25. *The Ultraviolet Spectra of Some αβ-Unsaturated Carbonyl Compounds.*

By M. H. Palmer and D. S. Urch.

Spectral studies of the π–π^* transition (*K* band) in the system, C:C·C:O, have been made on a series of αβ-unsaturated aldehydes, ketones, and acids, in ethanol (neutral but hydrogen-bonding conditions) and in concentrated sulphuric acid (protonating conditions). The results are interpreted by molecular-orbital theory and indicate protonation of the carbonyl-oxygen atom in all cases.

Lactonisation and cyclic ketonisation of olefinic acids are known [1] to occur virtually irrespectively of the position of the ethylene linkage. Thus migration of this linkage or of the derived carbonium-ion charge must precede the formation of lactones or ketones when the double bond is unfavourably placed in the starting material. Further, it is known [2] that γ- and δ-lactones may be interconvertible under strongly acid conditions and there is evidence for the equilibria:

$$\delta\text{-Lactone} \overset{H^+}{\rightleftharpoons} \gamma\text{-Lactone} \overset{H^+}{\rightleftharpoons} \text{Olefinic acid} \overset{H^+}{\rightleftharpoons} \text{Alkylcycloalkenone (or Alkylidenecycloalkanone)}$$

It is thus important to consider the behaviour, on protonation, of the alkenone species in these equilibria. We have therefore investigated the protonation of various αβ-unsaturated carbonyl compounds by spectroscopic studies of the π–π^* (*K* band) transition.

Experimental and Results

The spectra were obtained by using a Unicam S.P. 700 spectrophotometer and 1 cm. silica cells. 97% Sulphuric acid and 95% ethanol (S.V.R. grade) were used without purification. Most of the compounds were shown to be pure by their physical constants or by gas-chromatography; the 2-alkylidenecycloalkanones were contaminated with *ca.* 5% of the 2-alkylcycloalk-2-enone.

The results are shown in Table 1. In ethanol the series [3–6] of *cisoid* αβ-unsaturated aldehydes and ketones (II, III, V) absorb at longer wavelengths than the *transoid* [4–6] compounds (I, IV, VI, VII) although the number of α- and β-substituents is also important.[4,6] The hypsochromic shift already noted [8] for carboxylic acids when compared with aldehydes and ketones is evident in both ethanol and sulphuric acid solution (see also molecular-orbital calculations). In the latter solvent, a slight bathochromic shift occurs as the β-alkyl substituent increases in size.

It is apparent that protonating conditions, relative to ethanol, lead to a bathochromic shift of the first principal absorption maximum ($\log \varepsilon > 4$), of $\sim 6500 \pm 500$ cm.$^{-1}$, the extinction coefficient being virtually unchanged.

Thomas and Branch [9] observed two main absorption bands for a series of vinylogous aldehydes and ketones in weakly acid solution. The change in relative intensities on variation of acid strength of the solvent showed that the band at higher frequency arose from unprotonated molecules (the base), and the other from the conjugate acid of the base. Reinterpretation of their results shows that, for all the compounds studied by them, the frequency decrease in absorption maximum of the unprotonated base for the solvent change methanol to sulphuric–acetic acid was 1450 ± 550 cm.$^{-1}$. For the protonated species under

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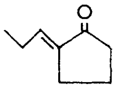
[1] Ansell and Brown, *J.*, 1958, 2955; Ansell, Coombs, and Emmett, personal communications.
[2] Ansell and Palmer, unpublished work.
[3] French and Wiley, *J. Amer. Chem. Soc.*, 1949, **71**, 3702.
[4] Evans and Gillam, *J.*, 1943, 565.
[5] Evans and Gillam, *J.*, 1941, 815.
[6] Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890.
[7] Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 72, 76.
[8] Gillam and Stern, "Electronic Absorption Spectroscopy," Arnold, London, 1960.
[9] Thomas and Branch, *J. Amer. Chem. Soc.*, 1953, **75**, 4793.

these conditions, the frequency decrease, relative to the base in methanol, was 6900 ± 700 cm.$^{-1}$, in good agreement with our results.

