Fluorescence of Simple Olefins

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Abstract

Weak fluorescence has been observed from propylene, cis-2-butene, trans-2-butene, 1-hexene, cis-2-hexene, trans-2-hexene, 2-methyl-2-pentene, and 2,3-dimethyl-2-butene in vapor and solution phases. Emission spectra and quantum yields are presented. The transitions are tentatively assigned as originating from the lowest singlet Rydberg state.

I. Introduction

The absorption spectra of the alkyl-substituted ethylenes⁽¹⁾ exhibit a strong $V + N$ transition which slightly red-shifts with increasing methyl substitution. To the red of this transition there appears, at least in the vapor phase, a somewhat weaker transition ($R + N$). In heptane solution the $V + N$ transition tends generally to red-shift slightly whereas the $R + N$ transition loses its rather well-defined vapor structure and appears to merge with the $V + N$ transition. Herer and Mullikan⁽²⁾ have summarized the evidence for assigning the $R-N$ system to a Rydberg transition and this assignment seems now to be generally accepted. A number of calculations have also indicated that the R state, unlike the V state, has an equilibrium geometry not too dissimilar from that of the ground state.⁽²⁾ As a consequence, the Einstein B coefficient in absorption should provide a reasonable estimate of the radiative constant of the R state. For many simple olefins this value is about $10^7 - 10^8 \text{ sec}^{-1}$ which is comparable to that of many aromatics. Yet whereas aromatics emit strongly, no fluorescence has ever been reported from the simple olefins although searches have been made.

With a recently developed capability for measuring emission yields as low as 10^{-6} for excitation at 184.9 nm we decided to seek an olefin fluorescence and present here in a preliminary report the results of recent observations of a weak emission in the region around 230-265 nm.

II. Experimental

The 184.9 nm Hg resonance line was obtained from an electrodeless lamp containing 3 torr of argon with power supplied from a 100 W, 2450 MHz microwave generator. The lamp was butted onto the entrance slit of a 0.5 m, f/11 McPherson Model 235 vacuum monochromator (grating blazed at 150 nm). An f/1.8 polished LiF lens was used to focus sharply the exciting beam onto the face of the sample cell at normal incidence. Two Suprasil quartz lenses f/1.0 and f/4.0 focused the fluorescence from the front surface of the sample cell onto the entrance slit of a 0.5 m, f/4.4 Bausch and Lomb monochromator (grating blazed at 200 nm). The optical axes of the exciting and analyzing system made a 45° angle. The remainder of the analyzing system consisted of a dry-ice-cooled EMI 62565 photomultiplier, Keithley 417 picoammeter, and a 1-sec potentiometric recorder. The exciting monochromator and the sample compartment were flushed with nitrogen to eliminate absorption of the 184.9 nm line by molecular oxygen. A gamma-ray-irradiated LiF disk (1 mm thick) was placed between the LiF focusing lens and the sample cell to reduce the level of stray 253.7 nm light. Also, a quartz cell filled with H₂O (1 cm path) was placed between two quartz lenses in the analyzing system to block entry of scattered 184.9 nm line into the analyzing monochromator.

The sample cell was a 7520 glass tube to which a sapphire window (10 mm diameter x 1 mm thick) was directly sealed (obtained from Scientific Services Co.). This direct-seal sapphire window was finally chosen to minimize a background light level originating from weak fluorescence from the empty cell. Suprasil quartz, MgF₂ and LiF windows attached with various materials were all found less satisfactory in this regard. The background was a broad band extending from ~260 nm to 500 nm. The subtraction of this background from the recorded sample spectra was made by using a spectrum obtained from the cell when filled with CCl₄.

The olefin samples were obtained from the following sources: ethylene, propylene, cis-2-butene, trans-2-butene from Air Products and Chemicals, Inc.; 1-hexene (99.9%), cis-2-hexene (96%), trans-2-hexene (99%), 2-methyl-2-pentene (99%), 2,3-dimethyl-2-butene (99%) from Chemical Samples, Co. These samples were used without further purification for the purposes of this preliminary study, although results with a few chemicals which were further purified by distillation or by percolation through Woelm silica gel showed no noticeable change in emission intensities or spectra.

III. Results

Figure 1 shows the fluorescence spectra of three olefin gases: propylene, cis- and trans-2-butene at 1 atm excited at $\lambda_{ex} = 184.9$ nm. All the spectra given in this report were obtained by multiplying the recorded intensity by λ^2 to give the relative intensity in units of photons/cm⁻¹, but have not yet been corrected for the spectral response of the analyzing system. (i.e., it is assumed here that the spectral response is constant over the pertinent spectral region.)

The intensity scale in each of the figures is normalized such that the peak intensity of 2×10^{-2} M p-xylene in nitrogenated cyclohexane for $\lambda_{ex} = 184.9$ nm (quantum yield = 0.30) is unity.

