E XTINCTION COEFFICIENTS FOR THE ALLYL RADICAL

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ABSTRACT

Electronic spectra in the 210–250 nm region, were reported for the allyl radical and subsequent reactions have been investigated by kinetic spectroscopy and gas liquid chromatography. The measured rate constant for allyl combination was 3.1×10^{10} mol^{-1} ls^{-1} at $295 \pm 2K$.

INTRODUCTION

The free allyl radical is the simplest example of a conjugated system, and its electronic structure has been investigated in several theoretical approximations. (Linnett 1963, Hirst 1962, Longuet-Higgins 1985, Moffit 1953.) The radical sould be planar in the ground electronic state, and the electron spin resonance spectrum, (Moffit 1953), is consistent with a molecule of C_{2v} symmetry: In the Hückel approximation, the
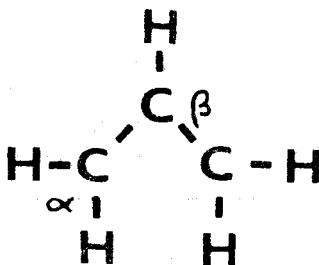
ground state π − system is composed of two b_1 bonding orbitals and a single a_2 nonbonding orbital $(b_1)^2$ (a_2), $^2A_2$, corresponding to an equality of electron density on each of the C atoms. The two lowest doublet-excited-states have $^2B_1$ symmetry, and result either from excitation of the a_2 electron to an antibonding b_1 orbital to fill the non-bonding a_2

orbital. In this approximation both electric dipole transitions would be strong and the excitation energies would be equal. More sophisticated theories predict excitation energies of about 3 and 5.5 eV for the $^2B_1$ states, the low energy optical transition is predicted to be weak, and the other to be strong, (Longuet-Higgins 1955), The excitation energy of the $^4A_2$ state, with one electron in each of the three orbitals, has been predicted to be about 5–6 eV, (Longuet-Higgins 1955, Moffit 1953), There should not be any other state of the radical which can cause a strong electronic transition in the quartz ultra-violet.

There have been several reports of the production of transient absorption bands in irradiated polyethylene at low temperature, which have been assigned to the short wavelength transition of the allyl radical incorporated in a hydrocarbon chain. (Bodily 1966), recorded an absorption maximum at 258 nm. and considered that the a, a' substitution causes a "bathochromic shift" from the theoretically predicted shorter wavelength for the unsubstituted radical. In the gas phase, (Currie 1966), have detected a weak and diffuse band system in absorption (40 m path), with an "apparent" 0–0 band at 408.3 nm in the flash photolysis of each of nine compounds containing the allyl group. Full deuteration caused a shift to shorter wavelength. They have provisionally assigned the spectrum to the long wavelength transition of the allyl radical.

On the basis of photochemical and structural evidence, spectra have been assigned to the allyl radical, the β– methallyl radical, the α– methallyl radical. They all exhibit intense band systems in the far ultra-violet, and the character of the electronic change is very probably similar in each case, corresponding to the transition from the $^2A_2$ to the higher of the $^2B_2$ states. The allyl spectrum has been detected in the flash photolysis of 8 compounds containing the allyl group, and the original assignment (Callear, 1967), has been strengthened by the observation of derivatives of the allyl radical produced in analogous photochemical processes.

EXPERIMENTAL

Flash Photolysis Apparatus – this employed two airfilled photolysis lamp in series, with a flash duration (1 /e) of 4 μ sec. at a discharge energy of 1125 J. Spectra were recorded on a Hilger medium quartz spectrograph, slitwidth 0.025 mm. The Ilford HP3 plates used were developed in Ilford PQ Universal developer.

Plate Photometry-The spectra were photometered an a Joyce-Loeble double beam recording microdensitometer model MK IIB. Calibrated optical densities on the phtographic plate were obtained with a seven-step filter (Hilger F 1273).

Materials – Dially and allyl bromide were from K and K, allyl alcohol and butene-1 from Hopkin and Willams, and the other organic chemicals from B.D.H. They were degassed and redistilled in vacuo before use. Nitrogen (Oxygen-free) was from B.O.C.

Pressure Measurement – low pressures of parent molecules (8×10^{-3} to 10 torr) were flashed after mixing with excess of nitrogen (at pressures up to 700 torr) to maintain isothermal conditions.

Pressures were measured with a McLeod gauge (up to 0.1 torr), a spiral gauge (0.1 – 50 torr), and above 50 torr, with a mercury manometer.

End-product Analysis-Products and residual parent molecules were dissolved in ethanol and the resulting solutions concentrated for analysis with Varian 3700/111 chromatography.

