One such experimental approach would be a determination of the effects of salts on the partial pressures of the *t*-butyl halides at various solvent compositions and temperatures. This method was used at zero salt concentration in aqueous methanol by Olson, Ruebsamen and Clifford.[13]

(13) A. R. Olson, W. C. Ruebsamen and W. E. Clifford, THIS JOURNAL, **76**, 5255 (1954).

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BATES COLLEGE]

The Effect of Solvent on the Visible Absorption Spectrum of Biacetyl

BY LESLIE S. FORSTER[1]

RECEIVED OCTOBER 5, 1954

The visible absorption spectrum of biacetyl has been measured in 25 solvents. The intensity of the long wave length peak is diminished when biacetyl is dissolved in solvents that contain oxygen, nitrogen and fluorine atoms. There is no correlation between this diminution and the following macroscopic solvent parameters: dipole moment, molar refraction, refractive index, dielectric constant, or hydrogen-bonding tendency. This effect is ascribed to intermolecular dispersion forces. The visible band is the result of two electronic transitions. The intensity of one of these transitions is strongly dependent on solvent.

The effect of solvent on absorption spectra has been the subject of many investigations.[2] Although most of these have been concerned with shifts in band position, a number have treated variations in band shape[3] and intensity.[4] The possibility that solvent effects may be used to characterize electronic transitions[5,3a,3b] has prompted this study, which is preliminary to an extensive investigation of the luminescence and photochemistry of biacetyl solutions.

In the visible absorption spectrum of a hexane solution of biacetyl there are four distinct maxima[6] which disappear when the solvent is changed to an alcohol.[7] The biacetyl vapor spectrum has been interpreted as a sharp singlet-triplet ($T \leftarrow S$) band superimposed on a broad singlet-singlet ($S' \leftarrow S$) band.[8] In this study, the absorption spectra of biacetyl in a variety of solutions have been determined with the purpose of explaining the loss of structure in alcohol solutions and attempting a determination of the number of electronic transitions involved.

Experimental

Purification of Materials.—Biacetyl, a Lucidol product, was dried for several weeks over anhydrous calcium sulfate, vacuum distilled, and the middle fraction stored under vacuum, in the dark at −78°. The refractive index, n^{19}_{D} 1.3940 (lit. $n^{18.5}_{\mathrm{D}}$ 1.3933), and the absorption spectrum were unchanged upon redistillation of the biacetyl. Biacetyl samples were withdrawn by freezing out shortly before use. The solutions were prepared and the spectra determined as quickly as possible thereafter. With the exception of aqueous and alcoholic solutions the extinction coefficients were unchanged with time.

All solvents were dried and distilled in an all-glass still. Small amounts of water had no effect on the absorption spectrum.

Spectrophotometric Measurements.—The absorption spectra were determined with a Beckman Model B spectrophotometer. The wave length scale was calibrated against a Corning 5120 filter (didymium glass). A correction of 4 mμ was added to all scale readings. The absorbance was determined every 10 mμ in the region 320–400 mμ, every 2 mμ from 400–415 mμ and every mμ from 415–450 mμ. Atmospheric oxygen was without effect on the spectra and no attempt was made to exclude it. A temperature variation of 10° had a negligible effect on the spectra and extinction coefficients of all solutions except biacetyl in water. When the biacetyl concentration exceeded 0.085 *M*, a 1-mm. cell was used, otherwise a 10-mm. cell was used. The spectrum of liquid biacetyl was determined by preparing a thin film of the pure liquid between two glass plates.

Molar extinction coefficients were calculated from the equation $\log I_0/I = \epsilon l c$, with l in cm. and c in moles/l.

Results

The biacetyl solutions may be divided into three classes, 1, 2 and 3, according to their general appearance. A representative spectrum from each of these classes is reproduced in Fig. 1, and the solvents are grouped according to class in Table I. In Fig. 2 the biacetyl vapor spectrum (redrawn[8]) is compared with the heptane and benzene solution spectra. Only in the heptane solution are the three distinct maxima discernible, the shapes of the remaining Class 1 solution spectra resemble that of biacetyl in benzene, although there are small differences in the maximum extinction coefficients, $\epsilon_{\max}$. The positions of the maxima, $\nu_{\max}$, and the $\epsilon_{\max}$ of the Class 1 solutions are tabulated in Table I. It will be noted that the long wave length peak (maximum II) is enhanced more than the short wave length peak (maximum I) when biacetyl is dissolved in Class 1 solvents (Fig. 2).

