[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

The X-Ray Diffraction and Infrared Spectra of Molecular Compounds of Acetamide and Long-chain Saturated Fatty Acids

BY ROBERT T. O'CONNOR, ROBERT R. MOD, MILDRED D. MURRAY AND EVALD L. SKAU

RECEIVED AUGUST 2, 1954

Infrared spectra and X-ray diffraction data have been obtained for the four molecular compounds formed between acetamide and lauric, myristic, palmitic and stearic acids. The infrared spectra in the rock salt region resemble those of the constituent molecules and, like the spectra of the saturated fatty acids, are identical for all members of the homologous series. Infrared spectra are not useful for the identification of the individual molecular compounds. From X-ray diffraction patterns "long" and "short spacings" have been measured. The "long spacings" of the molecular compounds have been shown to correspond in length to two molecules of saturated fatty acid and two molecules of acetamide. Each pattern also exhibits a weak "long spacing" identical to that of the "C" form of the parent acid. In addition the myristic acid-acetamide compound shows a very weak "long spacing" equal to that reported for an unstable third modification of a C_{14} fatty acid. These spacings can be accounted for by the sublimation of a small amount of acetamide from the saturated fatty acid–acetamide addition compounds during the exposure to the X-ray radiation. "Short spacings," obtained by the usual "powder" technique and useful for analytical identifications, are also reported.

Recently Magne and Skau[2] showed that 1:1 compounds of the general formula $RCOOH \cdot NH_2COCH_3$ are formed between acetamide and long-chain saturated fatty acids. They reported binary freezing point data and apparent molecular weights in 1,4-dioxane for the molecular compounds formed between acetamide and lauric, myristic, palmitic and stearic acids. Optical properties of these compounds have now been investigated. The infrared spectra in the rock salt region from 2 to 12 μ and the "long" and "short" crystal spacings from X-ray diffraction patterns are reported in this paper.

Experimental

The saturated fatty acids and acetamide were purified[2] and the molecular compounds prepared by fusing together equimolecular proportions of the acid and acetamide and allowing the melt to solidify. The infrared spectra were obtained both in chloroform solution and as Nujol[3] mulls with a Beckman[3] IR-2T infrared spectrophotometer. The instrument was housed in a room maintained at about 23° and 20% relative humidity and its temperature was maintained constant at 25 ± 0.1° by water circulated from a constant temperature bath. The X-ray diffraction patterns were obtained with a General Electric[3] Diffraction Unit Model XRD, using Cu Kα radiation with a nickel filter (0.0007 inch thick). The "long spacings" were measured from photographs obtained by pressing a small amount of sample, enough to produce a layer several tenths of a millimeter thick, on a thin piece of glass. This sample was mounted in the X-ray apparatus with a plate distance of 10 cm. and the mount was oscillated through an angle from 0 to 10°. The "short spacings" were calculated from patterns obtained by photographing the finely powdered samples in sealed capillary tubes at a plate distance of 6 cm. Exposure times for both "long" and "short" spacing patterns were 2.25 hours.

Infrared Spectra.—Infrared spectra were obtained both from chloroform solutions, containing about 25 g. of sample per liter of solution, and as finely ground Nujol[3] mulls. The solid and solution spectra were identical throughout the rock salt region, in spite of the fact that the molecular compounds are highly dissociated into fatty acid and acetamide molecules in solution.[2] This is not surprising in light of the fact that the addition compound contains no new vibrating groups. The molecular compound formation most probably involves hydrogen bonding with O–H· · ·O and N–H· · ·O groups, but these groups are also present in the spectra of fatty acids and acetamide, even in relatively dilute solution. The vibrating groups which give rise to the other characteristic bands in these molecules are likewise not perceptibly altered by the addition compound formation. Hence no change would be expected in going from the spectra of the addition compound in the solid form (Nujol mull) to a dissociated form (chloroform solution). Comparison of the infrared spectra of the molecular compounds with those of the fatty acids[4] and of acetamide[5] affords further confirmation. The spectra of the four molecular compounds in chloroform solution are shown in Fig. 1.

