5.   This precipitate can be redissolved upon the addition of acids and the resulting diazo compound will follow the normal decomposition.

6.   The solid diazotate has been prepared and its decomposition noted. The addition of acid to this solid causes it to redissolve and decompose normally.

WORCESTER, MASSACHUSETTS

ABSORPTION SPECTRA IN SOLUTION AT LOW TEMPERATURES

BY L. B. ARNOLD, JR., AND G. B. KISTIAKOWSKY

Introduction

Extended and systematic work on light absorption of carbon compounds in solution has been concerned mainly with the identification and quantitative study of rather broad absorption regions.   Each of these can be assigned to a definite electronic transition in the molecule, at least in cases where information on the absorption spectra in the gaseous state is available.   The main achievement of this work is the evidence that certain absorption regions, located mostly in the near and middle ultraviolet, can be identified with definite atomic groups like the carbonyl, double bond, benzene ring, etc.   Evidence has also been accumulated indicating that, if more than one such light absorbing group is present in a large molecule, the resulting spectrum can be represented in the first approximation as a sum of the component spectra.   A more detailed study, by the usual method of quantitative measurement of the light absorption coefficients, has revealed, however, that the summation rule holds only very approximately and that in general the rest of the molecule exerts an influence on the absorption by a given part of it.   Such an effect, as has been pointed out frequently, is altogether analogous to the alterations in the chemical properties of a group produced by the rest of the molecule, that are so common in organic chemistry.

The study of the spectral changes in solution is thus of considerable interest, at least in the domain of large and complicated molecules where neither the Raman spectra nor the absorption spectra in the vapor phase are sufficiently simple to offer a promise of a more rapid and direct solution of the problem.   An attempt at a closer theoretical treatment of the absorption coefficient data for homologous molecules is complicated, however, by the circumstance that this experimental method records simultaneously the effects of two essentially different phenomena.   In addition to alterations in the energy of electronic levels as well as to more or less mechanical changes in vibrational frequencies of an atomic group, resulting in a shift and modification of bands comprising an absorption

region, the light absorption coefficients are affected by changes in electronic transition probabilities. This latter phenomenon is much less accessible to theoretical treatment and so long as the effects of the two are not separated, an uncertainty is attached to speculations based on the study of the absorption coefficients describing only the large scale structure of absorption spectra. The difficulty is removed, in principle at least, by a study, not of the intensity of absorption, but of the locations of the vibrational bands within the absorption region due to the atomic group investigated and their alterations produced by changes in the structure of the rest of the molecule. The scarcity of work in this direction is due undoubtedly to the diffuseness and frequently to the complete absence of any finer structure in the absorption spectra of organic molecules in solution.

The existing literature indicates that the presence or absence of finer structure is typical of large classes of organic compounds and is not "accidental."

Hartley[1] has already pointed out that only aromatic hydrocarbons possess finer structure in their spectra, while aliphatic compounds show only continuous absorption. Stark[2] denied this conclusion and showed that some aliphatic hydrocarbons had banded spectra. However, the bands which he finds are of an altogether different appearance from those of aromatic hydrocarbons and comprise, judging from their width, many vibrational transitions, each probably representing a definite electronic level. Thus, on the whole, Stark's objections do not disprove the conclusion of Hartley, but show that it needs modification. The present contribution is concerned with this modification and amplification; it also deals with the problem of the mutual influence of two parts of a molecule as a function of their distance apart.

In an attempt to improve experimental conditions use was made of the old and well-known observation that low temperatures tend to sharpen and bring out the finer details in the spectra of solids and liquids.[3] Further improvement was expected and obtained by the use of an inert and nonpolar solvent, since the influence of the latter on the spectra of solutes is known to be considerable in some cases.[4]

Experimental Details

The experimental set-up consisted of a quartz hydrogen discharge[5] (E, Fig. 1) as a source of continuous ultraviolet light, a Dewar flask with quartz windows and a small

[1] Hartley and Dobbie, *J. Chem. Soc.*, **77,** 846 (1900); **39,** 153 (1881).

[2] Stark and Lipp, *Z. physik. Chem.*, **86,** 43 (1913).

[3] For recent work see particularly Kronenberger, *Z. Physik*, **63,** 494 (1930); Conant and Crawford, *Proc. Nat. Acad. Sci.*, **16,** 552 (1930).