A semi-quantitative study of the effect of increasing the acid strength of a solution of hex-2-enoic acid in aqueous sulphuric acid showed the formation of a longer wavelength shoulder, a broadened peak, and a long-wavelength peak with a shorter-wavelength shoulder. Analysis of these results indicated about 5000 cm.$^{-1}$ between the two peaks and a solvent effect of the order of 1500 cm.$^{-1}$.

It seems, therefore, that, both in Thomas and Branch's and in the present work, only about 1500 cm.$^{-1}$ of the bathochromic shift may be ascribed to solvent effect and the remainder to the formation of an ionic species in acid solution.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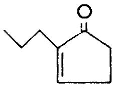
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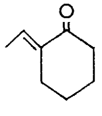
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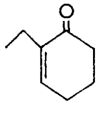
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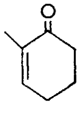
(VII)

TABLE 1.

Absorption maxima and extinction coefficients of αβ-unsaturated molecules.

	In ethyl alcohol		In 97% H_2SO_4		
Compounds	ν (cm.$^{-1}$)	$10^{-4}\varepsilon$	ν (cm.$^{-1}$)	$10^{-4}\varepsilon$	Δ' (cm.$^{-1}$) [1]
trans-Me·CH:CH·CO_2H	47,400	1·5 [2]	42,300 [3]	1·24	5100
trans-Et·CH:CH·CO_2H	48,400	1·29	41,700	1·66	6700
trans-Pr^n·CH:CH·CO_2H	48,050	1·47	41,400	1·37	6650
trans-Bu^n·CH:CH·CO_2H	47,000	—	41,300	—	6400
trans-C_5H_{11}·CH:CH·CO_2H	48,100	1·52	41,200	1·55	6900
trans-C_5H_{11}·CH:CH·CO_2Me	47,200	1·55	40,700	1·54	6500
MeEtC:CH·CO_2H	46,500	1·5	39,700	—	6800
trans-Me·CH:CH·CHO (I)	45,600	1·38 [2, 4]	38,800	2·32	6800
Me_2C:CH·COMe (II)	41,500 [4]	—	35,000 [5]	—	6500
(III)	40,700	0·733	33,700	0·937	7000
(IV)	43,800	0·563	37,800	0·607	6000
(V)	40,600 [6]	0·417	33,500	0·812	7100
(VI)	42,350 [7]	0·707	34,500	0·462	7850
(VII)	42,400 [8]	0·905	34,800	0·952	7600

[1] Δ' is observed bathochromic frequency shift (cm.$^{-1}$) on going from EtOH to 97% H_2SO_4. [2] Hausser, Kuhn, Smakula, and Hoffer (*Z. phys. Chem.*, 1935, *B*, **29**, 371) give crotonic acid $\lambda_{max.}$ 204 mμ (ε 11,700) and crotonaldehyde 217 mμ (ε 15,650) (both in EtOH). [3] Bandow (*Biochem. Z.*, 1938, **298**, 81) gives crotonic acid $\lambda_{max.}$ 230 mμ (in H_2SO_4). [4] Evans and Gillam (*J.*, 1941, 815) give mesityl oxide $\lambda_{max.}$ 235 mμ (ε 14,000) and crotonaldehyde 217 mμ (both in EtOH). [5] Nagakura, Minegishi, and Stanfield (*J. Amer. Chem. Soc.*, 1957, **79**, 1033) give mesityl oxide $\lambda_{max.}$ 284 mμ (ε 15,600) (in H_2SO_4). [6] Dreiding and Nicel (*J. Amer. Chem. Soc.*, 1954, **76**, 3965) give $\lambda_{max.}$ 250 mμ (ε 4000) (in EtOH). [7] Ansell and Brown (*J.*, 1958, 2955) give $\lambda_{max.}$ 235 mμ (ε 5500) (in EtOH). [8] Ansell and Coombs (unpublished results) obtained $\lambda_{max.}$ 234 mμ (ε 8500) (in EtOH).

The 2-alkylcycloalk-2-enones and 2-alkylidenecycloalkanones studied here have different absorption maxima under protonating conditions, showing that protonation occurs at the carbonyl-oxygen atom rather than at the other end of the unsaturated system. Attack at the latter site would give a common carbonium ion from the pairs (III–IV) and (V–VI), which is not observed.

