4. Small amounts of biacetyl greatly increase the fluorescence of acetone.

5. It is concluded that the fluorescent emitters are the same for both acetone and biacetyl, at least as regards the bands at 5000 Å. and longer wave lengths.

6. Mechanisms to account for these facts are advanced. An adequate explanation is based on a very probable deactivation of excited acetone molecules by biacetyl, the excited biacetyl being responsible for the fluorescence. However, fluorescence of the CH_3CO radical cannot be excluded.

PROVIDENCE, RHODE ISLAND RECEIVED MAY 6, 1938

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Absorption Spectrum of Biacetyl between 1500 and 2000 Å.

BY VICTOR R. ELLS

In connection with work on the spectroscopy and photochemistry of ketones it was thought advisable to study the absorption spectrum of biacetyl. This substance is formed during the photochemical decomposition of acetone[1] and is a possible product, along with other diketones, during the irradiation of ethyl methyl ketone. Since absorption coefficients of the ketones below 2000 Å. are far higher than in the near ultraviolet, it was hoped that the absorption spectrum might be used to detect even small amounts of biacetyl.

As would be expected the juxtaposition of two chromophoric groups causes a displacement of the absorption spectrum toward longer wave lengths. Thus in the near ultraviolet biacetyl vapor absorbs to 4670 Å.,[2] whereas acetone[3] and ethyl methyl ketone[4] show absorption to only between 3200 and 3300 Å. Below these absorption regions both biacetyl and the other ketones show a broad zone of transmission extending to below 2000 Å., where an intense absorption takes place.

Biacetyl shows bands with fine structure from 4670 to 4400 Å. at which point the bands become diffuse. Continuous absorption is observed below 2800 Å.[2] and extending to about 2500 Å.

Lardy[5] and Luthy[6] have investigated the spectra of biacetyl and of glyoxal, respectively, in hexane solution. In biacetyl four bands occur between 4512 and 4054 Å., a wide band at 2800 and another at 1950 Å. being observed also. Glyoxal between 4613 and 3119 Å. shows seventeen bands and in addition there are bands at 2800 and 1950 Å. The substitution of a CH_3 group for a hydrogen atom widens the narrow bands, reduces their number and increases the absorption coefficient.

Experimental

The biacetyl (Eastman) was fractionated several times before being introduced into the storage bulb, after which it was again fractionated three times at low pressures in the vacuum line. Calcium chloride was used as a drying agent and the boiling point of the fraction taken was 87–88°. The freezing point was approximately −4°, although no value is recorded in the literature. No vapor pressure data could be found, but the observed vapor pressures were about 0.01 mm. at −70°, 1 mm. at −30° and 13 mm. at 0°.

A quartz cell with relatively thin windows was interposed between the hydrogen discharge tube and the slit of the vacuum spectrograph to avoid introducing the biacetyl directly into the spectrograph. Thus an absorbing column about 15 cm. in length and vapor pressures from 0.01 to 15 mm. were used. The spectrograph has been described.[3] Ilford I plates were used.

The dispersion of the spectrograph with the setting used was found to be 8.48 Å. per mm. in the first order. The 1931.027 Å. line of C III and a number of the fourth positive bands of carbon monoxide were used[7] as wave length standards. Since a quartz cell was employed, the lower limit of observation was about 1550 Å.

Results

Twenty-six bands of biacetyl were found in all. These are listed in Table I, together with rough estimates of the intensities based on the pressure at which the bands appeared and their visually estimated intensities on the plates. The red edges of the bands appeared to be most sharp and are reported. Most of the bands were sufficiently

---

(1) Barak and Style, *Nature*, **135**, 307 (1935); Spence and Wild, *ibid.*, **138**, 206 (1936).

(2) *Cf.* Sponer, "Molekülspektren," Verlag von Julius Springer, Berlin, Vol. I, 1935, p. 117.

(3) Noyes, Duncan and Manning, *J. Chem. Phys.*, **2**, 717 (1934). This paper contains references to earlier work. See also Noyes, *Trans. Faraday Soc.*, **33**, 1495 (1937).

(4) Duncan, Ells and Noyes, THIS JOURNAL, **58**, 1454 (1936).

(5) Lardy, *Compt. rend.*, **176**, 1548 (1923).

