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Solvent and Substituent Effects upon the n → π* Transition of Aliphatic Carboxylic Acids and Esters

Lyman R. Caswell,* M. Francine Howard, and Therese M. Onisto

Department of Chemistry, The Texas Woman's University, Denton, Texas 76204

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The near-ultraviolet spectra of 13 aliphatic carboxylic acids, 13 ethyl esters, and 16 alkyl acetates were determined for solutions in *n*-hexane, acetonitrile, and water. The carbonyl n → π* transition for these compounds was found in the vicinity of 206 nm under hydrogen-bonding conditions, and around 212 nm in the absence of hydrogen bonding. The spectra of the carboxylic acids in acetonitrile solution showed that the carboxyl group is not involved in hydrogen bonding in this solvent. The absorption band of alkyl acetates was red shifted by increasing bulkiness of the *O*-alkyl group. The values of $\epsilon_{\max}$ ranged from 40 to 100 and were determined principally by the electron-donating abilities of the *C*-alkyl groups, for both acids and esters. The spectra of these compounds as neat liquids showed a very weak transition ($\epsilon_{\max} \simeq 10^{-2}$) in the vicinity of 275 nm.

The electronic absorption spectra of saturated aliphatic carboxylic acids and their alkyl esters display three absorption bands. The best known of these bands is the transition observed between 200 and 220 nm, with a molar absorptivity of 50–60.[1] A variety of arguments have been used to assign this band to the carbonyl n → π* transition of both the acids[2,3] and the esters.[4] In agreement with this assignment, this band in the spectra of esters is blue shifted with increasing solvent polarity.[5] Variation of either the *C*-alkyl or the *O*-alkyl group in the ester structure produces variations in the transition energy which appear to be more closely related to the overall conformation of the molecule than to variation of the electrical effects of these substituents.[5,6]

The n → π* absorption band is superimposed upon the end absorption of a much stronger band with its peak in the vacuum ultraviolet. This absorption band has been studied by Nagakura and his co-workers,[7,8] who found peaks in the range 155–165 nm, with molar absorptivities from 2500 to 4200, in the spectra of the vapors of formic and acetic acids, and of ethyl acetate. Theoretical considerations led these authors to the conclusion that this band is of mixed character, involving intramolecular charge transfer from the singly bonded oxygen to the carbonyl group, combined with a smaller contribution from the π → π* transition of the carbonyl.[8]

In 1931, Hartleb published a study of the absorption spectra of neat liquid carboxylic acids.[9] This study showed the presence of a shoulder on the end absorption, at 270–280 nm. The molar absorptivity at this shoulder was of the order of magnitude of 10^{-2}. The only ester which was examined in the study, tributyrin, failed to show this shoulder, which led Hartleb to the conclusion that the shoulder was due to an absorption band of the carboxylate anion. Since the spectra of salts of carboxylic acids do not show an absorption band in the vicinity of this shoulder, this interpretation is not tenable. No further mention of this shoulder has appeared in the literature.

Although Closson and co-workers[5,6] made an extensive examination of solvent and substituent effects upon the spectra of aliphatic esters, no comparable study of the spectra of the corresponding acids has been described. Since the hydrogen bonding and steric interactions in carboxylic acids are quite different from those of esters, it is to be expected that solvent and substituent variation will have different effects upon the n → π* transition of acids than upon this transition of esters. In order to examine these effects, we have undertaken the measurement of the spectra of a number of carboxylic acids and their esters in three different solvents. These solvents were *n*-hexane, as a representative nonpolar solvent, acetonitrile, as a representative polar aprotic solvent, and water, as a representative polar hydrogen-bonding solvent. With supplies of these carboxylic acids and their esters available, it was also convenient to examine the spectra of these compounds as neat liquids, in the region of the shoulder described by Hartleb.[9]

Results and Discussion

The near-ultraviolet absorption spectra of 13 aliphatic carboxylic acids (Table I), 13 ethyl esters (Table II), and 16 alkyl acetates (Table III) were determined for solutions in *n*-hexane, acetonitrile, and water, and for neat liquids. All of the measurements were made with the samples thermostated at 20.0 °C,[10] in 1-cm rectangular cells. The wavelengths of the peaks, $\lambda_{\max}$, were reproducible within ±0.3 nm; and the molar absorptivities, $\epsilon_{\max}$, of these peaks for the solution spectra were reproducible within ±8. Since the excitation energies are proportional to the wavenumbers of the peaks, $\bar{\nu}_{\max}$, these latter values expressed in kilokaysers have been calculated, and are recorded in the tables.

