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[CONTRIBUTION FROM THE CHEMISTRY AND CHEMICAL ENGINEERING DEPARTMENT, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Principal Electronic Absorption Bands of the Vinylogous Series Derived from Benzylaldehyde and Benzophenone

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The spectra of the vinylogous series $C_6H_5(CH{=}CH)_nCHO$ and $C_6H_5(CH{=}CH)_nCOC_6H_5$ were measured over the range from $n = 0$ to $n = 6$. The measurements were made in methanol, acetic acid and benzene solutions, and also in acetic acid containing enough sulfuric acid to obtain the principal bands of the ions of all of them except benzaldehyde and benzophenone. With the exception of benzophenone the neutral series obeyed the equation $\lambda^2_{max} = a + bn$ up to $n = 5$ for the aldehydes and $n = 4$ for the ketones. The ionic series obeyed the equation $\lambda_{max} = a + bn$. The wave numbers of the principal bands of the ions were smaller than those of the corresponding neutral compound whether the aldehydes or ketones were considered. The wave numbers of the principal bands of the ketones were found to be smaller than those of the corresponding aldehydes whether the neutral compounds or the ions were considered. The wave numbers of the principal bands of all four series were found to decrease with each interpolation of a vinyl group by amounts that decreased with every interpolation. Assuming that these decreases followed geometric progressions, empirical equations have been written for all four series. The same common factors were used for aldehydes and ketones. These equations were applicable as far as the measurements were made ($n = 6$). The equation for the ketonic series did not fit benzophenone. From the spectra, approximate values for the ratio of ion to base were made at a fixed acidity. The logarithms of these ratios were larger for ketones than for the corresponding aldehydes by approximately constant amounts. In both aldehydic and ketonic series these logarithms increase with each interpolation of a vinyl group by increments that decreased approximately by a geometric progression with the same common factor for both series. The logarithms, which are proportional to base strengths, therefore obeyed an equation similar to those obeyed by the wave numbers. It is pointed out that these equations are empirical and their accuracy must be largely fortuitous. However, they show that the effect on the energy of a reaction of interpolating vinyl groups in a conjugate system decreases with the length of the conjugate system.

Introduction

A compound and its vinylogs, $R(CH{=}CH)_nR'$ with $n = 0, 1, 2\ldots$, form a series that is homologous with respect to $CH{=}CH$. Such series can be called vinylogous series. In the spectra of a vinylogous series there generally are certain bands that show such a close relationship from member to member that they can be considered as a class common to the series. Often these bands are more intense or of longer wave lengths than the others and are called the principal bands of the series. The peaks of these bands move in a regular way toward the red as n increases.

The relationship between the position of the principal band and n varies with the series, but often can be expressed by a simple mathematical equation. For many series of the type $R_2\overset{+}{N}{=}CH(CH{=}CH)_nNR_2$, λ_{max} of the principal band is very nearly a linear function of n up to as large a value of n as have been obtained and including the first member ($n = 0$).[1] For the series $C_6H_5(CH{=}CH)_2C_6H_5$ the square of λ_{max} is linear with n, except for $n = 0$.[2] This square law is moderately applicable to several series in which the conjugate system is attached to a $C{=}O$ or $C{=}N$ group, but the measurements do not extend to values of $n > 4$.[3]

Our measurements of the spectra of the series $C_6H_5(CH{=}CH)CHO$ and $C_6H_5(CH{=}CH)_nCOC_6H_5$ are of interest because (1) measurements have been made up to $n = 6$, which allows the breakdown of the square law to be observed, (2) the first member of the ketonic series has a different symmetry to the other ketones and so does not conform to the series, and (3) the aldehydes and ketones are basic and form the new series $C_6H_5(CH{=}CH)_nCH\overset{+}{O}H$ and $C_6H_5(CH{-}CH)_nC\overset{+}{O}HC_6H_5$ in which a positive charge can be carried along the conjugate system without the separation of opposite charges necessary for the aldehydes and ketones.

A conjugate system allows the possibility of many stereoisomers. However a glance at Figs. 1 and 6 will convince the reader that such regularity could result only if all the compounds have the same stereo pattern.

Since the names and formulas of these compounds are long, we shall indicate each compound by a letter with a subscript. The letter A or K shows that it belongs to the aldehydic or ketonic series. The subscript number shows the number of vinyl groups. Thus A_2 is 5-phenylpentadienal and K_0 is benzophenone.

Materials and Methods

A_3,A_4,A_5,A_6.—These aldehydes were prepared by condensing crotonaldehyde with cinnamaldehyde or 5-phenylpentadienal in alcohol using piperidine acetate as the catalyst.[4] A_3 and A_5 were obtained from A_1, and were separated with toluene in which A_5 is insoluble in the cold. A_4 and A_6 were obtained from A_2 and were separated with ethyl acetate in which A_6 is insoluble. After recrystallizations these aldehydes were sublimed in vacuum. The freshly prepared final products were beautiful colored crystals. The yields were always less than 10% and sometimes less than 5%.

A_2.—Cinnamaldehyde and cyanacetic acid were condensed and the product was decarboxylated by heating with copper powder.[5] The resulting nitrile was reduced with $SnCl_2$ and HCl in dioxane.[6] After hydrolysis of the stannic complex compound the aldehyde was treated with

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(1) L. Brooker, *Rev. Modern Phys.*, **14**, 275 (1942).

(2) G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1934).

(3) L. Ferguson and G. Branch, THIS JOURNAL, **66**, 1467 (1944).

(4) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **12**, 496 (1929).

(5) G. Wittig and R. Kethur, *Ber.*, **69**, 2081 (1936).

(6) K. Hausser, *Z. Tech. Physik*, **15**, 10 (1839).