TABLE I

THE PRINCIPAL ABSORPTION BANDS IN THE INFRARED SPECTRA OF ACETAMIDE–SATURATED FATTY ACID MOLECULAR COMPOUNDS

Wave length of absorption max., μ	Probable vibrating group which gives rise to the obsd. absorption band
3.12	N-H stretching (only partially resolved from strong C-H stretching)
3.35	C-H stretching (any C-H group)
3.65	Weak shoulder, probably branch of O–H· · ·O (bonded (OH) stretching)
5.85	C=O stretching, characteristic of fatty acids
5.93	C=O stretching, amide; poorly resolved from C=O of fatty acids
6.28	NH_2 bending
6.67	N-H bending
6.87	Doubly degenerate CH_3 methyl deformation and symmetrical CH_2 methylene deformation
7.05 7.18	Symmetrical deformation of the methyl CH_3 groups
7.28	CH_2 methylene, and CH_3 methyl deformation
7.75	C–O stretching
8.00	C–O stretching
8.93	C–O stretching
9.54	CH_3 rocking
10.60	Characteristic of COOH, probably OH vibration in and out of plane of COOH

---

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

[2] F. C. Magne and E. L. Skau, THIS JOURNAL, **74**, 2628 (1952).

[3] Mention of names of firms or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

[4] Robert T. O'Connor, Elsie T. Field and W. Sidney Singleton, *J. Am. Oil Chem. Soc.*, **28**, 154 (1951).

[5] Robert T. O'Connor, unpublished data.

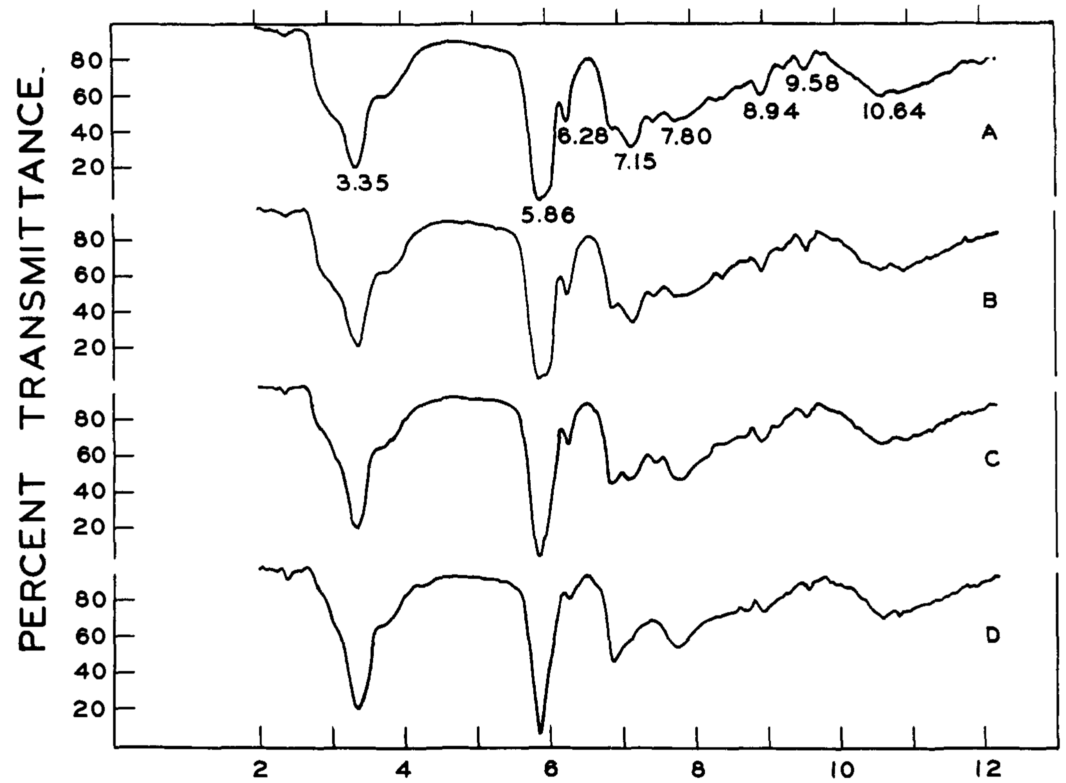


Fig. 1.—Infrared absorption spectra of chloroform solutions of: A, lauric acid–acetamide addition compound; B, myristic acid–acetamide addition compound; C, palmitic acid–acetamide addition compound; D, stearic acid–acetamide addition compound.

