[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

Spectra of Simple Amides in the Vacuum Ultraviolet[1]

BY H. D. HUNT[2] AND W. T. SIMPSON

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Absorption spectra from 2340 to 1500 Å. for dimethylformamide and from 2000 to 1220 Å. for formamide each show two broad adsorption bands. The absorption maxima for the former are at 1974 and 1621 Å., for the latter at 1717 and 1345 Å. Approximate extinction coefficients for the maxima, Einstein absorption coefficients, etc., are given for the two bands of dimethylformamide. A Rydberg series leading to an ionization potential of 10.2 e.v. is found for formamide. An orbital energy diagram is presented which accounts for the observations. The longer wave length and shorter wave length bands are assigned as NV_1 and NV_2, respectively, the assignments are discussed, and the effect of hyperconjugation is considered. An improvement in the use of the Lyman source is described, involving the use of a Teflon capillary.

The present paper is a report of an experimental investigation of the electronic spectra of dimethylformamide and formamide. These substances were chosen because they are volatile, and represent a large class of molecules conventionally described as containing four π-electrons in three π-orbitals; and also because a thorough understanding of the electronic structure of the amide linkage may be helpful in protein chemistry.

We have made correlative calculations pertaining to the π-electron dynamics, using the method of anti-symmetrized molecular orbitals, but the details will be reported in another paper.

Experimental

The Spectrograph.—A one-meter focus glass concave grating (~ 8.5 Å./mm. dispersion) was used,[3] arranged so that the light from the slit fell on the grating at approximately normal incidence. The slit widths were usually 0.08 mm. and the source was a Lyman discharge.[4] The sample was introduced directly into the tank of the spectrograph, so that no windows were needed.

The capillaries in the Lyman discharge tube were 2 mm. in diameter and 15 to 20 mm. in length. The Lyman continuum is overlaid with emission lines characteristic of the atoms in the material of the capillary. In order to increase the capacity to detect fine structure, capillaries were made using Teflon, a material quite different from the commonly used Pyrex or quartz; and which gave a continuum entirely free of silicon lines. Our procedure was, then, to use Pyrex and Teflon alternatively. It is believed that this is an improvement in instrumentation which has not been reported previously.

The detection was with Eastman Kodak 103-C plates, U.V. sensitized. The plates were developed in Eastman X-Ray developer to a gamma of approximately unity. Plate calibration was carried out with the flashing Lyman tube as a sensitometer. In view of the short duration and extreme intensity of each flash we do not feel that the sensitometric procedures are necessarily to be trusted; but we have not investigated them except to be reasonably sure that separate flashes in a short sequence each gave the same quantity of light.

The vacuum system was not unusual, and lower limit of pump pressures of approximately one micron were found sufficient.

Purity of Samples.—Care was exercised to introduce pure materials into the spectrograph. In addition, steps were taken to guard against the possibility that individual lines identified as belonging to the substance being investigated might belong instead to products of photodecomposition, or trace amounts of strongly absorbing impurities. The initial purification will be described first.

The dimethylformamide, Matheson #5974, seems to be quite pure. It was dried over magnesium sulfate for 24 hours, then over solid potassium hydroxide to remove water and formic acid. Finally it was carefully distilled at atmospheric pressure and a small middle fraction taken with corrected b.p. (760 atm.) 152.6 ± 0.5°. The refractive index n^{25}_{w} 1.4281 is to be compared with the values reported by others of 1.4269[5] and 1.4290.[6]

Formamide was obtained from Mr. Y. P. Hwang[7] who used repeated vacuum distillations to achieve a purity suitable for conductivity work.

With respect to the presence of spurious lines owing to products of photodecomposition it was found that long exposures gave plates very similar to the ones obtained with short exposures; but since the Lyman source is intermittent this is not conclusive. Moreover it did not appear fruitful to investigate the absorptions at different flow rates. However the plates were all carefully examined for absorption by specific impurities, so that it is felt that the final results reported below ought to be considered reasonably trustworthy. The impurities considered in detail were water, oxygen, hydrogen cyanide, carbon monoxide, formic acid, ammonia and dimethylamine.

