num is a pure element (that is, contains no isotopes), its atomic mass being 27. From the standpoint of the nuclear structure it belongs to the type having the nucleus composed according to the scheme $4n + 3$. The results reported here confirm the previously accepted value of slightly less than the sum of the nuclear masses of helium (4.00) and hydrogen (1.008), and although the three hydrogen nuclei are here satellites, the new value suggests that this loss of mass might be due to a disturbing effect of electromagnetic forces within the nuclear system.

I take pleasure in acknowledging my indebtedness to the Bohemian Academy of Prague for financial support in this investigation.

Summary

This paper records the synthesis and analysis of pure aluminum chloride.[12] The substance was prepared from very pure chlorine and the purest obtainable metallic aluminum. Eleven different fractions of the chloride, digested and repeatedly sublimed in nitrogen and in a vacuum, were analyzed. The ratio $AlCl_3:3Ag$ was determined, using three different samples of standard silver. The mean of these eleven determinations is $Al = 26.972$ (± 0.001), when silver is taken as 107.88, and chlorine as 35.458.

Prague, Czechoslovakia

[Contribution from the Sir Donald Currie Laboratories, The Queen's University of Belfast]

THE EMISSION SPECTRA OF ORGANIC COMPOUNDS

By William Hamilton McVicker, Joseph Kenneth Marsh
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Introductory

Owing to the disruptive effect of the ordinary spark discharge upon the vapors of organic compounds, it has hitherto been impossible to obtain characteristic emission spectra from the majority of carbon derivatives; for, as a general rule, only the spectra of carbon, its oxides, or cyanogen, are observed, which result from the decomposition of the compound under examination.

Wiedemann and Schmidt,[1] by selecting some specially stable polynuclear compounds, were able to produce characteristic spectra in the case of ten substances; but as they were unable to extend the field and as, further, their investigations were confined to the visible region of the spectrum, their results contributed very little to our knowledge.

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[12] During this work a new synthesis of aluminum chloride from pure aluminum oxide, sugar charcoal and chlorine has been commenced.

[1] Wiedemann and Schmidt, *Ann. Physik*, **56**, 20 (1895).

Kauffmann[2] at a later date attempted to trace a relationship between the chemical constitution of organic compounds and their power of emitting light when excited by Tesla discharges at ordinary pressures and at the boiling point. As he trusted entirely to eye-measurements of intensity and made no spectroscopic examination of the emitted radiation, his investigations did nothing to advance the quantitative side of the subject.

Last year we[3] were able to show that it is possible to obtain a series of well-marked emission spectra from organic compounds by the use of a Tesla transformer and a quartz ultraviolet spectrograph. These Tesla-luminescence spectra are in some cases extremely regular and complex; the spectrum of benzene, for example, contains seven distinct groups of bands, each group including in its system a set of bands all of which find their parallels in the remaining band groups, so that the wave numbers of the whole complicated band system are expressible by means of a simple formula.

Our investigations have included both the visible and the ultraviolet regions of the spectrum, and we have examined a number of derivatives of benzene as well as the parent substance. In the case of benzene itself, we have been able to show that our Tesla-luminescence spectrum is the complement of the absorption spectrum of benzene vapor. Our emission bands coincide in position with the absorption bands mapped by Hartley. Thus the Fraunhofer effect has now been exhibited in the case of complex organic compounds and is no longer confined to the case of elemental spectra.

Our investigation of the benzene derivatives demonstrated that each compound has its own characteristic spectrum; so that a new constitutive property has been discovered, taking its place alongside of absorption spectra, magnetic rotation, refractivity, etc.

The present paper deals with a number of compounds drawn from the most widely different groups of organic derivatives, our object being to show the applicability of our method to a whole series of classes of organic compounds; and thus to establish its generality.

Apparatus

The spectrograph employed by us was a Hilger quartz-prism instrument, size (c). Especially rapid plates were used for the ultraviolet region; and Panchromatics, developed with the aid of Desensitol, were employed when it was desired to photograph the red end of the spectrum. The medical Tesla transformer used by us has already been described in our first paper; it was driven by means of a 30cm. induction coil. The glass cell with quartz window, described in our original paper, has been sup-

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[2] Kauffmann, *Z. physik. Chem.*, **26**, 719 (1898); **27**, 519 (1898); **28**, 673 (1899); *Ber.*, **33**, 1725 (1900).

