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# Synchrotron-Radiation Study of Weak Fluorescence from Neat Liquids of Simple Alkenes: Anomalous Excitation Spectra as Evidence for Wavelength-Dependent Photochemistry

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**Abstract:** Fluorescence excitation spectra of *trans*-2-octene, *trans*-cyclooctene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene were measured by using synchrotron radiation as a tunable light source in the vacuum UV and UV region. The wavelength dependence of the fluorescence yields provides direct evidence for the long-proposed assignment that the emissive state is the $\pi$,R(3s) Rydberg state, which in turn gives the carbene-derived photoproducts.

Alkylated ethylenes are known to afford more than two photoproducts upon direct irradiation in the vacuum ultraviolet (VUV) region in the vapor and liquid phases.[2] These products are considered to arise through different reaction pathways involving geometrical and/or valence isomerizations. We have recently demonstrated that the relative ratio of individual photoproducts drastically varies depending upon the excitation wavelength employed, indicating intervention of distinctly different excited states for each photochemical process and slow mutual interconversion between the excited states involved.[3]

The photophysical behavior of the excited alkenes does not appear to have been investigated extensively,[4-6] probably because they are extremely poor fluorescers. Hirayama and Lipsky have, however, succeeded in observing very weak fluorescence from a series of alkylated ethylenes excited at 185 nm in the vapor and/or liquid phases.[5] With increasing alkylation, the fluorescence band maximum in the liquid phase moves from 231 nm (1-hexene, neat liquid) to 263 nm (2,3-dimethyl-2-butene, neat liquid) and the fluorescence quantum yield dramatically increases from $1 \times 10^{-6}$ to $1.5 \times 10^{-4}$, although unsubstituted ethylene does not fluoresce appreciably. Neat 2,3-dimethyl-2-butene has been reported to afford a higher fluorescence quantum yield of $2.7 \times 10^{-4}$ or $3.5 \times 10^{-4}$ when excited at longer wavelengths of 214 or 229 nm, respectively. For several reasons, the emissive state has been assigned tentatively to the $\pi$,R(3s) Rydberg excited state.[4,5]

Recently, Wickramaaratchi et al.[6] have reported a synchrotron-radiation study of 2,3-dimethyl-2-butene in the vapor and liquid phases, in which the authors recorded the fluorescence excitation spectrum and also measured the lifetime of the fluorescent state. The results reported, however, show several serious discrepancies with those of Hirayama and Lipsky,[5] although the excitation wavelengths employed in both studies were somewhat different (185-229[5] and 235 nm[6]) and it is not absolutely inconceivable that the emission would be very strongly wavelength dependent. Further investigation is obviously needed for the photophysics of this faintly fluorescent alkene.

In this paper we wish to report the fluorescence excitation spectra of di-, tri-, and tetraalkylethylenes, which differ in shape significantly from their absorption spectra but provide direct support for the assignment of the emissive state as $\pi$,R(3s) Rydberg rather than as a $\pi,\pi^*$ excited state. The anomalous wavelength dependence of the fluorescence quantum yield is further discussed in relation to the wavelength-dependent photochemical reactivity of the simple alkene.

## Experimental Section

**Materials.** Commercially available *trans*-2-octene (Nakarai), 2-methyl-2-butene (Tokyo Kasei), and 2,3-dimethyl-2-butene (Aldrich) were purified to >99% purity by preparative gas chromatography over a 8 mm × 2 m column of oxydipropionitrile at 50 °C. *trans*-Cyclooctene was prepared and purified up to 99.6% according to the procedures reported.[7] The major impurities in each alkene were the geometrical and/or positional isomers, and the purified samples did not show any appreciable emission upon excitation at >220 nm on a conventional spectrofluorometer. The purified alkene was introduced into a 1 × 10 × 50 mm Suprasil cell, purged with argon gas for 10 min at −60 °C, and then sealed under an argon atmosphere. Extra pure reagents of sodium salicylate, magnesium oxide, and barium sulfate were used as received.