RESULTS AND DISCUSSION

Fig. 1 show the main region of absorption of the $^2B_2 \leftarrow {}^2A_2$ short wavelength transition of the free allyl radical. Diallyl (1,5-hexadiene) and allyl bromide are the best sources of the radical with these particular experimental conditions, though it can be detected strongly in flashed butene-1, and also in flashed propylene. The radical has also been observed in the flash photolysis of allyl amine, diallyl ether and allyl cyanide. Except for allyl cyanide and butene-1, the only spectra recorded in the flash photolysis were those of allyl and methyl radicals. The hydrocarbons diallyl, propylene and butene-1 are the best sources of the spectrum, because they do not absorb strongly in the 220–230 nm. region. Even with these parent molecules, the selection of optimum conditions requires care because of the production of other species which absorb continuously. (Bayrakçeken, 1976).

Allene itself absorbs strongly in the same wavelength region as the allyl radical. The allyl spectrum could be detected only faintly, in the flash photolysis of allyl cyanide. The radical was detected weakly in the flash photolysis of transbutene-2 (as well as the α– methallyl radical), this being the only, compound which yielded the spectrum and does not specifically contain the allyl group ($H_2 C = CH — CH_2 —$).
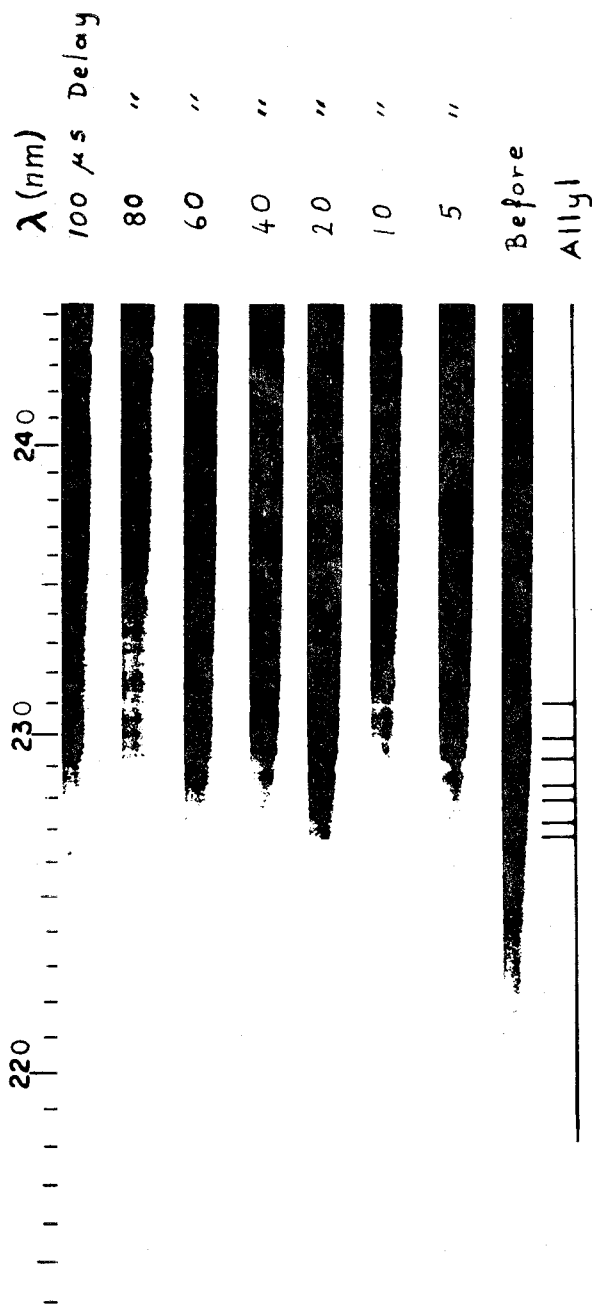
Fig. 1. Flash photolysis of 1,5-Hexadiene (0.2 torr) and Argon (200 torr) showing the spectrum of the allyl radical and its decay.

Flash energy = 1125 J

TABLE 1. ALLYL SPECTRUM

wavelength (nm)	intensity	cm^{-1}
245.7	w	40688
240.4	w	41583
237.2	w	42144
230.8	m	43314
229.5	m	43559
229.0	s	43711
228.1	m	43826
227.7	m	43904
227.0	s	44039
225.8	m	44272
224.8	vs	44469
224.3	m	44569
223.7	s	44687
222.6	m	44908
222.3	m	44970
221.5	m	45131

The evidence for the suggested assignments of the allyl and α– and β– methallyl radical arises not only from the detection of particular spectra from a variety of related parent molecules, but also in consideration of the different free radicals which may be prepared according to prediction from the initial structure. The type of initial structure is preserved following photodecomposition, which usually yields the radical by scission of the weakest bond. The individual photochemical reactions which are required to interpret the assignments, receive qualitative support from established photochemical mechanisms. (Lossing 1954, Heller 1965, Cvetanovic 1964, Maas 1964, Calvert 1966). The production of both allyl and α– methallyl free radicals in the direct photolysis of butene-2 has been postulated by (Chesick 1966).