[3] *J. Chem. Soc.*, **123**, 642, 817, 2147 (1923).

planted for the present by a simpler arrangement in which a quartz tube connects the evaporating flask and the receiver and is placed directly in front of the spectrograph slit. With an electrode at each end of the tube, the discharge produces a very satisfactory glow in the quartz tube. There is always a certain amount of decomposition or polymerization of the compound under examination, which necessitates cleaning the cell from time to time during an experiment. Every precaution has been taken, however, to eliminate any errors likely to arise from this cause.

The Tesla-Luminescence Spectra of Various Compounds

In the majority of cases dealt with in the present paper, the spectra take the form of a general emission over certain regions. As our object was to observe types of spectra rather than to make exact comparisons—which we propose to do later—the exposures were not kept constant but were varied according to the intensity of the radiation emitted. The results of our experiments are given in Table I.

Carbon Monoxide and Carbon Dioxide.—These two gases give identical spectra, which have been found to be the same as the ordinary spectrum obtained by the use of an ordinary induction coil. It seems evident that under the action of the Tesla discharge, an equilibrium mixture of the two gases is produced, and that our observed spectrum is that produced by this mixture.

Methyl Alcohol.—This also exhibits the spectrum of carbon dioxide, which is apparently produced by the decomposition of the alcohol by the discharge.

Diethylamine.—Even at pressures as low as 1 mm., no discharge could be induced to pass through the cell, and no emission was observed.

It may be pointed out that in cases of doubt, the experiments were repeated, but in no case was there any difference in the results.

Discussion of the Results

Inspection of the figures given in Table I at once brings to light the fact that each compound, if it emits luminescence at all, has its own characteristic spectrum. In addition to this, certain other inferences can be drawn from the results.

First, it is evident that compounds such as methyl alcohol, diethyl ether and diethylamine have no luminescent power either in the visible or the ultraviolet region of the spectrum; and it may be recalled that these substances have no absorption spectra either. It seems evident that hydroxyl, methoxy, and ammonia derivatives do not owe their luminescent qualities to the mere presence of the OH, MeO and NR_2 groups in their structure, though such groups may act as influencing factors on the nature of the spectrum emitted by compounds in which they are present.

TABLE I

RESULTS OF EXPERIMENTS

Substance	B. p. °C.	Exposure Min.	Temp. °C.	Pressure Mm.	Spectrum	Wave length	Remarks
Acetaldehyde	20.6–21.1	25	Room	38	Weak, continuous	3650–4750	Fading at end of shorter wave length
Propyl aldehyde	48.5–49.5	48	Room	16–19	Weak, continuous	3400–4850	Fading at end of shorter wave length
Paraldehyde	124–124.5	45	Vapor.[b]	9	Very weak, cont.	3650–4750	Fading at end of shorter wave length
Acetal	102.2–104.4	60	Room	3	Faint, continuous	3700–4800	
Acetone	56.3	60	Room	15	Weak, continuous	3650–4850	Fading at end of shorter wave length
Methylpropyl ketone	101.5–102.5	60	Room	12.5	Weak, continuous	3550–4850	Fading at end of shorter wave length
Methyl*iso*propyl ketone	93.5–95.2	35	Room	13	Weak, continuous	3600–4800	Fading at end of shorter wave length
Diethyl ketone	102–103.5	25	Room	14	Weak, continuous	3500–4850	Fading at end of shorter wave length
Mesityl oxide	130–131	60	Vapor.	1.5	None	....	
Cyclohexanone	156–156.2	45	Vapor.	2.5–6.0	Weak, continuous	3550–4850	Fading at end of shorter wave length
Benzoquinone	(pur. by subl.)	90	Volatil.[c]	1	......	5200–6680[a]	Diffusely banded on faint continuous
Pyruvic ester	85–92 (90–100 mm.)	10	Vapor.	3	None	....	Much sparking; exp. short to avoid decomp.
Ethyl aceto-acetate	78–82(11 mm.)	20	Vapor.	2	Very faint, cont.	3200–4800	Much sparking in cell
Acetylacetone	137.4–138.2	40	Vapor.	2	......	....	Only CO spectrum obs., prob. due to decomp.
Anisole	222.6–222.8 (750 mm.)	30	Vapor.	3	Intense, cont.	2840–4450	Fading at both ends
o-Anisidine	222.6–222.8 (750 mm.)	30	Vapor.	1.5	Faint, bands	2891–2909	
Anisaldehyde	247.5–250	27	Vapor.	1.5	Intense, cont.	3130–4500	Fading at end of greater wave length
					Continuous	3880–4700	Spectrum resembled that of acetone
					Three diffuse bands	3930, 4190, 4520 (approx.)	