All of these spectra were obtained by measuring against an equivalent amount of chloroform in the same absorption cell. Inspection of Fig. 1 reveals that the spectra of all four molecular compounds are essentially identical. Infrared spectra in the rock salt region are of no aid in identifying individual members of the homologous series of saturated fatty acids by means of their acetamide molecular compounds. The wave length positions of maxima of the most prominent bands in these spectra and the most probable vibrating groups giving rise to them are listed in Table I.

X-Ray Spacings.—Characteristic X-ray "long spacings" for the four molecular compounds are given in Table II, columns 2, 3 and 4. These "long spacings" are average values calculated from measurements of several diffraction orders, all of which gave closely agreeing results. From two to five diffraction patterns were obtained for most samples. The values reported in Table II are over-all averages from all diffraction orders measured from all films. Individual "long spacing" calculations were identical within negligible experimental differences, usually within ±0.2 Å. regardless of whether the samples were obtained by solidification of the original fusion or by recrystallization from a solvent.

Each of the acid–acetamide compounds shows two "long spacings," one strong and one weak, and in addition, the myristic acid–acetamide compound exhibits a third, very weak long spacing. On the basis of all the available evidence this multiplicity of "long spacings" can be attributed to the sublimation of a small amount of the acetamide from the sample caused by the slight rise in temperature during the exposure to X-radiation. This would result in formation of an equivalent amount of free acid which would appear as a minor constituent in the X-ray diffraction patterns.

This explanation is suggested by the observation that the weak "long spacing" is in each case practically identical to the accepted value for the characteristic "double spacing" of the "C" form of the corresponding long-chain, saturated fatty acid. These comparisons are shown in column 3 of Table II. The heading "2:0" indicates that the "long spacings" in this column, measured from the X-ray photographs, corresponds to the length of two fatty acid molecules and no acetamide molecules. The values in parentheses, in column 3, are published values for the "long spacings" of the "C" form of the four saturated fatty acids. The value for lauric acid is from Clark[6] and values for the other three acids are from Markley.[7]

Similarly the additional very weak "long spacing" in the patterns for the myristic acid–acetamide compound is in good agreement with that reported by Slagle and Ott[8] for an unstable modification of the C_{14} acid, as shown in column 4 of Table II. This spacing may result from the formation of this unstable form of myristic acid as an intermediate step in the formation of the stable

---

[6] George L. Clark, "Applied X-Rays," McGraw-Hill Book Co., Inc., New York, N. Y., 3rd Ed., 1940, p. 437.

[7] Klare S. Markley, "Fatty Acids," Interscience Publishers, Inc., New York, N. Y., 1947, p. 94.

[8] F. B. Slagle and Emil Ott, THIS JOURNAL, 55, 4396 (1933).

TABLE II

X-RAY DIFFRACTION DATA

VS = very strong, S = strong, M = medium, F = faint.

Mol. cpd. acetamide and	"Long spacings" 2:2[a]	2:0[a]	2:0[a]	"Short spacings"	
	Strong	Weak	Very weak		
Lauric acid	36.97 (8 orders) (38.8)[b]	27.26 (6 orders) (27.4)[c]		9.32 (M) 7.60 (M) 6.60 (F) 5.84 (F) 4.64 (S) 4.21 (VS) 3.90 (VS)	3.76 (S) 3.32 (S) 2.95 (M) 2.73 (F) 2.58 (F) 2.52 (F) 2.30 (M)
Myristic acid	42.37 (8 orders) (43.0)[b]	31.60 (5 orders) (31.60)[d]	37.03 (3 orders) (36.64)[e]	9.13 (M) 7.68 (M) 5.95 (M) 5.03 (F) 4.53 (F) 4.06 (VS) 3.77 (S) 3.61 (M) 3.44 (M) 3.24 (F) 2.97 (S) 2.79 (F)	2.67)M) 2.41 (S) 2.29 (F) 2.22 (S) 2.16 (F) 2.03 (F) 1.91 (F) 1.73 (F) 1.70 (F) 1.66 (F) 1.58 (F)
Palmitic acid	46.48 (8 orders) (47.0)[b]	35.59 (9 orders) (35.60)[d]		7.18 (F) 4.45 (M) 4.12 (VS) 3.72 (S)	3.28 (F) 2.94 (F) 2.47 (F) 2.21 (F)
Stearic acid	59.59 (12 orders) (51.15)[b]	39.72 (6 orders) (39.75)[d]		5.78 (F) 4.35 (F) 4.11 (VS) 3.68 (S) 3.27 (F)	2.95 (F) 2.48 (F) 2.33 (F) 2.25 (F) 2.19 (F)

