[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Ultraviolet Absorption and Fluorescence Spectra of Acetophenone

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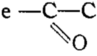
The absorption and fluorescence spectra of acetophenone vapor have been re-examined. Contrary to previously published results, an absorption region which is characteristic of the C=O group is present and the fluorescence spectrum in the blue shows vibrational structure. A similar structure is present in the fluorescence spectrum of the microcrystalline solid at 80°K. and in a solid solution of acetophenone (in E.P.A.) at 80°K. An attempt is made to interpret the vibrational structure in terms of two normal state frequencies, both characteristic of the  $—\underset{\diagdown O}{C}—CH_3$ part of the molecule.

The acetophenone molecule contains a phenyl and a carbonyl group, between which there is a strong probability of conjugation. This question, in relation to the absorption spectrum, has been discussed theoretically by McMurry.[1] There exists some confusion in interpretation of the absorption spectrum of acetophenone, probably because of the large shifts to the red of electronic bands associated with both the carbonyl and phenyl chromophoric groups relative to the spectra of simple ketones and benzene derivatives. Most investigations of the absorption have disclosed three bands[2-8] which may be interpreted as follows. The transition at 3200 Å. appears to be principally localized in the C=O group[1,2]; it disappears when C=O is replaced by C=C, it is absent[9] in the oxime of acetophenone, and it has the low intensity which is expected theoretically. The band at 2800 Å. is characteristic of a π-electron transition in the phenyl group and appears close to this position in a large number of benzene derivatives. The very strong band at 2200–2400 Å. appears to be associated with the C=O group and possibly has the same origin[10,11] as the bands near 1950 Å. in unconjugated ketones. These interpretations have been advanced in one or more of the above references. If they are correct, it may be concluded on the basis of wave length shifts and intensity increases that the interaction of unsaturation electrons in the ring and in the C=O is large, but certainly not large enough to indicate complete delocalization of the electronic transitions. Hence it is a convenient approximation to refer to localized transitions in the two chromophoric groups. Further indication of large conjugation is found in the lowering of the C=O frequency in the normal state, as shown by Raman[12] and infrared[2] spectra.

In previous research on acetophenone vapor,[13,14] no absorption near 3000 Å., associated with the C=O group was found. Indeed, it was stated[14] that this band was completely lacking. The present work does not support this observation, since we find absorption in the vapor corresponding to the absorption observed in solution near 3200 Å. The disagreement between solution and vapor spectra therefore does not exist.

The fluorescence spectra of simple ketones lies in the blue[15] and except in the case of acetone[16] consists of a broad continuous band. The fluorescence spectrum of acetophenone vapor was observed by Prileshajewa,[14] who reported a continuous band extending from 3900 to 4600 Å., excited by wave lengths 2400–2700 Å. Lewis and Kasha[17] found a phosphorescence spectrum of acetophenone in the same wave length region in a solid solution at low temperatures, but did not describe the details of the spectrum.

In a glow discharge,[18] acetone shows a blue emission spectrum which is apparently continuous, while acetophenone under the same conditions emits a spectrum composed of several broad bands. This interesting difference suggested that the fluorescence spectrum might show a similar structure. We have re-examined the fluorescence spectrum of acetophenone vapor, and in addition the fluorescence spectrum of the microcrystalline solid at 80°K., as well as the fluorescence of a solid solution of acetophenone in a rigid medium (E.P.A.) at 80°K. We also investigated the absorption spectrum of the vapor and of the solid solution.

Experimental Details

Purification of Materials.—Acetophenone (Eastman Kodak Co., White Label grade) was distilled twice and only the middle fractions were retained. E.P.A. was made from diethyl ether, isopentane and ethyl alcohol in the ratio 5:5:2 by volume. Only the isopentane required purification, which was accomplished by washing it with concentrated sulfuric acid. The mixed solvent was completely transparent to the limits of our observations (about 2200 Å.) and showed no fluorescence under the conditions of our experiments.