Substance	B. p. °C.	Exposure Min.	Temp. °C.	Pressure Mm.	Spectrum	Wave length	Remarks
Salicyl aldehyde	195.6–197 (751 mm.)	25	Vapor.[b]	1	None	....	Discharge passed with difficulty
Methyl salicylate	222.2 (751 mm.)	28	Vapor.	1.5	Medium, cont.	3490–5000	Terminates abruptly at both ends
					Centers of intens. at	3700–4600	
Diethylaniline	213.2–214 (738 mm.)	39	Vapor.	2	Very intense, cont.	3250–4750	Fading at end of greater wave length
Cinnamyl aldehyde	132 (20 mm.)	..	Vapor.	1.5–2	None	....	Much sparking
Furfural	160.5–161.2 (760 mm.)	20	Vapor.	2–3	Traces of carbon	....	Much sparking; discharge passed w. diff.
Thiophene	83.5–84.4	40	Room	10	None	....	Decomp.; discharge passed w. diff.
Pyrrole	128.4–132	20	Room	5	Only CN bands	....	Decomposition; cell quickly dirty
Pyridine	....	Various conditions			None	....	......
β-Picoline	141.2–143.4 (758 mm.)	57	Vapor.	1	Doubtful luminesc.	4700–5500	Discharge passed with difficulty
Quinoline	234.2–234.6 (727 mm.)	30	Vapor.	1	Weak, continuous	3320–4700	......
					Less intense	3700–4000	......
Isoquinoline	238.6–240.6 (730 mm.)	30	Vapor.	1.5	Medium, continuous	3380–4575	Fading at end of greater wave length
					Traces of heads	3520–3730	
Tetrahydroquinoline	247.7–249.2 (745 mm.)	30	Vapor.	1.5	Intense, continuous	3350–4600	Fading at end of greater wave length
					Luminescence	5100–6150	Observed in visual spectroscope
Diethyl ether	....	..	Room	1.5–2	None	....	......

[a] Bands noted as follows: 5340, distinct; 5445?, faint; 5700?, faint; 5860, distinct; 6150, medium; 6285, faint; 6530, distinct; 6680, distinct.

[b] "Vapor." means minimum vaporization temperature.

[c] "Volatil." means minimum volatilization temperature.

Second, while each luminescent compound possesses its own characteristic Tesla spectrum, a general similarity is traceable among the members of a particular chemical class of compounds. For example, the ketones and aldehydes all show luminescence in a specific restricted spectral region, different from that in which the luminescences of benzene and its congeners make their appearance. It is, therefore, evident that the Tesla-luminescence spectrum is a constitutional property of compounds; and the investigations which we have made up to the present, seem to indicate that even slight changes of chemical structure may exert a marked influence upon the spectral character, just as is the case in absorption spectra.

An example of these phenomena is to be found in the spectral limits of the luminescence in the cases of some carbonyl compounds.

	Spectral limits		Spectral limits
$CH_3.CHO$	3650 4750	$C_2H_5.CO.C_2H_5$	3500 4850
$C_2H_5.CHO$	3400 4850	$CH_3.CO.COOEt$	No emission due to compound
$CH_3.CO.CH_3$	3650 4850		
$CH_3.CO.CH(CH_3)_2$	3600 4800	$CH_3.CO.CH_2.COOEt$	3200 4800
$CH_3.CO.CH_2.CH_2.CH_3$	3550 4850	$CH_3.CO.CH_2.CO.CH_3$	No luminescence
		$CH_3.CO.CH{:}C(CH_3)_2$	No luminescence

Inspection shows that although all aldehydes and ketones in the first group emit a luminescence somewhere in the region between 3500 and 4850, yet in no two cases is there coincidence of any two spectra at both ends. Four of the compounds emit spectra ending at 4850, but in each case the other end of the spectrum occupies a different position.

The effect produced by slight changes in chemical character can be seen in the case of the two isomeric methylpropyl ketones, for which the whole spectrum of the normal compound is a hundred units longer than that of the *iso*propyl derivative. Again, while aceto-acetic ester gives distinct luminescence, the emission is extinguished when the ethoxy group is replaced by the methyl radical, or the group —CH_2.COOEt is replaced by —COOEt. Thus by very slight alterations in constitution, one of the longest of all the emission spectra is completely damped down.

The influence of substitution is equally well marked in the aromatic series. Salicylic aldehyde emits no spectrum, whereas methyl salicylate shows a luminescence of medium intensity between 3490 and 5000, with diffuse bands around 3700 and 4600. Thus, the exchange of a hydrogen atom for a methoxy group produces an alteration from no luminescence to the production of a banded spectrum.

Again, in the methoxy-phenyl series, equally striking results appear, as the following data show.