Because of the absence of spectral response data, exact values of intensity maxima (λ_f) and fluorescence quantum yields (ϕ_f) have not yet been determined. Therefore, in this report, only rough estimates of λ_f and ϕ_f can be given.

Emissions from the three olefin gases (1 atm) shown in Fig. 1 are characterized as follows: propylene ($\lambda_f = 223$ nm, $\phi_f = 1.5 \times 10^{-6}$); cis-2-butene (≈ 227 nm, $\approx 2 \times 10^{-6}$); trans-2-butene (≈ 230 nm, $\approx 3 \times 10^{-6}$) with half-widths

σ_f of ≈ 7.5 kK. No emission from ethylene gas (1 atm) has as yet been detected.

Figure 2 shows the fluorescence from neat liquids (nitrogenated) of 1-hexene, cis-2-hexene and trans-2-hexene for $\lambda_{ex} = 184.9$ nm. These emissions are characterized by: 1-hexene ($\lambda_f \approx 236$ nm, $\phi_f \approx 5 \times 10^{-6}$); cis-2-hexene (≈ 238 nm, $\approx 7 \times 10^{-6}$); trans-2-hexene (≈ 235 nm, $\approx 6 \times 10^{-6}$) with σ_f 8.8, 8.6 and 8.8 kK respectively. These emissions were found not to be quenched by dissolved oxygen (1 atm). The fluorescence of 1-hexene vapor (vapor pressure at 25°C with 1 atm N_2 added) blue-shifts about 5 nm with the intensity reduced to approximately one-half that of the liquid.

Figure 3 shows the fluorescence spectrum of neat 2-methyl-2-pentene, which is characterized by $\lambda_f = 253$ nm, $\phi_f \approx 13 \times 10^{-6}$ and $\sigma_f \approx 8.5$ kK. The spectrum of the vapor (at 25°C with 1 atm N_2) is similar to that of the liquid except for slight broadening ($\lambda_f \approx 253$ nm, $\sigma_f \approx 9$ kK) and with ϕ_f reduced to $\approx 9 \times 10^{-6}$.

Figure 4 shows the absorption and fluorescence spectra of 2,3-dimethyl-2-butene (23DMB) in four different conditions: neat liquid, 5% solution in pentane, 5% solution in perfluorohexane and vapor (at 25°C with 1 atm N_2).

Neat 23DMB fluoresces with much higher quantum yield ($\phi_f \approx 2 \times 10^{-4}$) than any of the other olefins studied. It has an intensity maximum at 264 nm with $\sigma_f \approx 6.5$ kK (Fig. 4a). In pentane solution, ϕ_f is reduced to approximately one-third but with little change in spectral distribution (Fig. 4b). In perfluorohexane solution, ϕ_f is further reduced to $\sim 15\%$ that of the neat liquid accompanied by ~ 5 nm blue-shift (Fig. 4c). The vapor spectrum is broader ($\sigma_f \approx 9$ kK), ϕ_f is reduced by about 0.2, but λ_f remains at ≈ 264 nm.

IV. Discussion

With the exception of azulene⁽³⁾ and some of its derivatives,⁽⁴⁾ the most intense emission that is observed from a polyatomic system contained in a condensed phase is from the S_1 state regardless of excitation wavelength.⁽⁵⁾ Non-radiative transitions appear to deplete the upper states S_n so rapidly and to populate the lower states with sufficient efficiency to cause immense disparity in emission intensities from S_n and S_1 even when the S_n radiative constant is several orders of magnitude larger than that of S_1 .⁽⁶⁾ Unless the simple olefins are still other exceptions to this general behavior, it follows, that our solution fluorescence is from S_1 and therefore, most plausibly, should be assigned as R + N.⁽²⁾

Unfortunately, for most of the compounds we have so far studied the R + N vapor absorptions are insufficiently resolved from the V + N absorptions to permit correlation with our observed emission spectra. However, for unsubstituted olefins it is expected that both V-N and R-N systems should shift to similar extent with increasing number of carbon atoms and therefore we expect peaks of the V + N absorption of these compounds (e.g., propylene: 58.1 kK, cis-2-butene: 57.5 kK, trans-2-butene: 56.2 kK, 1-hexene: 56.5 kK) to correlate with peaks of the emission (e.g., 44.8 kK, 44.1 kK, 43.5 kK, 43.3 kK, respectively) and indeed this is approximately satisfied. Nevertheless it is perhaps significant to note that whereas the V-N absorptive peak of cis-2-butene is 1.3 kK to the blue of trans-2-butene,⁽¹⁾ in the emission from these compounds this separation is reduced to 0.6 kK. This would be consistent with an R + N assignment for the emission were the V-R energy gap of the cis compound larger than that of the trans and indeed the absorption spectrum gives some hint of this.⁽¹⁾

The V + N absorption of 1-hexene red shifts by about 0.9 kK on solution in n-heptane⁽¹⁾ and very likely even further red shifts on condensation to the neat

liquid. The emission of neat liquid 1-hexene is about 0.9 kK red shifted from that of the vapor. Assuming that the emission is indeed $R \rightarrow N$, we would conclude then that, at least for this compound, the R state is red shifted on condensation although perhaps not as much as is the V state.