Procedure for Obtaining a Spectrum.—Dimethylformamide was bled into the spectrograph continuously. The comparatively high vapor pressure at 25° (4 mm.) made it possible to achieve an entirely suitable steady state concentration. The formamide was distilled into the spectrograph where it condensed on the inside walls. The spectrum was obtained while the distillation was taking place, so that an effective pressure somewhat above the room temperature vapor pressure was probably obtained.

A typical plate contained five blank exposures (2, 4, 9, 14, 20 flashes) and two sample exposures (14 flashes). The source was operated at 12,000 volts.

Plates were traced manually with a Hilger Microdensitometer. The most important reference lines used were boron (2067.9 and 2066.4 Å.), carbon (1550.8 and 1548.2 Å.) and oxygen (1371.3 Å.).

Results. The Broad Absorptions.—The spectra are recorded in Figs. 1 and 2, referring, respectively, to dimethylformamide and formamide. In the former case it will be noted that the ordinate is absolute extinction coefficient *k* (based on 1 cm. path, $\log_{10}$ and concentration in moles/liter). This coefficient was obtained by scaling the vacuum ultraviolet curve to fit one obtained on the Beckman U.V. Spectrophotometer. For the Beckman determination the material was gaseous, with a concentration determined from the temperature, according to data supplied by E. I. du Pont de Nemours & Company.[8] There are various sources of error in the absolute intensity, which were not really overcome. These include reciprocity failure, scattered light and stray light in the Beckman and in the vacuum spectrograph, and higher orders in the vacuum spectrograph showing up differently in blank and sample. We have considered these errors semi-quantitatively, but believe that the recorded intensities may actually be in error by as much as 25%. The relative intensities are presumably much more accurate.

To summarize, for dimethylformamide the absorption maxima taken as 1974 and 1621 Å. have *k* values, respectively, of 8700 and 6960. Other workers have found similar values, as 7200 for the long wave length band in diglycyl.[9]

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[1] Supported in part by the Air Force under Contract R-351-20-2.

[2] Taken from the writer's Ph.D. thesis.

[3] W. A. Noyes, Jr., A. B. F. Duncan, W. M. Manning, *J. Chem. Phys.*, **2**, 721 (1934), describe the grating.

[4] R. E. Worley, *Rev. Sci. Instruments*, **13**, 67 (1942).

[5] J. R. Ruhoff and E. E. Reid, THIS JOURNAL, **59**, 401 (1937).

[6] J. R. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).

[7] Y. P. Hwang, Master of Science Thesis, University of Washington (1952).

[8] Product Information Bulletin, "Dimethylformamide."

[9] J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **20**, 335 (1952).

The Einstein absorption coefficients were determined from

$$B = \int k \, \mathrm{d} \log_{10} \nu / 2.509 \times 10^{-17}$$

and of course depend on the process for dividing the spectrum into bands. This division was made by classifying the absorption as consisting, for the present purposes, of two bands, called the 1974 and 1621 bands. The long wave length side of the 1621 curve was given the same shape as observed for the long wave length side of the 1974 band. This determined the shape of the short wave length side of the 1974 band by subtraction, and subsequently this shape was also assumed for the 1621 band. The coefficients are $B_{1974} = 1.86 \times 10^{19}$ and $B_{1621} = 1.39 \times 10^{19}$.

The oscillator strengths given by

$$f = 4.31 \times 10^{-9} \int k \, \mathrm{d}\nu$$

are $f_{1974} = 0.237$ and $f_{1621} = 0.209$. The "lifetimes," calculated as A^{-1} where A is the Einstein spontaneous emission probability are, respectively, 2.35×10^{-9} and 1.97×10^{-9} sec. The transition moments squared, calculated from the B values, are 0.44×10^{-16} cm.^{2} (1974 band) and 0.33×10^{-16} cm.^{2} (1621 band).

