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The Near Ultraviolet Absorption Spectrum of Propargyl Aldehyde[1]

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The absorption spectrum of propargyl aldehyde vapor has been examined in the 3000–4000 Å. region, under sufficient resolution to permit a vibrational analysis based upon infrared and microwave data. The transition is identified as N → A (n-π) from its general appearance and its similarity to the corresponding absorption in acrolein. A simplified Franck–Condon calculation has been performed for the principal vibrational progression observed. A small blue shift, relative to acrolein, has been noted and ascribed to differences in conjugation and electronegativities in the two molecules. Solution spectra also were obtained for this and the 2140 Å. region.

Introduction

The near ultraviolet absorption spectra of a number of unsaturated conjugated aldehydes have appeared in the literature. Much of this work has been summarized by McMurray[2]; in addition, the work of Price[3] has extended the region of observation to include the vacuum ultraviolet for acrolein, crotonaldehyde and related molecules. In general, each of these conjugated aldehydes exhibits two regions of absorption in the visible and/or near ultraviolet. The first of these is a very weak absorption showing long progressions and having a maximum around 3300 Å.; the structure and intensity of this transition is quite similar to the one appearing in saturated aldehydes which possesses a maximum around 2900 Å.[4] The second of these transitions is similar in appearance to the N–V type observed for a number of unsaturated hydrocarbons; it is more intense than the 3300 Å. transition. Although the position of this transition varies somewhat with the particular molecule in question, it can be expected to occur around 2000 Å. for molecules similar to acrolein.

Although the ultraviolet spectra of conjugated aldehydes having carbon–carbon double bonds are well known, few ultraviolet spectra are available for the analogous triple-bonded, or acetylenic, compounds. However, for the simplest such molecule, propiolic aldehyde ($H{-}C{\equiv}C{-}CHO$), there are available, from microwave[5a] and infrared[5b] studies, considerable data which are at least indirectly applicable to the electronic problem.

From Stark effect studies in the microwave spectrum, it is found that the magnitude of the dipole moment vector is 2.46 D, and that the vector lies 25-30° from the carbonyl bond toward the aldehyde hydrogen. Further, it is estimated from relative intensity measurements on "satellite lines" that there are two low-lying bending modes at about 150 and 230 cm.$^{-1}$. Other fundamental frequencies of interest are those of the $C{\equiv}C$ and $C{=}O$ stretching modes; these are determined from the infrared spectrum to be 2115 and 1706 cm.$^{-1}$, respectively.

Comparison of these data with similar data for the analogous ethylenic compound, acrolein, suggests that interesting differences occur between the two molecules. On the other hand, one can postulate a simplified model for propiolic aldehyde which allows interaction of only two π-electrons from the triple bond with the carbonyl group; this would suggest that the gross structure of the electronic spectra of the two molecules might be of a similar nature. One can thus hope that the main features of the propiolic aldehyde electronic spectrum can be explained in terms of the better known acrolein spectrum while differences in the details of the spectra for the two molecules will yield further information on the differences between the two molecules. The results described below confirm to some extent this expectation.

Experimental

Propiolic aldehyde was prepared from commercially available propargyl alcohol by chromic acid oxidation according to the method of Wille and Saffer.[6] Purification was effected by distillation under reduced pressure at room temperature into a receiver cooled by Dry Ice–acetone slush. The purified sample was kept frozen at Dry Ice temperature until ready for use in order to prevent decomposition, which occurs readily at room temperature. No differences were noted in the spectrum of a freshly purified sample and of one which had been kept frozen for two weeks.

The instrument employed for scanning the vapor phase spectra was a single beam Leeds and Northrup model 6750-PL grating spectrometer with photomultiplier detector. In the region scanned the second-order spectrum was employed; filters were placed in the sample beam to ensure no interference from the first-order spectrum in the red.

Wave lengths were determined by linear interpolation between reference points on the recorder trace at about 50 Å. intervals. The reference points themselves were placed manually on the chart during a scan by reading the wave length dial. With this method, the error in reading the chart is about 0.3 Å. Differences between observed and reported wave lengths for mercury lines in the 3000–4000 Å. region fell within this reading error with the result that no attempt to correct for instrument calibration has been made. Vacuum corrections have been applied to facilitate comparison with other studies. It is estimated that difference frequencies in this region are reproducible to about 12 cm.$^{-1}$.