In the spectra of Class 2 solutions, maximum II is no longer present and only a broad shoulder remains, while in Class 3 solutions even this shoulder disappears. The relevant data for these two classes are listed in Table I. The variation in appearance of the Class 2 spectra can be seen in Fig. 1 (ether) and Fig. 3. The spectra of biacetyl in chloroform, fluorobenzene and anisole are nearly identical in shape.

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[1] Supported by a Frederick Cottrell grant from The Research Corporation.

[2] For references see L. N. Ferguson, *Chem. Revs.*, **43**, 394 (1948).

[3] (a) H. P. Stephenson, *J. Chem. Phys.*, **22**, 1077 (1954); (b) F. Halverson and R. Hirt, *ibid.*, **19**, 711 (1951); (c) H. Ungnade, THIS JOURNAL, **75**, 432 (1953); (d) N. Coggeshall and E. Lang, *ibid.*, **70**, 3283 (1948); (e) H. Ungnade and R. Lamb, *ibid.*, **74**, 3789 (1952).

[4] (a) L. Jacobs and J. R. Platt, *J. Chem. Phys.*, **16**, 1136 (1948); (b) N. Chako, *ibid.*, **2**, 644 (1934); (c) R. Mulliken and C. Rieke, *Rep. Prog. Phys.*, **8**, 231 (1941).

[5] (a) J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951); (b) M. Kasha, *Disc. Faraday Soc.*, No. 9, 14 (1950).

[6] L. Light, *Z. physik. Chem.*, **122**, 419 (1926).

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[8] G. N. Lewis and M. Kasha, *ibid.*, **67**, 994 (1945).

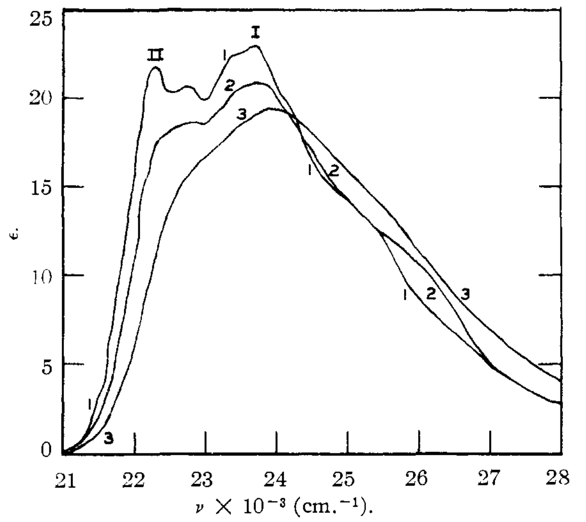

Fig. 1.—Biacetyl in: 1, heptane (Class 1); 2, ether (Class 2); 3, acetone (Class 3). The biacetyl concentrations are 0.0253, 0.0660 and 0.0547 *M*, respectively. Maximum I and maximum II are indicated on the heptane spectrum.