Table I. Ultraviolet Absorption Spectra of Alkanoic Acids, RCO_2H, at 20.0 °C

		Neat liquid			In *n*-hexane			In acetonitrile			In water		
R	Registry no.	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}
H	64-18-6	*a*			206.8	48.36	45.1	214.5	46.62	48.3	205.9	48.57	48.2
$Cl(CH_2)_2$	107-94-8	*b*			~208^c	~48.1		*a*			~207^c	~48.3	
CH_3	64-19-7	*a*			202.6	49.36	50.3	210.8	47.44	36.7	*a*		
C_2H_5	79-09-4	273.6	36.55	0.0184	204.6	48.88	57.8	211.4	47.30	37.6	202.8	49.31	52.4
n-C_3H_7	107-92-6	268.9	37.19	0.0522	205.1	48.76	59.3	213.1	46.93	43.5	203.8	49.07	51.2
i-C_4H_9	503-74-2	273.8	36.52	0.0455	206.8	48.36	68.4	213.8	46.77	45.4	204.9	48.80	63.8
n-C_4H_9	109-52-4	~275 ^{c}	~36.4		206.5	48.43	63.9	211.7	47.24	48.1	205.0	48.78	61.3
n-C_5H_{11}	142-62-1	*a*			205.6	48.64	68.7	213.0	46.95	46.0	202.1	49.48	63.7
Cyclohexyl	98-89-5	*a*			207.0	48.31	87.5	218.8	45.70	66.9	~208^c	~48.1	
i-C_3H_7	79-31-2	270.2	37.01	0.0592	206.1	48.52	74.5	212.9	46.97	54.2	206.2	48.50	68.7
Cyclopentyl	3400-45-1	*a*			207.6	48.17	95.1	214.8	46.55	75.3	206.8	48.34	81.0
sec-C_4H_9	116-53-0	~277 ^{c}	~36.1		206.4	48.45	86.5	213.4	46.86	60.4	208.2	48.03	77.0
t-C_4H_9	75-98-9	*b*			207.9	48.10	99.1	213.9	46.75	68.1	208.7	47.92	84.4
Average^d		271.6	36.82	0.0438	206.1	48.53	71.4	213.5	46.84	52.5	205.4	48.68	65.2
		± 2.5	± 0.33	± 0.0178	± 1.5	± 0.33	± 17.5	± 2.1	± 0.45	± 12.5	± 2.2	± 0.48	± 12.6

[a] End absorption only. [b] Solid at 20.0 °C. [c] Shoulder. [d] ± One standard deviation; calculated only for peaks.

Table II. Ultraviolet Absorption Spectra of Ethyl Alkanoates, $RCO_2C_2H_5$, at 20.0 °C

