fragment ions by dissociative charge-transfer and/or by insertion and elimination are probably dominant product channels for these alcohols with lower ionization potentials (IP): IP values of CH_3OH , C_2H_5OH , $n-C_3H_7OH$ and $i-C_3H_7OH$ are 10.83, 10.47, 10.22 and 10.12 eV respectively.¹⁶

CH(A—X) LIF spectra exclusively from $v'' = 0$ were detected from the reactions of $C(^1D, ^1S)$ with the same substrates as in the case of CH_3OH . This suggests that no energy is channelled into the CH(X) vibration. Possible reaction pathways of $C(^1D, ^1S)$ + alcohols leading to CH(X) radicals are direct abstraction of a hydrogen atom and insertion into a CH or OH bond followed by elimination of CH(X) through a long-lived intermediate. In the simplest case, namely that of $C(^1D, ^1S)$ reaction with methanol, the following pathways are possible:

As shown before, processes (4) and (6) are unimportant, though corresponding processes can not be ruled out in the cases of the other larger alcohols. In general, processes such as (3) and (4) can be distinguished from insertion/elimination processes (5) and (6) by observing the product vibrational excitation.^{25,29} A large fraction of available energy is channelled into CH(X) vibration in the former case, while a much smaller fraction is deposited into CH(X) vibration in the latter case. On the basis of the present spectral observation, it is reasonable to assume that CH(X) radicals are produced in the reactions of $C(^1D, ^1S)$ with aliphatic alcohols via an insertion on a CH bond to form a long-lived intermediate species followed by elimination of the newly formed CH group. Most of available energy is probably released as an internal energy of alkoxy radical and relative kinetic energies of products. However, the possibility that lifetimes of chemically activated intermediate complexes are sufficiently long to allow collisional deactivation by the He buffer gas cannot be completely ruled out under the relatively high He pressure used in the discharge flow system. In order to understand specific behaviors of low vibrational excitation and site selectivity in the $C(^1D, ^1S)$ + alcohol reactions to form CH(X), further experimental studies such as measurements of rotational distribution and angular distribution of products are required under single collision conditions.

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