[4] Klingstedt, *Compt. rend.*, **176,** 1550 (1923).

[5] Kistiakowsky, *J. Opt. Soc. Am.*, **2,** 549 (1931).

Hilger quartz spectrograph (F). The construction of the flask will be seen from Fig. 1. (A) are four quartz to Pyrex graded seals, (B) are polished quartz windows sealed to the ends of these and (C) is the absorption cell of quartz, 4 cm. long, placed in line with the windows. Cooling was accomplished by means of liquid nitrogen, whose level was kept somewhat below the absorption cell. A small electric heater (D) placed in the bottom of the flask generated a steady stream of dry nitrogen which kept the absorption cell cool and prevented frost from forming on it and on the inner windows. Exposures were made on Hammer Special plates sensitized with vaseline. The wave length determinations were made by comparison with the copper arc spectrum. Solutions were made by dissolving a weighed amount of the substance in pentane, transparent within the limits of the set-up, and introducing a small known amount of this solution into liquid propane. This procedure was adopted because solutions in the pentane showed a strong tendency to freeze on cooling.
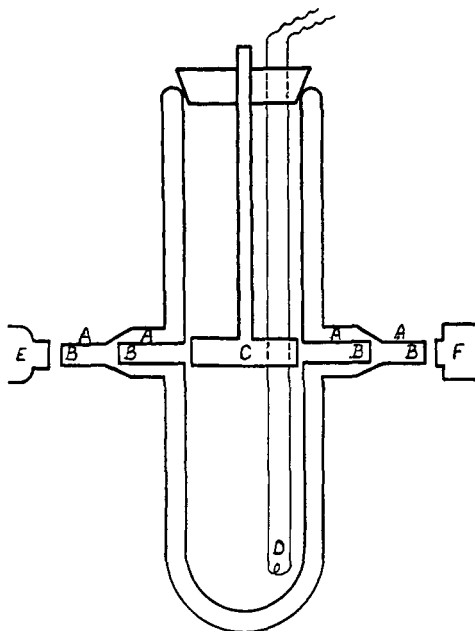

Fig. 1.

In the following a short résumé is given of the more essential points in the preparation and purification of the compounds and solvents used.

Purification of Solvents

Propane.—Gaseous propane from a commercial cylinder was passed successively through spiral wash bottles containing 15% fuming sulfuric acid, concentrated sulfuric acid, saturated permanganate solution containing 10% sodium carbonate, dilute potassium hydroxide solution, and a drying tower filled with sticks of solid potassium hydroxide. It was condensed by solid carbon dioxide.

Pentane.—Shell Pentane Solvent was shaken with saturated potassium permanganate solution containing 10% sodium carbonate until it no longer reduced the permanganate solution. It was then successively washed with water, dilute sulfuric acid and concentrated sulfuric acid. To remove aromatic hydrocarbons the pentane was shaken for four hours with one-fourth its volume of 15% fuming sulfuric acid. After this it was successively washed with concentrated sulfuric acid, dilute sulfuric acid, 10% sodium carbonate solution and finally with distilled water. The pentane was dried over calcium chloride and distilled over sodium. The material all boiled under 34°. It was tested spectrographically for transparency and if any bands persisted the fuming sulfuric acid treatment was repeated. The original material was of such purity that purification was readily obtained. The solvent used was transparent to 2250 Å., which was the limit of the complete apparatus when empty.

Preparation and Purification of Compounds

Benzene.—Eastman thiophene-free benzene was dried over sodium and distilled through a five-foot column. The boiling point was 80.4°.

$\Delta^{1,3}$-Cyclohexadiene.—This was prepared by removing hydrogen bromide from 1,2-dibromocyclohexane with sodium ethylate according to Hoffmann and Damm.[6] The product was repeatedly distilled over sodium in a stream of carbon dioxide until the refractive index[7] was n_D^{20} 1.4740 ±0.0002 and the boiling point was 80.25–80.75°.

Cyclohexene.—Eastman cyclohexene was repeatedly distilled over sodium through a silver spiral fractionating column until a constant absorption spectrum was obtained. The spectrum shows no structure.[8]

Dimethylbutadiene.—This compound was prepared from pinacol. The product was redistilled over sodium until its boiling point was 68.8–69.4°.