Cells.—A cylindrical fused quartz cell, 20 cm. long, 25 mm. diameter, with plane end windows fused on, was used

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[2] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

[3] G. Scheibe, F. Backenhöler and A. Rosenberg, *Ber.*, **59**, 2617 (1926).

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[9] J. Meisenheimer and O. Dormer, *Ann.*, **502**, 156 (1933).

[10] H. L. McMurry, *J. Chem. Phys.*, **9**, 231 (1941).

[11] A. B. F. Duncan, *ibid.*, **8**, 444 (1940).

[12] M. J. Murray, F. F. Cleveland and R. H. Saunders, THIS JOURNAL, **64**, 1181 (1942).

[13] S. Kato and F. Someno, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **34**, 912 (1938).

[14] N. Prileshajewa, *Acta Physicochim. U.S.S.R.*, **3**, 195 (1935).

[15] W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, **16**, 223 (1948).

[16] G. W. Luckey, A. B. F. Duncan and W. A. Noyes, Jr., *ibid.*, **16**, 407 (1948).

[17] G. N. Lewis and M. Kasha, THIS JOURNAL, **66**, 2100 (1944).

[18] H. Schuler and A. Woeldike, *Phys. Z.*, **42**, 390 (1941).

for the absorption and fluorescence spectra of the vapor. An excess of purified liquid, outgassed under high vacuum, was maintained at a series of definite temperatures in a side tube furnished with an external heating coil. The main portion of the cell was kept several degrees hotter with another heating coil, which was wrapped on a form which protruded sufficiently past the end windows to avoid condensation of vapor. The entire cell was covered with asbestos paper, except the windows and a small portion of the cylindrical wall near one end window for admission of light to excite fluorescence. Temperatures were measured with thermocouples in contact with the walls of the cylindrical tube and side arm, and the pressure was determined from the vapor pressure curve of acetophenone. The cell was sealed off under high vacuum after purification of the acetophenone, and it was shown that the conditions of the experiment produced no measurable thermal or photochemical decomposition.

Absorption and fluorescence experiments with acetophenone dissolved in E.P.A. were made in a fused quartz 15-mm. diameter test-tube, which was suspended in a brass framework in liquid N_2, which was contained in a fused quartz Dewar. For fluorescence of the microcrystalline solid, about 3 cc.of purified acetophenone was outgassed in a 6 mm. diameter fused quartz tube and this was sealed off under high vacuum. This tube was supported rigidly in the quartz Dewar, immersed in liquid N_2.

Light Sources.—A conventional hydrogen discharge tube furnished the continuous background for absorption spectra. The fluorescence spectra were excited by .an Hanovia "Alpine" quartz mercury lamp or an AH-6 mercury lamp, or a spark between zinc electrodes. Suitable filters were used to remove visible radiation and to isolate parts of the ultraviolet spectrum used for excitation.

Spectrographs, Plates.—Absorption spectra were photographed with a Hilger E-484 quartz spectrograph, using Eastman 33 plates. This spectrograph was used also in attempts to observe fluorescence in the neighborhood of the absorption bands. Fluorescence spectra in the visible region were photographed with a three-prism glass spectrograph (camera aperture $f = 2.8$), with Eastman Super Panchro-Press plates. The dispersion of this spectrograph in the neighborhood of 4358 Å. was approximately 35.7 A./mm.

Experimental Results

Absorption Spectrum of Vapor.—At room temperature (about 1 mm. pressure) we observed three bands at 2832, 2770 and 2695 Å. in a 20-cm. path. These bands had been observed previously.[13] At this pressure we find complete absorption below 2400 Å. As the pressure is increased a long wave limit at 2960 Å. appears at about 15 mm. pressure (20-cm. path), which we interpret as the beginning of the transition associated with the phenyl ring. This wave length limit remains about constant and fairly sharp up to about 100 mm. pressure. At about 60 mm. pressure a new absorption band appears with a center at about 3250 Å. It is developed best at about 86 mm. (see Fig. 1). This band, which we interpret as associated with the C=O group, has not been found before in the vapor. The long wave length edge of this band remains fairly constant at 3600 Å. between 100 and 150 mm. pressure.