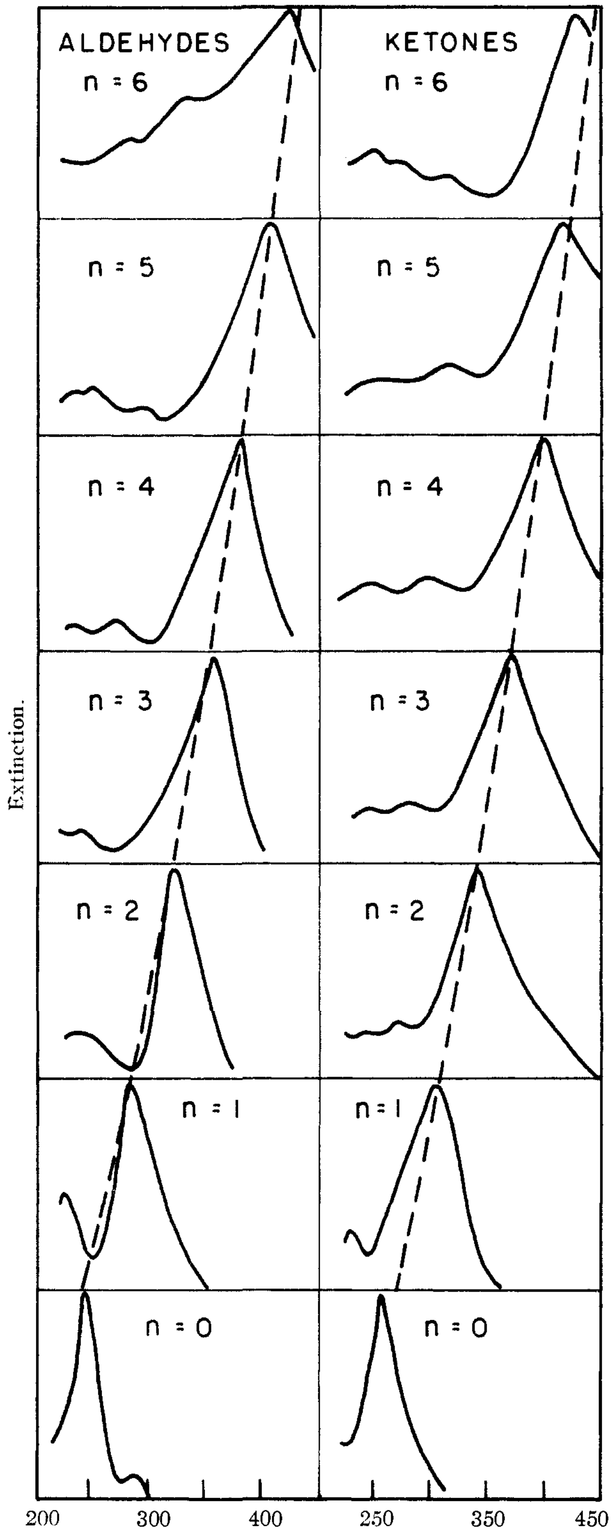

Fig. 1.—Spectra of the series $C_6H_5(CH{=}CH)_nCHO$ and $C_6H_5(CH{=}CH)_nCOC_6H_5$ in methanol. Extinctions are arbitrary, the peaks of the principal bands being drawn to reach the tops of the appropriate sections. The broken lines correspond to the equation $\lambda^2 = a + bn$. For the values of the constants, see the text.

$NaHSO_3$ and SO_2. The crystalline bisulfite compound was recrystallized from water, and hydrolyzed. The resulting aldehyde was extracted with ether, the ether driven off and the residue distilled in vacuum. It was then crystallized from petroleum ether, from which it separated as colorless crystals. It did not keep in this form except in an atmosphere of nitrogen.

K_1,K_2,K_3,K_4,K_5,K_6.—The ketones were prepared by condensing the freshly prepared aldehyde with one less double bond with acetophenone[7]; stirring, 10°, sodium hydroxide as catalyst and alcohol as solvent were the normal conditions. With higher aldehydes the solubility was increased by using ethyl acetate as the solvent and an excess of acetophenone. After two to four hours the product was filtered off and recrystallized. This was done with alcohol for the lower members and ethyl acetate for the higher. The yields were good (50–80%).

The spectra were measured with a Beckman spectrophotometer, using 1-cm. cells and solutions of about 10^{-5} *M*. In most cases the solutions were made from a weighed quantity of compound in a measured volume of solvent. The solutions of the very slowly dissolving compounds A_5, A_6 and K_6 were made by treating an excess of solid with the solvent and filtering off the solutions. No molal extinction coefficients were obtained for these compounds.

Most of these compounds are unstable toward light and air, and generally a repeated measurement of a spectrum with the original solution did not check with the first measurement. The positions and relative intensities of the bands were no different, but the extinctions of the second spectrum were less than those of the first. The positions of the bands given in this paper can be taken to have normal accuracy, but the molal extinction coefficients have large errors; in spite of this their measured values have been given. However, the molal extinction coefficients are not given in the figures, where arbitrary extinctions are shown.

TABLE I

THE COMPOUNDS INVESTIGATED AND SOME OF THEIR PROPERTIES

Compound in code	M.p., °C.	M.p. (lit.), °C.	Sublimation	Color
A_0	Liq.	Liq.	...	Colorless
A_1	Liq.	Liq.	...	Colorless
A_2	40–41	38–40	...	Colorless
A_3	115–116	116	110° (0.1 mm.)	Yellow
A_4	142–144	144	135° (0.1 mm.)	Orange
A_5	183–184	183	170° (0.1 mm.)	Orange-red
A_6	210–213	213	200° (0.02 mm.)	Crimson
K_0	48	48	...	Colorless
K_1	55–57	55–57	...	Pale yellow
K_2	102–103	102–103	...	Yellow
K_3	79–82	...	...	Deep yellow
K_4	123–124	...	...	Orange-yellow
K_5	164–165	...	...	Orange
K_6	Dec. 185	...	...	Red

Spectra of the Aldehydes and Ketones

The spectra were measured in methanol to 220 mμ, in acetic acid to 240 mμ and in benzene to 280 mμ.

The spectra of all the substances in methanol are shown in Fig. 1. In this figure the units of extinction are arbitrarily chosen, so that principal bands have the same heights, and each reaches the top of its appropriate section. Through the spectra of the aldehydes a broken line has been drawn, the curvature being such that the line crosses each section at a wave length given by the equation $\lambda^2 = a + bn$ with the values of a and b so chosen as to obtain the best fit between observed values of λ and those calculated from the above equation. A similar dotted line is drawn in the section reserved for ketones. The coincidence between the dotted lines and the peaks of the bands shows the correlation between the observed values and those calculated from the above equation.

Figure 1 shows that there is no uncertainty in

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[7] M. Scholtz, *Ber.*, **28**, 1730 (1895).

selecting the principal bands, and that in both series λ_{max} increases in an orderly way with n, except for K_0.

The λ_{max} values and their molal extinction coefficients in the three solvents are shown in Table II with the exceptions of those of A_0 and K_0 in benzene and ϵ values for A_5, A_6 and K_6. As already explained the values for the molal extinction coefficients are subject to large errors. Nevertheless the values shown in Table II have the normal characteristic of vinylogous series of increasing with m. The exceptions, A_3 and A_4 in methanol, and K_2 and K_3 in acetic acid, are obviously due to error.

TABLE II

SPECTRAL DATA OF THE PRINCIPAL BANDS

	CH_3OH		C_6H_6		CH_3COOH	
Comp.	λ, mμ	$\epsilon \times 10^{-4}$	λ, mμ	$\epsilon \times 10^{-4}$	λ, mμ	$\epsilon \times 10^{-4}$
A_0	244	1.2	...	...	250	1.0
A_1	285	2.5	287	2.3	287	2.3
A_2	323	4.3	323	3.9	325	4.0
A_3	355	5.4	350	4.8	360	5.1
A_4	382	5.1	378	6.0	387	6.1
A_5	408	...	404	...	410	...
A_6	425	...	425	...	430	...
K_0	254	2.0	...	...	254	1.8
K_1	305	2.5	308	2.2	310	2.3
K_2	342	3.9	342	3.6	343	3.6
K_3	373	4.6	370	4.6	376	3.1
K_4	400	6.0	395	6.2	402	5.7
K_5	418	6.6	418	7.7	418	6.4
K_6	430	...	435	...	445	...

The principal bands in acetic acid and benzene are only a little displaced from those in methanol. The displacement is toward the red in acetic acid and, on an average, toward the violet in benzene. These displacements vary for different compounds, for acetic acid from 0 to 15 mμ, for benzene from +5 to −5 mμ. The average displacement is 4 mμ for acetic acid and 1 mμ for benzene.

The principal bands are without structure in methanol and acetic acid. This is also the case in benzene where $n < 3$, but with $n \geqq 3$, the principal band has a shoulder in each side, that on the red side being the more pronounced.

Sample spectra are shown in Figs. 2, 3, 4 and 5. Figures 2 and 3 show the spectra of A_2 and K_2, where $n < 3$. Figures 4 and 5 show the spectra of A_5 and K_3, where $n \geqq 3$. A_5 has been chosen to show that the trailing bands of the methanol solutions (see Fig. 1) appear in the more opaque solvents, when n is sufficiently large.

In Fig. 1 the peaks of the principal bands of A_0, A_1, A_2, A_3, A_4, A_5, K_1, K_2, K_3 and K_4 fall on or near the broken lines. This corresponds to an agreement between the observed λ_{max} values and those calculated from the equations $\lambda^2 = 5.95 \times 10^4 + 2.18 \times 10^4\, n$ for the aldehydes and $\lambda^2 = 7.2 \times 10^4 + 2.18 \times 10^4\, n$ for the ketones. The same agreement between observed and values calculated from the equation $\lambda^2 = a + bn$ can be obtained for benzene and acetic acid solutions, if slight changes are made in the values for the constant a.