The formamide spectrum is qualitatively similar, and again the broad absorption is classified as consisting of two bands. Here the maxima are taken to be 1717 and 1345 Å. It may be asked why maxima and not so called zero–zero wave lengths are quoted. The zero–zero values are difficult to estimate, but more important, the maximum intensity values are considered as best for the purpose of eventual comparison with theoretical calculations. These are usually made at assumed ground state nuclear configurations believed to be the equilibrium ones. It will be seen that formamide exhibits a rich line spectrum, which will be discussed next.

Results. The Finer Structure.—The peaks in the formamide spectrum are listed in Table I, while the dimethylformamide peaks are listed in Table II. The sharpness of many of the formamide peaks below 1500 Å. suggested that it should be possible to find Rydberg series. After much searching a progression was found which fits the formula

$$\nu = 82566 - R/(n + 0.361)^2$$

This gives an ionization potential of 10.2 e.v. which is a reasonable value (the value for the lone pair on formaldehyde is 10.8 e.v.). The calculated and observed Rydberg maxima are tabulated in Table III and it will be seen that the fit is about as good as for many progressions which have been identified in the literature as Rydberg series.

TABLE I

ADSORPTION PEAKS IN FORMAMIDE

Wave lengths, Å.			
1751	1529	1408	1312
1716.9	1468	1373	1303
1677	1448	1364	1290
1651	1442	1356	1282
1626	1432	1345	1270
1608.7	1426	1333.	1253
1567.1	1419	1325	

TABLE II

ABSORPTION PEAKS IN DIMETHYLFORMAMIDE

Wave lengths, Å.					
2225	2055	1953	1800	1645	1543
2160	2012	1910	1732	1621	1495
2090	1975	1840	1689	1578	

TABLE III

ABSORPTIONS FOR THE FORMAMIDE RYDBERG SERIES

	cm.$^{-1}$		
n	Obs.	Calcd.	Difference
2	62162	62880	−718
3	72830	72851	−21
4	76800	76796	4
5	78750	78748	2
6	79860	79854	6

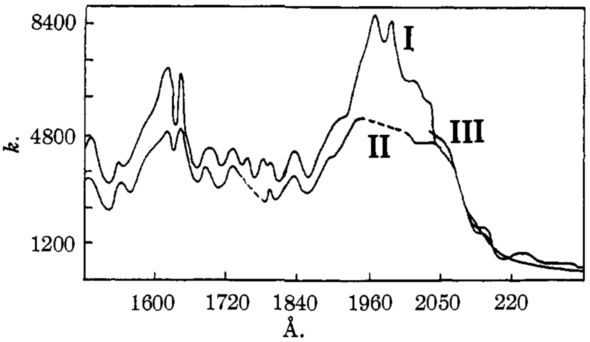

Fig. 1.—Dimethylformamide (I is with Pyrex capillary, II, with Teflon capillary and III is curve obtained on Beckman U.V. spectrophotometer).

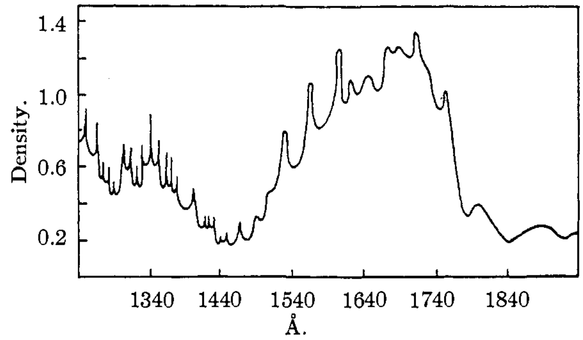

Fig. 2.—Formamide.

The question of coupling of vibrational with electronic terms has not been considered. However, it seems reasonable to attribute the absence of easily identifiable Rydberg lines for dimethylformamide (the investigation was carried to below 1300 Å.) either to a sort of pressure broadening in which the molecule "collides" with its own methyl groups, or to actual pre-dissociation.