		Neat liquid			In *n*-hexane			In acetonitrile			In water		
R	Registry no.	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}
H	109-94-4	*a*			215.6	46.38	78.9	213.6	46.82	68.5	208.1	48.05	73.3
$Cl(CH_2)_2$	623-71-2	271.9	36.78	0.0956	212.8	46.99	58.3	211.2	47.35	58.1	202.6	49.36	65.6
CH_3	141-78-6	*a*			210.5	47.51	58.4	209.0	47.85	58.1	202.9	49.29	62.7
C_2H_5	105-37-3	~282 ^{b}	~35.50		208.0	48.08	67.3	208.1	48.05	65.3	204.3	48.95	77.6
n-C_3H_7	105-54-4	281.7	35.50	0.0208	213.3	46.88	66.2	212.4	47.08	63.8	206.2	48.50	74.3
i-C_4H_9	108-64-5	~272 ^{b}	~36.8		208.3	48.01	69.0	208.2	48.03	77.6	205.4	48.69	85.8
n-C_4H_9	539-82-2	271.8	36.79	0.0501	212.4	47.08	65.3	211.8	47.21	67.2	205.9	48.57	73.0
n-C_5H_{11}	123-66-0	~284 ^{b}	~35.2		211.6	47.26	71.8	209.2	47.80	73.6	204.4	48.92	*c*
Cyclohexyl	3289-28-9	*a*			218.0	45.87	90.4	215.7	46.36	92.0	207.0	48.31	*c*
i-C_3H_7	97-62-1	279.3	35.80	0.0317	213.4	46.86	80.4	209.1	47.82	80.4	207.6	48.17	107
Cyclopentyl	5453-85-0	*a*			214.8	46.55	88.3	212.6	47.04	89.7	208.6	47.94	92.3
sec-C_4H_9	7452-79-1	~275 ^{b}	~36.4		214.0	46.73	77.1	212.2	47.13	90.3	207.9	48.10	102
t-C_4H_9	3938-95-2	*a*			215.0	46.51	101	214.3	46.66	95.0	208.1	48.05	96.7
Average^d		276.2	36.22	0.0496	212.9	46.98	74.8	211.3	47.32	75.4	206.1	48.53	82.8
		± 5.1	± 0.67	± 0.0330	± 2.8	± 0.63	± 12.8	± 2.4	± 0.55	± 13.1	± 2.0	± 0.48	± 14.9

[a] End absorption only. [b] Shoulder. [c] Saturated solution. [d] ± One standard deviation; calculated only for peaks.

The only spectra which showed fine structure were those of formic acid, ethyl formate, and methyl acetate. The fine structure blurred with increasing polarity of the medium and disappeared from the spectra of methyl acetate in polar solvents. The fine structures of the spectra of formic acid[11] and of alkyl formates[5] have been described elsewhere.

Only four compounds provided high enough concentrations in the vapor phase, under the conditions of these measurements, to give satisfactory results in the determination of the vapor spectra. These compounds were formic acid, λ_{max} 204.0 nm ($\bar{\nu}_{max}$ 49.02 kK); ethyl formate, λ_{max} 215.5 nm ($\bar{\nu}_{max}$ 46.40 kK); methyl acetate, λ_{max} 208.7 nm ($\bar{\nu}_{max}$ 47.92 kK); and ethyl acetate, λ_{max} 209.8 nm ($\bar{\nu}_{max}$ 47.66 kK). The red shifts of the spectra of these compounds in going from the vapor state to solutions in *n*-hexane are attributable to the dispersion effects of the solvent.[12] These effects for a nonpolar solvent with low dielectric constant, such as *n*-hexane, are generally sufficiently small, in comparison with dipole–dipole and hydrogen-bonding effects, that the spectra in this solvent may be taken as approximating the vapor spectrum for purposes of comparison with spectra for polar solvents.

Using a set of four methyl esters, Closson and Haug[5] described a correlation between the excitation energies, E_T, and the Taft polar substituent constants,[13] σ^*, for the *C*-alkyl groups of the esters. In order to facilitate search for such relationships, the data in Tables I–III were assembled in order of decreasing σ^* of the alkyl groups, that is, in order of increasing electron-donating ability. The wavenumbers of the excitations, $\bar{\nu}_{max}$, in kilokaysers, are directly proportional to the excitation energies, and can be converted to kilocalories per mole by multiplying by 2.859.[14] If the correlation of E_T with σ^* of the *C*-alkyl group actually existed, we would expect to see a gradual decline in the values of $\bar{\nu}_{max}$ from top to bottom in Tables I and II, and constancy of $\bar{\nu}_{max}$ in Table III. In fact, the variation of $\bar{\nu}_{max}$ for the carboxylic acids (Table I) and for the ethyl esters (Table II) is no greater than the variation for the alkyl acetates (Table III), as long as all measurements are made in the same solvent.