However, the values of λ_{max} for A_6, K_5 and K_6 do not fit the equations, as can be seen by the separation of the broken lines from the peaks of these bands in Fig. 1. For K_6 in methanol the deviation is 20 mμ. No change in the constants of the equation can make the calculated and observed values fit. Of course one can make calculated and observed values even for K_6 agree by the requisite changes of the constants a and b; but this destroys the agreement for other ketones. One must conclude that the equation $\lambda^2 = a + bn$ is only an approximation for these series. Though it is a close one when n is small, it fails lamentably for large values of n. This casts no aspersions on the square law for the series $(C_6H_5)(CH{=}CH)_3C_6H_5$, where it is known to be accurate up to $n = 7$.

The first members of homologous series are often anomalous, as for instance water taken as the first member of the series $H(CH_2)_nOH$. In this instance we find that λ_{max} of benzaldehyde is normal for the aldehydic series, but λ_{max} for benzophenone is anomalous for the ketonic series (see Fig. 1).

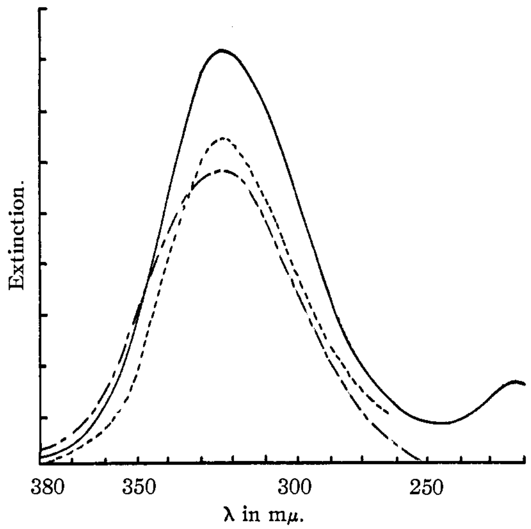

Fig. 2.—Spectra of $C_6H_5(CH{=}CH)_2CHO$: —, in methanol; - - - -, in benzene; — — — —, in acetic acid. Extinctions are arbitrary, being chosen to keep the curve for benzene distinct.

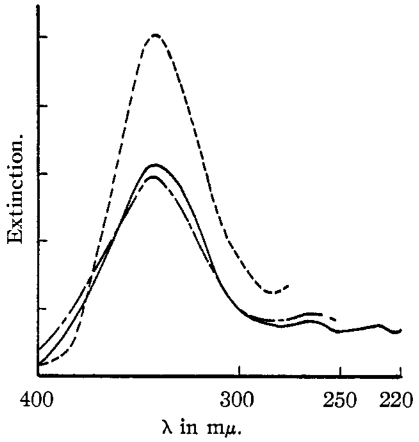

Fig. 3.—Spectra of $C_6H_5(CH{=}CH)_2COC_6H_5$: —, in methanol; - - - -, in benzene; — — — —, in acetic acid. Extinctions are arbitrary, being chosen to keep the curve for benzene distinct.

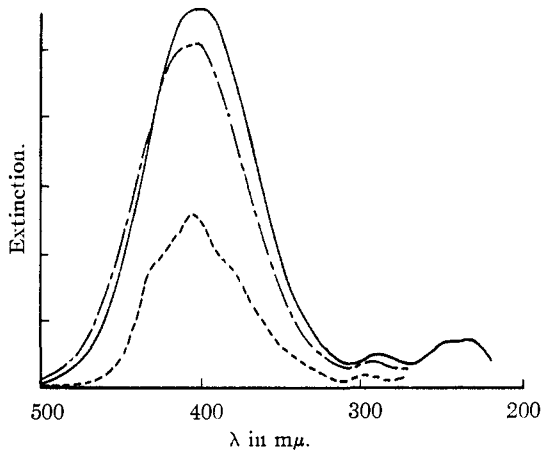

Fig. 4.—Spectra of $C_6H_5(CH{=}CH)_5CHO$: —, in methanol; - - - -, in benzene; — — — —, in acetic acid. Extinctions are arbitrary, being chosen to keep the curve for benzene distinct.

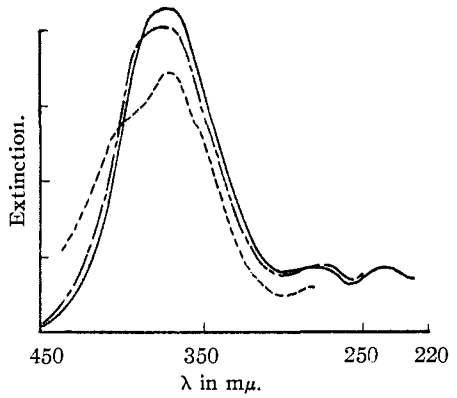

Fig. 5.—Spectra of $C_6H_5(CH{=}CH)_3COC_6H_5$: —, in methanol; - - - -, in benzene; — — — —, in acetic acid. Extinctions are arbitrary, being chosen to keep the curve for benzene distinct.

It seems probable that this is connected with the presence of an axis of symmetry through the carbonyl group and between the phenyl groups. There is no such axis of symmetry in the other members of the ketonic series, and there is no such specific axis in benzaldehyde.

In these series the principal bands are distinguished from the others by their greater intensities. The smaller bands are nearly all at shorter wave lengths than the principal bands, and most of them are visible only in methanol, the most transparent solvent used in these measurements. The following are wave lengths for the small peaks observed in methanol: 280 mμ for A_0, 224 mμ and 235 mμ for A_2, 245 mμ for A_3, 235 and 270 mμ for A_4, 240, 250 and 292 mμ for A_5, 280 and 330 mμ for A_6, 227 mμ for K_1, 240 and 270 mμ for K_2, 242 and 276 mμ for K_3, 245 and 293 mμ for K_4, 250, 255 and 218 mμ for K_5, 250, 270 and 310 mμ for K_6.

Spectra of the Ions

The spectrum of each of the substances was measured in acetic acid with 5, 10 and 20% by volume of concentrated sulfuric acid (d. 1.84). One of these solutions was diluted with acetic acid to insignificant concentrations of sulfuric acid, and its spectrum measured. The obvious difficulties that would be involved in this last measurement were overcome by making a solution in the mixed acids concentrated with respect to the substance, and diluting a portion with the appropriate mixture of sulfuric and acetic acids, and another portion with pure acetic acid.

The spectrum in a mixture of acetic and sulfuric acids normally shows two strong bands; one of these can be identified as the principal band of the aldehyde or ketone. We shall call this the P-band. The other band is nearer the red end of the spectrum. This we shall call the I-band. The normal behavior is that the I-band grows at the expense of the P-band with increase of acidity, the respective increase and decrease being of the same order of magnitude. On dilution the I-band disappears and what we shall call the R-band takes its place. The R-band is indistinguishable from the principal band in pure acetic acid.

The greater value of λ_{max} of I- than of P-bands shows that the conjugate system is maintained in the action of sulfuric acid, but acquires more positive charge. The old explanation that the sulfuric acid neutralizes the base (aldehyde or ketone) to form the ion $C_6H_5(CH{=}CH)_nCROH^+$ is satisfactory.[8]

Rapidly reversible reactions of the ions in which the conjugate system and the charge are maintained (*e.g.*, esterification) are possible. If the bands of the product of such a reaction are resolved from those of the ion in our procedure, the reaction is demonstrable, but if these bands were not resolved the reaction is not distinguishable from a solvent effect of sulfuric acid. In our experiments the I-bands were never duplicated by excess of sulfuric acid, and we shall treat the effects of change of concentration of sulfuric acid on them as solvent effects.