(6) Luthy, *ibid.*, **176**, 1547 (1923).

(7) Read, *Phys. Rev.*, **46**, 571 (1934).

sharp so that the error should not exceed ten wave numbers, although a few of the more diffuse bands may not be accurate to better than 30 cm.$^{-1}$. Bands measured only once may be considered to be somewhat doubtful.

TABLE I

BIACETYL BANDS, 1600–2000 Å.

Wave length, Å.	Wave number cm.$^{-1}$	Relative intensities	No. times measured
1691.45	59121	75	8
1705.09	58648	50	8
1720.13	58135	20	2
1730.88	57774	40	8
1745.35	57295	100	9
1883.77	53085	2	3
1905.45	52481	3	5
1928.08	51865	4	3
1951.07	51254	12	11
1960.78	51000	1	1
1962.44	50957	4	5
1963.56	50928	4	4
1964.64	50900	4	4
1965.95	50866	5	8
1967.30	50831	1	1
1968.16	50809	3	1
1969.05	50786	3	1
1970.06	50760	4	3
1970.99	50736	8	8
1972.08	50708	6	12
1973.09	50682	12	12
1974.45	50647	12	15
1975.82	50612	2	3
1977.14	50578	2	2
1982.87	50432	1	1
1984.40	50393	1	1

One upper electronic state probably leads to all the bands in the table except the first five. These twenty-one bands are found in three regions, as are those from 50,634 to 53,119 cm.$^{-1}$ in ethyl methyl ketone[4] and those from 51,000 to 54,954 cm.$^{-1}$ in acetone (four regions). The bands present many similarities in all three compounds.

In biacetyl, as in the other two ketones, the structure is sharpest in the region of longest wave length and very diffuse in the other two.

From intensity considerations the 50,647 band is probably the origin of the system. Absorption is practically complete above 56,000 cm.$^{-1}$ at the optimum pressure for observing the bands from 50,600 to 54,000.

The prominent bands in the three regions referred to above are separated by about 1200 cm.$^{-1}$ as follows:

50,647		51,865		53,085
	1218		1220	

It is true that frequency differences very close to this seem to be found in other ketones,[8] but it is less clear with biacetyl whether this difference is significant, since it is possible to put five of the important bands in a progression using a frequency approximately half as great:

50,647		51,254		51,865		52,481		53,085
	607		611		616		604	

However, similarities to the spectra of the other ketones would indicate the 1200 cm.$^{-1}$ frequency to be characteristic of the upper state of the carbonyl group, especially since the bands 50,647, 51,865 and 53,085 belong in different regions.

The Raman spectrum of biacetyl is probably not known in detail, although Kohlrausch and Pongratz[9] have found the following frequencies (intensities in parentheses): 375 (0), 690 (2), 1275 ($^1/_2$), 1444 (0), 1725 (2), 2940 (3), 3023 ($^1/_2$). Frequency differences of 375 and 690 do not occur prominently, if at all, in the bands in Table 1. Therefore it is impossible to identify, even tentatively, any transitions from upper vibration levels in the ground state.

Some eight differences of approximately 220 cm.$^{-1}$ occur. This is rather low to be a fundamental frequency of either the upper or lower state and may possibly be ascribed to a difference between upper and lower state fundamentals. Further attempts at a vibration analysis seem inappropriate at present.

The first five bands in Table I doubtless involve a second upper electron state as do the bands 60,086 to 62,529 in acetone and 58,110 to 59,360 in ethyl methyl ketone. 1350 occurs twice and 475 occurs twice as frequency differences among these bands, but the significance of these numbers is uncertain.

Since a quartz cell was used, the spectrum below 1550 Å. was not investigated. In acetone Duncan[10] found a Rydberg series among the bands at shorter wave lengths, but such a series, if it exists, could not have been found in the present experiments.

As the pressure is increased continuous absorption appears at the shorter wave lengths studied and gradually spreads until it reaches 2000 Å. In this respect biacetyl somewhat resembles the other ketones.

---

(8) Henri, *Compt. rend.*, **199**, 849 (1934); **203**, 67 (1936); Eastwood and Snow, *Proc. Roy. Soc.* (London), **A149**, 434 (1935); see Noyes, *J. Phys. Chem.*, **41**, 81 (1937).