The model 6750-PL spectrometer was adapted to absorption work by placing the 10 cm. quartz sample cell between a xenon arc source and the spectrometer. Radiation leaving the sample cell was focused on the entrance slit by a quartz lens. No emission of absorption lines were detected in the region of interest with either air or the evacuated cell in the beam.

The sample cell was evacuated and filled using a standard glass vacuum system. Pressures were measured with the requisite accuracy by a mercury manometer attached to the manifold of the system. The spectra reported here were scanned with a sample pressure of about 27 mm. although higher pressures were occasionally employed.

The intense xenon source was found to cause rapid photolytic decomposition of the sample with the resultant formation of a visible brown film on the windows of the cell. That this material was not responsible for the observed absorption was shown by freezing the sample out of the cell

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(1) This research was sponsored in part by the Office of Ordnance Research, U. S. Army.

(2) H. L. McMurray, *J. Chem. Phys.*, **9**, 241 (1941).

(3) W. C. Price, *Trans. Faraday Soc.*, **41**, 498 (1945).

(4) H. L. McMurray, *J. Chem. Phys.*, **9**, 231 (1941).

(5) (a) J. A. Howe and J. H. Goldstein, *ibid.*, **23**, 1223 (1955); (b) work in progress at this Laboratory.

(6) F. Wille and L. Saffer, *Ann.*, **568**, 34 (1950).

into a side arm; with the sample thus removed, no absorption bands were detected for the dirty cell. When the side arm was allowed to warm, the volatile sample vaporized into the cell and the usual spectrum was then obtained. Corning filters No. 9700 and No. 9863 were placed between the source and the sample cell in order to filter out far ultraviolet radiation; however, this had no apparent effect on the rate of decomposition. The only observed difficulty introduced by the decomposition was the lessening of sample pressure, and consequent decrease in intensity of absorption, during the 20 minutes or so required to scan the 3000–4000 Å. region.

The solution spectrum in the 3000–4000 Å. region was obtained with a Beckman model DU spectrophotometer equipped with a photomultiplier detector. The usual cell in-cell out technique was used with a pair of matched 10 cm. cells with quartz windows. Spectral grade 2,2,4-trimethylpentane was employed as the solvent in making up the 10^{-2} molar solutions used in this study.

The scan of the solution spectrum in the 2140 Å. region was made with a Cary recording spectrophotometer by the Wood River, Illinois, laboratories of the Shell Oil Company. Comparison scans made in this region with the model DU spectrophotometer showed essentially the same features, at least for solutions sufficiently dilute to minimize the effect of stray non-monochromatic radiation.

Results

In the 2000–4000 Å. region, propiolic aldehyde possesses two regions of absorption. The first of these extends from about 2000 to 2200 Å.; under low resolution, this absorption appears to consist of three separate peaks with the most intense of the three having a maximum extinction coefficient of about 4.7×10^2 l./mole-mm. The second absorption extends from about 2950 to 3950 Å.; under low resolution, it consists of at least five distinct peaks with the maximum absorption occurring at 3340 Å. with an extinction coefficient of about 1.7 l./mole-mm. Thus, the second absorption is about 10^{-2} as intense as the first one.

Medium resolution scans of the long wave length absorption region confirm the coarse features seen in the low resolution scans and afford considerably more data. Under these conditions, the most noticeable feature is the occurrence of four intense peaks, each of which is separated from its neighbor by an average frequency of 1291 cm.$^{-1}$. On going from the last of these peaks toward higher frequency, the spectrum becomes diffuse and then begins to fall rapidly to low intensity. Each of these main peaks, except for the lowest frequency member, has associated with it a number of less intense peaks lying to both high and low frequencies from the parent absorption; the intensity of these subsidiary peaks is found to decrease as the separation between it and the parent peak increases. Although experimental error prevents accurate determination of difference frequencies, it appears that separations between subsidiary peaks in a given group, or between a subsidiary and its parent, can be expressed approximately as a linear combination with integral coefficients of the numbers 170 and 80 cm.$^{-1}$.

A more nearly complete description of the low frequency absorption region of propiolic aldehyde is afforded by Table I, which lists frequencies and relative intensities of transitions which could be reproducibly observed in this region. Figure 1 is a reproduction of the recorder trace from the Leeds and Northrup spectrophotometer which shows much of the region of interest in the vapor phase work; this chart would appear to show some resolution of the rotational sub-structure. Figure 2 shows the extinction coefficient as a function of wave length for the 3000–4000 Å. region as determined with the Beckman DU spectrophotometer. Such information as is available for the high frequency absorption region is summarized in Fig. 3, which is a plot of extinction coefficient *vs.* wave length as determined with the Cary spectrophotometer.