Table III shows λ_{max} and molal extinction coefficients of the P-, I- and R-bands in the three concentrations of sulfuric acid and of the P-bands in pure acetic acid for all the substances. Except where specifically mentioned no R-bands were observed in the neighborhood of the I-bands. As in Table II, the ε-values were subject to considerable error. The errors were probably greater than those for the neutral compounds.

A_0, A_1, K_0 and K_6 did not behave normally. A_0 and K_0 gave no I-bands. They are too weakly basic to form ions with 20% sulfuric acid.

On acidification, the decrease of the P-band of A_1 was much greater than the increase of its I-band (more than nine to one). Dilution restores the P-band to its normal intensity. Presumably the compound of A_1 and sulfuric acid is only about 10% ionized. The un-ionized compound would not absorb much light, since it has lost the carbon to oxygen double bond.

That this un-ionized species is formed in appreciable quantities only in the aldehyde with one vinyl group, suggests that it is not the hydroxy bisulfate, but the 1,4-addition product, $HCOH{=}CH{-}CHOSO_3HC_6H_5$ or its anhydride. Otherwise the

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(8) A. Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923).

TABLE III

SPECTRAL DATA FOR SOLUTIONS IN MIXTURES OF ACETIC AND SULFURIC ACIDS

Comp.	0% H_2SO_4 λ, mμ	0% H_2SO_4 $E \times 10^{-3}$	5% H_2SO_4 λ, mμ	$E \times 10^{-3}$	λ, mμ	$E \times 10^{-3}$	10% H_2SO_4 λ, mμ	$E \times 10^{-3}$	λ, mμ	$E \times 10^{-3}$	20% H_2SO_4 λ, mμ	$E \times 10^{-3}$	λ, mμ	$E \times 10^{-3}$	Diluted with CH_3COOH λ, mμ	$E \times 10^{-3}$	Orig. H_2SO_4, %
A_0	250	1.0	250	1.0			250	0.4			250	1.3			250	1.0	20
A_1	287	2.3	295	2.1			295	2.1			300	0.7	(355)[a]	0.17	287	2.3	20
A_2	325	4.0	330	3.6	(400)	0.4	335	3.0	400	1.0	340	2.0	404	2.2	325	3.3	20
A_3	360	5.1	365	4.0	450	0.8	372	3.1	458	1.9	382	1.8	468	3.7	359	4.2	20
A_4	387	6.1	392	4.0	512	0.8	400	3.0	520	3.0	(395)[a]	1.4	525	5.4	386	5.5	10
A_5[b]	410	...	415	...	560	...	430	...	570	...	(436)[a]	...	580	...	410	...	5
A_6[b]	430	...	435	...	620	...	445	...	625	...	(445)[a]	...	630	...	430	...	5
K_0	254	1.8	253	1.7			255	1.6			260	1.4			253	1.6	20
K_1	310	2.3	312	2.3			315	2.1	(390)[a]	0.2	320	1.8	390	0.74	310	2.3	20
K_2	343	3.6	350	3.2	450	0.43	355	2.7	455	1.2	370	1.65	460	2.9	344	3.6	20
K_3	376	3.1	382	2.8	520	0.59	387	2.2	520	2.0	(400)[a]	1.0	530	4.0	376	3.1	5
K_4	402	5.7	407	3.6	588	2.0	414	2.5	585	3.7	(415)[a]	0.87	585	5.2	403	5.4	5
K_5	418	6.4	430	3.1	630	2.2	435	1.65	640	3.7	(440)[a]	0.7	650	5.2	418	5.4	5
K_6[b]	445	...	450	...	735	...	455	...	710	...	(470)[a]	...	735	...	[c]		

[a] Parentheses have been put around these numbers to indicate that their accuracy is not as great as in other cases because the bands are somewhat weak, or mixed with absorption from another species. [b] The concentrations of A_5, A_6 and K_6 were not measured and so no molal extinction coefficients can be given. However, the ratio of extinctions at the I- and P-bands can be measured from the spectra without knowing the concentrations. These values were 0.457 at 5% H_2SO_4, 1.39 at 10% and 3.7 at 20% for A_5; 0.59 at 5% H_2SO_4, 1.7 at 10% and 4.0 at 20% for A_6; 1.8 at 5% H_2SO_4, 2.8 at 10% and 4.0 at 20% for K_6. [c] Two strong R-bands were obtained with K_6, at 436 and 745 mμ from a solution in 5% H_2SO_4. From a solution in 1% H_2SO_4, R-bands were obtained at 440 and 745 mμ.

greater resonance of the aldehyde than of the hydroxy bisulfate would make the un-ionized compound easier to form with A_0 than with A_1. The extra resonance of extra vinyl group favors ionization of the compound, hence it was not detected in the higher aldehydes. The extra phenyl group of K_1 would have the same effect. Also addition products are less stable toward ketones than they are toward aldehydes.

The I-band of K_6 was not lost on dilution of a 5% H_2SO_4 solution. The experiment was confirmed using 1% H_2SO_4. After dilution the concentration of the acid was well below 0.1%, yet the I-band was still strong. The λ_{max} values observed for the I-band varied in a very irregular manner. It was 745 mμ in the diluted solutions, 735 mμ in 5% H_2SO_4, 710 mμ in 10% H_2SO_4, and 735 mμ in 20% H_2SO_4. Dilution did not restore the P-band to its location in pure acetic acid. Thus R-bands were obtained at 436 and 440 mμ from 5 and 1% H_2SO_4, respectively, while λ_{max} in pure acetic acid is 445 mμ. The ratio of intensities of the I- to P-bands in 5% H_2SO_4 was also anomalously high. The whole behavior of K_6 suggests that some other strongly colored substance was formed, but to varying extents in the different experiments.

To properly understand the behavior of K_6 one must know that the method of making its solutions was not like those for the other compounds. To overcome the difficulty of solution excess of the solid was added and the solution warmed until there was sufficient color for a measurement, cooled and the clear supernatant liquid decanted. When the solution was destined for dilution (5 and 1% H_2SO_4) a very strong solution must be made, and greater heating was necessary than for direct measurements. Thus for the less acid solutions the treatment was more drastic than for the more acid solutions. The treatment was least drastic for the solution in 10% H_2SO_4.

The R-band found at 745 mμ suggests that the structure of the compound formed is similar to that of the ion. The R-bands found 436 and 440 mμ suggest that the structure is similar to that of K_6. This contradiction can be explained if the substance is tautomeric, the structures of the tautomers being similar from a spectroscopic aspect to K_6 and its ion. That is both have six vinyl groups and one a C=O and the other a $C{=}OH^+$ group. If we assume that the reaction is sulfonation, then the product has a group that is very strongly acid in acetic acid and the basic group $(CH{=}CH)_6CO$. Partial neutralization between these groups results in the tautomeric mixture

$$C_6H_5CH{=}CSO_3H(CH{=}CH)_5COC_6H_5 \rightleftarrows C_6H_5CH{=}CS\overset{-}{O}_3(CH{=}CH)_5C\overset{+}{O}HC_6H_5$$

The position chosen for the sulfonic acid group is arbitrary, there being no evidence of its location.