DISCUSSION

In this discussion the simplified molecular-orbital theory of Hückel[10] will be used and the symbols have their usual meaning.[11] In order to make calculations for the $\overset{1}{C}{:}\overset{2}{C}\cdot\overset{3}{C}{:}\overset{4}{O}$ system it was necessary to estimate the coulomb integral for carbonyl-oxygen and the resonance integral for the 2,3-bond. This bond is long in acraldehyde,[12] so it is

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[10] Hückel, *Z. Phys.*, 1931, **70**, 204, 227.

[11] Coulson, "Valence," Oxford Univ. Press, 1919, p. 60.

[12] Mackle and Sutton, *Trans. Faraday Soc.*, 1951, **47**, 691.

reasonable to suppose that the resonance integral will be less than for the 1,2-bond. To estimate the necessary parameters preliminary calculations were made for acetone ($n \rightarrow \pi^*$ $\lambda_{\text{max.}}$ 275 mμ; $\pi \rightarrow \pi^*$ $\lambda_{\text{max.}}$ 150 mμ),[13] and for 3-methylcyclohex-2-enone ($n \rightarrow \pi^*$ $\lambda_{\text{max.}}$ 310 mμ; $\pi \rightarrow \pi^*$ $\lambda_{\text{max.}}$ 235 mμ).[5] Let the increased electronegativity of the 2*p*-orbital of carbonyl-oxygen relative to the 2*p*-orbital of carbon be $h\beta$ where β is the $C_{(1)}$–$C_{(2)}$ resonance integral. The C–O resonance integral is also assumed to be β. $k\beta$ is the $C_{(2)}$–$C_{(3)}$ resonance integral. The energies of the molecular orbitals as a function of h were plotted for acetone and 3-methylcyclohex-2-enone (with $k = 1{\cdot}0$, $1/\sqrt{2}$, and $0{\cdot}5$) by the method suggested by one of us.[14] Correlation with the observed transitions was found for $h = 0{\cdot}4$, $k = 1/\sqrt{2}$, and $\beta = 30{,}000$ cm.$^{-1}$.

TABLE 2.

Δ for protonated ketones in units of β (30,000 cm.$^{-1}$).

k: *h*	0·4	0·5	0·6	0·7	0·8	0·9	1·0	1·1	1·2	1·3	1·4
0·1	0·65	0·80	0·92	1·07	1·20	1·32	1·42	1·49	1·56	1·63	1·70
0·2	0·68	0·82	0·96	1·08	1·20	1·32	1·42	1·49	1·56	1·63	1·70
0·3	0·70	0·85	0·97	1·09	1·21	1·32	1·42	1·49	1·56	1·63	1·69
0·4	0·74	0·88	0·99	1·12	1·23	1·33	1·42	1·50	1·56	1·63	1·68
0·5	0·80	0·93	1·03	1·14	1·24	1·34	1·43	1·50	1·57	1·63	1·67
0·6	0·86	0·96	1·07	1·16	1·26	1·35	1·43	1·50	1·57	1·62	1·67
0·7	0·92	1·01	1·11	1·18	1·28	1·35	1·43	1·50	1·57	1·62	1·66
0·8	0·98	1·05	1·14	1·20	1·29	1·36	1·43	1·49	1·56	1·61	1·66
0·9	1·04	1·10	1·17	1·23	1·30	1·37	1·43	1·49	1·55	1·60	1·65
1·0	1·09	1·14	1·20	1·25	1·31	1·38	1·43	1·49	1·54	1·59	1·64
1·1	1·14	1·18	1·22	1·27	1·32	1·38	1·43	1·49	1·54	1·59	1·63
1·2	1·18	1·21	1·23	1·28	1·32	1·38	1·42	1·48	1·53	1·58	1·62
1·3	1·21	1·23	1·25	1·29	1·33	1·38	1·42	1·48	1·53	1·57	1·61
1·4	1·23	1·24	1·26	1·30	1·33	1·38	1·42	1·47	1·52	1·56	1·60

