Near Ultraviolet Absorption Spectra of Acrolein and Crotonaldehyde

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Near ultraviolet absorption spectra of a number of aldehydes and ketones have been studied by many workers[1]. It is well known that these compounds have a weak absorption in 33300~25000 cm^{-1} region, and that this absorption arises from the transition of an electron from a non-bonding orbital to an excited orbital. We have also studied recently the effects of solvents on the near ultraviolet absorption spectra of some conjugated aldehydes and ketones[2]. In order to study the electronic properties of the carbonyl group in these molecules, we treated in this paper acrolein and crotonaldehyde which have conjugated systems. E. Eastwood and C. P. Snow[3] carried out a vibrational analysis for the n-π^* absorption spectrum of acrolein. The purpose of the present paper is to analyze the n-π^* absorption bands of acrorlein and crotonaldehyde, and also to estimate the amount of elongation of the C=O bond of these molecules during the n-π^* transition from the relative intensities of the C=O progression bands using the method of J. A. Howe and J. H. Goldstein[4].

Experimental

Acrolein and crotonaldehyde (Tokyo Kasei G. R. grade) were distilled before the experiment.

Carbon tetrachloride used as a solvent was boiled with dilute alkali several times. The carbon disulfide free solvent thus obtained was then washed several times with water, dried over phosphorus pentoxide, and distilled. Absorption spectra were measured by a Hitachi E. P. S. double beam automatic recording spectrometer. The absorption cell of 10 or of 40 cm. was used, depending upon the vapor pressure of the sample. All the absorption measurements were made at room temperature. Solution spectra were obtained with 1 cm. cell. For the purpose of checking that the transition in this region is of the n-π^* type, the effects of solvent on the absorption spectra were also studied by changing the solvent from carbon tetrachloride to ethanol.

Result and Discussion

Both of the compounds have weak absorption in 33300~25000 cm^{-1} region in solution and vapor states. In carbon tetrachloride solution each of the absorption spectra exhibits four distinct shoulders. On addition of ethanol

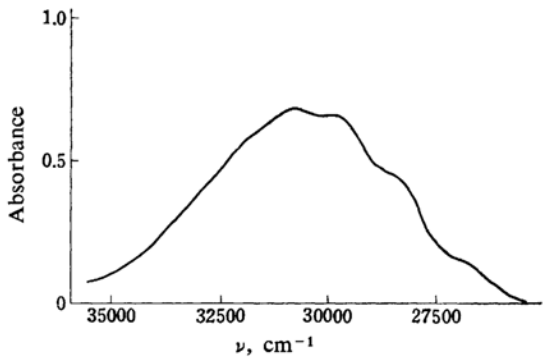

Fig. 1. Spectrum of acrolein in carbon tetrachloride solution.

1) For example, H. L. McMurry, *J. Chem. Phys.*, **9**, 241 (1941); J. W. Sidman, *Chem. Revs.*, **58**, 689 (1958).
2) M. Ito, S. Inuzuka and S. Imanishi, *J. Am. Chem. Soc.* 82, 1317 (1960).
3) E. Eastwood and C. P. Snow, *Proc. Roy. Soc.*, **149A**, 446 (1935).
4) J. A. Howe and J. H. Goldstein, *J. Am. Chem. Soc.*, **80**, 4846 (1958).

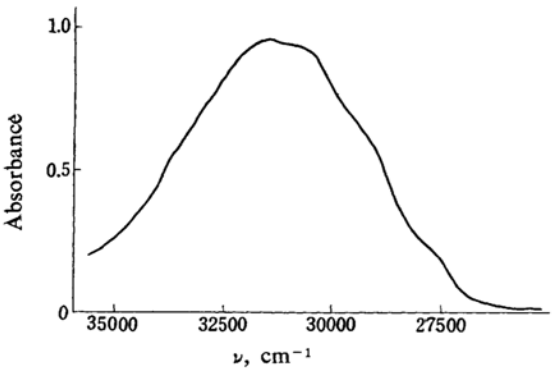

Fig. 2. Spectrum of crotonaldehyde in carbon tetrachloride solution.

to carbon tetrachloride solution the absorption shifts towards shorter wavelengths, and in pure ethanol solution the acrolein maximum shifts to the shorter wavelengths, by 400 cm^{-1} compared with the pure carbon tetrachloride solution. In the case of crotonaldehyde also the blue-shift of 900 cm^{-1} was observed. These blue-shifts indicate the n-π^* nature of the electronic transition.