The λ_{max} values of the P- and I-bands increase with increase of the concentration of sulfuric acid Notable exceptions are the λ_{max} values of the I-bands of K_3 and K_4. In general the bathochromic effect of the sulfuric acid on the I-bands are more marked in the aldehydes than in the ketones. These effects are greater than the solvent effect of acetic acid compared with methanol, and they are even more irregular. When, as in this case, a reagent reacts with a substrate to form a new product with a greater λ_{max}, the reagent tends to be bathochromic on the bands of both substrate and product. This is the result of incomplete resolution of the bands. However, the peaks of the P- and I-bands are on an average 150 mμ apart, and even though the bands are not very sharp the lack of resolution is hardly sufficient to account for all of the bathochromic effect of sulfuric acid. Whatever the cause of this bathochromic action comparisons between the λ_{max} values of the I-bands are best made at a single sulfuric acid concentration.

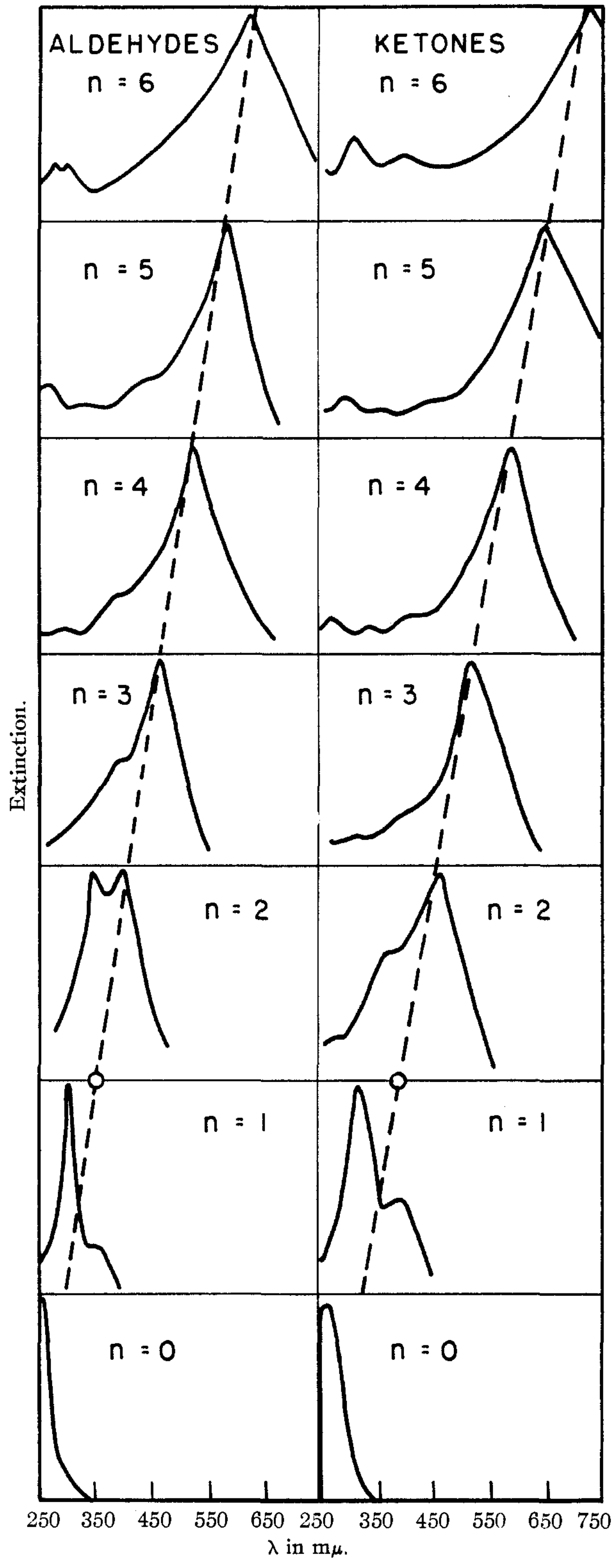

Fig. 6.—Spectra of $C_6H_5(CH{=}CH)_nCHO$ and $C_6H_5(CH{=}CH)_nCOC_6H_5$ in acetic acid 20% by volume with respect to commercial H_2SO_4. Extinctions are arbitrary, the peaks of strongest bands being drawn to reach the appropriate sections. Where the I-band is less intense than the P-band a circle has been drawn at the top of the section at the wave length of the I-band. The broken lines correspond to the equation $\lambda_{max} = a + bn$. For the values of the constants see the text.

This has been done in Fig. 6 where all the spectra in 20% H_2SO_4 are given.

The spectra in Fig. 6 have been drawn so that the peak of the stronger band reaches the top of its section. Where this band is the P-band a circle has been put at the top of the section at the wave length of the peak of the I-band. The straight lines corresponding to the equations $\lambda = 301 + 55n$ and $\lambda = 325 + 65n$ have been drawn through the halves reserved for the aldehydes and ketones, respectively. The correspondence between these straight lines and the peaks of the I-bands or the circles that replace them measures the extent to which the relationships between the λ_{max} values of the ions and n are linear. Except for K_6 the correspondence is as good as could be expected.

Quite similar relationships can be shown for the solutions in 5 and 10% H_2SO_4. The same coefficients of n can be used, but small changes in the other constants are required. In 10% H_2SO_4, λ_{max} for K_6 fits the equation.

From the spectra of the bases and ions one can make the following generalizations: the values of λ_{max} for ketones are greater than those of the corresponding aldehydes whether the bases or the ions are compared. The difference tends to get smaller for the bases but greater for the ions, when n is increased. The values of λ_{max} for the ions are greater than those of the corresponding bases. This effect is greater for the ketonic than for the aldehydic series. In both cases the difference increases when n is increased.

These compounds can be considered as carbonium ions in which the charge is supplied from the $C{=}O$ or $C{=}\overset{+}{O}H$ group. In both cases the extra phenyl group of the ketone increases the range of the positive charge and hence makes λ_{max} greater than that of the corresponding aldehydes. The $C{=}\overset{+}{O}H$ group donates more charge to the conjugate system than the $C{=}O$ group does, and hence λ_{max} for an ion is greater than that for the base, and this difference increases as more scope is given to the charge by extra vinyl groups. It is difficult to see why the difference between ketonic and aldehydic ions increases with n. It is as well to note that this difference would decrease rather than increase had the wave numbers instead of the wave lengths been used for the comparison.

Sample spectra are shown in Figs. 7, 8, 9 and 10. The substances are A_4, A_5, K_3 and K_4, and the spectrum of each is shown in the three concentrations of sulfuric acid. The relative values of the extinctions in different parts of the same curve are correct, but the relative values of extinctions in different curves, even if they are in the same figure, are meaningless.

These spectra illustrate the points discussed above. They also show that the relative intensity of the I-band to that of the P-band is greater for the ketones than for the aldehydes, and increases with the acidity and the number of vinyl groups.

Relative Strengths of the Bases

The error in the molal extinction coefficients due to the deterioration of the substances makes it impossible to measure the relative strengths of these

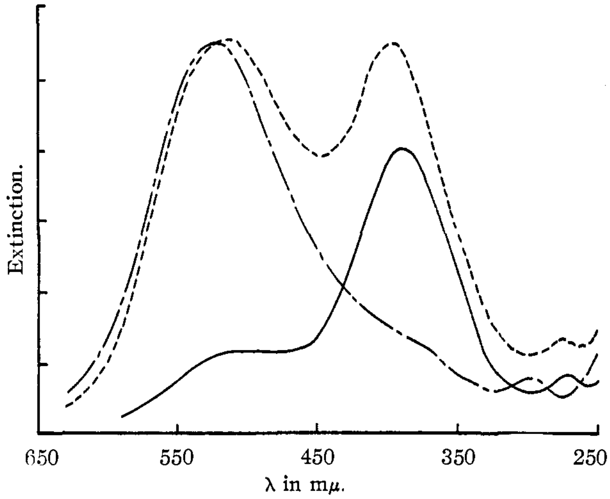

Fig. 7.—The spectra of $C_6H_5(CH{=}CH)_4CHO$ in mixtures of acetic and sulfuric acids: —, 5% by volume H_2SO_4; — — — —, 10% by volume H_2SO_4; - - - -, 20% by volume H_2SO_4. The extinctions are arbitrary.