TABLE I

Solvent	Maximum I $\nu_{max.}$ (cm.$^{-1}$)[a]	 $\epsilon_{max.}$[b]	Maximum II $\nu_{max.}$ (cm.$^{-1}$)	 $\epsilon_{max.}$
None (vapor)[8]	24,000	21.0	22,700	16.8
Class 1				
Heptane	23,700	22.7	22,300	21.4
Benzene	23,600	23.3	22,350	21.6
CCl_4	23,600	24.4	22,300	22.9
CS_2	23,450	27.8	22,200	26.5
C_2H_5I	23,600	24.3	22,350	22.5
Toluene	23,600	25.0	22,350	23.4
Chlorobenzene	23,650	23.6	22,350	21.8
Iodobenzene	23,550	25.8	22,300	24.3
Diphenyl ether	23,650	24.0	22,400	22.6
Class 2				
Ether	23,700	20.9		. .
Fluorobenzene	23,750	23.8		21.2[c]
C_6F_{14}	23,850	[d]		. .
Anisole	23,700	23.0		20.7[c]
Chloroform	23,700	22.8		19.8[c]
Class 3				
Water	24,500	5.2[e]		
Methanol	24,000	5.2[e]		
Butanol	23,750	20.2[f]		
Octanol	23,700	22.0		
Acetone	23,900	19.4		
Acetic acid	24,000	20.4		
Acetonitrile	24,000	19.7		
Nitromethane	24,000	19.6		
Pyridine	23,800	19.9		
Dioxane	23,900	21.0		
Biacetyl[g]	23,900	. .		

[a] Relative wave numbers are accurate to 50 cm.$^{-1}$, absolute wave numbers to 100 cm.$^{-1}$. [b] Relative $\epsilon_{max.}$ (for maximum I and II) are accurate to 0.1 unit, absolute $\epsilon_{max.}$ to 0.3 unit. [c] Corresponds to horizontal portion of shoulder. [d] Insufficient solvent for accurate measurements. [e] Changes rapidly with time, equilibrium value is listed. [f] Changes slowly with time, this value was obtained 2 min. after mixing biacetyl and butanol. [g] Thin layer of pure biacetyl, no $\epsilon_{max.}$ could be calculated. (Path length unknown.)

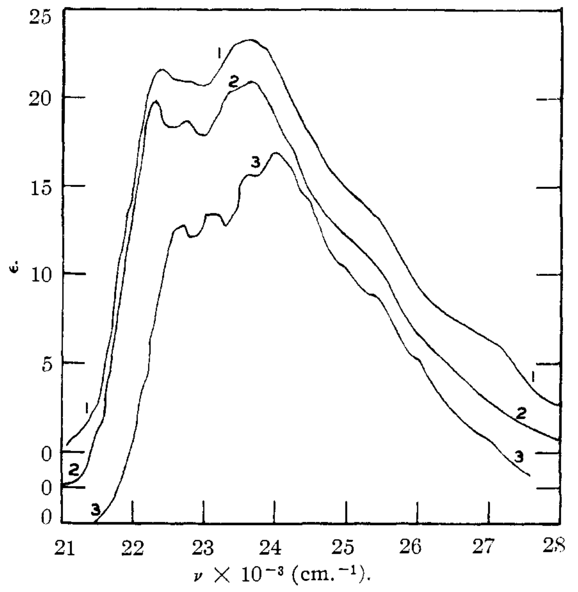

Fig. 2.—Biacetyl in: 1, benzene (0.0497 *M*); 2, heptane (0.0253 *M*); 3, biacetyl vapor (redrawn[8]). Spectra are displaced for clarity.

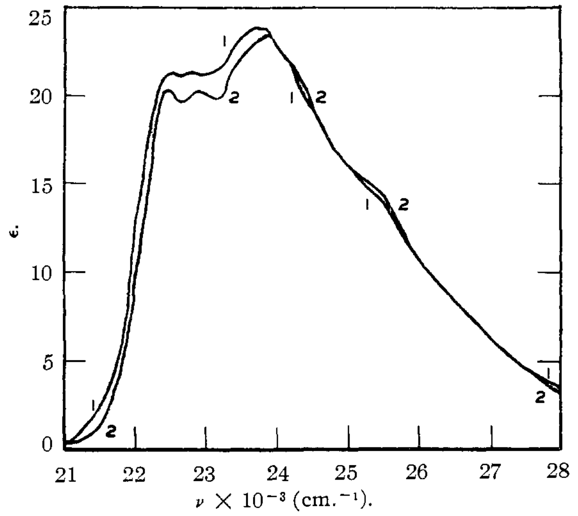

Fig. 3.—Biacetyl in: 1, fluorobenzene (0.0587 *M*); 2, perfluorohexane. The values of ε for perfluorohexane are relative.