TABLE I

VAPOR PHASE ABSORPTION SPECTRUM OF PROPIOLIC ALDEHYDE

Band	Frequency, cm.$^{-1}$	Designation	Intensity
1	26,160	0–0	vs
2	26,235		vw
3	27,122		w
4	27,273		w
5	27,461	0–1	vs
6	27,470	0–1	vs
7	27,553		w
8	27,637		w
9	27,808		vw
10	27,919		vw
11	28,226		vw
12	28,421		w
13	28,568		w
14	28,746	0–2	vs
15	28,761	0–2	vs
16	28,932		w
17	29,103		w
18	29,181		vw
19	29,524		w
20	29,691		s
21	29,846		s
22	30,032	0–3	s
23	30,198		w

The near ultraviolet absorption spectrum of acrolein, which is of interest for purposes of comparison, has been reported previously by several authors[7,8] and will not be given in detail here. For the present purpose, it will be sufficient to describe the results of scans of the 3000–4000 Å. region with the Leeds and Northrup instrument.

Results of these scans show that the absorption spectrum of acrolein in this region is quite similar to that of propiolic aldehyde. The four most prominent peaks occur with a mean separation of 1272 cm.$^{-1}$ and there is the same onset of diffuseness as one proceeds from the last of these toward higher frequency. However, as is to be expected, the vibrational detail differs considerably for the two molecules. Associated with each of the main peaks in acrolein, there is a peak lying to higher frequencies which is only slightly less intense than the main one; the mean separation between one of these and its parent is 480 cm.$^{-1}$. Assignment of other difference frequencies is difficult since there is no longer the smooth intensity variation which enables grouping most of the propiolic aldehyde peaks into systems. Two differences which appear to recur frequently are 90 and 130 cm.$^{-1}$. In agreement with Eastwood and Snow,[8] the lowest frequency member of the series consisting of the

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(7) A. Luthy, *Z. physik. Chem.*, **B107**, 285 (1923).

(8) E. Eastwood and C. P. Snow, *Proc. Roy. Soc.* (*London*), **A149**, 446 (1935).

four prominent peaks mentioned above is assigned to the O–O transition; this transition occurs at 25,847 cm.$^{-1}$.

As a result of his work, and that of McMurray, Price[3] has assigned the 3000–4000 Å. transition in acrolein to the N→A transition. This transition is expected to be weak and involves the transfer of one electron from a non-bonding oxygen p orbital to the lowest lying anti-bonding conjugated orbital.

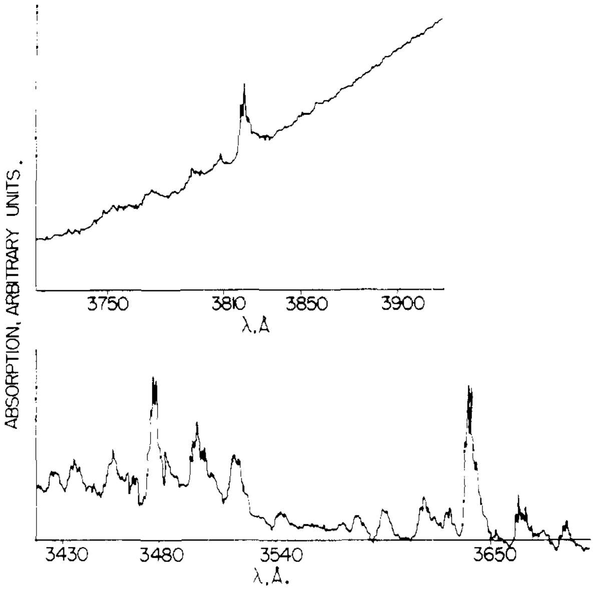

Fig. 1.—Vapor phase spectrum of propargyl aldehyde in the 3400–4000 Å. region, under medium resolution.

As stated previously, one can postulate a simplified model for propiolic aldehyde in which the molecule can be considered to be "acrolein plus ethylene." This model is constructed by allowing only one pair of the acetylene π-electrons to interact with those of the carbonyl group. The other pair of acetylene π-electrons is then considered to interact only with the appropriate oxygen lone-pair electrons; this interaction can be taken to be small because of the relatively great distance separating the interacting centers. There is thus some theoretical basis for expecting certain transitions in propiolic aldehyde to be quite similar to those in acrolein.