Since it has been shown above that substituted-vinyl ketones are protonated at the carbonyl-oxygen atoms, calculations were made by assuming $\overset{1}{\mathrm{C}}{:}\overset{2}{\mathrm{C}}{\cdot}\overset{3}{\mathrm{C}}{:}\overset{4}{\mathrm{O}}{}^{+}\text{–H}$ to be the species present in concentrated sulphuric acid: $H_{12} = \beta$, $H_{23} = \beta/\sqrt{2}$, $H_{34} = k\beta$, $\alpha_{\mathrm{O}}-\alpha_{\mathrm{C}} = h\beta$. Two parameters h and k were introduced since it is expected that protonation will cause the 2*p*-orbital that conjugates with the π-system to become more tightly bound. h will therefore be larger than for carbonyl-oxygen, and k will be reduced, since the more tightly bound orbital will be smaller and so overlap less with that of $C_{(3)}$. Families of energy levels were computed as a function of h for fixed values of k (0·1—1·5 at 0·1 intervals). From these graphs, Δ, the frequency of the first intense absorption band (top bonding level to lowest anti-bonding level) was found for different values of h and k. The results are presented in Table 2, in units of β (30,000 cm.$^{-1}$).

From Table 1 it can be seen that protonation of ketones produces an average bathochromic shift of 7300 cm.$^{-1}$ [except for the strained compound (IV)] of which 1500 cm.$^{-1}$ may be ascribed to solvent effect. Reasonable parameters are, therefore, $k = 0{\cdot}7$—$0{\cdot}6$ and $h = 0{\cdot}85$—$1{\cdot}1$.

To confirm these figures and to seek to determine the parameters more exactly calculatations were made for an αβ-unsaturated carboxylic acid, $\overset{1}{\mathrm{C}}{:}\overset{2}{\mathrm{C}}{\cdot}\overset{3}{\mathrm{C}}(\overset{5}{\mathrm{O}}\mathrm{H}){:}\overset{4}{\mathrm{O}}$, H_{35} being assumed to be $\beta/\sqrt{2}$. Other parameters were $H_{12} = \beta$, $H_{23} = \beta/\sqrt{2}$, $H_{34} = \beta$, $\alpha_4-\alpha_{\mathrm{C}} = 0{\cdot}4\beta$, $\alpha_5-\alpha_{\mathrm{C}} = h\beta$. The variations of three of the energy levels (ψ_1 top bonding, ψ_2 "non-bonding," and ψ_3 lowest anti-bonding), with h were plotted graphically. For $h = 0{\cdot}85$, the energies were found to be $\psi_2 \longrightarrow \psi_3 = 1{\cdot}34\beta$ (40,200 cm.$^{-1}$) and $\psi_1 \longrightarrow \psi_3 = 1{\cdot}63\beta$ (48,900 cm.$^{-1}$).

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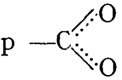
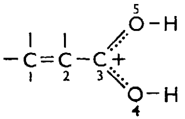
[13] Lake and Harrison, *J. Chem. Phys.*, 1959, **30**, 361.

[14] Urch, *J.*, 1958, 4767.

The relative intensities of these transitions may be considered as follows. If the group  is assumed to be symmetric it belongs to the class C_{2v}.[15] The three π-molecular orbitals will have symmetries, $\psi_1, B_2 : \psi_2, A_2 : \psi_3, B_2$ $(x, B_1 : y, B_2 : z, A_1)$. Thus a transition between ψ_1 and ψ_3 will be permitted $(\Gamma_{\psi_1} \times \Gamma_y \times \Gamma_{\psi_3} = A_1)$ but between ψ_2 and ψ_3 will be forbidden, $(\Gamma_{\psi_2} \times \Gamma_{x, y, \text{ or } z} \times \Gamma_{\psi_3} \neq A_1)$.[15,16] We assume that distortion of this simple model, to form CO_2H, will cause these rules to be relaxed but that $\psi_2 \longrightarrow \psi_3$ will remain weak and $\psi_1 \longrightarrow \psi_3$ will be strong. In confirmation of these calculations and expectations, acrylic acid [17] (in hexane) has weak absorption ($\log \varepsilon \sim 2$) at 41,000 cm.$^{-1}$ and strong absorption ($\log \varepsilon > 4$) at 48,500 cm.$^{-1}$. Other examples in Table 1 also show strong absorption in the region of 48,000 cm.$^{-1}$.

The ultraviolet spectra of possible products of the protonation of carboxylic acids may now be calculated, as follows.