Unfortunately, we do not yet have vapor data for the cis- or trans-2-hexenes. However, it is interesting to note that whereas in heptane solution the $V \rightarrow N$ absorption of the cis compound is about 0.6 kK higher than that of the trans compound, in the neat liquid it is the trans compound that emits about 0.6 kK higher than that of the cis. This is also consistent with an $R \rightarrow N$ assignment if once again we postulate that the V-R gap is larger for the cis than the trans compound as is indeed indicated here too by the vapor absorption spectra.⁽¹⁾

For the methyl substituted olefin 2-methyl-2-pentene the $R \rightarrow N$ absorption now stands out quite clearly from the $V \rightarrow N$ absorption and for 2,3-dimethylbutene these two absorptive transitions are even much further displaced.⁽¹⁾ For 2-methyl-2-pentene the vapor $V \rightarrow N$ absorption is rather flat in the vicinity of its maximum extinction and as a consequence it is difficult to obtain the spectral shift of this transition upon solution of the compound in heptane. However, it is probably not much different from the 0.9 kK shift observed for 1-hexene. The emission, however, is unaffected by condensation to the neat liquid suggesting that there is now a strong repulsive interaction between the R state and N states of neighboring molecules that effectively cancels their attractive dispersive interaction.

For 2,3-dimethylbutene the $V \rightarrow N$ transition red-shifts by about 1 kK on solution in n-heptane whereas the fluorescence is unaffected upon similar solution in n-pentane or on condensation to the neat liquid. Once again this suggests that the dispersive or polarization effect of the solvent on the R state is mitigated by a strong repulsive interaction. In support of this we find that in

perfluorinated hexane solution, where the polarization effect is strongly reduced, as indicated by the absence of spectral shift of the $V + N$ transition, the emission is now blue-shifted by about 0.7 kK.

From the integrated vapor absorption spectrum of the R-N system of 2,3-dimethylbutene we obtain a radiative constant of $\approx 5 \times 10^7 \text{ sec}^{-1}$. Using this together with a vapor fluorescence quantum yield of 6×10^{-5} provides a value for the non-radiative constant of $8 \times 10^{11} \text{ sec}^{-1}$. The state that emits therefore must live about $1.2 \times 10^{-12} \text{ sec}$ which raises the interesting question that if indeed this is the R state and it is S_1 , what can be the nature of the decay channel that so rapidly depopulates it?⁽⁷⁾ For the other olefins investigated, if their R + N absorptive transitions are not weaker than that of 2,3-dimethylbutene, since their emission quantum yields are much reduced their lifetimes must be an order of magnitude smaller still (i.e., for propylene $\approx 3 \times 10^{-14} \text{ sec}$).

In general, the quantum yields seem to decline with decreasing molecular complexity and although the origin of this trend is not known, it may be the reason for our inability to observe ethylene emission. Already the quantum yield of propylene of 1.5×10^{-6} is just about at our limit of detectability.

Once again we wish to emphasize that our results here are preliminary and further work is required to substantiate our assignment of the emission to an olefinic Rydberg transition. Also to be remembered is that we have not yet corrected for spectral response of the analyzing system and although the correction should not be too large, nevertheless some of our comparisons between emission maxima and $V + N$ absorptive peaks may require alteration.

References and Footnotes

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7. Of course, were the assignment $V \rightarrow R$, an even shorter lifetime of $\approx 10^{-13}$ sec would be obtained but decay to the R state could be invoked to explain the short lifetime. Nevertheless, one would still wonder why the lower R state did not emit.

Figure Captions

- Fig. 1. Fluorescence spectra of: a) propylene; b) cis-2-butene; and c) trans-2-butene in gas phase (1 atm) excited at 184.9 nm.
- Fig. 2. Fluorescence spectra of nitrogenated neat liquids of: a) 1-hexene; b) cis-2-hexene; and c) trans-2-hexene excited at 184.9 nm.
- Fig. 3. Fluorescence spectrum of nitrogenated neat liquid 2-methyl-2-pentene excited at 184.9 nm.
- Fig. 4. Fluorescence and absorption spectra of 2,3-dimethyl-2-butene: a) neat liquid; b) 5% solution in pentane; c) 5% solution in perfluorohexane; and d) vapor (vapor pressure at 25°C in the presence of 1 atm N_2). Excitation was at 184.9 nm.

Fig. 1

Fig. 2

Fig. 3

Fig. 4