In the vibrational analysis of the vapor spectrum of acrolein we have taken the strong band at 25873 cm^{-1} as the 0—0 band, which is accompanied on its lower frequency side by three very weak bands at 24647, 24912 and 25555 cm^{-1}. From the higher frequency region of the 0—0 band, we may pick out three vibrational frequencies of 1427, 1271 and 498 cm^{-1} all of which forming long progressions. The progression formed by 1271 cm^{-1} frequency is the most prominent feature in the spectrum. For crotonaldehyde, the 0—0 band taken at 26518 cm^{-1} which is accompained by no prominent band on its lower frequency side. On the high freguency side there are three progressions with the separations of 1360, 1237 and 450 cm^{-1}, respectively, the one with the 1237 cm^{-1} separation being the strongest. For acrolein, E. Eastwood and C. P. Snow[3] found two fundamental vibrational frequencies 1260 and 500 cm^{-1} of the excited state. They assigned the former to the C=O stretching vibration and the latter to an oscillation of the methylene group about the C=C double bond. As it is well known that in ketone and aldehyde n-π^* spectra the C=O stretching vibration generally gives rise to the main progression, the frequencies 1271 cm^{-1} in acrolein and 1237 cm^{-1} in crotonaldehyde may be assigned to the C=O stretching vibration in their excited states. Futhermore, since vibrational modes involving the motion of hydrogen generally do not appear prominently in the electronic spectra it seems to be more reasonable that the 498 cm^{-1} in acrolein and the 450 cm^{-1} in crotonaldehyde should be assigned to the skeletal bending modes instead of the assignment otherwise made by E. Eastwood and C. P. Snow. The frequencies 1427 cm^{-1} of acrolein and 1360 cm^{-1} of crotonaldehyde may be assigned to the C=C stretching vibration in the excited state, corresponding to the ground state vibration frequencies 1618[5] cm^{-1} and 1642[6] cm^{-1}, respectively, observed in Raman spectra. The blue-shift by 645 cm^{-1} of the 0-0 band of crotonaldehyde relative to that of acrolein is in accordance with the fact that the methyl substitution generally leads to the blue-shift of the n-π^* absorption[7,8].

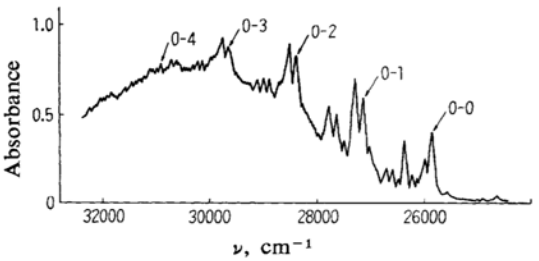

Fig. 3. Absorption spectrum of acrolein vapor.

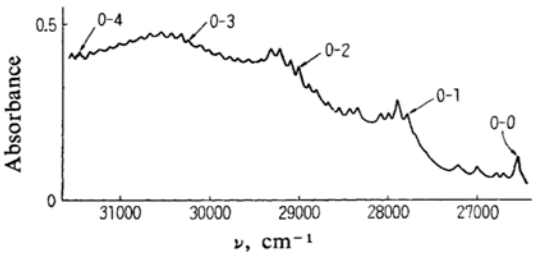

Fig. 4. Absorption spectrum of crotonaldehyde vapor.