(9) Kohlrausch and Pongratz, *Ber.*, **67B**, 976 (1934).

(10) Duncan, *J. Chem. Phys.*, **3**, 131 (1935).

Certain of the bands of biacetyl occur, as would be expected, at longer wave lengths than similar bands for the other ketones hitherto investigated. Since absorption coefficients in the absorption regions below 2000 Å. are, generally speaking, very high, it probably would be possible to use these bands for a semi-quantitative as well as a qualitative estimate of the amount of biacetyl present along with acetone and ethyl methyl ketone.

In conclusion the author wishes to express his appreciation to Dr. W. A. Noyes, Jr., who suggested this problem.

Summary

The absorption spectrum of biacetyl vapor has been investigated with a vacuum grating spectrograph between 2000 and 1550 Å. Absorption regions are found which correspond in general to those in acetone and ethyl methyl ketone, although they are displaced to longer wave lengths as would be expected due to the juxtaposition of two carbonyl groups. A prominent frequency difference of about 1220 cm.$^{-1}$ is found in the upper state, although the presence of another difference almost exactly half as great renders the interpretation ambiguous. Certain bands occur at wave lengths sufficiently displaced from those in acetone and ethyl methyl ketone to permit them to be used for the identification of biacetyl in the presence of these other substances.

PROVIDENCE, R. I. RECEIVED MAY 6, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Phase Rule Studies of Soap Systems.
I. Applicability of the Phase Rule

BY J. W. McBAIN, R. D. VOLD AND M. J. VOLD*

The purpose of this introductory paper is to justify the application of the phase rule to soap systems.

It has been shown[1] that many colloid systems are formed spontaneously from their crystalloidal components, and exhibit properties which are independent of previous history and are solely dependent upon composition and temperature, and that they are thermodynamically stable in the same sense as are crystals or solutions of sugar or salts. It will be shown that therefore the phase rule in its usual form, $(F = C + 2 - P)$, must apply to all thermodynamically stable colloid systems, without the introduction of any new variable.

Empirically, it has been found in many contributions since that of McBain and Burnett in 1922 that the behavior of systems of soap, water and electrolytes can be represented quantitatively on the usual Gibbs triangular diagram.[2] A large body of knowledge has been thus assembled and the work of previous authors[3] also has been found to fit into the same systematic description and analysis. The results have led to a greatly clarified understanding of the processes and phenomena of soap-boiling.

The same phases occur for sodium palmitate,[4] potassium laurate,[5] and potassium oleate.[6] The observations of temperatures at which phase changes occur and the analytical data on the composition of separated phases fit into the phase rule diagrams. Similar results have been obtained in experiments on the mixed fatty acids from coconut oil and in the experiments of Elford with commercial oils and fats on a full commercial scale. Ferguson and Richardson[7] likewise found that the phases of commercial soaps are the same as those in soaps from a single fatty acid.

---

* Née M. J. Young.

(1) J. W. McBain and A. J. Burnett, *J. Chem. Soc.*, **121**, 1320 (1922); J. W. McBain, Fourth Colloid Symposium Monograph, **4**, 7 (1926); *Kolloid-Z.*, **40**, 1 (1926); THIS JOURNAL, **58**, 2610 (1936); **60**, 223 (1938).

(2) See also J. W. McBain and E. Walls, Fourth Colloid Report of the British Association for the Advancement of Science, 1922, p. 244.

(3) F. Merklen, "Études sur la Constitution des Savons du Commerce," Marseilles, 1906; German edition by F. Goldschmidt, Halle-a.S., 1907; T. Richert, Diss., "Über das Aussalzen von Seifen," Karlsruhe, 1911; F. Bätz, Diss., Karlsruhe, 1918; M. Thörl, Diss., Karlsruhe, 1918.

(4) J. W. McBain and G. M. Langdon, *J. Chem. Soc.*, **127**, 852 (1925); also J. W. McBain, L. H. Lazarus and A. V. Pitter, *Z. physik. Chem.*, **A147**, 87 (1930); this paper contains an extensive bibliography.

(5) J. W. McBain and M. C. Field, *J. Phys. Chem.*, **30**, 1545 (1926).

(6) J. W. McBain and W. J. Elford, *J. Chem. Soc.*, 421 (1926).

(7) R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, **24**, 1329 (1932).