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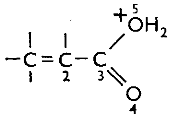
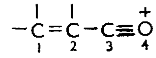


(IX)



(X)

(VIII). $H_{12} = \beta$, $H_{23} = \beta/\sqrt{2}$, $H_{34} = H_{35} = \beta/\sqrt{2}$, $\alpha_4 - \alpha_C = \alpha_5 - \alpha_C = 0{\cdot}85\beta$. The first strong absorption was calculated to be at $1{\cdot}43\beta$ (42,900 cm.$^{-1}$, 233 mμ).

(IX). Addition of a proton to the hydroxyl group removes the lone-pair *p*-electrons from conjugation with the π-system of the molecule. The effect of $-OH_2^+$ will therefore be purely inductive on $C_{(3)}$. We thus have: $H_{12} = \beta$, $H_{23} = \beta/\sqrt{2}$, $H_{34} = \beta$, $H_{35} = 0$, $\alpha_4 - \alpha_C = 0{\cdot}4\beta$, $\alpha_3 - \alpha_C = h\beta$.

In Table 3, Δ is calculated as a function of h.

TABLE 3.

h	(Initial acid)	0·1	0·2	0·3	0·4	0·5
Δ (β)	1·63	1·38	1·35	1·32	1·30	1·29
Δ': (β)	—	0·25	0·28	0·31	0·33	0·34
(cm.$^{-1}$) *	—	7500	8400	9300	9900	10,200

* For comparison with Table 1 it is necessary to add ~1500 cm.$^{-1}$ owing to solvent effects.

TABLE 4.

k	(Initial acid)	1·1	1·2	1·3
Δ (β)	1·63	1·50	1·56	1·63
Δ': (β)	—	0·13	0·07	0
(cm.$^{-1}$) *	—	3900	2100	0

* See footnote to Table 3.

(X). If an acylium ion were formed the triple bond between $C_{(3)}$ and $O_{(4)}$ would cause a shortening of this bond. The resonance integral H_{34} will therefore increase. Now the four-electron π-system is similar to that considered in Table 2, and the result of an increase in H_{34} may be observed for $k > 1{\cdot}0$. The variation of Δ with probable values of H_{34} is shown in Table 4.

The calculations presented above are of a general nature. However, the effect of substituents will be of the same order for both the charged and uncharged molecules and the shift of frequency (Δ') calculated should be unaffected. This expectation is clearly borne out by the results (Table 1). It remains to determine which of the three possible

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[15] Mulliken, *Phys. Rev.*, 1933, **43**, 279.

[16] Duncan, " Technique of Organic Chemistry, Vol. IX, Chemical Applications of Spectroscopy," Interscience Publ. Inc., New York, 1956, p. 587.

[17] Lüthy, *Z. phys. Chem.*, 1923, **107**, 285.

species best fits the observed frequency shift of about 6500 cm.$^{-1}$ (less 1500 cm.$^{-1}$ solvent effect).

A suitable value of k for the shortened bond in the ion (X) would be about 1·2, which gives a value of Δ' much smaller than that observed. Further, stable acylium ions seem to require special structural features for their formation.[18]

In the ion (IX) the inductive effect of OH_2^+ might well amount to $h = 0{\cdot}2$—$0{\cdot}3$, which corresponds to a much larger bathochromic shift than is observed.

Only ion (VIII) gives Δ' of the right order of magnitude; with the parameters used above it is in fact about 1000 cm.$^{-1}$ too large. However, Δ' is very sensitive to changes in the resonance integral, $H_{34} = H_{35}$. Although H_{34} was taken to be $\beta/\sqrt{2}$ since good agreement was achieved with a simple unsaturated carboxylic acid, values within the range $0{\cdot}75\beta$—$0{\cdot}65\beta$ are admissible. Corresponding bathochromic shifts are 4200—8700 cm.$^{-1}$.

Model (VIII) is thus in best agreement with the experimental results, from which it is concluded that αβ-unsaturated carboxylic acids are protonated on the carbonyl-oxygen atom in strong acid, in agreement with previous observations on substituted benzoic acids.[19]

The authors are indebted to the D.S.I.R. for an award to M. H. P.

Queen Mary College,
Mile End Road, London, E.1.

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[18] Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 52.

[19] Stewart and Yates, 133rd Meeting Amer. Chem. Soc., San Francisco, April 1958, p. 40N; *J. Amer. Chem. Soc.*, 1960, **82**, 4059.