We wish to thank Professor S. C. Lind for suggesting the method of attack and Professor W. H. Hunter for his interest in our work and helpful suggestions.

Summary

A new method is proposed which permits the determination of oxygen during the combustion of organic compounds containing carbon, hydrogen and oxygen. The amount of oxygen consumed is measured volumetrically. The arrangement of the combustion train in a closed circulating system insures complete combustion.

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[CONTRIBUTION FROM THE BAKER CHEMICAL AND ROCKEFELLER PHYSICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF BENZENE AND TOLUENE IN ALCOHOLIC SOLUTION. THE SPECTROSCOPIC DETECTION OF BENZENE AS AN IMPURITY IN ORGANIC COMPOUNDS[1]

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Since Henri[4] succeeded in ordering the numerous lines in the absorption spectra of benzene vapor, in accordance with the modern view of band spectra, there has been a revival of interest in the absorption of the aromatic hydrocarbons. Henri and Walter[5] followed with a study of the vapor of toluene and Klingstedt[6] reported on its absorption spectrum in hexane solution. The latter was able to show that the relatively broad solution bands follow the same law that applies to the band heads in the vapor spectrum. Kronenberger and Pringsheim[7] have measured the absorption spectrum of solid benzene at −180°. They found that the diffuse bands of liquid benzene break up into many narrow bands of about 1 Å. in width, of which they record 62. These vary considerably in intensity, the most prominent being associated with the strong bands

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[4] Henri, *J. phys. radium*, **3**, 181 (1922). For a fairly complete bibliography of the early work on the absorption spectra of benzene and toluene, see "Report of the British Association for the Advancement of Science," **1916**, p. 131.

[5] Henri and Walter, *Compt. rend.*, **176**, 746 (1923).

[6] Klingstedt, *ibid.*, **175**, 1065 (1922); *Acta Acad. Abo. Math. Phys.*, **3**, 1 (1924).

[7] Kronenberger and Pringsheim, *Z. Physik*, **40**, 75 (1926).

reported by Henri[4] for a pentane solution.[8] Kronenberger and Pringsheim call attention to the general similarity of the absorption of benzene at the low temperature and in the vapor state and attempt to arrange the bands on energy level diagrams, while pointing out the theoretical difficulties in the way of accepting any of the arrangements proposed. Despite the fact that the mechanism is obscure, the general equation deduced by Henri is still applicable, and with certain simplifications for the cases of solid and liquid (or dissolved) benzene, it expresses the data very satisfactorily. For the vapor spectra, the equation takes the form

$$\nu = \nu_0 + an - (bp + b'p^2) - \alpha(m^2 - q^2) \qquad (1)$$

where ν_0 is the frequency attributed to electronic vibrations, a and b correspond to intramolecular vibrational frequencies in the excited and unexcited states, b' is a correction introduced by the non-harmonic nature of the vibrations and α gives the molecular rotational frequency; n, p, m and q are quantum numbers. In the solid and liquid states, molecular rotation is absent, as evidenced by the lack of fine structure in the individual bands and the equation can be simplified to

$$\nu = \nu_0 + an - bp \qquad (2)$$

The factor in b' is neglected, since its value of 0.2 mm.$^{-1}$ as determined from the vapor spectra of benzene is less than or, at best, of the same order of magnitude as the probable error in the location of band heads for solution spectra.

In a recent paper, Smith, Boord, Adams and Pease[9] have ascribed the ultraviolet bands in benzene vapor to the presence of the carbon-hydrogen linkage, on the basis of the numerical relationship with the infra-red bands of benzene. This accordance is achieved by neglecting the factor ν_0 and considering only the contributions to the energy of the molecule given by the vibrational factors a and b. However, a closer examination of the available data[10] shows that of the infra-red bands of benzene, some are characteristic of all compounds containing the CH_2 and CH_3 groups, others occur only in compounds containing the ethylenic bond, while still others are characteristic of benzene alone. This makes it appear very doubtful whether there is any justification for attributing the ultraviolet bands merely to the carbon-hydrogen linkage. The evidence adduced by Smith and his collaborators in support of their view indicated that a number of organic compounds of radically different types, such as cyclohexene, diethyl ether, methyl-*n*-amyl ether and ethylene chlorohydrin in the vapor state, all showed exactly the same bands, in position and

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[8] It would seem to be more appropriate to compare the bands in solid benzene with those in the liquid state, which Henri also measured, as this brings out more precisely the effect of change of state and decrease in temperature on the absorption.