The spectra of biacetyl dissolved in various mixtures of acetone and heptane are shown in Fig. 4. It can be seen that with progressive addition of acetone to a heptane solution, the spectrum gradually changes from that of Class 1 to Class 2 and finally to Class 3.

The spectra of alcoholic and aqueous biacetyl solutions are of interest in that the extinction coefficients change with time and approach an equilibrium value while the spectral shape is unchanged. This indicates that a colorless product is formed and that the low values for ϵ_{max} in methanolic and aqueous solutions are due to the change in biacetyl concentration and do not imply a diminution in the "true" extinction coefficients. The rate of this reaction decreases in the order, water, methanol, butanol and octanol. The blue shift in ν_{max} decreases

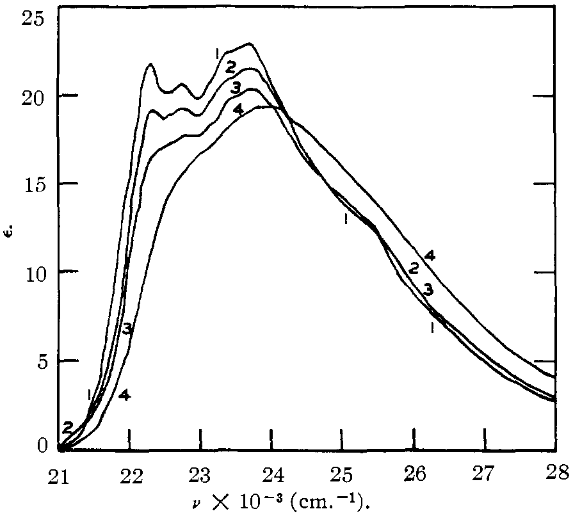

Fig. 4.—Biacetyl in the mixed solvent heptane–acetone. The mole % of acetone is: 1, 0%; 2, 7.7%; 3, 18.2%; 4, 100%.

in the same order (Fig. 5). The apparent reaction of biacetyl with water is consistent with the assumption, made as a result of polarographic studies, of a slow equilibrium between hydrated and unhydrated biacetyl molecules.[9]

Discussion

In general, when the solvent is varied, the shape, position and intensity of an absorption band may change simultaneously. Indeed, these spectral properties are not independent. If an absorption band results from two or more electronic transitions, the shape of the band is dependent on the relative intensities of these transitions. A shift in relative band positions makes an analysis of the solvent effect even more difficult. In the case of biacetyl, the shifts in band position are rather small (except for aqueous and methanolic solutions) and the change in spectral shape is primarily due to the change in the relative intensity of the maxima.

Beer's law is obeyed and the spectrum is unchanged in acetone solutions of biacetyl in the concentration range 0.005–0.75 *M*. This indicates that the solvent effect results from the interaction between solvent and biacetyl molecules rather than from the influence of the solvent on the degree of polymerization of biacetyl.

An examination of the results fails to reveal any correlation between spectral shape and the following macroscopic solvent parameters: dipole moment, molar refraction, refractive index, dielectric constant or hydrogen-bonding tendency. It will therefore be necessary to seek an explanation in terms of microscopic solvent properties, *i.e.*, the interaction between the biacetyl molecule and part of the solvent molecule. All Class 2 and 3 solvents (with the exception of chloroform) contain at least one oxygen, nitrogen, or fluorine atom and all Class 1 solvents (excepting diphenyl ether) do not contain these atoms. It would appear that the suppression of maximum II is related to the presence of these atoms, which can interact with one of the oxygen atoms in biacetyl.

