[CONTRIBUTION FROM INSULATING MATERIALS SECTION, CHEMICAL AND METALLURGY, DIVISION OF GENERAL ELECTRIC CO.]

Infrared Spectra of α,β-Unsaturated Esters

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A number of ester families have been shown to have characteristic absorptions in the 10–15 μ region. These absorptions are quite constant in wave length for all members of the ester family (*i.e.*, esters derived from the same acid). The esters which show such absorptions are those that have unsaturation α,β- to the ester group. It is postulated that the vibration responsible for the most prominent of the absorptions is an out-of-plane deformation at the ester carbon atom. However, the interaction of this vibration with other out-of-plane vibrations is probable and, therefore, more or less of such other vibration is also presumed to be involved. Some evidence suggests that the vibration type may be general for 4-atom systems with a given "Y" structure even including some saturated types. However, the vibration is not necessarily so prominent in the saturated types and the more limited generalization that the absorption is prominent in coplanar unsaturated types is thus of greater value for prediction purposes.

Introduction

The recognition of esters by their infrared spectra generally is based on the observation of strong absorption bands resulting from the C=O and the two C–O–C stretching modes. The bands due to the latter two modes may overlap, however, and appear as one. Therefore, with two, or at most three, bands to utilize, recognition of esters in mixtures frequently is quite unsatisfactory and further characteristic bands are needed. If in addition to locating such bands the vibrational modes giving rise to them can be elucidated, then their applicability can be defined more readily and their utility enhanced.

Recent work[1] on the spectra of maleates and fumarates showed that the fumarates have a fixed absorption at 12.9 ± 0.05 μ which is insensitive to the alcohol of the ester. The maleates, on the other hand, showed no constant absorption bands in the 10 to 15 μ range. This feature was puzzling and merited further investigation. The present paper presents a possible assignment of the 12.9 μ fumarate absorption band which not only explains the difference between maleates and fumarates but also leads to a generalization concerning this type of vibration in α,β-unsaturated esters.

Thompson and Torkington, in a paper[2] treating extensively the C–O stretching vibrations of esters, also noted some peaks in the region beyond 10 μ. There were two peaks of relatively constant frequency for acetate and propionate esters near 16 μ, one of which they associated with the whole ester group skeleton and one with a part of the ester group skeleton. All other constant peaks beyond 10 μ seemed relatable to the hydrocarbon part of the acid moiety—or else these workers simply found no basis for any assignment more specific than to the ester family. The present work attempts to supplement this knowledge of ester spectra by providing more correlations and an assignment in the 10–15 μ region.

Generalization

A step toward the development of the generalization was the theoretical consideration of an effect which was first proposed by Price,[3] that the ester groups are both coplanar with the ethylene in fumarate esters whereas this is not the case in the maleates. (This structual feature was then used by Price to explain the fact that fumarates copolymerize better than maleates. This he explained was due to *absence* of steric hindrance to the approach of a growing free radical to the ethylene linkage in fumarates.) On exploring several types of esters, it was found in the present work that only one ester group conjugated with an unsaturated group was needed to give absorption like the 12.9 μ peak of a fumarate. As detailed below, there is evidence that the liquid maleates have no ester group coplanar with the ethylene structure.

The generalization may be stated as follows: wherever an ester group is conjugated with an unsaturated linkage and the ester group is free to assume one of its normal positions coplanar to that linkage a prominent absorption occurs which is constant for (and therefore *characterizes*) the ester family. By means of polarized infrared coupled with examination of oriented crystal films, this absorption has been shown to be due to an out-of-plane vibration. Further it is postulated that the specific vibration is the out-of-plane deformation at the ester carbon atom.

The following ester families fulfill the requirements of the generalization: fumarates, acetylenedicarboxylates, acrylates, methacrylates and *trans*-crotonates. They all have been found to show strong characterizing absorptions, all in the range 11.8–13.5 μ. Maleates constitute the one well explored negative case (*i.e.*, a case in which a conjugated system is present and the ester groups are constrained from coplanarity by steric and electrostatic forces). Halogenated esters have not been examined and, in general, the question of size or electrical charge of a group in the α-position or β-*cis* position necessary to interfere with coplanarity has not been studied.

The generalization has been investigated briefly for possible application to types other than esters, and it appears that several other types may fit. The types which appear to match the "family" absorptions are the corresponding acids, amides, alkyl amides, acid halides and nitro compounds. Further, the several types have their characterizing peak at approximately the same wave length as the esters. This weakens the analytical value of such a peak as a guide to the recognition of an ester—but it extends the range of its value as a means to the recognition of the grouping which directs the absorption to the region.