An electronic transition of the allylic group confined in a ring structure, is likely to incur little change in geometry and result in absorption in a restricted wavelength region. The position of the band is considerably displaced from the absorption detected by (Bodily and Dole 1966). The free allyl spectrum is widely different from that observed in pulsed radiolysis experiments (Burrell 1967). The initial act of light absorption at $\sim$ 185 nm. Corresponds to about 150 kcal/Einstein, of which 70–80 kcal/mole are required to produce allylic type free radicals. If, on fragmentation, the energy is distributed with equal accessibility amongst the quantum states, practically all the excess would be retained in the allylic radical. The results suggest that such vibrationally excited radicals decompose unless stabilized by collision within about 2 x 10^{-8} sec. This scheme is open to investigation by direct photolysis at low pressures.

The decay of all bands could be fitted well to second order plots with slope consistent with their relative optical densities at the respective wavelengths. A typical example is shown in figure 2. Measurements commenced at 5 µ s delay, when the photolysis flash is virtually over. Table 2, shows the rate constants and extinction coefficients for 1, 5–Hexadiene. Figure 1. shows the allyl absorption spectrum and its decay in the vapor phase.
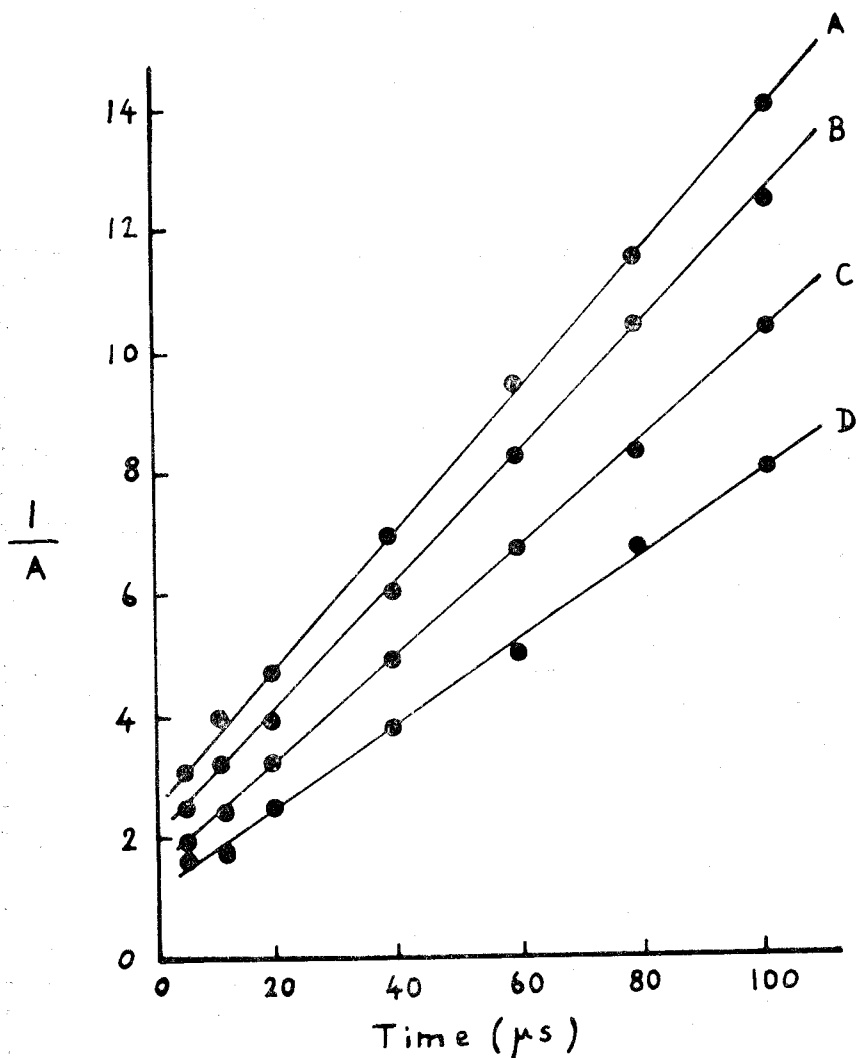

Fig. 2. Second order plot for the decay of the allyl redical measured at A, 229, B, 227, C, 224. 8 and D, 223.7 nm.

TABLE 2

Compound	k (10⁴ A⁻¹ s⁻¹)	λ (nm)	ε (10⁴ mol⁻¹ l cm⁻¹)
1, 5- Hexadiene	11.5	229.0	0.37
	10.5	227.0	0.33
	8.4	224.8	0.27
	7.0	223.7	0.22

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