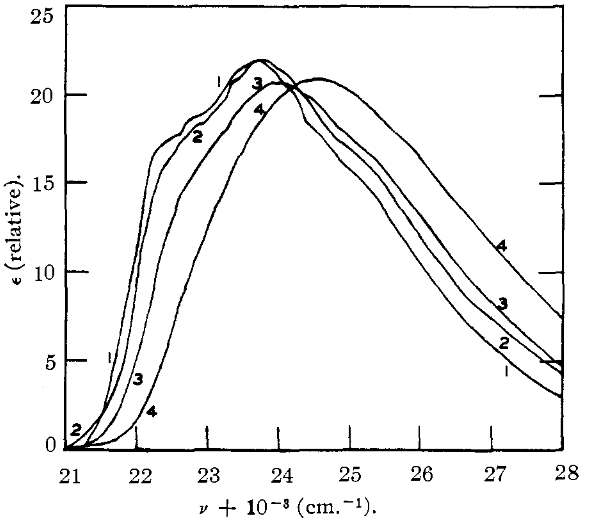

Fig. 5.—Biacetyl in: 1, octanol (0.0236 *M*); 2, butanol (0.0491 *M*); 3, methanol (0.218 *M**); 4, water (0.173 *M**); *The concentration of the absorbing species is less than this value (see text). See Table I for values of ϵ_{max}.

This conclusion is strengthened by the spectra in mixed solvents (Fig. 4). It is apparent from the gradual manner in which the spectrum changes with the addition of acetone, that the phenomenon is a statistical one. The visible biacetyl spectrum is probably the result of two (or more) electronic transitions. The intensity of one of these is markedly diminished when the acetone oxygen atom is close to a biacetyl oxygen atom at the moment of the absorption act. As the fraction of acetone molecules to heptane molecules increases, the probability of this favorable configuration is increased. Thus, the division into solvent classes is arbitrary and no clear-cut distinction exists. It is obvious that the solvents acetic acid and biacetyl will behave in much the same way as acetone. Analogously, in pyridine and acetonitrile, the suppression of maximum II results from the interaction of the nitrogen atom in the solvent and the biacetyl oxygen atom. The other Class 3 solvents are discussed below.

The shape of the ether spectrum can now be understood in terms of the above explanation. In ether there are fewer orientations that will allow a close oxygen–oxygen approach than in acetone. Thus, the proper orientation will not always occur at the moment of absorption. This may not be the only reason for the Class 2 nature of ether (see below). It would be expected that the replacement of the ethyl group(s) in ether by phenyl group(s) would further reduce the probability of proper orientation. This expectation is borne out by the spectra of anisole and diphenyl ether solutions (Fig. 6). The steric hindrance is so great in diphenyl ether that it behaves as a Class 1 solvent.

Additional evidence in support of this statistical interpretation comes from a comparison of the spectra in the mixed solvents, ether–heptane and dioxane–heptane. The C–O–C angle is nearly the same in both of these molecules. From simple

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[9] R. Pleticha, *Chem. Listy*, **46**, 69 (1952).

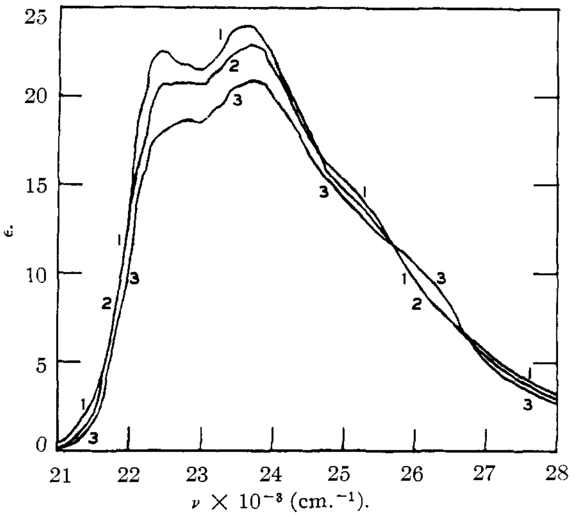

Fig. 6.—Biacetyl in: 1, diphenyl ether (0.0544 *M*); 2, anisole (0.0386 *M*); 3, ether (0.0660 *M*).

probability considerations, one would expect dioxane to be somewhat more than twice as effective as ether because of the two oxygen atoms per molecule. Actually it is about four times as effective; approximately the same spectrum results from 6.7 mole % dioxane as from 30 mole % ether (Fig. 7). This discrepancy may be partly due to the comparatively small size of dioxane. Also, the naive assumption that both oxygen atoms in dioxane act independently is probably incorrect. In any event, the effect is in the right direction.