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[1] W. L. Walton and R. B. Hughes, *Anal. Chem.*, **28**, 1388 (1956).

[2] H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945).

[3] C. C. Price, *J. Polymer Sci.*, **1**, 86 (1946).

TABLE I

ASSIGNED VIBRATIONS COMPARED WITH ACETATE ESTER ABSORPTIONS

Compound	λ, μ	Assignment	λ, μ	Assignment	Reference
Sodium acetate	16.26	⊥ rocking of CO_2	15.50	In-plane deformation of CO_2	5
Acetate esters	16.34	"Part of the ester group skeleton"	15.61	"Ester group skeleton"	2
Nitromethane	16.68	⊥ rocking of NO_2	15.46	In-plane deformation	6

Discussion of Assignment of "Family Absorption"

Since the simplest α,β-unsaturated ester is a many-atomed molecule of low symmetry, it is not surprising that no vibrational analysis of any example of the type has been reported. Thus no wholly trustworthy model is available in the literature for comparison with the compounds treated here. On the other hand, in the case of the particular fundamental which we are proposing, there are a number of parallels worthy of consideration.

If the type be defined broadly as the planar structure illustrated by Fig. 1 in which, first, all atoms are heavier than hydrogen[4] and second, the BC and BD bonds are highly polar, whereas the AB bond is of a low order of polarity, then the models to consider are nitromethane and sodium acetate. Table I shows the assignments compared with the acetate esters.

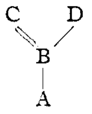

Fig. 1.

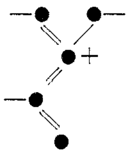

Fig. 2.

An analysis of the equal and opposite actions in the whole molecule permits a mode which is reasonably well described as out-of-plane deformation at the central atom in the Y structure, and this clearly is that which is termed perpendicular "rocking" (Table I), in the cases of sodium acetate and nitromethane.

Now since, in α,β-unsaturated esters, a degree of double bond character is present at the bond between the central atom and the α-atom, added restraint against bending is present and the frequency of the vibration will be greater.[7]

The absorption in the 15.5 μ region of the spectra of nitromethane and sodium acetate was assigned to a vibration which consists of in-plane-bending of the two oxygen atoms. The motion alternately increases and decreases the angle at the central atom with a relatively smaller motion of the central atom itself. Therefore, this second vibration is less subject to influence by the bond strength of the bond between the central and the α-atom.

The fact that *two* peaks are insensitive to the alcohol group in the acetate esters[2] suggests strongly that they are due to the acetate moiety only. That all the frequencies of the table should be so much "of a pattern" would also seem to be more than chance.

If the restriction that the A–B bond in Fig. 1 must be non-polar be discounted, then a number of even better known parallels are available for comparison. The nitrate and carbonate salts are completely symmetrical Y, planar structures. Their fundamental vibrations have all been assigned and besides highly similar absorption patterns are observed for the two types as theory predicts. In the calcium salts containing these ions, the out-of-plane deformation is at 11.54 μ for $CO_3^{=}$ and at 12.11 μ for NO_3^-, whereas the second vibration noted above is at 14.00 and 14.20 μ, respectively.[8] The out-of-plane vibration is thus found in much the same region as the absorptions we have observed in α,β-unsaturated esters.

Still another similar structure is that of the organic nitrates which were compared with nitric acid and in which the out-of-plane vibration has been assigned[9] to the peak at 13.29 μ.

In summary it seems reasonable to state that the evidence from the literature of similar type compounds indicates that the vibration illustrated in Fig. 2 for α,β-unsaturated esters should be in the region 10–15 μ.

Experimental

Spectra.—The spectra were run on a Perkin-Elmer, model 21, double beam spectrophotometer. Capillary films of pure liquid between optical rock salt plates were used except where otherwise noted. Scanning times (2.0–15.5 μ) were 14–25 minutes with suppression setting of two units. Slit schedule 3 and sodium chloride prism were used.

Films were prepared for the polarized spectra by the steps of: 1, heating the compound in question between square rock-salt plates to slightly above its melting point; 2, differentially cooling the "sandwich"; and 3, seeding the melt at the coldest corner.

The preparation was then checked by microscopic examination between crossed nicols to ascertain that uniform, and nearly parallel, crystal structure was available for study.