Benzaldehyde.—Commercial benzaldehyde was purified through the bisulfite derivative. The sample taken boiled at 66° (10 mm.).

Phenylacetaldehyde.—Phenylacetaldehyde diethyl acetal was prepared and hydrolyzed to phenylacetaldehyde after the method of Woods and Comley.[9] The aldehyde boiled at 195–198° at atmospheric pressure. The semicarbazone melted at 152° and the oxime at 93–95°. The aldehyde was purified through the bisulfite derivative from which it was regenerated by steam distillation from a solution made slightly alkaline with sodium carbonate.

Hydrocinnamic Aldehyde.—Eastman hydrocinnamic aldehyde was purified through the bisulfite derivative. The sample taken boiled at 106–108° (10 mm.).

Chlorobenzene.—c. p. chlorobenzene was redistilled until its boiling point was 132°.

Benzyl Chloride.—Eastman benzyl chloride was redistilled several times. The fraction boiling at 176–179° was filtered through activated charcoal, dried over calcium chloride and distilled again. The sample taken boiled at 178–178.5°.

β-Phenylethyl Chloride, γ-Phenylpropyl Chloride, δ-Phenylbutyl Chloride and ω-Phenylheptyl Chloride.—The preparation of these compounds has been described by Conant and Kirner.[10] The samples were generously loaned by Professor J. B. Conant.

Results and Discussion

It seemed desirable to investigate the relation between the width of absorption bands and molecular structure using the simplest and most similar representatives of the aromatic and aliphatic series. As such, benzene, cyclohexadiene, cyclohexene and dimethylbutadiene were chosen. At room temperature benzene possesses fairly sharp bands while cyclohexadiene has only one wide band according to the work of Stark,[11] which we were able to confirm. The other two compounds show only a gradually increasing absorption toward the short wave lengths. Figure 2 presents microphotometer records[12] of the spectra of the first two compounds at

[6] Hoffmann and Damm, *Mitt. schles. Kohlenforschungsinst. Kaiser-Wilhelm-Ges.*, **2**, 97–146 (1927); *Chem. Abstracts*, **22**, 1249 (1928).

[7] Hoffmann and Damm[6] reported n_D^{20} 1.4755 and Willstätter, *Ber.*, **45**, 1464 (1912), reported n_D^{20} 1.47439.

[8] Stark and Lipp, *Z. physik. Chem.*, **86**, 43 (1913).

[9] Woods and Comley, *J. Soc. Chem. Ind.*, **42**, 429T (1923).

[10] Conant and Kirner, THIS JOURNAL, **46**, 241 (1924).

[11] Stark and Levy, *Jahr. Radioakt. Electronik.*, **10**, 179 (1913).

[12] We take this opportunity to thank Professor Plaskett of the Harvard Observatory for permission to use the Moll microphotometer belonging to the Observatory.

liquid nitrogen temperature. Cyclohexene and dimethylbutadiene are not shown as no significant changes have been obtained on cooling. The reproduction brings out clearly the sharpness of the benzene bands[13] and also the resolution of the cyclohexadiene absorption into three bands. The half width of the bands in the two spectra is, however, strikingly different, being *ca.* 130 cm.$^{-1}$ for benzene and about 700 cm.$^{-1}$ for the other compound. This difference seems to be quite general and the literature presents no evidence, which we could locate, of bands observed with aliphatic compounds in solution which even approach the narrowness of benzene bands. The acetaldehyde absorption spectrum, which is resolved into
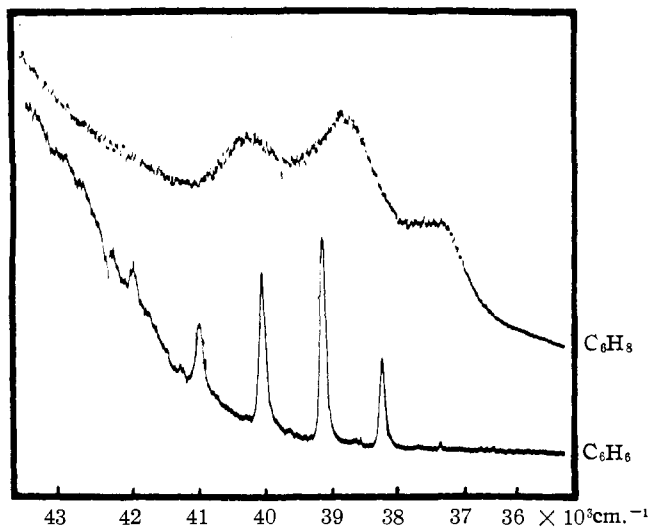