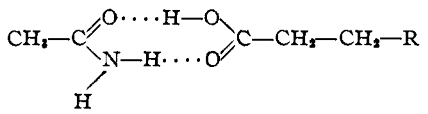
[a] Ratio of saturated fatty acid groups to acetamide groups in repeating cell unit—see text. [b] Calculated as sum of "double spacing" of "C" form of acid and "double spacing" of acetamide—see text. [c] Reference 6. [d] Reference 7. [e] Reference 8.

"C" form of the acid by sublimation of acetamide from the addition compound. Such behavior would be in accord with Ostwald's law of successive reactions which explains the formation of metastable forms not otherwise obtainable.[9]

The validity of this explanation of the apparent multiplicity of "long spacings" for these molecular compounds was confirmed by heating a sample of the stearic acid–acetamide compound for 24 hours at 50°. A loss in weight was observed which corresponded to about 11% of the acetamide present. As expected, the X-ray diffraction pattern for this specimen indicated the presence of a higher concentration of stearic acid. That is, the lines corresponding to the long spacing of the "C" form of stearic acid were more intense, relative to other lines on the pattern. The excellent agreement between the values for the "double spacings" of the "C" form of the acids and those reported in the literature is a criterion of the precision of the present measurements.

The "long spacings" in column 2 of Table II are the most intense and are undoubtedly "double spacings" of the acetamide addition compounds. Measurements on pure acetamide gave a "double spacing" of 11.4 Å., in good agreement with the value (11.44 Å.) reported by Senti and Harker[10] for one of the dimensions of the hexagonal unit cell. Using this value for the "long spacing" of the acetamide, the "long spacings" for the molecular compounds can be computed as combinations of saturated fatty acid and acetamide chains. A comparison of values computed in this manner (shown in parentheses) and the results obtained from the measurements reported here are shown in column 2. The heading "2:2" indicates that the perpendicular distance between planes of identical composition corresponds to the length of two molecules of the long-chain saturated fatty acid and two molecules of acetamide.

The addition compounds formed between the long-chain, saturated fatty acids and acetamide are probably hydrogen-bonded complexes of the form



Such an addition compound requires that the ratio of acid to amide be 1:1, as confirmed by freezing point data[2] and by isolation and analysis,[11] and that the two ends be inactive to further hydrogen bonding.

The agreement between observed and calculated values in column 2 of Table II indicates that the tilt, or β, angle is the same in the addition com-

---

[9] Alexander Findlay, "The Phase Rule and Its Applications," Dover Publications, 8th Ed., 1945, New York, N. Y., p. 50.

[10] F. Senti and D. Harker, THIS JOURNAL, **62**, 2008 (1940).

[11] E. L. Skau, unpublished data.

pounds as in the homologous series of the long-chain, saturated fatty acids. A molecular arrangement in the crystal which would be in agreement with these observed data can be postulated:

···MX·YR·RY·XM·MX·YR·RY·XM·MX·YR···
| repeating unit | repeating unit |

Where M is the CH_3 radical, X is the $CONH_2$ group, Y is the COOH group, and R is the long-chain $C_n H_{2n+1}$.

Such an arrangement would result in a 1:1 ratio of acid to amide, both ends would be inactive to further hydrogen bonding, and the repeat pattern of the unit cell would be equal to the sum of the "double spacing" of the "C" form of the acid and the "double spacing" of the acetamide. The values in parentheses in column 2 of Table II are maximum values for this sum. The actual spacing of the 2:2 addition compounds must be somewhat less than this sum since the acetamide must be inclined at some angle to the 001 planes. Hence it cannot make its full contribution to the "double spacing" of the complex. It will be noted that in column 2 the observed 2:2 spacings are less than the calculated spacings (in parentheses) in every case, except for the stearic acid–acetamide compound. Measurements from five different diffraction patterns give values about 8 units higher than expected for this spacing.