Discussion

Classification According to Orbital Theory.—It is considered that there are filled orbitals up to and including two π non-localized molecular orbitals and a non-bonding oxygen 2p-orbital. The transitions may be interpreted as including excitation of the electrons in these orbitals into a remaining unfilled orbital (NV and $n\pi$ transitions) and into orbitals which are linear combinations of atomic orbitals with principal quantum number greater than two (first Rydberg members) and into hydrogen-like orbitals (higher Rydberg members).

An orbital energy diagram which is believed to represent the electron dynamics reasonably well is given in Fig. 3. Incidentally, the energies are those computed according to simple LCAO theory for allyl, and are in units of the integral

$$\gamma = \int \varphi_i H \varphi_j \mathrm{d}\tau - \int \varphi_i \varphi_j \mathrm{d}\tau \int \varphi_i H \varphi_i \mathrm{d}\tau$$

with the usual Coulomb integral taken as zero. The subscripts +, 0 and − represent, respectively, bonding, non-bonding and anti-bonding (valence shell), "CH_3" refers to dimethylformamide only, p_0 is the lone pair oxygen orbital,[10] and the numbered subscripts refer to assumed principal quan-

[10] p_0 is identical to the oxygen orbital which is part of the π-electron system, except that it is in a perpendicular direction. It is considered to have approximately the same energy as π_0 (compounded of oxygen and nitrogen orbitals, opposite in phase, but non-adjacent, a fact which leads to the classification as non-bonding).

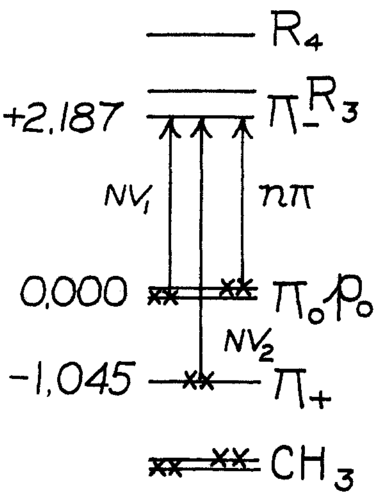

Fig. 3.—Orbital energy diagram. Energies are according to simple LCAO theory.

tum numbers for the various Rydberg members. The NV_1/NV_2 transition energy ratio as calculated by simple LCAO theory for allyl is 0.68. The intensity of the NV_1 transition for allyl as calculated on the basis of the simplifying assumption that overlap may be neglected is (1.15 Å.)^2. The orbitals used are obtained in the conventional way, and are

$$\pi_- = 0.50a - 0.707b + 0.50c$$
$$\pi_0 = 0.707a - 0.707c$$

The atomic orbitals, corresponding in the amide to N, C and O orbitals are a, b and c. The interatomic distance was taken as 1.33 Å. which is not characteristic of allyl but represents an average for amides. This facilitates later comparison with experiment. The one-electron moment has been multiplied by $2^{1/2}$ because there are two electrons in the highest filled orbital.

The orbital picture may be thought of as more general than the LCAO MO treatment which is included in the description given above. But the use of very simple LCAO MO theory without anti-symmetrization seems to furnish a useful semi-quantitative basis for classification in this and many other cases. In fact, we believe that the study of all-carbon-atom model substances (which may be isoelectronic to substances of greater complexity) should, whenever possible, be adopted as a companion procedure to the examination of the valence bond structures.

Assignment of the Broad Bands.—It may be of interest to discuss the classification of the first broad band as NV_1 (see Figs. 1 and 2) even though most molecular spectroscopists would agree with this assignment. All the evidence for this classification cannot be stated in a small space but the following is fairly complete. The spectroscopic behavior of compounds related to cyanine dyes, as for example

$$[R_2\overset{+}{N}{=}CH(CH{=}CH)_n\text{-}NR_2]^+$$

is nicely understood in terms of Mulliken's NV theory, as exemplified by the simple LCAO approximation. A particular example, the amidic substance

$$Me_2N{-}CH{=}CH{-}CH{=}CH{-}CH{=}O$$

absorbs at λ_{max} = 3860 Å. (in water).[11] Moreover it is well-known that the related adsorptions in vinylogous progressions are increased approximately 1000 Å. per double bond. The strong broad adsorption of dimethylformamide at 1974 Å. is therefore almost surely a first member of the vinylogous progression, and hence is classified as NV_1.