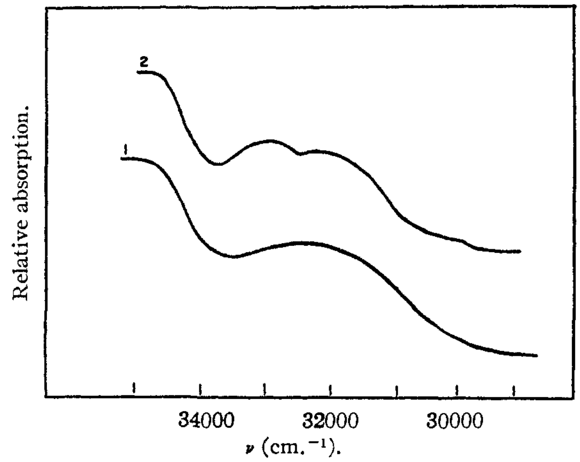

Fig. 1.—Absorption curves of acetophenone: 1, vapor, 86 mm. pressure; 2, solution in E.P.A. at 80°K.

Absorption Spectrum in E.P.A.—The concentrations used were 0.1 to 10 cc. of acetophenone per liter of E.P.A. The solution froze to a clear glass at 80°K. The liquid N_2 was filtered through glass wool just before use. At the lowest concentrations the absorption spectrum duplicated the absorption of the vapor, with some shift of the bands to the violet. The C=O band appeared at a concentration 1 cc./liter and appeared to be split into two bands separated by about 1500 cm.$^{-1}$. A density curve of this absorption is shown in Fig. 1. At the highest concentration, the long wave length limit is at about 3600 Å., very closely equal to the limit found in the gas.

Fluorescence of Acetophenone.—Under the most favorable conditions (80–90 mm. pressure, liquid temperature, 129°) the fluorescence of the vapor is extremely weak. Most experiments were made with radiation from an AH-6 mercury arc filtered by 6 mm. of Corning 9863 glass (red-purple Corex) which removed most of the visible radiation. The exciting light was focussed in the quartz tube containing the vapor and the fluorescence at 90° from the incident beam was photographed. An eight-hour exposure showed a system of three diffuse bands, with indications of others at longer wave lengths. The wave numbers of the three bands which could be measured are shown in Table I.

TABLE I

FLUORESCENCE BANDS OF ACETOPHENONE[a]

Phase	Wave no. of band centers, cm.$^{-1}$	Suggested assignment
Vapor	23600	$\nu_{01}(g)$
	21930	$\nu_{01}(g) - v_1$
	20500	$\nu_{01}(g) - (v_1 + v_2)$
Solid solution	25500	$\nu_{01}(s.s.) + v_2'$
	24100	$\nu_{01}(s.s.)$
	22470	$\nu_{01}(s.s.) - v_1$
	21050	$\nu_{01}(s.s.) - (v_1 + v_2)$
	19250	$\nu_{02}(s.s.)$
	17600	$\nu_{02}(s.s.) - v_1$
Microcrystals	24500	$\nu_{01}(c)$
	22860	$\nu_{01}(c) - v_1$
	21260	$\nu_{01}(c) - 2v_1$
	19700	$\nu_{01}(c) - 3v_1$
	23400	$\nu_{03}(c)$
	21930	$\nu_{03}(c) - v_2$
	20520	$\nu_{03}(c) - 2v_2$
	19200	$\nu_{02}(c)$
	17560	$\nu_{02}(c) - v_1$

[a] Estimated error is ±50 cm.$^{-1}$.