It has therefore been assumed that for each set of compounds $\bar{\nu}_{max}$ has a constant value for each solvent, and, further, that the two sets of esters can be considered as a single group for purposes of comparing solvent effects and for comparison with the carboxylic acids. By comparing the average values of the transition energy for a set of compounds in two different solvents, using only those compounds which show well-defined peaks in both solvents, we can achieve a measure of the solvent

Table III. Ultraviolet Absorption Spectra of Alkyl Acetates, CH_3CO_2R, at 20.0 °C

		Neat liquid			In *n*-hexane			In acetonitrile			In water		
R	Registry no.	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}	λ_{max}, nm	$\bar{\nu}_{max}$, kK	ϵ_{max}
$Cl(CH_2)_2$	542-58-5	*a*			209.9	47.64	57.7	207.9	48.10	55.4	203.0	49.26	58.3
CH_3	79-20-9	276.5	36.17	0.0989	210.2	47.57	54.6	206.5	48.43	63.4	202.7	49.33	55.3
C_2H_5	141-78-6	*a*			210.5	47.51	58.4	209.0	47.85	58.1	202.9	49.29	62.7
n-C_3H_7	109-60-4	273.5	36.56	0.0465	211.3	47.33	57.9	207.8	48.12	57.5	203.0	49.26	59.4
i-C_4H_9	110-19-0	*a*			211.1	47.37	60.5	207.0	48.31	65.5	201.3	49.68	59.5
i-C_5H_{11}	123-92-2	313.4	31.91	0.106	212.1	47.15	59.9	209.4	47.76	59.0	201.3	49.68	60.7
n-C_4H_9	628-63-7	*a*			210.5	47.51	60.6	208.5	47.96	56.9	202.3	49.43	61.9
n-C_5H_{11}	142-92-7	*a*			212.6	47.04	53.8	209.2	47.80	62.7	202.5	49.38	57.6
Cyclohexyl	622-45-7	~324 [b]	~30.9[b]		211.7	47.24	65.0	210.2	47.57	63.9	~208[b]	~48.1	
$C_2H_5CH(CH_3)CH_2$	624-41-9	*a*			211.6	47.26	57.2	208.7	47.92	54.2	*a*		
$(CH_3)_3CCH_2$	926-41-0	277.6	36.02	0.115	208.7	47.92	66.8	209.1	47.82	64.2	*a*		
i-C_3H_7	108-21-4	*a*			211.4	47.30	58.8	208.5	47.96	56.1	204.2	48.97	59.5
Cyclopentyl	933-05-1	296.9	33.68	0.0846	212.2	47.13	63.2	210.4	47.53	61.8	*a*		
sec-C_4H_9	105-46-4	~281 [b]	~35.6		212.2	47.13	65.2	210.9	47.42	63.8	204.1	49.00	61.1
t-C_4H_9	540-88-5	*a*			218.0	45.87	57.2	215.2	46.47	66.0	208.9	47.87	55.4
t-C_5H_{11}	926-41-0	*a*			215.9	46.32	63.1	213.7	46.79	67.0	210.0	47.62	57.1
Average[c]		287.6 ± 17.1	34.87 ± 2.00	0.0902 ± 0.0268	211.9 ± 2.3	47.21 ± 0.50	60.0 ± 3.8	209.5 ± 2.3	47.74 ± 0.51	61.0 ± 4.2	203.8 ± 2.8	49.06 ± 0.65	59.0 ± 2.4

[a] End absorption only. [b] Shoulder. [c] ± One standard deviation; calculated only for peaks.

effects upon the spectra. In the case of the esters, the overall average value of the blue shift from *n*-hexane to acetonitrile was 0.45 ± 0.27 kK, or 1.3 ± 0.8 kcal/mol.[15] Such a shift is in agreement for the effect of a polar solvent on an n → π* transition in the absence of hydrogen bonding.