In order to check the above assignments, the relative intensities of the member bands in the main C=O progression were calculated with the method used by Hose and Goldstein[4] and were compared with the observed intensities*. Figs. 3 and 4 show the vapor spectra of acrolein and crotonanldehyde. The procedure of this calculation was detailed by D. P. Craig[9]. The C=O group in the molecle was assumed to be a simple diatomic moleclue harmonically bound. The intensity of the 0-n band is given by

5) P. Lambert and J. Lecomtte, *Compt. rend.* **208**, 740 (1939).
6) K. W. F. Kohlrausch und A. Pongratz, *Z. physik. Chem.*, **B27**, 176 (1934).
* The intensity of a band was assumed here to be proportional to the observed optical density value. The intensity contribution from satellite bands was assumed to be the same for all the bonds forming the C=O progression.
7) H. Baba, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 341 (1951).
8) L. E. Orgel, *J. Chem. Soc.*, 121 (1955).
9) D. P. Craig, ibid., 2146 (1950).

$$I_n = (\omega_n/\omega_0)\left[\int\psi_0(\xi_1)\psi_n(\xi_2)\mathrm{d}\tau\right]^2$$

where $\psi_i(\xi_j)$ is the i-th simple harmonic oscillator wave function of the j-th electronic state, and ω_n is a frequency of the n-th band in the progression. Craig has given a formula for evaluating the overlap integral as a function of the separation of the origins of coordinate q of the two reduced oscillators in the electronic states 1 and 2, and also as a function of the ratio of frequencies $\rho = \nu_1/\nu_2$ where ν_1 and ν_2 are the C=O stretching frequencies in the ground and excited states.

The results of calculation for acrolein and crotonaldehyde are shown in Tables I and II. As seen in these tables, calculated intensities for acrolein with $q = 0.11$ Å are in fairly good

TABLE I. RELATIVE INTENSITIES OF THE C=O PROGRESSION BAND IN ACROLEIN

Band	$q=$ 0.10 Å	$q=$ 0.11 Å	$q=$ 0.12 Å	Obsd. intensity
0—0	1.00	1.00	1.00	1.00
0—1	1.81	1.99	2.60	1.48
0—2	1.90	2.27	3.76	2.07
0—3	1.50	1.93	3.94	2.20
0—4	0.99	1.36	3.40	1.95

TABLE II. RELATIVE INTENSITIES OF THE C=O PROGRESSION BANDS IN CROTONALDEHYDE

Band	$q=$ 0.11 Å	$q=$ 0.115 Å	$q=$ 0.12 Å	Obsd. intensity
0—0	1.00	1.00	1.00	1.00
0—1	2.17	2.37	2.62	2.00
0—2	2.74	3.23	3.83	3.04
0—3	2.59	3.28	4.10	3.63
0—4	2.04	2.74	3.65	3.35

agreement with the observed values listed in the last column of the tables. Similarly, for crotonaldehyde the calculated values with $q = 0.115$ Å are in reasonably good agreement with the observation.

On the other hand, an empirical relation between the C=O bond length and its vibrational frequency has been given by Layton et al.[10]. From using this empirical relation the q values

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

TABLE III.

	Acrolein	Crotonaldehyde
q(Layton)	0.11 Å	0.11 Å
q(calc.)	0.11 Å	0.115 Å

were estimated, and were compared with our calculated q values given in Table III. The agreement is quite satisfactory. From the above results we may conclude that the C=O bond distances of acrolein and crotonaldehyde increase by about 0.1 Å during n-π^* transition. In this calculation q values may be correct within 0.01 Å.

Summary

The positions vibrational structures and blue-shifts of absorption spectra of acrolein and crotonaldehyde in 33300~25000 cm^{-1} region suggest that the transition is of the n-π^* type. They are similar in vibrational structure except that the crotonaldehyde absorption is shifted towards higher frequencies with respect to that of acrolein. The vapor frequency of the 0–0 band is 25873 cm^{-1} for acrolein, smaller by 654 cm^{-1} than that of crotonaldehyde. The acrolein absorption has 1427, 1271 and 498 cm^{-1} progressions, which are assigned to the C=C stretching frequency, the C=O stretching frequency and skeletal bending frequency in the excited state, respectively. For the crotonaldehyde there are 1360, 1237 and 450 cm^{-1} progressions, which are assigned to the C=C stretching frequency, the C=O stretching and the skeletal bending vibration in the excited state, respectively According to our calculation, the elongation q in the carbonyl bond length during the n-π^* transition, is estimated to be approximately 0.1 Å.

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