The fluorescence in E.P.A. is greatly intensified. The three bands observed in the vapor appear to be shifted about 400–500 cm.$^{-1}$ toward the violet, but the frequency separations were the same as observed in the vapor, as were the relative intensities and density contours. In addition a new and much weaker band appears at 25500 cm.$^{-1}$ and two weaker bands at 19250 and 17600 cm.$^{-1}$. A schematic density curve is shown in Fig. 2, which indicates the positions of the principal bands observed in vapor solid solution and microcrystalline phases, and gives crude indications of relative intensities of bands observed in one phase, but which gives no relation between intensities in different phases.

The fluorescence spectrum of microcrystalline acetophenone is very intense. The angle between the incident and fluorescent beams was about 90°. The penetration of the incident beam into the crystals was very slight. Uneven illumination of the slit by fluorescence from individual crystals was avoided by slightly defocussing the fluorescent image. The spectra of the crystals are more narrow than the spectra of vapor and solid solution and there are more bands distributed over the same spectral region. The wave numbers are recorded in Table I.

A single experiment was made in which the exciting light was confined by filters to fall within the absorption band characteristic of the phenyl group (2700–2900 Å.). The fluorescence spectrum was exactly the same as in the other cases, where light was absorbed only by the C=O group, or by both groups.

We have made a very careful search for resonance fluorescence in acetophenone near the regions of the absorption bands (2830–3000, 3250–3600 Å.). Even with very long exposures we have not found any such fluorescence. These experiments are complicated by the difficulty of removing the exciting lines from the fluorescent beam. However, the scattering of incident light was not too troublesome in E.P.A. solutions, and we believe that resonance fluorescence could have been detected, if it was present. It may be concluded safely that any resonance fluorescence is very much weaker than the fluorescence in the blue, probably by several powers of ten.

Discussion

The fluorescence spectra of acetophenone, taken as a whole, show little difference from the fluorescence spectra of unconjugated ketones and do not resemble the fluorescence spectra of substituted benzenes. Furthermore the spectra are independent of the electronic level which is reached on absorption, since absorption in the 2800 Å. region (characteristic of the phenyl group) or in the 3200 Å. region (characteristic of the C=O group) results in the same spectra. This latter fact gives an indication that the excitation remains principally localized in the C=O group, or if the excitation occurs from the π-electrons of the phenyl group, it is transferred with high probability to the C=O group.

A detailed interpretation of the vibrational structure of the fluorescence is probably not justified, in view of the large number of vibrational frequencies. The situation is complicated by the diffuse nature of the bands. We have measured intensity maxima from microphotometer tracings with an estimated error of ±50 cm.$^{-1}$. A much larger subjective error may exist if the maxima of some bands and the minima of other bands are the significant parts. Nevertheless the agreement between the separations between vibrational transitions in vapor and solid solution phases has led us to a tentative interpretation, which is certainly not to be regarded as final. The interpretation offered for the microcrystalline fluorescence is more questionable.

The frequencies of the fluorescence maxima in the acetophenone vapor, solid solution (E.P.A.) and microcrystalline solid states are collected in Table I, where the following notation is used. An upper initial state for fluorescence in labeled ν_{0i} (g, s.s. *or* c) with i = 1, 2, 3, and the phases distinguished by letter in parentheses. The normal state vibrational frequencies are designated v_1 and v_2, and an upper state vibrational frequency by v_2'. v_1 may be attributed probably to the C=O vibration (1686 in the infrared,[2] 1679 in the Raman effect[12]). The meaning of v_2 (1400–1430 cm.$^{-1}$) is less clear; frequencies 1428, 1450 and 1483 cm.$^{-1}$ in the Raman effect are attributed[12] to C–H vibrations in the methyl group. If this interpretation of v_2 is correct, the final levels of the fluorescence are all characteristic of the –CO—CH$_3$ part of the molecule rather than of the phenyl part.