[9] Smith, Boord, Adams and Pease, THIS JOURNAL, **49**, 1335 (1927).

[10] Henri, "Études de Photochimie," Paris, **1919**, p. 113.

relative intensity, as benzene. The suspicion that these bands were actually due to the presence of benzene as an impurity has been confirmed by experiments carried out in this Laboratory, following in general the same procedure that was used by the above authors.[11]

The diethyl ether used was a sample of Kahlbaum's, distilled over sodium. The methyl-*n*-amyl ether, cyclohexene and ethylene chlorohydrin were obtained from the Eastman Kodak Company. These were first examined without any previous attempt at purification. The diethyl ether and cyclohexene showed no indication of benzene bands, while both the ethylene chlorohydrin and methyl-*n*-amyl ether gave the characteristic vapor bands very strongly. The latter two substances were then carefully distilled and again examined, with the result that the ethylene chlorohydrin now gave no trace of the benzene bands, while with the methyl-*n*-amyl ether no change in the intensity of the bands was apparent. Following a suggestion from Dr. H. T. Clarke of the Eastman Kodak Company, the ether was purified by dissolving in concd. sulfuric acid, blowing dry air through the cold solution for one hour, then diluting with ten volumes of water and distilling. The vapor from the sample so obtained was found to be perfectly transparent, with no trace of the characteristic bands of benzene.

The question of the possible source of benzene in the contaminated samples was also considered. In the case of ethylene chlorohydrin, we were informed that benzene was used as the dehydrating agent in the course of its purification, which satisfactorily accounts for the 0.06% found in the product. The presence of benzene in methyl-*n*-amyl ether may be explained either by the fact that the commercial diethyl ether used in its preparation by the Grignard reaction might have been contaminated by benzene or that the methyl-*n*-amyl ether might have absorbed benzene vapor from the atmosphere of the laboratory during its preparation. Commercial ether has, at times, been manufactured from alcohol denatured with benzene, although a sample of technical ether from current production at the U. S. Industrial Alcohol Co. showed no indication of benzene as an impurity. The second suggestion appears, therefore, to be the more probable, especially as it was found that when a sample of some pure non-volatile organic liquid, such as ethylene chlorohydrin, was allowed to stand in an open container near an open vessel of benzene for ten hours its absorption spectrum revealed the presence of appreciable traces of benzene.

As the form of vapor apparatus used in the above experiments does not permit of quantitative determination of the benzene content of the

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[11] Since obtaining our data, de Laszlo, This Journal, **49**, 2106 (1927), has shown experimentally that ethylene chlorohydrin, when carefully purified, exhibits no trace of benzene bands.

samples, an examination of the liquids was undertaken with the Hilger sector photometer, following the method previously described.[12] It was found that both methyl-*n*-amyl ether and ethylene chlorohydrin contained sufficient benzene to give the characteristic solution bands of that substance. The following procedure was developed for its quantitative determination in the ethylene chlorohydrin. A series of exposures was made at different sector openings, using the original, contaminated sample in the solution cell and the twice redistilled material in the solvent cell. From the plate an approximate determination of the benzene concentration could be obtained by reference to the absorption curve for the alcoholic solution (see below). A solution of equivalent concentration was then prepared by dissolving a weighed amount of benzene in a given volume of pure ethylene chlorohydrin. The absorption of this solution was determined in the usual manner against pure ethylene chlorohydrin as standard and from the curve so obtained it was at once possible to calculate the concentration of benzene in the contaminated sample. To carry out the calculation, a curve is drawn for the known solution, plotting absorption coefficient against frequency numbers, the absorption coefficient being defined by the relation

$$\beta = \frac{m}{cd} \log \frac{1}{T}$$

where m = molecular weight, c = concentration in g./liter, d = thickness of cell and $1/T$ = reciprocal of the transmittance. For the unknown solution, a series of exposures is made for different values of log $1/T$ and the corresponding values of the frequency numbers are determined from the plate. From the curve for the known solution, the values of β corresponding to these frequency numbers are read off and, by substituting in the above expression, c can be calculated. The sample of ethylene chlorohydrin, as received, contained 0.06% of benzene, while it was estimated by a somewhat cruder method that the methyl-*n*-amyl ether contained about 0.7–0.8% of benzene.