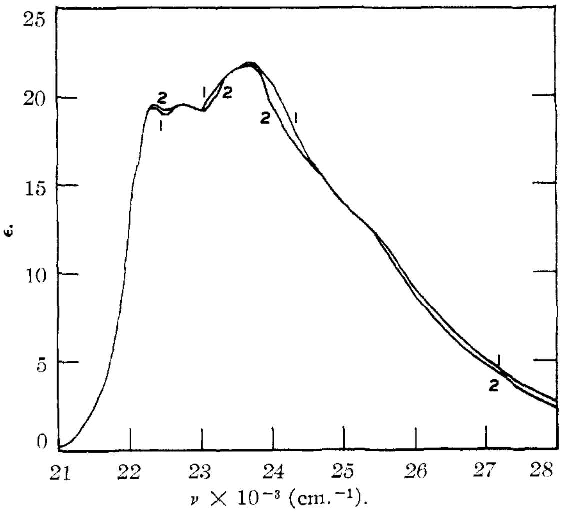

Fig. 7.—Biacetyl in mixed solvents: 1, 6.7 mole % dioxane in heptane; 2, 30 mole % ether in heptane.

If the oxygen–oxygen distance is the critical factor, then it is clear that dipole–dipole forces cannot be the only factor responsible for the attraction between biacetyl and solvent molecules, for these would be repulsive in many cases. Attractive forces of the dispersion type must be sufficiently large to overcome the dipole–dipole repulsion. This is not unreasonable for a molecule such as biacetyl with a conjugated system of double bonds.[10] These attractive dispersion forces fall off much more rapidly with distance than do the repulsive dipole forces. This explains the Class 1 character of a solvent such as iodobenzene which has a highly polarizable atom but due to the large atomic size of iodine cannot approach the biacetyl oxygen atom very closely.

It is not evident whether the intermolecular attraction between biacetyl and the alcohols results from hydrogen-bonding or dispersion forces, but the force between biacetyl and chloroform can only be due to a hydrogen bond.[11] The Class II nature of ether may result, in part, from the comparative weakness of the intermolecular forces as well as from the difficulty of proper orientation. The smaller polarizability of a single-bonded oxygen compared to that of a doubly-bonded oxygen would result in weaker dispersion forces. The fact that dioxane falls into Class 3 is evidence against this conclusion. The Class 2 character of fluorobenzene and perfluorohexane may be ascribed to the smaller dispersion forces.

The data appear to indicate that the visible absorption of biacetyl results from two electronic transitions. One of these (corresponding to maximum II) is much weaker than the other. The intensity of the weaker transition is markedly reduced as the solvent–biacetyl interaction increases. This two-transition interpretation is similar to that of Lewis and Kasha.[8] However, the discovery[12] of a weak absorption (T ← S) around 20,000 cm.$^{-1}$ casts doubt on their assumption that T ← S absorption contributes to the strong visible band.

A similar solvent effect has been observed for the spectra of pyridine solutions.[3a,3b] In that case the spectral changes were explained as arising from the shift of the weak long wave length maximum to the blue with the result that this transition was obscured by the more intense band. This explanation cannot be valid for biacetyl solutions because the reduction in the intensity of maximum II is not accomplished by an increase in the intensity of maximum I.

McConnell has discussed the use of band shifts as a means of distinguishing n-π^* from π-π^* transitions.[13] He found the blue shift of n-π^* transitions can be correlated with solvent polarity. The stronger transition in the visible spectrum of biacetyl has been identified as n-π^*.[14] The effect of solvent on this band appears to be independent of that on the weaker band. In Fig. 4 it can be seen that the intensity of maximum II is much more sensitive to the solvent than is the blue shift in maximum I. The dipole moments of the alcohols are nearly the same,[15] yet the blue shift increases in the order, methanol, butanol, octanol (Fig. 5). This might be due to some sort of "cage effect"[16] or may merely result from the greater difficulty of orientation of the larger alcohol molecule. In the latter case, McConnell's interpretation would be

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(10) J. H. Hildebrand and R. Scott, "Solubility," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 57.

(11) Ref. 10, p. 171.