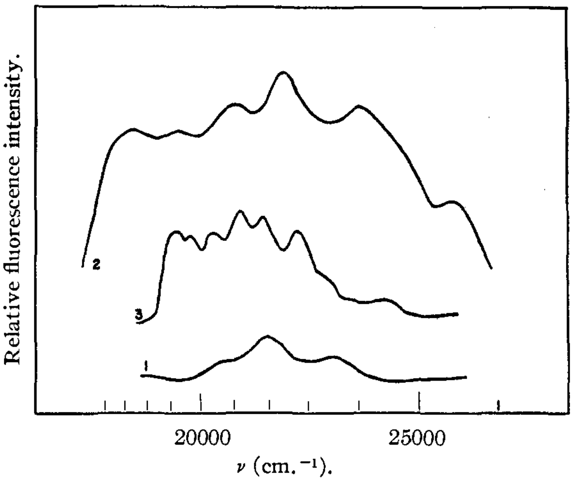

Fig. 2.—Fluorescence of acetophenone: 1, vapor, 86 mm. pressure: 2, solution in E.P.A. at 80°K.; 3, microcrystalline solid at 80°K.

With this assignment, except for the 25500 band observed only in solid solution and shifts associated with change of phase, there is little difference in the principal features of the spectra in the three phases. The similarity of transitions from ν_{01} (g) and ν_{01} (s.s.) is particularly striking. The solid solution and crystal spectra show an upper level ν_{02} which is not found in the vapor, but this is probably a question of absolute intensity, since the vapor fluorescence is considerably weaker.

The weak 25500 cm.$^{-1}$ transition has been found only in solid solution. Its absence from the vapor spectrum might be explained on the basis of intensity, but its absence from the crystal spectra cannot be explained in this way since the latter are considerably more intense than the solid solution spectra. It is suggested that the upper state for this transition is an excited vibrational level of ν_{01} (s.s.). This assignment implies that loss of vibrational energy to the rigid solvent should be less efficient than to other acetophenone molecules in a crystal. The band may come from another upper electronic level, but as evidence against this we were able to show qualitatively that the mean lifetime associated with the 25,500 band was not significantly different from the lifetime of other bands coming from the ν_{01} (s.s.) level.[19]

While our interpretation is based on reasonable ground state differences assigned to v_1 and v_2, the nature of the upper levels ν_{01}, ν_{02} and ν_{03} is far from clear. The most simple explanation of these levels would attempt to identify them with triplet states. The relatively long lifetime of the fluorescence[20] is evidence in favor of this interpretation. The differences $\nu_{01} - \nu_{02}$ (5300, 4850 cm.$^{-1}$) are large enough to be differences between electronic levels. If this is true, then a reinvestigation of the mean lifetimes of bands above and below 20000 cm.$^{-1}$ might show a difference in lifetime. The difference ν_{01}(c) $-$ ν_{03}(c) may arise from the same cause.

Finally it should be pointed out that the fluorescence as reported here may be incomplete, particularly the vapor fluorescence. Also the spec-

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[19] The lifetime measurements were made by Mr. D. Neuberger in this Laboratory, to whom we are indebted.

[20] D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

trum should be reinvestigated with greater resolution in the hope of finding more details of the vibrational structure.

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Temperature Coefficient of the Intermolecular Carbon Isotope Effect in the Decarboxylation of Normal Malonic Acid