**Instruments.** Electronic spectra at >200 nm were recorded with the neat liquid alkene prepared above on a Jasco UVDEC-660 or Ubest-50 spectrometer. Attempted fluorescence measurements were carried out on a Jasco FP-770 instrument with excitation above 220 nm.

**Synchrotron Radiation Study.** The light source in the vacuum UV and UV region was synchrotron radiation from the beam line BL-7B of the Ultraviolet Synchrotron Orbital Radiation Facility (UVSOR), the Institute for Molecular Science, operated at 750 MeV and 100-mA beam current in the 16-bunch mode.

A block diagram for the fluorescence measurement is illustrated in Figure 1. The radiation was made monochromatic through a 1-m Seya-Namioka monochrometer with a grating of 1200 lines/mm and a slit width of 2 mm, which corresponds to 3.2-nm resolution. The monochromatic light was introduced into a low-vacuum sample chamber though a lithium fluoride window, which was used to separate the sample chamber from the high-vacuum system of the beam line. The sample was irradiated at an angle of ca. 45° from the side opposite to the observation window in order to reduce the reflected and scattered light from the cell. Whole emission from the sample was passed through appropriate filters (e.g., Toshiba UV-25 + KL-260 or UV-27 + UV-D33S) and was soft-focused with a quartz lens on a Hamamatsu R1564U-03 (two-stage multichannel plate (MCP) operated at −3 kV) or R2286U-02 (three-stage MCP operated at −3.6 kV) photomultiplier. The light intensity and collection efficiency at every excitation wavelength were calibrated by a sodium salicylate actinometer, assuming that the fluorescence quantum yield from crystalline sodium salicylate is constant over the wavelength range 160-250 nm. The stray light from the monochrometer was evaluated by placing a scattering plate of fine powder of barium sulfate, magnesium oxide, or nonglossy aluminum foil at the sample holder, and the appropriate correction was made, although its contribution was minimal even at longer wavelengths.

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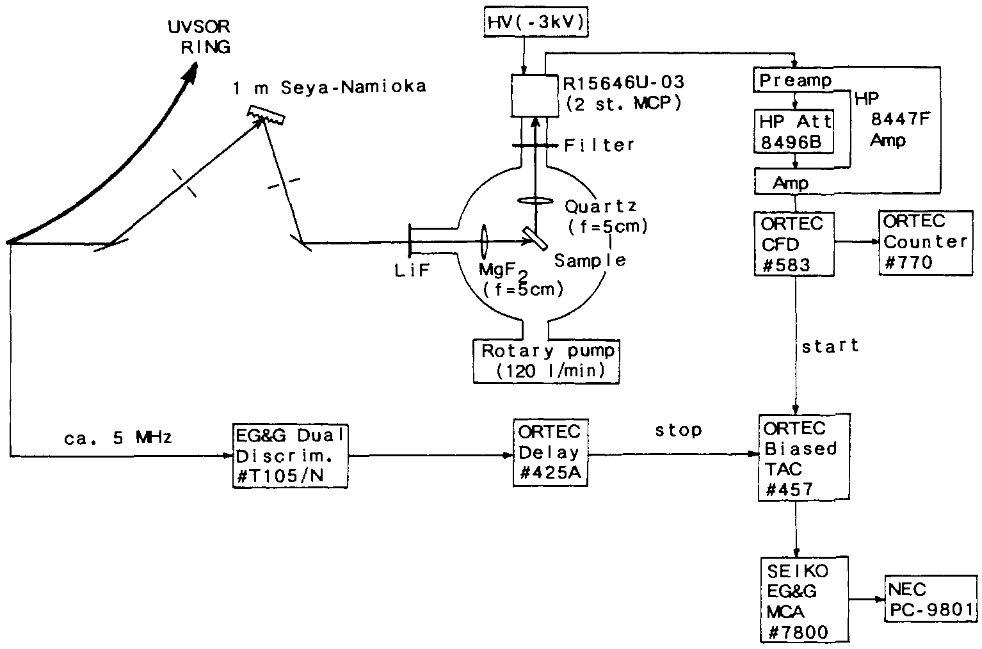

**Figure 1.** Typical block diagram for the measurement of weak fluorescence from alkylethylenes upon excitation in the vacuum-UV and UV regions.