43   42   41   40   39   38   37   36 $\times 10^3$cm.$^{-1}$

Fig. 2.

seven component bands at liquid air temperature (see Fig. 3, A) has half-widths of about 400 cm.$^{-1}$. About the same half-width persists in the spectra of the carbonyl group attached to the benzene ring (Fig. 3), while the latter retains the narrow bands practically unchanged in their width in all derivatives which we investigated. Various publications dealing with the spectra of aromatic compounds at room temperature indicate that this behavior is typical of other derivatives of benzene and other aromatic carbon rings, showing that a significant difference exists between their spectra and those of aliphatic compounds. This difference, however, is not the absence of bands, as assumed by Hartley, but their different half-width.

At 80°K. the rotational energy of molecules is so small that on this

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[13] Fainter but similarly narrow bands located between the strong ones have been observed visually on our other photographs of the benzene spectrum (see also Kronenberger[3]).

account alone vibrational bands should all appear at least as sharp as those of benzene, particularly so long as only compounds of approximately the same molecular weight are compared. The unequal width observed is due therefore to other causes. One of these, probably the most important, is that many aliphatic compounds have in the vapor phase only continuous or diffuse spectra owing to photochemical dissociation and predissociation. These spectra, of course, cannot show structure in solution no matter how low the temperature. It is somewhat doubtful, though, whether this explanation suffices for those cases, like cyclohexadiene or the carbonyl group, where vibrational structure is obtained in the liquid state and where at least the long wave length part of the gaseous spectrum is discrete.[14]
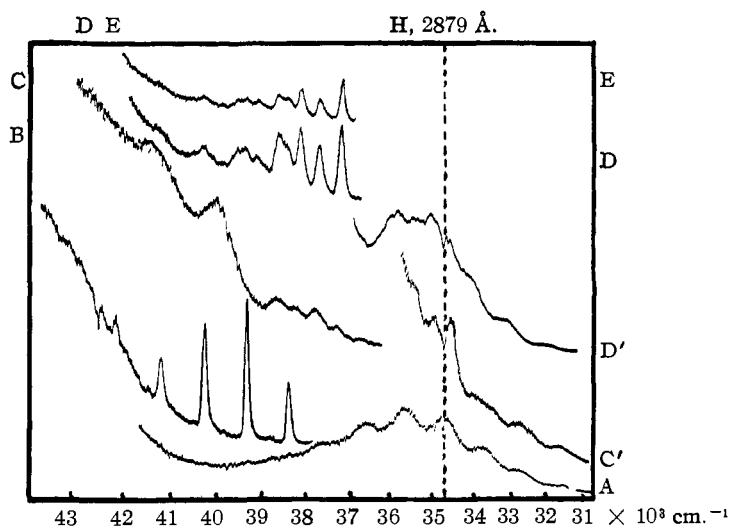

Fig. 3.

It seems more probable that in solution the fields of the surrounding molecules cause considerable broadening of the absorption bands by disturbing the electronic levels. The work of Kronenberger[3] also points to this. He found by direct comparison that the bands of benzene in solution are more diffuse than those of benzene crystals. In the latter case, owing to the regular spacing of the molecules, the broadening should be reduced to a minimum. The present work shows that the disturbing influence of the solvent is much greater with aliphatic compounds whether they be small atomic groups or even rings with double bonds. Thus the electronic states in aromatic rings appear to be exceptionally stable against external influences. Perhaps this can be adduced in favor of the central bond theory for such molecules, since neither the ring structure, nor the

[14] V. Henri, "Structure des Molecules," Paris, 1925.

conjugated double bond, both being present in cyclohexadiene, show this phenomenon.   At any rate the present experiments indicate that the sharpness of absorption bands in solution can be utilized as a supplementary method in investigating the structure of large molecules and thus completely confirm the conclusions reached in a recent communication by Conant and Kamerling.[15]

Although the problem of mutual influence of spectra by two groups in a molecule has already received considerable attention, some new evidence on the subject seemed to be desirable and with this purpose in view a series of aryl aromatic aldehydes has been chosen together with some aryl aromatic monochlorides.   The choice was guided by the consideration that the carbonyl group and the benzene ring both have well-defined and not overlapping absorption spectra in an easily accessible spectral region.