$MeO{-}C_6H_4{-}H$	Intense spectrum	2840–4450	Two bands
$MeO{-}C_6H_4{-}CHO$	Very intense	3130–4500	No bands
$MeO{-}C_6H_4{-}NH_2$	Medium spectrum	3880–4700	Three bands

The presence of long chains of conjugated double bonds does not appear to have a stimulative effect, but rather the reverse, so far as can be seen. For example, benzaldehyde shows a well-marked spectrum with a series of well-defined bands in the blue region, whereas cinnamyl aldehyde, in which the chain of conjugation is lengthened by the interposition of the double bond between the phenyl nucleus and the aldehyde groups, shows no luminescence at all.

Turning to the heterocyclic series, it is found that the five-membered monohetero rings yield no emission, so that it is clear that the apparent parallelism between benzene and thiophene cannot be maintained in this field, since benzene gives one of the most complicated band systems, whereas thiophene yields no spectrum whatsoever.

The six-membered heterocylic compounds promise results of greater immediate interest. As mentioned above, pyridine itself shows no emissive property; and the introduction of a single methyl radical into its structure appears to have little influence, since the emission of β-picoline is so faint that we are in doubt as to its reality. But when a benzene ring is fused with the pyridine nucleus, a marked change is produced; and a further alteration is brought about by the reduction of the pyridine ring in the bicyclic compound, as the following data show.

Pyridine	No emission	
Quinoline	Weak	3320–4700, a less intense region at 3700–4000
Isoquinoline	Medium	3380–4575, with bands at 3520 and 3730
Tetrahydroquinoline	Intense	3350–4600 and 5100–6150
Diethylaniline	Very intense	3250–4750

The inference to be drawn from these facts seems plain. The pyridine ring in itself contains no luminescent structure; it shows luminescence only when fused with a benzene ring. But since the benzene ring system is one of the most delicate producers of Tesla-luminescence spectra, it seems probable that the part played by the hetero ring in quinoline and isoquinoline is merely that of a modifier, altering the character of the emission from the benzene nucleus and shifting the spectrum approximately a hundred units towards the end of greater wave length. This idea seems to be strengthened by the fact that when the hetero ring is reduced, as in tetrahydroquinoline, the emission still goes on in the region 3350–4600, but changes from a weak spectrum to an intense one.

Further evidence on this point is found in an examination of the spectrum of diethylaniline. This substance emits a very intense spectrum which covers the whole of the region occupied by that portion of the tetrahydroquinoline luminescence which lies outside the visible region; so that it may reasonably be assumed that the origins of these two almost identical luminescences are much alike. Now obviously in the case of diethylaniline, we are dealing with a spectrum which does not originate in the amino group, since diethylamine yields no luminescence whatever. It thus seems logical to suppose that the machinery of the diethylaniline spectrum lies in the benzene ring as modified by the presence of the adjacent substituted amino radical. But if this assumption is correct, it seems equally applicable to the case of tetrahydroquinoline, for that compound also has a substituted amino radical in immediate proximity to the benzene nucleus.

We wish to express our thanks to the Chemical Society of London for a grant made from the Research Fund towards the expenses of this research. Some of the materials used in the work were obtained from the Eastman Kodak Company, and we wish to thank them for specially pure specimens, the use of which saved us much trouble. Part of the apparatus used in the investigation was procured with the aid of the Heron Fund of this University.

Summary

An examination has been made of the Tesla-luminescence spectra of a number of organic compounds belonging to various classes, and it has been shown that while each compound yields its own characteristic spectrum, the members of a given class show a general resemblance in the spectra which they emit. It has been found that slight changes in structure make their influence felt in the Tesla-luminescence spectra. A study of some heterocyclic compounds indicates that while furfurole, thiophene, pyrrole and pyridine emit no characteristic spectra of their own, the pyridine nucleus exerts a very marked influence when it is fused with a benzene ring, as in quinoline; and reduction of the pyridine structure produces a marked alteration in the spectrum of the compound.

BELFAST, NORTHERN IRELAND

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE MECHANISM AND THERMOCHEMISTRY OF THE REACTION BETWEEN CALCIUM CARBIDE AND NITROGEN

BY H. J. KRASE AND J. Y. YEE

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When calcium carbide reacts with nitrogen, calcium cyanamide and carbon are the end products of the reaction. There is, however, ample evidence that the reaction does not go as simply as is indicated by the equation,

$$CaC_2 \text{ (solid)} + N_2 \rightleftharpoons CaCN_2 \text{ (solid)} + C \text{ (solid)} \qquad (1)$$

for it appears that the system is not a monovariant one with three separate solid phases.

The evidence which demonstrates that the system is not a monovariant