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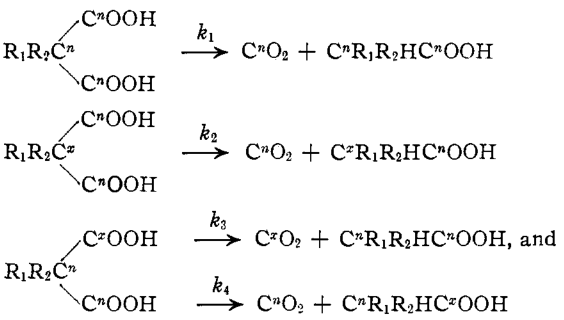
The intermolecular carbon isotope effect in the decarboxylation of isotopically normal malonic acid has been measured in 80% aqueous sulfuric acid in the range 56 to 129°. The magnitudes of the results are in accord with predictions based on the simplified model of Bigeleisen, but their mode of temperature dependence is not. The temperature coefficients of the possible corresponding oxygen isotope effects (O^{17} and O^{18}) have been found to be negligible. It is concluded that the mechanism of decarboxylation in 80% sulfuric acid is similar to that in dilute hydrochloric acid solution, as reported by Hall.

Introduction

Isotope effects in the thermal decarboxylation of malonic acids have been the subject of a number of studies.[1-7] In the notation introduced by Bigeleisen and Friedman,[2] (where n and x denote different isotopes or concentrations of isotopes of carbon), the deviation from unity of the ratio k_4/k_3 is a measure of the *intra*molecular isotope effect, while that of $k_1/2k_3$ is one measure of the *inter*molecular effect. The former can be determined from analysis of the carbon dioxide obtained by complete decarboxylation to acetic acid, while the latter is gotten from analysis of the first carbon dioxide evolved.



Bigeleisen and Friedman,[2] and Lindsay, Bourns and Thode[3] have determined the intermolecular isotope effect at the melting point of solid malonic acid. Material from several sources was employed. Lindsay, Bourns and Thode[5] have reported measurements of this effect at several temperatures above the melting point. Bigeleisen,[8] in a revision of previous calculations,[9] has shown that theoretical predictions of the magnitudes of the effects observed are in accord with these experiments, except that the latter do not show the predicted temperature coefficient. The predictions and experimental results are summarized in Table I.

TABLE I

INTERMOLECULAR ISOTOPE EFFECT IN DECARBOXYLATION OF NORMAL MALONIC ACID (C^{13} EFFECT)

T, °C.	$100[(k_1/2k_3) - 1]$ Calcd.	$100[(k_1/2k_3) - 1]$ Obsd.	Ref.
137.5	3.5	3.7 ± 0.2	2, 10
138	3.5	4.6	3, 10
137	3.5	3.4	5, 11
149	3.4	4.1	
173	3.3	3.4	
196	3.1	3.6	

In all of these experiments the carbon isotope ratio was determined on the first 1% or so of carbon dioxide evolved after the initiation of decarboxylation by submersion of the reaction vessel in a high temperature bath. The interpretation which has been made of results so obtained is subject to challenge because the rates of melting and of decarboxylation of malonic acid are not very different. For example, in order that the isotopic constitution of the first 1% of carbon dioxide evolved reflect the influence of temperature it is necessary that much less than 1% decarboxylation occur before the solid malonic acid has melted. Actually there is considerably more than 1% decarboxylation (at bath temperatures of 140 or 200°) before melting is complete, and this effect introduces another complication into the interpretation of results from these experiments because under such conditions the intermolecular isotope effect cannot be measured directly.[12]

Fry and Calvin[6] have measured the intramolecular C^{14}-isotope effects in decarboxylations of phenyl- and α-naphthylmalonic acids at the melting points and at several lower temperatures in dioxane–aqueous hydrochloric acid solution. While the effect of temperature on results obtained from solution decarboxylation is masked by their stated errors in radioactivity measurement, the difference between results from solution runs at low temperatures and pure solid runs at about 100° higher is so

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(2) J. Bigeleisen and L. Friedman, *ibid.*, **17**, 998 (1949).

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(8) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

(9) J. Bigeleisen, *J. Chem. Phys.*, **17**, 425 (1949).

(10) Eastman Kodak Co. malonic acid.

(11) British Drug Houses malonic acid.

(12) If decarboxylation were rapid compared with melting, only an intramolecular isotope effect could be observed.