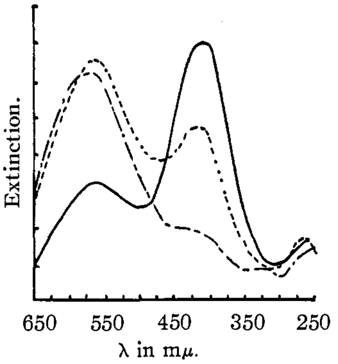

Fig. 8.—The spectra of $C_6H_5(CH{=}CH)_5CHO$ in mixtures of acetic and sulfuric acids: —, 5% by volume H_2SO_4; — — — —, 10% by volume H_2SO_4; - - - -, 20% by volume H_2SO_4. The extinctions are arbitrary.

compounds by methods that involve comparisons of extinctions from different samples. We have, therefore, estimated the relative strengths of these bases from comparisons of I- and P-bands from individual samples.

To do this one must assume (1) that the absorptions at the peaks of the I- and P-band are due to the ion and the base, respectively, and (2) that the ratio of molal extinction coefficients of ion to base at the peaks of their bands is the same for all the compounds. Were these assumptions strictly true the relative values of E_I/E_P, where E_I and E_P are the extinctions at the peaks of the I- and P-bands at a single acidity, would be a measure of the relative strengths of the bases.

The first assumption is most nearly correct when the acidity is such that both I- and P-bands are well formed and clearly separated. This means that 10% H_2SO_4 should be chosen for the fixed acidity. This does not allow a measurement on A_1. We have estimated the value of E_I/E_P for A_1 as 0.06 by dividing the value at 20% H_2SO_4 (0.24) by 4, the average ratio of E_I/E_P at 20 and 10% H_2SO_4.

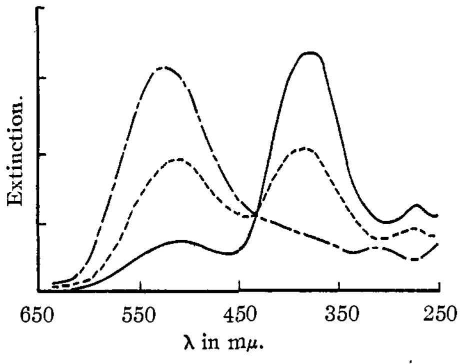

Fig. 9.—The spectra of $C_6H_5(CH{=}CH)_3COC_6H_5$ in mixtures of acetic and sulfuric acids: —, 5% by volume H_2SO_4; — — — —, 10% by volume H_2SO_4; - - - -, 20% by volume H_2SO_4. The extinctions are arbitrary.

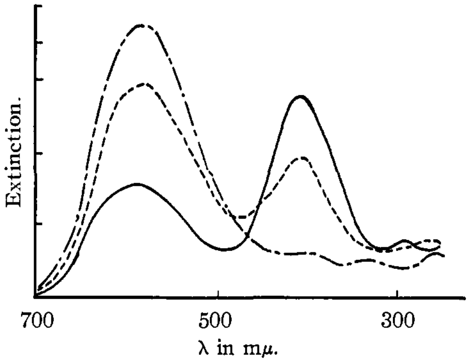

Fig. 10.—The spectra of $C_6H_5(CH{=}CH)_4COC_6H_5$ in mixtures of acetic and sulfuric acids: —, 5% by volume H_2SO_4; — — — —, 10% by volume H_2SO_4; - - - -, 20% by volume H_2SO_4. The extinctions are arbitrary.

Some idea of the accuracy of the second assumption was obtained by the ratio of increase of E_I to decrease of E_P in changing from one acidity to another. When the first assumption is valid and Beer's law holds even for changes in acidity, the ratio of increase of I-band to the decrease of the P-bands is the ratio of molal extinctions of the salt and base at the peaks of their respective bands.

For highly ionized salts this is the ratio of molal extinctions of ion and base. The salt of A_1 is weak and A_1 cannot be included in these measurements. The same error may exist to lesser degrees for other salts, but since the weak salt has no resonance interaction with a $C{=}\overset{+}{O}H$ group, the degrees of ionization must increase rapidly with *n*.

In the higher numbers in 20% H_2SO_4 the extinction at the P-band must include much absorption by the ion. However A_2, A_3, A_4, K_2, K_3 and K_4 are available for measurement. The ratio of increase of I-band to decrease at P-band was measured for each for the changes from 5–10% H_2SO_4 and from 10–20% H_2SO_4. The two measurements on each substance differ from the mean by 13% on an average, in a haphazard way. These mean values range from 1.2 to 2.0 in a haphazard way. The average value is 1.5 with a mean deviation of 10%. From these results the second assumption may be estimated to be valid within 20%.

The values of E_I/E_P in 10% H_2SO_4 and their common logarithms are shown in Table IV. The logarithms are shown because when the conditions are constant the logarithms are proportional to free energies. Since the changes in entropies should be very much the same for all the compounds, the differences in log E_I/E_P are a measure of the energy changes produced by variations of structure. The variations of structure are the substitutions of a phenyl group for a hydrogen atom in the aldehyde, and the interpolation of vinyl groups between phenyl and carbonyl groups. The energy changes are the differences between the interaction energies of groups with $C{=}\overset{+}{O}H$ and $C{=}O$.

TABLE IV

RELATIVE BASE STRENGTHS

Concn. about 10^{-5} M, solvent 10% by volume of H_2SO_4 (d. 1.84) in acetic acid, T, 22 ± 3°.

Comp.	E_I/E_P	$\log_{10}(E_I/E_P)_{\text{obsd.}}$	$\log_{10}(E_I/E_P)_{\text{calcd.}}$
A_1	0.060	−1.22	−1.16
A_2	0.33	−0.482	−0.56
A_3	0.61	−0.215	−0.20
A_4	1.00	0.00	+0.02
A_5	1.39	+0.143	+0.15
A_6	1.70	+0.230	+0.22
K_1	0.095	−1.022	−0.98
K_2	0.445	−0.352	−0.38
K_3	0.91	−0.041	−0.02
K_4	1.48	+0.170	+0.20
K_5	2.2	+0.342	+0.33
K_6	2.8	+0.447	+0.40

Inspection of the log (E_I/E_P) values in Table IV shows (1) that they are greater for the ketones than for the corresponding aldehydes by a nearly constant amount, and (2) that for both aldehydes and ketones log (E_I/E_P) increases with each additional vinyl group, but by increments that decrease with n in a way that is approximately the same for aldehydes and ketones.

The first of these observations can be attributed to the resonance interaction of the phenyl group, as the energy of this interaction must be greater with a $C{=}\overset{+}{O}H$ group than with a $C{=}O$ group. However, the difference is 0.18, which corresponds to about 240 cal. With the large effect of the phenyl group on the base strength of aniline this seems a very small effect. This difficulty is resolved if we note that the phenyl group has an inductive as well as a resonance effect. In aniline, these effects are combined, and according to the most recent estimates are of about equal importance.[9] In these compounds the inductive effect opposes the resonance, since the resonance is greater in the positive ion than in the base, while the inductive effect is electronegative and opposes the formation of the ion.

Interpolation of the vinyl group increases the resonance energy of the ion more than it does that of the base. This is markedly greater than the inductive effect of the interpolation. The net effect can be estimated as 1360 cal.