Hydrogen-bonding effects must be considered in the case of water as the solvent and with the carboxylic acids, since the nonbonding pair of electrons of the carbonyl is the acceptor site for the hydrogen bond. Brealey and Kasha[16] have shown that the excitation energy of an n → π* transition in a hydrogen-bonding solvent includes the energy which must be added to break the hydrogen bond. In water this hydrogen-bond energy constitutes most of the energy difference of the blue shift from a nonpolar solvent. The overall average value of the blue shift for the esters in the current study was 1.71 ± 0.48 kK, or 4.9 ± 1.4 kcal/mol, for the difference between *n*-hexane and water.

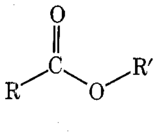
Carboxylic acids exist as hydrogen-bonded dimers in the vaper state and in solution in nonpolar solvents, as well as having the ability for hydrogen-bonding interaction with water. Comparison of the spectra of the acids with those of the esters shows that the spectra of the acids in *n*-hexane and in water are very similar to the spectra of the esters in water, that is, under hydrogen-bonding conditions. An unanticipated finding is noted, however, in the spectra of the acids in acetonitrile, which are similar to those of the esters in *n*-hexane. It must be concluded that the carboxylic acids are not involved in hydrogen-bonding interactions of any sort in acetonitrile. This conclusion is supported by nuclear magnetic resonance[17] and infrared[18] spectral studies of acetonitrile solutions of carboxylic acids. A study[19] of the vapor spectrum of acetic acid at elevated temperatures has shown a shift of λ_{max} from 200 nm for the dimer at 75 °C, to 210 nm at 200 °C, where acetic acid is almost entirely monomeric.[20] Reference to Table I shows 202.6 nm for the dimer in *n*-hexane, and 210.8 nm for the monomer in acetonitrile. These values are excellent agreements if one allows for the dispersion effects of the solvents. Similar solvent effects upon the π → π* transitions of three α,β-unsaturated acids have also been observed, and similarly interpreted.[21]

Using only data for acids that gave well-formed peaks in each pair of solvents, calculation of the blue shift from monomer in acetonitrile to dimer in hexane, and of the blue shift from acetonitrile to water, gave the same value for both shifts, 1.69 ± 0.35 kK, or 4.8 ± 1.0 kcal/mol, a remarkably good agreement with the value of the blue shift for esters. Using similar methods, Balasubramanian and Rao[22] have obtained a value of 4.8 kcal/mol for the energy of the hydrogen bond between acetone and water. Two conclusions must be made from this remarkable coincidence of values: first, for the systems examined here (though not necessarily under all conditions), water and carboxylic acids have comparable hydrogen-bond donating abilities; and, second, the nonbonding electrons of the singly bonded oxygen cannot be involved in either the hydrogen-bonding or the n → π* excitation of the acids and esters. The latter conclusion is further supported by protonation studies.[23] The infrared and Raman spectra of acetic acid in strong sulfuric acid solutions showed that the carboxyl is protonated on the carbonyl oxygen to give $CH_3C(OH)_2^+$, rather than the less symmetrical $CH_3(CO)OH_2^+$ ion which would result from the protonation of the singly bonded oxygen. This protonation of the carbonyl oxygen also suppressed the n → π* absorption band. In the current study, it was found that protonation of ethyl acetate by hydrochloric acid at concentrations as low as 0.1 N was sufficient to suppress the n → π* transition, leaving only end absorption.

Balasubramanian and Rao[22] found that the solvent-induced blue shifts of the n → π* transitions of methyl ketones, $RCOCH_3$, correlate fairly well with the σ* values for the alkyl groups, R, of these ketones. Despite the evidence that an electronically comparable transition is present in the absorption spectra of the acids and the esters, no such correlations could be detected in the spectral data for these compounds. The Taft σ* functions are measures solely of electronic influences of alkyl groups upon the carbonyl groups to which they are bonded. The failure of these functions to correlate with either the excitation energies or the solvent-induced changes in excitation energies means that other factors, in addition to the electronic effects of the *C*-alkyl groups, are significant in determining the experimental values of the excitation energies. Two such factors can be identified. The first of these is the increment of the experimental transition energy added by the end absorption of the 160-nm absorption band.