(12) J. Sidman and D. S. McClure, paper presented at the American Chemical Society meeting, New York, Sept., 1954.

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correct. This point warrants further study.

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LEWISTON, MAINE

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

Photochemical Studies. LI. The Photochemistry of Biacetyl at 3650 and 4358 Å. and its Relationship to Fluorescence[1]

BY GEORGE F. SHEATS[2] AND W. ALBERT NOYES, JR.

RECEIVED SEPTEMBER 25, 1954

Quantum yields of carbon monoxide, of ethane and of methane from biacetyl vapor have been determined at 3650 and 4358 Å. as functions of intensity, of pressure and of temperature up to 100°. A few results were obtained at about 2700 A. to permit correlation with the work of Blacet and Bell. Methods of estimating primary quantum yields are discussed. At room temperature at 2700 and at 4358 Å. equal numbers of methyl and of acetyl radicals seem to be formed in the primary process. At 3650 Å. this primary process may compete with one in which two acetyls are formed. At 4358 Å. at room temperature the yield is proportional to the intensity and only slightly dependent on pressure. At 3650 Å. the yield decreases as the pressure increases, a fact which can be correlated with a corresponding increase in fluorescence efficiency. As the temperature is raised yields at 4358 Å. decrease and then increase at the same time that they become independent of intensity. Many of the photochemical facts can be correlated with the data on fluorescence to provde a fairly consistent picture for the primary process.

The fluorescence of biacetyl vapor has often been studied.[3] At 3650 Å. the fluorescence efficiency increases with increase in pressure, thus suggesting that collisions "stabilize" excited molecules which might otherwise dissociate.[3d,3g] On the basis of this simple picture the photochemical quantum yield would be expected to decrease as the fluorescence efficiency increases. At 4358 Å. pressure has little effect on the fluorescence efficiency and would be expected to have little effect on the photochemical yields. The present work indicates that the photochemical behavior is complicated at this wave length.

The photochemical decomposition of biacetyl vapor has also been investigated[4] but mainly at wave lengths shorter than 3650 Å. The secondary reactions proposed by Blacet and Bell agree well with published facts and as far as can be ascertained with the present work. Little evidence concerning the nature of the primary process is available, although Khan, Norrish and Porter[5] from a study of the flash photolysis conclude that there may be two modes of primary dissociation, one leading to $2CH_3 + 2CO$ and the other to $2CH_3CO$. The present work is in essential agreement with this conclusion, although a slightly different language for describing what takes place is preferred. In biacetyl as in acetone there is some ambiguity arising from the effect of radical recombination reactions in reducing the over-all yields.[6] Constants derived from the work on acetone may be used in estimating primary quantum yields in biacetyl.

A study of the photochemistry of biacetyl at 3650 and at 4358 Å. is considered to be of interest because of the possibility of correlating the photochemical and fluorescence behaviors.

Experimental

The preparation of the biacetyl has been described.[3l] Analyses for methane, ethane and carbon monoxide were performed by techniques which have been described in earlier papers from this Laboratory. Monochromatic 3650 Å. radiation was obtained in the preliminary runs by a combination of Corning glasses 5840 and 7380. In all runs reported in Table I, 5 mm. of No. 5860 were used alone. Wave length 4358 Å. was obtained by a combination of Corning glasses No. 3389 (2.5 mm.) and 5113 (2.0 mm.). The filter for 2700 Å. has been described.[7] General Electric Co. AH-6 and British Thompson-Houston Type ME/D lamps were used.

Estimates of quantum yields were made by measurement of the fraction of the incident radiation absorbed with an S5 response photoelectric cell. The intensity of the incident radiation at 3130 Å. (later at 2700 Å.) was measured by use of diethyl ketone at 75° for which the quantum yield of carbon monoxide is unity. From the sensitivities of the photocell at various wave lengths the incident intensities at 3650 and at 4358 Å. could be measured with an accuracy of about 20%. At these two wave lengths quantum yields are markedly dependent on conditions so that it would be very difficult to achieve high reproducibility in any case.

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(2) Hanovia Chemical and Manufacturing Company Predoctoral Fellow during 1953–1954.

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