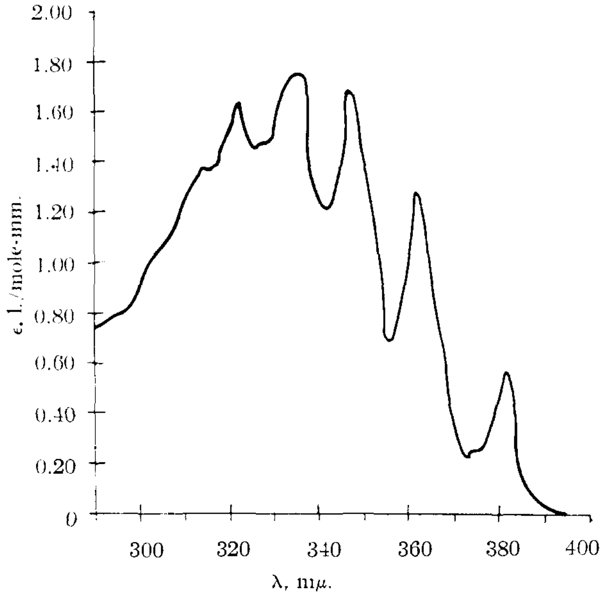

Fig. 2.—Near ultraviolet absorption spectrum of propargyl aldehyde in isoöctane solution.

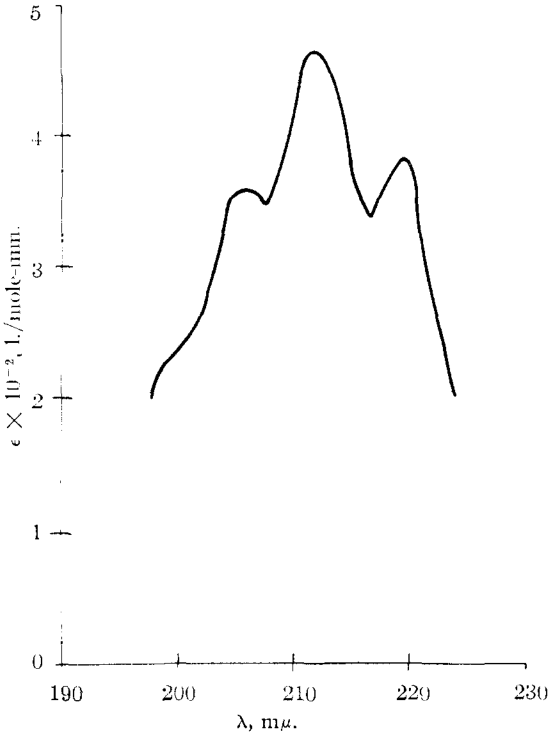

Fig. 3.—2140 Å. absorption of propargyl aldehyde in isoöctane solution.

The observed long wave length absorptions for acrolein and propiolic aldehyde appear to be two such transitions since they exhibit approximately the same intensity, frequency and principal vibrational structure. Thus, by analogy with acrolein, the 3000–4000 Å. transition in propiolic aldehyde is assigned to the N→A transition and the O–O band is taken to lie at 26,160 cm.$^{-1}$ (see Table I).

As a consequence of this assignment, it is to be expected that the excitation process responsible for the N→A transition is largely localized in the carbonyl group. Hence, long progressions should be observed for those fundamental frequencies which involve principally motions of the carbonyl group. For this reason, and by analogy to a number of similar molecules, the 1291 cm.$^{-1}$ frequency is assigned to the C=O stretch fundamental in the A state. Similarly, the excited-state frequencies of 170 and 80 cm.$^{-1}$ are believed to correspond to the 230 and 150 cm.$^{-1}$ frequencies observed for the N state. It is also of interest to note that deviations from harmonic behavior for the C=O stretch fundamental in the A state are not observable, within experimental error.

Although the N→A transition is formally allowed in propargyl aldehyde, it is expected to be weak because of small n-π overlap. It is probable that vibrational-electronic mixing provides most of the intensity, since the extinction coefficient is comparable to that obtained in aldehydes and ketones where mixing is known to be the principal source of intensity.