No rational correction for this end absorption can be made without a knowledge of the course and shape of this band deep into the vacuum ultraviolet for each compound and for the same experimental conditions. Such information is not experimentally accessible for spectra of solutions.

The second influencing factor is steric distortion of the chromophore away from a fully coplanar geometry. Since the n → π^* transition of the carbonyl group is symmetry forbidden, some sort of small distortion of the group geometry, probably vibrational in origin, is necessary for the transition to be spectroscopically observable. Since the molar absorptivities of carboxylic acids and their esters are some five to six times larger than those of simple aldehydes and ketones, additional factors must be at work in the former compounds to enhance the probability of the transition. It has been shown[24] that acyclic esters prefer the s-trans conformation (1) to the s-cis (2). The studies of Closson and co-workers[6] with lactones have shown that the s-cis conformation has a transition energy some 4 kcal/mol less than the s-trans. This difference is presumably largely due to the differences between the ground-state energies of the two conformations, with the s-trans conformation having the lower ground state energy. The preferred s-trans conformation places the O-alkyl group of the ester on the same side of the molecule as the carbonyl oxygen. The resulting steric interaction distorts the molecule out of coplanarity by an appreciable amount.[24] In the carboxylic acids, this distortion should be much smaller, but the generally accepted structure for the hydrogen-bonded dimer of these compounds requires that they also have the s-trans conformation in the dimeric state.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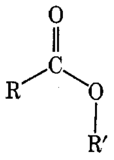
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Increasing bulk of the O-alkyl group should increase the steric interaction of this group with the carbonyl oxygen, and result in further deviation from coplanarity in the ester group. This will necessarily result in a decline of resonance stabilization energy, and will increase the energy of the ground state. The presence of bulky O-alkyl groups should thus produce a decline in excitation energy, assuming that these steric factors do not similarly affect the excited state energy. A good example of this effect may be observed with the alkyl acetates (Table III). Using dipole moment data, Pinkus and Lin[25] have recently calculated the dihedral angles, or angles of twist about the C–O single bond, in four alkyl acetates to be methyl acetate, 31°; ethyl acetate, 38°; isopropyl acetate, 39°; and *tert*-butyl acetate, 45°. The excitation energies of these esters, in kilocalories per mole, for solutions in *n*-hexane, acetonitrile, and water, respectively, are methyl acetate, 136.0, 138.5, and 141.0; ethyl acetate, 135.8, 136.8, and 140.9; isopropyl acetate, 135.2, 136.7, and 140.0; and *tert*-butyl acetate, 131.1, 132.9, and 136.9. The steric effect in the *tert*-butyl acetate is large enough that resonance interaction in this molecule is largely inhibited. It would be interesting to learn how this inhibition affects the charge-transfer band in the vacuum ultraviolet.

Ethyl formate has a smaller excitation energy than most of the other ethyl esters (Table II). The data of Closson and Haug[5] show that methyl formate also has a lower excitation energy than other methyl esters, and that alkyl formates generally have smaller excitation energies than the corresponding alkyl acetates. If the inductive effect of the C-alkyl group, as measured by the σ^* function, were the dominating factor in determining the excitation energy, we would expect to see larger excitation energies for the alkyl formates, rather than smaller ones. There is evidence[26] that the preferred conformation of alkyl formates may be s-cis rather than s-trans. Such a conformation certainly appears reasonable, since the hydrogen atom should offer less steric hindrance to the O-alkyl group than the carbonyl oxygen. The excitation energies of alkyl formates may thus not be electronically comparable with those of other esters as the result of a quite different geometry of charge distribution. It is interesting to note that the excitation energy of formic acid is similar to that of other carboxylic acids in *n*-hexane, but is considerably smaller in acetonitrile. In *n*-hexane, the formic acid should be locked into the s-trans conformation in the hydrogen-bonded dimer, but in the absence of hydrogen bonding in acetonitrile, each molecule is free to find its stablest conformation. In addition to these conformational effects, the excitation energies of formic acid and the formates are also lowered by the absence of C-alkyl hyperconjugation with the carbonyl group. The absence of this hyperconjugation, which raises the π^* level, has been used to explain why the excitation energy of acetaldehyde is less than that of acetone.[27]