The data for Tables II and III were taken mainly from spectra which were accumulated over a period of about two years. Wave length values quoted are believed to be accurate to ±0.5 μ except where otherwise noted.

Compounds.—In the preparation of methyl acetylenedicarboxylate a 15 molar portion of anhydrous methanol was refluxed 15 hr. with 1 mole of acetylenedicarboxylic acid and 0.01 mole of toluenesulfonic acid. The mixture was then cooled, diluted with water and extracted with benzene. The benzene solution was washed with 5% sodium bicar-

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(4) Should one of the atoms be hydrogen, mechanical effects would cause the bond to the hydrogen to become the primary site of the vibration and the frequency of vibration would then be substantially increased.

(5) L. H. Jones and E. McLaren, *J. Chem. Phys.*, **22**, 1796 (1954).

(6) D. C. Smith, C. Y. Pan and J. R. Nielsen, *ibid.*, **18**, 706 (1950).

(7) It has been pointed out by a referee that the out-of-plane bending vibration of the methyl group should interact strongly with the out-of-plane Y-deformation, one result of which would be that the vibrations would move farther apart in frequency. Further, according to the assignments of this methyl frequency,[5,6] the effects would be to *lower* the out-of-plane Y-deformation and increase the out-of-plane methyl bending frequency from what would otherwise have been their normal values. If equally strong interaction is not present in the α,β-unsaturated esters, then the effect will be in the same direction as that argued above. Thus, a second reason for predicting the out-of-plane deformation absorption of α,β-unsaturated esters at a wave length shorter than the 16 μ region of the models above is encountered.

(8) T. Y. Wu, "Vibrational Spectra and Structure of Polyatomic Molecules," Second Ed., Edwards Brothers, Ann Arbor, Mich., 1946, p. 207.

(9) J. F. Brown, Jr., THIS JOURNAL, **77**, 6348 (1955).

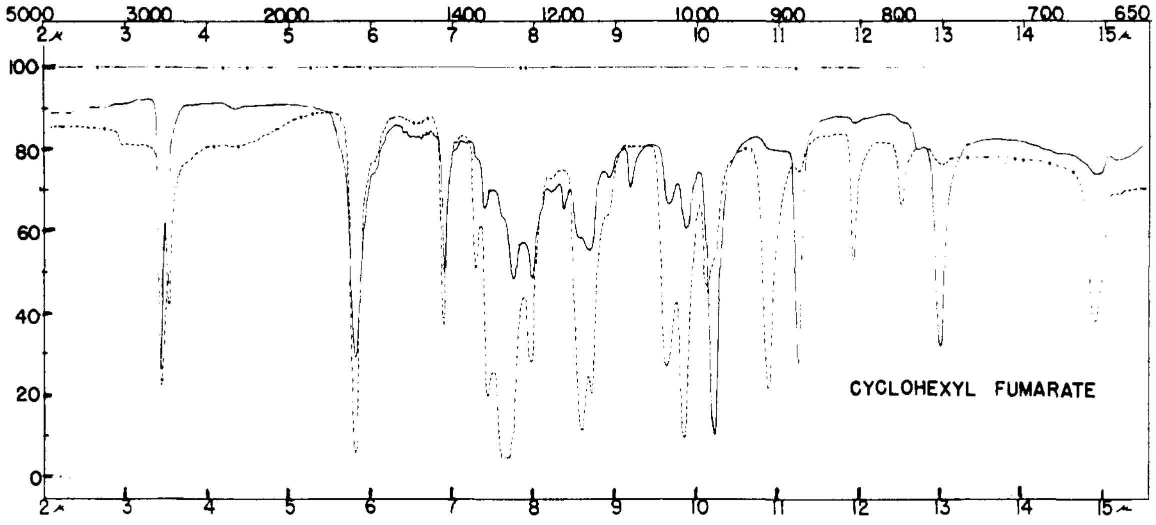


Fig. 3.

bonate solution and then with water and concentrated by distillation, using benzene to dry the ester azeotropically.

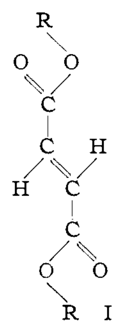
It was found that methyl acetylenedicarboxylate prepared by this method contained a considerable amount of an impurity which was higher boiling. On consulting the literature it was found that this side reaction had been explained.[10] The spectral data are in complete accord with Mommaerts interpretation that methanol added to this triple bond yielding an α-methoxy maleate which was partially removed by distillation with rejection of the higher boiling materials. The spectrum of the methyl acetylenedicarboxylate shown in Fig. 4 shows an absorption at 6.05 μ due to remaining impurity of this methoxy maleate ester.