Since the conventional time-averaging measurement of the emission did not give any significant signal distinguishable from the noise, we adopted the time-correlated single-photon-counting method to improve the S/N ratio. The signal was processed by the devices shown in Figure 1 and accumulated for 50–300 s in a multichannel analyzer (Seiko EG&G MCA-7800) as a series of emission peak trains synchronized with the bunches of the storage ring. Using a homemade software run on an NEC PC-9800 computer, only the emission signal above the noise level was integrated over a fixed number (mostly 10) of peak trains to give a fluorescence intensity at each wavelength.

It was shown that the present system, utilizing the synchrotron radiation as a tunable light source in the VUV and the single-photon-counting method for detection, does work well for the measurement of excitation spectra of very weak fluorescer(s) whose quantum yields are as low as $10^{-6}$.

## Results and Discussion

Since the intensity of monochromatic light from the UVSOR was substantially weaker than the radiation from conventional resonance lamps employed by Hirayama and Lipsky[5] and by Inoue et al. in photochemical reactions,[3] we first examined 2,3-dimethyl-2-butene, which has been reported to emit the most intense fluorescence among the simple alkenes.[5] The time profile of the emission signal was practically identical with the pulse shape of the UVSOR (ca. 450 ps fwhm), irrespective of the excitation wavelength. This is not unexpected in view of the extremely short fluorescence lifetime (15 ps) of the neat alkene estimated by Hirayama and Lipsky,[5] although a much longer lifetime of 10 ns has also been reported under a comparable condition.[6,8] The integrated emission intensity was measured at a 5-nm interval over a wavelength range 160–250 nm and was plotted as a function of exciting wavelength. As can be seen from Figure 2, the maximum fluorescence intensity was obtained by excitation at 229 nm, while the excitation at longer or shorter wavelengths resulted in an abrupt or gradual decline of the fluorescence intensity. The excitation spectrum obtained, though entirely different in shape from that reported recently,[6,8] qualitatively reflect the relative fluorescence intensity obtained by discrete excitations at 185, 214, and 229 nm[5] as discussed below.

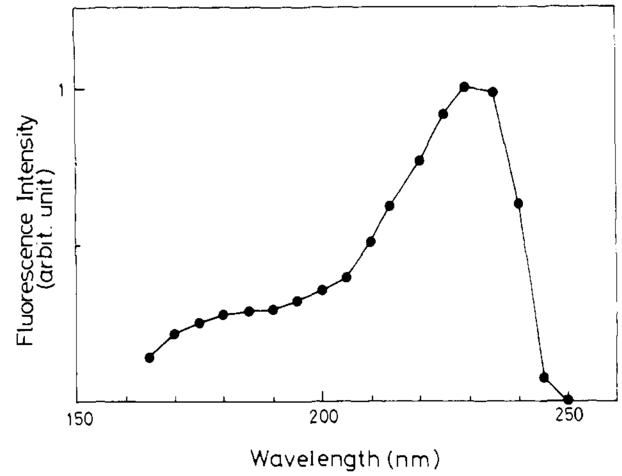

**Figure 2.** Fluorescence excitation spectrum of 2,3-dimethyl-2-butene (neat liquid).

**Table I.** Absorption and Fluorescence-Excitation Band Maxima of Some Simple Alkenes

| alkene | abs,[a] nm<br>V–N(π,π*) | <br>R–N(π,R(3s)) | fluorescence exc,[b] nm |
|---|---|---|---|
| *trans*-2-octene | 179 | (201)[c,d] | 195 |
| *trans*-cyclooctene | 197 | 207 | 214 |
| 2-methyl-2-butene | 177,[e] 181,[f] 184[g] | 206, 215,[f] 216[g] | 229 |
| 2,3-dimethyl-2-butene | 187, 187,[d,g] 190[f] | 218, 230,[g] 231,[f] 232[d] | 229 |