In determining the absorption spectra of benzene and toluene in alcoholic solution, special precautions were taken, because of their high volatility and the intense absorption of their vapors, to exclude them from the atmosphere of the laboratory and particularly to prevent local concentration between the light source and the slit of the spectrograph. The ends of the cell tubes for holding the solutions were carefully ground to prevent leakage and were filled completely, thus avoiding the presence of small bubbles which would be saturated with active vapor. As a final check, photographs of the absorption spectra of the vapors of benzene and toluene were made and compared with those of the solutions. A study of the relative positions and character of the vapor and solution

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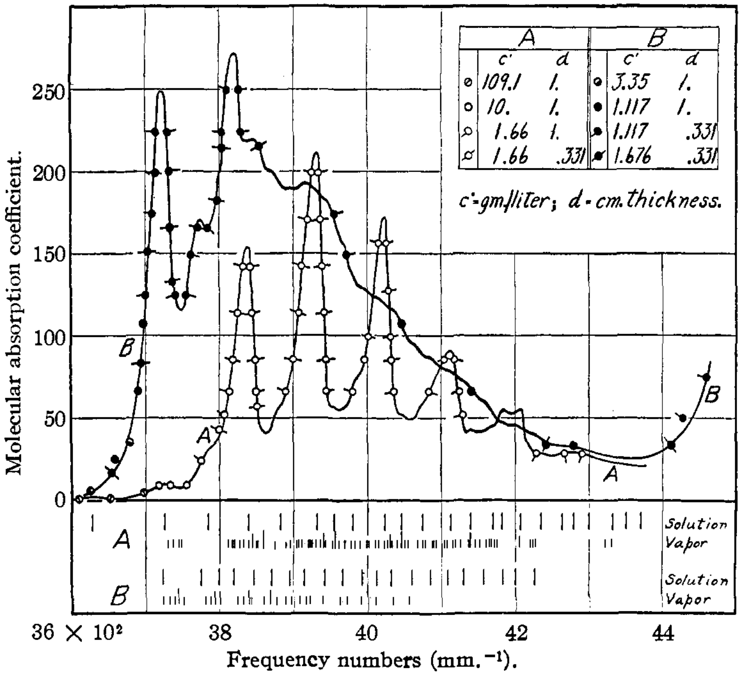
[12] Orndorff, Gibbs and McNulty, This Journal, **47**, 2767 (1925).

bands showed conclusively that none of the absorption bands found in solution could be ascribed to vapor. Two samples of benzene were examined, the first being redistilled from Kahlbaum's thiophene-free product, the other prepared from pure benzoic acid and redistilled. Both samples had a boiling point of 79° at 739.5 mm. They gave entirely concordant results. The toluene used was redistilled from a pure Kahlbaum sample. Its boiling point was 108.8° at 743 mm.

The absorption curves for absolute ethyl alcohol solutions of benzene and toluene are sketched in Fig. 1. The positions of the bands have been indicated on the same diagram, together with our measurements on the vapor spectra. Our apparatus was quite unsuited for bringing out the already well-known finer structure of these vapor bands, but they are included here primarily as evidence of the lack of consistent coincidence with the fainter solution bands. It will be noted that between frequency numbers 3600 and 4400 there are 23 solution bands for benzene and 21 for toluene, as against 8 tabulated by Henri[13] for benzene and 16 listed by Klingstedt[6] for toluene in hexane solution. Henri recorded but 7



A, Benzene; B, Toluene.

Fig. 1.—Neutral absolute alcohol solution.

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[13] Henri's curve indicates the presence of six more weak bands, whose positions he did not tabulate in frequency numbers.

bands for an alcoholic solution of benzene, his values being in very close agreement with ours. As pointed out by Henri, there is an average displacement of 5 mm.$^{-1}$ toward higher frequency numbers for the bands in an alcoholic solution of benzene as compared with their position in a hexane solution. Comparing Klingstedt's data with ours, the same average shift is found in the corresponding case for toluene. As shown in Fig. 1, the intensity of absorption is, on the whole, greater for toluene than for benzene in alcoholic solution. For hexane solutions, however, Klingstedt's curves show benzene to have a greater intensity, and toluene a lesser intensity, than our data show for the corresponding alcoholic solutions.