The effects of interpolated vinyl groups diminish with each interpolation. Using the geometric progression with a fractional common factor as the basis of an empirical equation one obtains $R(1 - \gamma^n)/(1 - \gamma)$ as the sum of the effects of n interpolated vinyl groups. Then $\log (E_I/E_P) = T + R(1 - \gamma^n)/(1 - \gamma)$, where the same values of R and γ may be applicable to aldehydes and ketones, but T is 0.18 greater for ketones than for aldehydes. The values of log (E_I/E_P) calculated by this equation using $R = 1$, $\gamma = 0.6$ and $T = -2.16$ for the aldehydes and -1.98 for the ketones are shown in Table IV. The agreement is better than the accuracy of the measurements. Nevertheless, one must remember that the equation is too simple to be anything but empirical. The effect of structural change on an equilibrium, even if one can discount effects on the entropy of the reaction, involves the difference of the interactions on reactant and product. So unless $\gamma = 0.6$ can be considered as a universal constant for the dropping off of the effects of interpolated vinyl groups in a conjugate system, it would be highly improbable that the above equation were exact.

The actual strengths of the bases depend on the activity of hydrogen ion in a 10% by volume solution of commercial sulfuric acid. This solution is 1.79 M with respect to sulfuric acid and 0.46 M with respect to water. In acetic acid water is a base comparable with diphenylamine in water. The water is practically completely neutralized, which makes the sulfuric acid about 1.33 M. The acidity function of 1.33 M H_2SO_4 in acetic acid is about -3.[10] Using 1.5 as the approximately constant value of ϵ_I/ϵ_P, log E_I/E_P is log C_i/C_b + 0.18, where C_i and C_b are the concentrations of the ion and base and 0.18 is the $\log_{10}$ of 1.5. The pK of one of these bases is then log $E_I/E_P - 3 - 0.18$. The pK values of the bases in Table IV cover the range -4.4 to -2.7. This range of basicity includes 2,4-dichloro-6-nitroaniline ($pK = -3.67$).[10]

Base Strength and Wave Number

The wave number of a band is proportional to the energy difference between a normal molecule and an activated one. The effect of a conjugate system of vinyl groups on the wave number is proportional to the difference of the energy of interaction of the conjugate system with the activated and the normal molecules.[11] In this case the activation can be treated as some change in the carbonyl group. This location of the activation to a group is a method of analysis. The carbonyl group and the conjugate system form a single unit in which all parts change together when light is absorbed.

From this point of view the effects of structural changes on the wave number must be very similar to their effects on log (E_I/E_P). In the latter the two forms of the group are $C{=}\overset{+}{O}H$ and $C{=}O$, in the former activated $C{=}O$ or $C{=}OH$ and normal $C{=}O$ or $C{=}\overset{+}{O}H$.

The same generalizations should hold for wave number of the principal bands as for log (E_I/E_P), except that when log (E_I/E_P) increases the wave number should decrease. These generalizations are (1) the wave number of the ketone should be less for ketones than for the corresponding aldehydes by about the same amount for each member

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[9] B. Webster, *Rec. trav. chim.*, **71**, 1171 (1952).

[10] M. Hall and W. Spengeman, THIS JOURNAL, **62**, 2489 (1940).

[11] L. Ferguson, "The Electron Structure of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 284.

of the series, though not necessarily by the same amount for base or ion, and (2) the wave number decreases for each interpolated vinyl group by amounts that decrease with each additional vinyl group. One cannot help trying the same equation

$$\bar{\nu} = T - R(1 - \gamma)^n/(1 - \gamma)$$

with appropriate changes of the values of the constants.

Obviously T must be a very large number, and be greater for aldehydes than for ketones. Since activation represents absorption of a large amount of energy, R must be much larger for effects on $\bar{\nu}$ than on log (E_I/E_P), for it is the difference of interaction energy of an interpolated vinyl group on two very differently energized groups in the former case and on the two rather similar groups $C{=}\overset{+}{O}H$ and C=O in the latter. One cannot say much concerning γ except that it seems to depend on the opposed forms of the carbonyl group, and not on whether the series is aldehydic or ketonic.

The solvent effects are small and somewhat irregular. The same is true of the bathochromic effects of sulfuric acid. In theory all the constants should depend on the solvent and concentration of sulfuric acid. In practice changes in T are all that are necessary to produce the maximum agreement between calculated and observed values. Obviously these cannot be much better than the regularity of the effects of solvents and acid.

The values for the constants for the different series, different solvents and different concentrations of sulfuric acid are shown in Table V. One case for the P-bands in a mixture of acetic and sulfuric acid has been included.

TABLE V

CONSTANTS FOR THE CALCULATION OF WAVE NUMBERS

Series	Solvent	T, cm.$^{-1}$	R, cm.$^{-1}$	γ
Aldehydes	CH_3OH	40980	5900	0.7
Aldehydes	C_6H_6	41080	5900	.7
Aldehydes	CH_3COOH	40780	5900	.7
Aldehydes	CH_3COOH (10% H_2SO_4)	39830	5900	.7
Ketones	CH_3OH	37790	5000	.7
Ketones	C_6H_6	37890	5000	.7
Ketones	CH_3COOH	37590	5000	.7
Aldehydic ions	CH_3COOH (5% H_2SO_4)	34450	5300	.77
Aldehydic ions	CH_3COOH (10% H_2SO_4)	34250	5300	.77
Aldehydic ions	CH_3COOH (20% H_2SO_4)	33950	5300	.77
Ketonic ions	CH_3COOH (5% H_2SO_4)	30740	4800	.77
Ketonic ions	CH_3COOH (10% H_2SO_4)	30640	4800	.77
Ketonic ions	CH_3COOH (20% H_2SO_4)	30540	4800	.77

The units of R and T are in cm.$^{-1}$. A unit of log (E_I/E_P) is equal to 471 cm.$^{-1}$. This is also the value of R for the basicities. On the basicities the difference in T between aldehydes and ketones is 84.8 cm.$^{-1}$, the corresponding differences in the spectra are 3200 and 3600 cm.$^{-1}$ for bases and ions, respectively. This marked difference between the effects of the phenyl group on the base strengths and on the spectra is due to the opposed resonance and inductive effects in the former where the reaction is the addition of a positive charge. In the spectra changes of dipole may occur, but the activation of the molecule does not involve any change in the charge.

In Table VI some calculated and observed values are compared, series being chosen as examples of the principal bands of aldehydes, ketones, aldehydic ions and ketonic ions and P-bands. Wave lengths not wave numbers have been used in this comparison. The ions are indicated by adding H^+ to the code symbol of the base. Thus AH^+ stands for the positive ion of 5-phenylpentadienal.