Examination of the standard deviations for the average molar absorptivity values in each of the tables reveals an interesting difference. The average of the standard deviations from the average of each set of ϵ_{max} values for carboxylic acids and ethyl esters is ±13.9, while the average for the alkyl acetates is only ±3.5, only one-fourth as much. Recalling that the estimated experimental error in measurement of ϵ_{max} was ±8, it must be concluded that ϵ_{max} can be considered constant for the alkyl acetates, but is variable for the carboxylic acids and their ethyl esters. Generalizing this conclusion leads to the prediction that, under comparable conditions of measurement, the value of the molar absorptivity is determined by the C-alkyl group, and the contributions of the O-alkyl group to its value are negligible. The data of Closson and Haug[5] for the molar absorptivities of six alkyl formates in isooctane, with an average value of 77 ± 4, support this conclusion.

Closer inspection of the data in Tables I and II shows that the ϵ_{max} values for each solvent increase rather regularly with increasing electron-donating ability of the C-alkyl group, in both the series of carboxylic acids and ethyl esters. Since this is the sequence of decreasing σ^* values, it was of interest to determine if the ϵ_{max} values for these sets of compounds could be correlated with the ϵ_{max} values for the C-alkyl groups. We therefore assumed the simple straight-line relationship

$$\epsilon_{max} = \rho^*\sigma^* + \epsilon^0_{max}$$

and calculated the least-squares slopes ρ^*, intercepts ϵ^0_{max}, and correlation coefficients *r*, using the points for seven alkyl groups: ethyl, *n*-propyl, isobutyl, *n*-butyl, isopropyl, *sec*-butyl, and *tert*-butyl. Three of the data sets yielded correlation coefficients which met Jaffé's criterion[28] for a "satisfactory" correlation, namely $r > 0.95$. These sets were for the carboxylic acids in *n*-hexane, with $\rho^* = -209 \pm 9$, $\epsilon^0_{max} = 38$, and $r = 0.977$; carboxylic acids in acetonitrile, with $\rho^* = -144 \pm 7$, $\epsilon^0_{max} = 27$, and $r = 0.974$; and ethyl esters in *n*-hexane, with $\rho^* = -173 \pm 9$, $\epsilon^0_{max} = 46$, and $r = 0.965$. The correlation coefficients for the other three data sets, carboxylic acids in water, ethyl esters in acetonitrile, and ethyl esters in water, were all less than 0.9, Jaffé's minimum limit for a "fair" correlation. It is not surprising that the correlations are better with the carboxylic acids than with the esters, considering the difference between steric effects in the two classes of compounds. It is also not surprising that the best correlations exist where the magnitude of interaction with the solvent is least. But it is surprising that these correlations exist at all. Their existence supports the conclusion that ϵ_{max} for carboxylic acids and their esters is determined mainly by the electrical effects of the C-alkyl group.

Since ethyl acetate was the reference compound in evaluation of the σ^* values, the methyl group is automatically assigned a σ^* value of zero.[13] This leads to the expectation that the intercepts ϵ^0_{max} should equate with the ϵ_{max} values for acetic acid and ethyl acetate. Inspection of Tables I and II shows that the experimental ϵ_{max} values are significantly larger than the calculated ϵ^0_{max} values for these compounds. The sparse data for the only two available groups with positive σ^* values, $ClCH_2CH_2$ and H, suggest that the ϵ_{max} vs. σ^* curve may pass a minimum somewhere between $\sigma^* = -0.1$ and $\sigma^* = 0$, and show a positive slope for positive σ^* values. An alternate explanation is that the methyl group is actually more electron donating than is implied by the zero value for σ^* that is obtained when methyl is compared with itself; that is, the "real" value of σ^* for the methyl group should lie between −0.1 and 0.0.