In the last column of Table II are given the "short spacings" for each of the molecular compounds. These values, obtained by the usual Pyrex capillary tube "powder" method, are the data required for chemical analyses by the method of Hull[12] as described in detail by Hanawalt, Rinn and Frevel.[13]

Acknowledgments.—The authors acknowledge with thanks the helpful suggestions of Leopold Loeb of this Laboratory and of Merrill E. Jefferson of the Soil and Water Conservation Research Branch of the Agricultural Research Service in the preparation of this manuscript. They are indebted also to Mrs. Elsie F. DuPré for the infrared absorption curves.

(12) A. W. Hull, THIS JOURNAL, **41**, 1168 (1919).

(13) J. D. Hanawalt, H. W. Rinn and L. K. Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 457 (1938).

NEW ORLEANS, LA.

NOTES

Electron Impact Data on Substituted Acetylenes: Propyne and 2-Butyne[1]

BY FRED H. COATS AND ROBBIN C. ANDERSON

RECEIVED AUGUST 20, 1954

To obtain further information on energy relations for acetylenic compounds, ionization and appearance potentials of various ions from substituted acetylenes are being determined. Some data on propyne have been reported earlier.[2] The experimental measurements have now been extended to 2-butyne.

Experimental

The instrument used in this work was a Westinghouse type LV mass spectrometer which employs a conventional 90° momentum filter. Its resolution is at least 1 mass unit in 120. Focussing is accomplished by adjusting the magnetic field to encompass the desired mass range and varying the accelerating electric field by means of a decade potentiometer.

The general procedure used in the appearance potential measurements was to determine, simultaneously, the ionization probability curves for the ionic fragment to be studied and for a reference ion, such as that of argon, the ionization potential of which has been accurately measured. The curves are compared by the method of vanishing ion currents[3] in which the lower non-linear portion of each of the curves is extrapolated to zero ion current. Tailing of the curves at very low ion currents gives rise to considerable uncertainty in the extrapolation. To reduce this effect, an intermediate electrode in the electron gun was maintained at a small constant negative potential with respect to the filament. The general problems arising from the energy spread of the electron, and corrective modifications, have been discussed by Fox, Hickam, Kjeldaas and Grove.[4]

The acetylene was commercial product purified from acetone by treatment with concentrated sulfuric acid. The propyne and 2-butyne were obtained from Farchan Laboratories. Preliminary checks in the mass spectrometer gave no indication of peaks from impurities which would interfere with the determination of appearance potentials.

Results

The appearance potentials for ions from acetylene were measured to furnish a check of the method and apparatus. The experimental values in each case were in agreement with those of Kusch, Hustrulid and Tate[5] and with ionization potentials reported by Price[6] and Franklin and Field.[7] These data are compared in Table I.

TABLE I

APPEARANCE POTENTIALS FOR IONS FROM ACETYLENE

Ion	A_R (These exp.), v.	A_R (lit.), v.
$C_2H_2^+$	11.4 ± 0.1	11.2 ± 0.1[a] 11.40[b] 11.46 ± .01[c]
C_2H^+	17.8 ± .5	17.8 ± .2[a]
C_2^+	23.3 ± .5	23.8 ± .3[a]

[a] Kusch, Hustrulid and Tate, electron impact. [b] Price, spectroscopic. [c] Franklin and Field, electron impact.

---

[1] This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command.

[2] F. H. Coats and R. C. Anderson, paper presented at Southwestern–Southeastern Regional Meeting of Am. Chem. Soc., New Orleans, Dec., 1953.

[3] *Cf.* L. G. Smith, *Phys. Rev.*, **51**, 263 (1937).

[4] R. E. Fox, W. M. Hickam, T. Kjeldaas and D. J. Grove, *ibid.*, **84**, 859 (1951).

[5] P. Kusch, A. Hustrulid and J. T. Tate, *ibid.*, **52**, 843 (1937).

[6] W. C. Price, *ibid.*, **47**, 444 (1935).

[7] J. L. Franklin and F. H. Field, THIS JOURNAL, **76**, 1994 (1954).