The spectra obtained at low temperatures, although considerably sharper and showing more fine structure than those reported previously from the work at room temperature, proved to be insufficiently resolved for an attempt at vibrational analysis.   Accordingly in Table I are reported only the wave numbers of the observed bands, while Fig. 3 brings out the salient points and shows the microphotometer records of the spectra of acetaldehyde (A), benzene (B), phenylacetaldehyde (C) and (C'), hydrocinnamic aldehyde (D) and (D'), and phenylheptyl chloride (E).   Turning first to the absorption of the benzene ring it will be seen that the substitution of a carbonyl group produces profound changes in the vibra-

TABLE I

WAVE NUMBERS OF OBSERVED BANDS

Bands, cm.$^{-1}$	Half width cm.$^{-1}$	Bands, cm.$^{-1}$	Half width, cm.$^{-1}$	Bands, cm.$^{-1}$	Half width, cm.$^{-1}$
Phenylacetaldehyde		Hydrocinnamic aldehyde		Phenylbutyl chloride*	
30490	500	32010	400	36660	
31630	540	33150	330	37110	
32770	580	34160	340	37360	
33800		35150		37880	
34590		35970		38290	
35000		37260	150	38570	
35190		37720	130	38760	
35460	200	38150	150	39220	
36750	140	38340	100	39430	
37340	110	38620	130	39670	
37750	210	39060	150	39780	
38290	130	30370	130	39980	
38690		30490	150	40140	
39870		40290		40340	
41430		41240		41190	

[15] Conant and Kamerling, THIS JOURNAL, 53, 3522 (1931).

TABLE I (Concluded)

Bands, cm.⁻¹	Half width cm.⁻¹	Bands, cm.⁻¹	Half width cm.⁻¹	Bands, cm.⁻¹	Half width cm.⁻¹
Benzene		**Propionaldehyde**		**Benzyl chloride***	
37790	120	30490	370	34630	
38410	120	32070	360	34870	
39270	140	33210	350	36890	
40200	140	34250	360	37400	
41200	120	35160	410	37610	
42160	110	36190	370	37790	
42410	110	37270	340	38310	
		38380	320	38570	
Cyclohexadiene				39280	
37310	620	**Chlorobenzene**		39430	
38910	780	36870		39830	
40210	730	37410			
		37850		**Phenylpropyl chloride***	
Benzaldehyde		38310		36940	
26940		38810		37400	
27560	170**	39260		37880	
28270	220**	39830		38300	
29020	150**	40290		38570	
29440	270**	40870		38780	
30550	490*	41930		39030	
31660	460**			39200	
32820	470**	**Phenylethyl chloride***		39460	
34510	200	37410		39730	
34950	150	37880		39980	
35290	150	38310		40180	
35640	150	38630		40440	
36620	100	38870		41240	
38340		39050			
39700		39280		**Phenylheptyl chloride**	
41000		39510		37190	110
		39740		37710	150
Acetaldehyde		40420		38120	140
30500		40770		38310	120
31510	400	41000		38600	130
32780		41310		39050	100
33800	410	42460		39320	130
34780	510			39480	100
35710	480			40230	340
36600	500			41250	400 (?)
37290	350				

Bands for compounds marked with (*) are computed from comparator measurements and in the case of benzaldehyde half-widths are estimated by comparison with bands of known half-width on other plates; benzaldehyde bands marked (**) are from a microphotometer record of this section of the benzaldehyde spectrum.   Heptyl aldehyde shows within the limits of experimental error the same absorption spectrum as propionaldehyde.   The benzaldehyde band marked (*), judging from the microphotometer record, is comprised of two bands with half-width about 200 cm.⁻¹.

tional structure, as should have been expected from the altered symmetry conditions alone. Further changes are produced by interposing one and two —CH_2— groups between the carbonyl group and the ring, but at this stage the spectrum has reached its final form, as can be noticed by comparison with phenylheptyl chloride, both being identical in so far as the positions of the bands are concerned.