A possible source of error which must be considered throughout these measurements is the effect of the rapid opening of the slits that occurs as the scan approaches the cutoff point of the instrument at 200 nm, especially in the 205–200-nm range.[5] Measurements of the slit widths for the three solvents were determined at 5-nm intervals between 215 and 200 nm and are recorded in the Experimental Section. The slit opening was serious only for *n*-hexane in the 200–205-nm range. Since, however, this affects only two spectra (acetic and propionic acids in *n*-hexane), we do not feel that the slit-opening effect has any seriously significant bearing on the experimental data or the general interpretation thereof.

The $n \rightarrow \pi^*$ transition of the carbonyl group is totally submerged when there is present in the molecule a stronger chromophore insulated from the carbonyl group, but with its λ_{max} near that of the carbonyl group. We examined the absorption spectra of phenylacetic and β-phenylpropionic acids and their ethyl esters, and of benzyl and β-phenethyl acetates. The spectra of these compounds were very similar to the spectra of toluene and ethylbenzene, with a very small blue shift of the λ_{max} values. This blue shift became smaller as the number of carbon atoms between the carbonyl group and the ring increased. The ϵ_{max} values were nearly identical with the values for the 205-nm band of the alkylbenzenes. Similar effects were observed for the 260-nm aromatic absorption band.

All of the acids and esters which are liquid at 20 °C showed evidence of an absorption band in the vicinity of the shoulder described by Hartleb[9] in the spectra of neat liquid fatty acids. In many cases this band was detectable only as a straightening out of the curvature of the end absorption, for which no specific λ_{max} value could be defined. In other cases there were shoulders similar to those described by Hartleb. A few cases gave very broad, low peaks in the vicinity of 275 nm.[29] Inspection of the data for alkyl acetates (Table III) shows that this peak is subject to red shifts by bulky *O*-alkyl groups, suggesting that the excitation energy is decreased by steric interaction between the *O*-alkyl group and the carbonyl oxygen. The extremely small molar absorptivity for this absorption band suggests that it is due to a singlet → triplet transition of the carbonyl group.

Experimental Section

The *n*-hexane used in these studies was Aldrich Gold Label spectrophotometric grade. The acetonitrile was Burdick and Jackson "distilled in glass" uv grade. The carboxylic acids and most of the esters were the highest purity grades commercially available. Four esters, ethyl α-methylbutyrate, ethyl cyclohexanecarboxylate, ethyl cyclopentanecarboxylate, and cyclopentyl acetate, were also synthesized in our laboratory, using standard esterification methods.

All absorption spectra were determined with a Cary Model 15 recording spectrophotometer, using a matched pair of 1-cm rectangular cells. Solutions were prepared using volumetric glassware calibrated for 20 °C, and the sample cell was thermostated at 20.0 ± 0.1 °C during measurement of all spectra.[10] Prior to each measurement, a baseline was established by a blank scan through the spectral region of interest, using solvent in both cells. The baseline absorbance at each peak was deducted from the absorbance at the peak. The resulting corrected absorbances were used for calculating absorptivities only if they fell within the range 0.2–0.9. The spectra were determined with a scale expansion of 1 nm per division of the chart paper. Slit widths were those automatically programmed by the instrument. These were for *n*-hexane 0.13 mm at 215 nm, 0.19 mm at 210 nm, 0.29 mm at 205 nm, and 0.51 mm at 200 nm; for acetonitrile, 0.12 mm at 215 nm, 0.14 mm at 210 nm, 0.20 mm at 205 nm, and 0.31 mm at 200 nm; and for water; 0.12 mm at 215 nm, 0.13 mm at 210 nm, 0.18 mm at 205 nm, and 0.24 mm at 200 nm.

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