As a further check for possible inconsistencies in our assignments, we have calculated relative intensities for the members of the carbonyl stretch progression. These calculations assume separability of electronic and nuclear motions and also assume that the molecule can be approximately represented as a linear diatomic harmonic oscillator with the oxygen atom being one mass point and the rest of the molecule being the other. With these assumptions, the intensity of the 0–n peak relative to that of the 0–0 peak is given by

$$I_n = \omega_n/\omega_0[\int \psi_0(\xi_1)\psi_n(\xi_2)\,dx]^2$$

where ψ is a simple harmonic oscillator wave function. Craig[9] has given a formula, in closed form, for evaluating these vibrational overlap integrals as a function of separation of origins, q, of the two reduced oscillators in electronic states 1 and 2, and as a function of the ratio of frequencies, $\rho = k_1/k_2)^{1/2}$.

For propiolic aldehyde $\omega_1 = 1706$ cm.$^{-1}$ and $\omega_2 = 1291$ cm.$^{-1}$, so that $\rho = 1.321$. Table II lists the calculated relative intensities as a function of q and compares these with the observed intensity distribution. From these data, it is seen that $q = 0.10$ Å. results in a reasonably good fit, at least for small n where the harmonic approximation is more nearly valid. It is of interest to note that the 0-4 peak should appear in observable intensity in this approximation although it has not yet been observed experimentally.

TABLE II

RELATIVE INTENSITIES OF C=O PROGRESSION

Band	$q =$ 0.095 Å.	$q =$ 0.107 Å.	$q =$ 0.131 Å.	Obsd.[a]
0–0	1.00	1.00	1.00	1.00
0–1	2.67	3.37	5.04	2.28
0–2	3.17	5.20	11.95	2.97
0–3	2.18	4.78	17.53	3.07
0–4	0.95	2.93	17.98	..

[a] Approximate values; based on maximum extinction coefficients from Fig. 2.

Several empirical relations between force constants and bond lengths are known, *cf.* Garforth, *et al.*[10]; also, Layton, *et al.*,[11] recently have given an empirically derived curve for carbonyl bonds.

From these relations were obtained the q values listed in Table III. These are in good agreement with that obtained from the relative intensity calculation.

TABLE III

	r_2/r_1	q, Å.[a]
Badger's rule	1.091	0.11
Clark's rule	1.097	.12
Layton, *et al.*	1.089	.11

[a] Assumed $r_1 = 1.23$ Å.

Discussion

The position, intensity and vibrational structure of the 3000–4000 Å. absorption region of propargyl aldehyde indicate that this is a single transition of the N-A (n-π) type. The observed structure is relatively simple, compared to that for acrolein, and the three postulated intervals, 1291, 170 and 80 cm.$^{-1}$, may be reasonably assigned to excited-state vibrational modes involving the carbonyl grouping. It should be pointed out that the microwave intensity measurements, from which the ground-state values of 150 and 230 cm.$^{-1}$ were inferred, are uncertain to perhaps 30 cm.$^{-1}$, but nevertheless unequivocally identify these as fundamental frequencies. Moreover, both must be skeletal modes, and one of them, probably the lower, is necessarily non-planar. Both the planar (A′) and non-planar (A″) vibrational progressions are permitted by symmetry.

The entire transition is shifted to the blue relative to acrolein. Thus, for example, the O–O peak occurs some 313 cm.$^{-1}$ higher then the corresponding peak in the latter. From a simple orbital point of view, this could mean that one or both of two factors are involved: the non-bonding electron could lie lower than in acrolein, or the π-orbital could be higher. The first factor is indicated by the greater electro-negativity of the acetylenic substituent, as compared to the ethylenic group in acrolein. It is also supported by the fact that the dipole moment of propargyl aldehyde is not only lower than that of acrolein, 2.46 *D* *vs.* 3.07 *D*, but is even lower than that of a typical saturated aldehyde, *ca.* 2.7 *D*. This suggests a decreased electron density at the oxygen atom and a correspondingly greater ionization potential. The second factor follows the reasonable expectation that conjugation should be less effective in the acetylenic aldehyde, by analogy with the sequence: butadiene, acrolein and glyoxal. It is not possible to estimate the relative importance of these two factors, but it seems likely that both are involved.

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(9) D. P. Craig, *J. Chem. Soc.*, 2146 (1950).

(10) F. M. Garforth, C. K. Ingold and H. G. Poole, *ibid.*, 508 (1948).

(11) E. M. Layton, R. D. Kross and V. A. Fassel, *J. Chem. Phys.*, **25**, 135 (1956).