TABLE VI

COMPARISON OF CALCULATED AND OBSERVED VALUES OF λ_{max}

Substance	Solvent	λ_{max} mμ	λ_{max} (calc.)	Deviation
A_0	CH_3OH	244	244	0
A_1	CH_3OH	285	285	0
A_2	CH_3OH	323	323	0
A_3	CH_3OH	355	356	1
A_4	CH_3OH	382	382	0
A_5	CH_3OH	408	405	3
A_6	CH_3OH	425	423	2
A_0	CH_3COOH + 10% H_2SO_4	250	251	1
A_1	CH_3COOH + 10% H_2SO_4	295	295	0
A_2	CH_3COOH + 10% H_2SO_4	335	336	1
A_3	CH_3COOH + 10% H_2SO_4	372	372	0
A_4	CH_3COOH + 10% H_2SO_4	400	402	2
A_5	CH_3COOH + 10% H_2SO_4	430	424	6
A_6	CH_3COOH + 10% H_2SO_4	445	445	0
K_0	CH_3OH	254	265	11
K_1	CH_3OH	305	305	0
K_2	CH_3OH	342	342	0
K_3	CH_3OH	373	373	0
K_4	CH_3OH	400	398	2
K_5	CH_3OH	418	418	0
K_6	CH_3OH	430	433	3
A_1H^+	CH_3COOH + 10% H_2SO_4	(345)[a]	345	0
A_2H^+	CH_3COOH + 10% H_2SO_4	400	402	2
A_3H^+	CH_3COOH + 10% H_2SO_4	458	460	2
A_4H^+	CH_3COOH + 10% H_2SO_4	520	518	2
A_5H^+	CH_3COOH + 10% H_2SO_4	570	573	3
A_6H^+	CH_3COOH + 10% H_2SO_4	625	625	0
K_1H^+	CH_3COOH + 10% H_2SO_4	390	387	3
K_2H^+	CH_3COOH + 10% H_2SO_4	455	452	3
K_3H^+	CH_3COOH + 10% H_2SO_4	520	518	2
K_4H^+	CH_3COOH + 10% H_2SO_4	585	585	0
K_5H^+	CH_3COOH + 10% H_2SO_4	640	648	8
K_6H^+	CH_3COOH + 10% H_2SO_4	710	708	2

[a] This band was not strong enough to measure. The value was estimated by taking 55 mμ (the average difference between adjacent members of the series of aldehydic ions from λ_{max} of A_2H^+.

Except for K_0 the agreement between calculated and observed values is as good as can be expected in view of the irregularities of solvent and acid effects. This can be illustrated by the case of K_5H^+ where the bathochromic effect of acid is abnormally large. In 20% H_2SO_4 the observed and calculated values for K_5H^+ agree fairly well. On the other hand K_4H^+ where there is no bathochromic effect of acid on the I-band, perfect agreement is obtained at 10% H_2SO_4, but at 20% H_2SO_4 the deviation is the average extra effect of 20% H_2SO_4 over 10% H_2SO_4.

Just as K_0 did not fit the square law, so it does not fit this equation. The activated form of K_0 does not belong to the vinylogous series of the other ketones.

For both aldehydic and ketonic bases the equation fits very much better than the square law ($\lambda^2 = a + bn$). In the ionic series the agreement between calculated and observed values is only slightly better than that obtained from the linear equation ($\lambda = a + bn$). It is unfortunate that we did not succeed in measuring the spectra of still higher members of the series. With $n = 8$, the difference between the two equations would be demonstrable.

The spectra of all vinylogous series show $\bar{\nu}$ decreasing by decreasing amounts with increase in n, but the way in which they decrease is not always that shown in the above equation. It is true that in the series $C_6H_5(CH{=}CH)_nC_6H_5$ up to $n = 7$ values of T, R and γ can be chosen so that the spectrum fits the equation, except when $n = 0$. With the same exception the spectra also fits the equation $\lambda^2 = a + bn$. But the spectra of series of the type $R_2\overset{+}{N}{=}CH(CH{=}CH)_n\text{-}NR_2$ do not fit the equation, no matter what choice is made for T, R and γ. However, the spectra of these vinylogous series obey the more general equation $\bar{\nu} = T - \sum_n f(n)$, where $f(n)$ is the effect of interpolating the nth vinyl group and decreases with n but does not become negative. It is probable that the expression $\sum_n f(n)$ with the above restrictions of $f(n)$ always gives the effect of the conjugate system $(CH{=}CH)_n$ on the energy of a reaction of a functional group with which it is in resonance, but that the agreement obtained by using $f(n) = R\gamma^n$ in these experiments is largely fortuitous.

Berkeley, California

[Contribution from the Department of Chemistry and the Radiation Laboratory, University of California, Berkeley]

The Heat of Formation of Thorium Sesquisulfide[1]

By LeRoy Eyring[2a] and Edgar F. Westrum, Jr.[2b]

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The heat of solution of thorium sesquisulfide was determined in 6.000 molar HCl at 25° to ascertain the stability of the thorium(III) halides. The molal heat of formation of Th_2S_3 from rhombic sulfur and crystalline thorium is calculated as 258.6 kcal.

The stability of the thorium(III) oxidation state is a matter of considerable interest in understanding the nature of the actinide elements. As a prelude to attempts to prepare a trihalide of thorium, we determined the heat of solution of thorium sesquisulfide (Th_2S_3) in aqueous hydrochloric acid and calculated its heat of formation. These quantities are of interest in considering the applicability of thorium sesquisulfide as a refractory material and in deducing the probable stabilities of thorium(III) halides.

Experimental

These measurements were made with a calorimeter, the calibration and operation of which are described elsewhere.[3] Frequent electrical calibrations were in complete accord with previous determinations of the heat capacity of the calorimeter.

A two-gram sample of thorium sesquisulfide prepared by Dr. Leo Brewer and his co-workers[4] was made available to us. Tests indicated that 96.95 ± 0.2% of the thorium sesquisulfide sample dissolved in aqueous HCl, liberated H_2 and H_2S, gave a solution with a S/Th ratio of 1.500 ± 0.005, and left 3.05 ± 0.2% of an insoluble residue of ThOS or ThO_2.[5] Accurately weighed quantities of thorium sesquisulfide were sealed into thin bottomed sample bulbs under an atmosphere of anhydrous nitrogen. In the calorimeter, each sample reacted with 6.000 M HCl which had been standardized against mercuric oxide and saturated with H_2. The amount of thorium dissolved was determined by gravimetric analysis of the calorimeter solution after each run.

The quantity of H_2S which remained dissolved in the calorimeter was established in order that appropriate corrections could be made for it. The solution from the calorimeter was filtered rapidly and transferred to a sealed flask fitted with a delivery tube. Upon boiling the solution, the H_2S distilled over into a flask containing an excess of aqueous silver nitrate. The Ag_2S residue was filtered, washed with hot water, dissolved in concentrated nitric acid, and titrated with 0.1 M KSCN.

To determine thorium, the calorimeter solution was neutralized with 15 M ammonium hydroxide, heated to boiling, and the thorium precipitated as thorium oxalate upon very slow addition of an excess of aqueous oxalic acid solution. The precipitate was allowed to stand several hours and was then filtered, washed and ignited to constant weight as ThO_2. A small, empirically determined correction was required to correct for the complexing action of the fluosilicate present in certain determinations. The six determinations of the heat of reaction of Th_2S_3 in acid solution are tabulated in Table I. Runs A, B and C were made with 6.000 M HCl and in each the reaction lasted 10 to 12 minutes. Determinations D, E and F were made in precisely the same way except that the hydrochloric acid was 0.005 M with respect to Na_2SiF_6. In these runs the reaction time was 6 to 8 minutes. The fluosilicate was added in order that the data could be compared without correction with heat of solution data of the metal dissolved in the fluosilicate HCl solvent.[6] The experiments were performed at 25.00°. The molecular weights of Th_2S_3 and ThO_2 are taken as 560.42 and 264.12, respectively.

The Heat of Formation of Th_2S_3

The series of reactions represented in Table II are the basis for the calculation of the heat of formation. The small concentration of fluorosilicate in the 6.0 M HCl is understood to be present. The heat of reaction (1) is evaluated from the heat of

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(1) This work was performed under Manhattan District Contract W-31-109-Eng 38 in 1946 at the Radiation Laboratory, Berkeley.

(2) (a) Department of Chemistry, State University of Iowa, Iowa City, Iowa. (b) Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

(3) E. F. Westrum, Jr., and H. P. Robinson, "National Nuclear Energy Series, Vol. 14B, The Transuranium Elements, Part I, Research Papers 6.50 and 6.51," McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(4) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, This Journal, **72**, 4019 (1950).

(5) L. Brewer, Manhattan Project Documents, MB-LB-123 and MB-LB-126 (1945).

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