We have identified a second broad region in the spectrum of formamide and the dimethyl derivative, and propose to classify it as NV_2. Since a band with an effective maximum at the very short wave length of 1345 Å. is being classified as arising from π-shell transitions, some justification is required.

Evidence favorable to the proposed classification is scant, but this is not unusual for NV_2 assignments. The shape and breadth, which may be studied in Fig. 1 and 2 is characteristic. The NV_1/NV_2 transition energy ratio is observed to be 0.785 for formamide and 0.822 for the dimethyl derivative. The simple LCAO picture given above as a part of the classification scheme gives, for the isoelectronic system allyl, an NV_1/NV_2 energy ratio of 0.68.[12]

The NV_1/NV_2 intensity ratio, which is observed to be 1.34, is at first sight quite low. (The NV_2 intensity for allyl is zero on the grounds of symmetry). However we do not feel that this is a serious objection to the classification, and in fact have estimated semi-quantitatively that the effect of heteroatoms might well account for the strength of the NV_2 transition. Incidentally the NV_2 can be considered to borrow from the NV_1 as computed for the symmetrical allyl. The sum of the observed intensities corresponds to a transition moment of (0.87 Å.)^2, and this value compares favorably with the one obtained for NV_1 by the simple LCAO calculation for allyl (1.15 Å.).^{2}

Hyperconjugative Effect.—It will be shown that the change in NV_1/NV_2 ratio on methyl substitution as well as the change in NV band positions may be explained in a unified fashion by assuming π-components of the two methyl group carbon orbitals in weak interaction with the π-electron system. Consider a "methyl orbital" (Fig. 3) to lie below the lowest filled π-orbital. It will then push π_+ up, and to a lesser extent will also push π_0 up. Thus the π_-, π_0 energy difference will change so that the absorption goes to longer wave lengths (observed, 1717 to 1974 Å.) and the π_-, π_+ energy difference will change so that the absorption shifts even by a greater amount on the energy scale (observed, 1345 to 1621 Å.). This in turn makes the NV_1/NV_2 energy ratio closer to unity after methyl substitution (observed, 0.785 to 0.822). Actually there are uncertainties connected with obtaining the position of the absorption maximum which make this last comparison tentative.

The Non-bonding Electrons.—In this final section several points related to the non-bonding

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(11) Unpublished research, W. T. S.

(12) More elaborate calculations, which may be more trustworthy, also give ratios nearly equal to the observed. For example for allyl anion (ASMO method with configurational interaction) the ratio is 0.66; but when allowance is made for the effect of heteroatoms (but without employing configurational interaction) the ratio becomes 0.82.

π-electrons on the oxygen will be mentioned. First to be considered is the complicated structure which overlaps the NV$_1$ bands over their entire breadth. According to the plan summarized in Fig. 3 the $n\pi$-transition (p_0, π_-) should be in the NV$_1$ region but it is clearly impossible to pick any one part of the NV$_1$ band as being $n\pi$ on the basis of structure alone. In fact the various maxima in the broad NV$_1$ region surely represent vibronic details and possible Rydberg transitions.

An interesting effect may sometime be observed related to the (assumed) approximate equality of the energies of the p_0- and π_0-orbitals. The states of the molecule which are considered to be represented fairly accurately by wave functions based on the configurations

$$\pi_+{}^2\,\pi_0{}^1\,\mathrm{p}_0{}^2\,\pi_-{}^1 \quad (\mathrm{V}_1)$$

and

$$\pi_+{}^2\,\pi_0{}^2\,\mathrm{p}_0{}^1\,\pi_-{}^1$$

are approximately degenerate so that, for example, the lifetime of the V$_1$ state might be abnormal.