[a] Gas-phase absorption maxima; ref 4, unless noted otherwise. [b] Neat liquid alkene; this work; accuracy ±5 nm. [c] Value for *trans*-2-hexene is shown, since the corresponding value is not available. [d] Reference 5. [e] Reference 9. [f] Johnson, K. E.; Johnston, D. B.; Lipsky, S. *J. Chem. Phys.* **1979**, *70*, 3844. [g] Reference 13.

Similar fluorescence measurements with 2-methyl-2-butene, *trans*-cyclooctene, and *trans*-2-octene, performed under comparable conditions, gave much weaker emissions, especially for the latter two dialkylethylenes. The observed maxima of the excitation spectra have been listed for each alkene in Table I, along with the reported absorption maxima for V–N and R–N transitions.[4,5]

Interestingly, the excitation spectra of simple alkenes thus obtained differ substantially from their absorption spectra reported.[4,5,9,10] Taking into account the broad bandwidth of ex-

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(8) Although we have no plausible rationalization at present for the apparent discrepancies with the reported fluorescence lifetime (10 ns) and excitation spectrum in ref 6, it is evident from the present measurement that the lifetime must be well below 100 ps, which is compatible with the estimation (15 ps) in ref 5. A picosecond-laser photolysis study of the excited 2,3-dimethyl-2-butene is planned in order to answer this problem.

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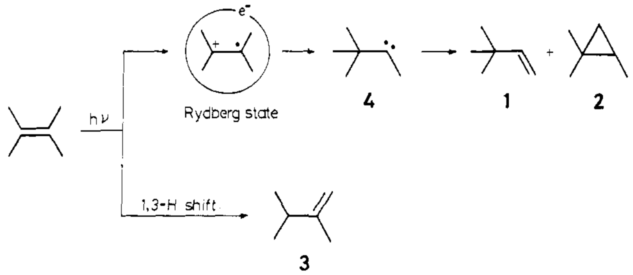
**Table II.** Fluorescence Intensity and Relative Ratio of Photolysis Products upon Excitation at 185–229 nm in Neat (Fluorescence) or 10 mM Solution (Photolysis) of 2,3-Dimethyl-2-butene

| exc wave-length, nm | fluorescence | | product ratio "carbene"/"1,3-shift"[c] |
|---|---|---|---|
| | quantum yield[a] | rel int[b] | |
| 185 | $1.5 \times 10^{-4}$ | ≡1 | 0.36 (≡1) |
| 214 | $2.7 \times 10^{-4}$ | 2.2 | 0.78 (2.2) |
| 229 | $3.5 \times 10^{-4}$ | 3.5 | 5.9 (16) |

[a] Reference 5. [b] This work. [c] References 3 and 12.

**Scheme I.** Photochemistry of 2,3-Dimethyl-2-butene in Solution



citation light and the different phase employed, the maximum of fluorescence excitation spectrum shows good agreement with the absorption maximum of the R–N transition band for each alkene, although a somewhat larger difference is seen with 2-methyl-2-butene.[11] Furthermore, the relative intensity of the fluorescence from 2,3-dimethyl-2-butene excited at 185, 214, and 229 nm coincides nicely with the relative quantum yield reported,[5] as shown in Table II. These results provide further evidence in support of the assignment that the emissive state is a $\pi$,R(3s) Rydberg state rather than a $\pi,\pi^*$ excited state.