Similar conclusions are reached with respect to the absorption of the carbonyl group. Considerable alterations in the band positions occur until two CH_2 groups have been introduced between the aldehyde group and the benzene ring (A, C', D' in Fig. 3), or—in case of aliphatic aldehydes—until the carbon chain is two atoms long. With longer chains the carbonyl absorption spectrum remains practically unchanged. Thus the bands belonging to hydrocinnamic, propionic and heptyl aldehydes have identical positions within the experimental errors of their determination, but with benzaldehyde the carbonyl spectrum is shifted to the visible somewhat and the bands are narrower.

Purvis[16] pointed out some time ago that the mutual influence of the groups on their respective spectra decreases as their spacing in the molecule increases. The present work confirms this conclusion and gives it a more precise illustration in the case of the aromatic aldehydes, which show that a very short interposed carbon chain suffices to make the vibrations and the electronic levels of the two groups quite independent of each other. Attention may be called to the fact that this distance of two —CH_2— groups nearly coincides with the distance at which two such groups as carbonyl and halogens cease to affect appreciably their respective chemical properties in the straight chain compounds. The frequencies of the Raman lines attributed to vibration of certain atomic linkages also cease to be appreciably influenced by the size of the remainder of the molecule when the attached carbon chain is longer than two or three atoms.

In conclusion we wish to express our appreciation for the useful suggestions of Professor J. B. Conant, which have added greatly to the success of this work. We are much indebted to the Cyrus M. Walker Fund of the American Academy of Arts and Sciences for a grant which enabled us to purchase a spectrograph used throughout this work.

Summary

1. An apparatus is described for studying the ultraviolet absorption spectra in solution at low temperatures.

2. It is shown that aromatic rings are characterized by narrow absorption bands in solution at low temperatures, while the spectra of aliphatic groups remain diffuse.

[16] Purvis, *J. Chem. Soc.*, **99**, 2318 (1911); **127**, 9 (1925). This phenomenon was also noticed by Baly and Collie, *ibid.*, **87**, 1332 (1905).

3.   The mutual influence of the spectra of two such groups as the carbonyl and benzene rings extends through carbon chains not more than two atoms long.   At greater distances in the molecule the spectra become entirely independent of each other.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SEPARATION AND DETERMINATION OF THE ALKALI METALS USING PERCHLORIC ACID. IV. THE PERCHLORATO–CHLOROPLATINATE METHOD FOR THE DETERMINATION OF POTASSIUM IN THE PRESENCE OF SODIUM

BY G. FREDERICK SMITH AND A. C. SHEAD[1]

Introduction

The separation and determination of potassium in the presence of sodium and lithium are most commonly carried out following the semi-extraction process of Fresenius.[2]   Chloroplatinic acid is used to convert the aqueous solution of the mixed chlorides to the corresponding chloroplatinates, followed by the extraction of sodium and lithium chloroplatinates with ethyl alcohol to produce 80–85% of the latter.   Many advantages result from the use of lithium chloroplatinate in place of chloroplatinic acid in the separation of potassium from sodium by the Fresenius process as shown by the present authors.[3]   Very distinct improvements in the perchlorate method in the separation of potassium from sodium have been developed as a result of previously published research from this Laboratory[4] which seem to justify claims of superiority for the perchloric acid method over the chloroplatinate separation.   In addition the use of perchloric acid facilitates the separation of sodium from lithium.[5]

The present paper demonstrates the advantage resulting from the simultaneous application of both perchloric and chloroplatinic acids to the separation and determination of potassium in the presence of sodium. Four distinct advantages result from this method of attack.   Only enough chloroplatinic acid is employed to convert the potassium present to potas-

[1] Holder of "The J. T. Baker Chemical Company Fellowship in Analytical Chemistry" for the year 1930–1931.   Submitted in partial fulfilment of the requirements for the Ph.D. degree in the Graduate School of the University of Illinois by the junior author.

[2] Fresenius, Z. anal. Chem., 15, 224 (1876); 16, 63 (1877); 21, 234 (1882).

[3] Smith and Shead, THIS JOURNAL, 53, 947 (1931).

[4] Smith, ibid., 45, 2073 (1923); 47, 762 (1925).   Smith and Ross, ibid., 47, 774 (1925); 47, 1020 (1925).

[5] Willard and Smith, ibid., 44, 2816 (1922).