Also by reason of the equality of the n- and π-energies, there is an uncertainty in assigning the Rydberg limit as the π-electron or lone-pair ionization potential.

It is believed that the spectra together with the interpretation given will be found typical of other simple amides, and in fact of many other systems which consist of four π-electrons in three π-orbitals (esters, oximes, etc.).

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Hydrogen Isotope Exchange between Anthracene and Sulfuric Acid[1]

BY V. GOLD[2] AND F. A. LONG

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The hydrogen isotope exchange between sulfuric acid and anthracene proceeds more rapidly at the *meso*-positions than at the other positions of anthracene. The kinetics of deuterium loss from the 9-position of anthracene by the action of sulfuric acid have been followed by experiments on the two-phase system, carbon tetrachloride–sulfuric acid. The velocity of the exchange reaction increases steeply with acidity. Analysis of the kinetic results, based on a model of the reaction which associates the yellow color of a solution of anthracene in sulfuric acid with a conjugate acid of anthracene in which a proton is added at a *meso*-position, leads to a value for the rate constant of proton loss from this conjugate acid. The rate of the proton loss decreases with acid concentration, and the rate of proton addition to anthracene appears to be insensitive to the composition of the acid in the range 84–90% H_2SO_4 by weight.

Exchange reactions of the type

$$C_6H_6 \xrightarrow{D^+} C_6H_5D + C_6H_4D_2, \text{ etc.}$$

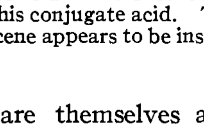
and

$$C_6H_5D \xrightarrow{H^+} C_6H_6$$

represent probably the simplest examples of aromatic substitution. It was established a number of years ago[3] that the isotope exchange between benzene derivatives and sulfuric acid-D$_2$ followed the known rules for electrophilic aromatic substitution reactions, as regards the dependence of orientation and reaction velocity on the nature of substituent groups already present in the benzene ring. At the same time it was qualitatively shown that the potency of an acid reagent depended on what was termed its "hydrion donating power."

There are other electrophilic aromatic substitution reactions, *e.g.*, nitration, for which the rate is governed by the "hydrion donating power" (or acidity) of the reaction medium. A distinction must, however, be made between these two cases. In the isotope exchange reaction a "kinetic acidity"—which will depend on the *rate* of proton (or deuteron) transfer reactions—is involved; in the latter case the term "acidity" is understood to mean the thermodynamic solvent property which controls the *equilibrium* concentrations of some reagent species (which are themselves acidic or basic). These thermodynamic acidities of strongly acidic solvents have been quantitatively described by the acidity functions H_0[4] and J_0.[5] There has been no corresponding analysis of the "kinetic acidity" of an acid solvent system.

The present study is concerned with the isotope exchange between anthracene and sulfuric acid in a stirred two-phase system, carbon tetrachloride being used as solvent for anthracene. The kinetics of the reaction under these conditions can be analyzed in some detail since the distribution of anthracene between the two phases can be measured independently by ultraviolet spectrophotometry. The particular choice of anthracene arose out of earlier experiments[6] in which it was found that anthracene is soluble in concentrated sulfuric acid with the formation of a species having a different ultraviolet absorption spectrum (and a yellow color) and to which the structure



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was assigned on the basis of its absorption spectrum. In all experiments with anthracene and sulfuric acid, a certain amount of loss of anthracene through

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[1] Presented in part at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

[2] du Pont Grant-in-Aid Fellow at Cornell, 1951–1952.

[3] C. K. Ingold, C. G. Raisin and C. L. Wilson, *Nature*, **134**, 734 (1934); *J. Chem. Soc.*, 915, 1637 (1936).

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[6] V. Gold and F. L. Tye, *ibid.*, 2172, 2184 (1952).