The frequency numbers (mm.$^{-1}$) of the absorption bands of benzene and toluene are arranged in Table I according to equation (2).

TABLE I

DATA FOR BENZENE AND TOLUENE

Frequency Numbers (mm.$^{-1}$) of Bands

Benzene							Toluene						
3628		..		..		..							
(98)													
3726		..		..		..	3723		..		..		..
(114)							(97)						
3840		..		..		..	3820		..		..		..
(92)							(95)						
3932		..		3785		..	3915	(68)	3847	(71)	3776		..
(92)				(98)			(97)		(96)		(95)		
4024	(69)	3955	(72)	3883		..	4012	(69)	3943	(72)	3871	(71)	3800
(89)		(91)		(98)			(97)		(90)		(96)		(96)
4113	(67)	4046	(65)	3981		..	4109	(76)	4033	(66)	3967	(71)	3896
(95)		(94)		(94)			(91)		(97)		(94)		(97)
4208	(68)	4140	(65)	4075		..	4200	(70)	4130	(69)	4061	(68)	3993
(92)		(95)		(95)					(96)		(96)		(92)
4300	(65)	4235	(65)	4170		..	..		4226	(69)	4157	(72)	4085
		(97)		(94)									(98)
..		4332	(68)	4264	(81)	4183	..		..		..		4183
				(87)		(96)							
..		..		4351	(72)	4279							
						(92)							
..		..		..		4371							

Attention may be called to one point raised by Kronenberger and Pringsheim[7] regarding the separation of the bands in benzene. It will be noted that there is an average separation of 94 mm.$^{-1}$, with a single exception where the deviation is too large to be overlooked, the bands at 3726 and 3840 being separated by 114 mm.$^{-1}$. As the band corresponding to that at 3726 is the first one recorded by them, they have assumed that, if any bands of lower frequency numbers existed, they would be characterized also by this exceptional separation value. Our plates reveal, however, a band with relatively low intensity, at frequency number 3628, yielding a separation of 98 mm.$^{-1}$. As this band is sharply defined and easily measured, there is no doubt as to its exact location. It is possible that by using greater thicknesses of solid benzene at the low temperature this band might be observed and its position checked under those conditions. The data for toluene, when tabulated in a similar manner, show an average separation of 95 mm.$^{-1}$, which compares favorably with that of 94.3 mm.$^{-1}$, found by Klingstedt for a hexane solution.

Since the above article was submitted for publication, a correction by Smith, Boord, Adams and Pease to their previous article[9] has appeared in THIS JOURNAL, **49,** 3137 (1927).

Summary

1. The absorption curves of benzene and toluene in absolute ethyl alcohol solution have been determined and their relations discussed.

2. An analysis of their spectra shows that with one possible exception all of the observed bands of benzene and toluene can be arranged in series, in accordance with a simple mathematical expression.

3. The results recently reported by Smith, Boord, Adams and Pease indicating a benzene-like structure for the absorption spectra of diethyl ether, methyl-*n*-amyl ether, cyclohexene and ethylene chlorohydrin have been proved to be due to the presence of benzene as an impurity in these compounds.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE REACTIVITY OF THE METHYLATED SUGARS. II. THE ACTION OF DILUTE ALKALI ON TETRAMETHYL GLUCOSE

BY M. L. WOLFROM[1] WITH W. LEE LEWIS

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The conversion of one sugar into another and the chemistry of sugars in alkaline media are matters of interest to the biologist and pathologist, as well as the chemist. The course of these transformations can never be fixed with exactness until the underlying fundamental chemistry has been elucidated. The interconversion of simple sugars by alkali has been explained by assuming intermediate enol formation, but no direct proof of this has been obtained. Thus, the reciprocal interconversion of *d*-glucose, *d*-mannose and *d*-fructose, discovered by Lobry de Bruyn and

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[1] Abstracted from a dissertation submitted by M. L. Wolfrom to the Graduate School of Northwestern University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.