From the photochemical point of view, the present result is crucial in identifying the excited state involved in the photoreaction of 2,3-dimethyl-2-butene.[2,3] As shown in Scheme I, the direct irradiation of 2,3-dimethyl-2-butene in solution phase gives three major photoproducts, **1**–**3**. The combined yield of rearrangement products **1** and **2**, which are derived from a carbene **4**, increases with increasing excitation wavelength from 185 to 214 and then to 229 nm, whereas the yield of 1,3-hydrogen-shift-derived product **3** decreases compensatorily.[3,12] As a result, a dramatic change in the relative ratio of "carbene" to "1,3-shift", i.e., (**1** + **2**)/**3**, is observed as shown in the last column of Table II. It is noted that the relative fluorescence yield is in good agreement with the relative product ratio (**1** + **2**)/**3**. This coincidence reinforces the reaction mechanism proposed by Kropp[2] and Inoue et al.[3] that the carbene **4** arises from the $\pi$,R(3s) Rydberg state, in which the cation-radical-like electronic configuration around the molecular core[13] promotes the alkyl shift to the cation center.

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**Registry No.** *trans*-2-Octene, 13389-42-9; *trans*-cyclooctene, 931-89-5; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1.

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(11) The different phases employed in the measurements of absorption and fluorescence excitation spectra would be responsible for the difference in both maxima, although the Rydberg transitions typically shift to shorter wavelengths with considerable broadening of the bandwidth in going from vapor to condensed phase.

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# Determination of the $\beta$-Silicon Effect from a Mass Spectrometric Study of the Association of Trimethylsilylium with Alkenes

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**Abstract:** A mass spectrometer equipped with a high-pressure ion source and pulsed electron beam has been used to study the association of alkenes with trimethylsilylium: $Me_3Si^+ + \text{alkene} \rightleftharpoons Me_3Si\text{–alkene}^+$ (7). The equilibrium constants for reaction 7 have been measured for a series of alkenes over a range of temperatures, and from the resulting van't Hoff plots the following $-\Delta H_7°$ (kcal mol$^{-1}$) and $-\Delta S_7°$ (in brackets; cal K$^{-1}$ mol$^{-1}$) values are obtained: ethene, 23.6 ± 0.3 (38.5 ± 0.8); propene, 30.6 ± 0.4 (42.5 ± 0.8); *trans*-2-butene, 30.9 ± 0.6 (41.5 ± 1.5); isobutene, 36.5 ± 1.1 (42.7 ± 2.1); 2-methyl-2-butene, 38.2 ± 0.5 (48.0 ± 1.1); cyclohexene, 32.9 ± 1.0 (45.6 ± 2.1); styrene, 36.6 ± 0.7 (42.4 ± 1.4). The $\beta$-silicon effect, defined as the stabilization energy resulting from a silicon atom in a position $\beta$ to a carbenium carbon, is given by $\Delta H°$ for the isodesmic reaction $Me_3Si{\cdot}X^+ + XH_2 \rightleftharpoons Me_3SiXH + XH^+$ (X = alkene). $\Delta H_f°(Me_3SiX^+)$ is obtained from $\Delta H_7°$ using $\Delta H_f°(Me_3Si^+) = 141$ kcal mol$^{-1}$; $\Delta H_f°(Me_3SiXH)$ is estimated. The stabilization energies (kcal mol$^{-1}$) are the following: X = ethene, 48.2; propene, 38.4; *trans*-2-butene, 38.2; isobutene, 28.1; 2-methyl-2-butene, 28.8; 2,3-dimethyl-2-butene, 25.8; styrene, 21.8. These values are grouped according to the number of substituents $\alpha$ to the carbenium carbon in classically drawn structures and are consistent with the theoretically predicted large hyperconjugative interaction between the Si–C $\sigma$-bond and the formally empty p orbital on the carbenium carbon.

Organosilicon compounds are finding increasing use in synthetic organic chemistry,[1] but unfortunately the basic thermochemical information required to predict the mechanistic properties of organosilicon molecules is very sparse and what little there is should be treated very critically.[2] Quantitative information is required regarding the effects on the kinetics and thermochemistry of reactions caused by the introduction of silicon-containing substituents into organic molecules. One aspect of organosilicon

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