Other esters of acetylenedicarboxylic acid were prepared by the method of Jeffery and Vogel.[11]

Spectra of Ester Families. Fumarates and Coplanarity.—Coplanarity of the ethylene and carbonyl in conjugated esters is generally accepted in the literature from which it would follow that the ester groups in a diester, such as a fumarate, would also be coplanar. Moreover, in the case of the fumarates some direct evidence of coplanarity can be deduced from the infrared spectra.

The carbonyl stretching absorption is at longer wave length by approximately 0.02 μ than the corresponding maleates. This indicates a greater degree of resonance stabilization.

Further, a peak at about 6.06 μ in maleates and fumarates is assigned to stretching of the C=C bond. With maleates, the 6.06 μ peak is regularly more intense and broader than the corresponding peak of fumarates. This constitutes one point of evidence since, in coplanar fumarate structures, two of the three pseudo-isomers would be centrosymmetric throughout the fumarate part of the structure. Defining s-*cis* (single-bond *cis*) as the case in which the C=C and C=O lie on the same side of the single bond, it is the s-*cis*, s-*trans* structure II which is non-centrosymmetric. Thus, barring substantial contribution to dissymmetry from the alcohol portion of the fumarates, one would anticipate weaker infrared activity in this band (since only one isomer in three is infrared active) than in the maleates which are incapable of assuming a centrosymmetric configuration.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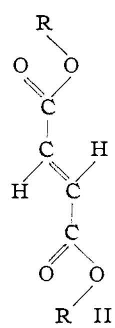
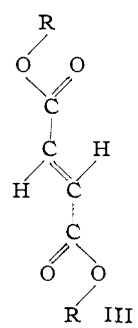

II


III

The third line of evidence that the fumarates are coplanar is based on observations of oriented crystal films with polarized infrared light.

Figure 3 shows the spectra of an oriented crystalline film of cyclohexyl fumarate. The solid curve was run with the polarizer setting such that the electric vector of the polarized beam was parallel to the direction of crystal growth of the sample. The dotted curve was run with the sample in the same position but with the polarizer rotated 90° from the first position. The carbonyl stretching absorption is intense in this preparation, but shows a greater absorption at the polarizer setting 90° from the direction of crystal growth. As both C–O peaks (7.4–8.0 μ and 8.6–8.7 μ) are intense with this same setting of the polarizer, it follows that both ester groups are essentially planar and normal to the direction of crystal growth. This most fortunate circumstance permits an easy analysis of the data, which might otherwise have been very complex. The C–O stretching vibrations are necessarily non-parallel because of the oxygen valence angle and would have yielded low dichroic ratios or considerably different angles of maximum absorption by any other orientation. Thus, this most fortunate orientation is clearly the actual one.

The out-of-plane ethylene hydrogen bending which is that consistently noted at 10.2 μ in fumarate esters is of moderate dichroism and is oriented as expected. The 12.9 μ appears slightly displaced (13.0 μ) but clearly identifiable as the strongest absorption is this region and of approximately the same intensity relative to say 10.2 μ as in liquid spectra. (Its intensity in relation to oppositely oriented peaks is normal as shown by mull spectra or this same crystal preparation without use of a polarizer.)

The spectrum of crystalline cyclohexyl fumarate is not appreciably different from that of the liquid as regards any of the absorptions noted above. It is different in that the C=C absorption at about 6.1 μ is very weak. Thus, evidently structure II above is eliminated in the crystallization process.

Our preparations of crystalline methyl fumarate have not provided high dichroic ratios, but the low ratios which were obtained were qualitatively in the same direction for each of the above-mentioned absorptions.

Acetylenedicarboxylates.—The spectra of six acetylenedicarboxylic esters are shown in Fig. 4. These spectra show peaks at 13.4 and 14.9 μ which are remarkably constant. Further, as in the case of the fumarates,[1] the lower frequency absorption is the less intense.

The first significant theoretical point learned from the acetylenedicarboxylates is that the fixed peaks are clearly not generated by hydrogen atom vibrations. And, since they are quite similar in frequency and intensity to the 12.9

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(10) Henri Mommaerts, *Bul. soc. chim. Belg.*, **52**, 79 (1943).

(11) Geo. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 658 (1948).

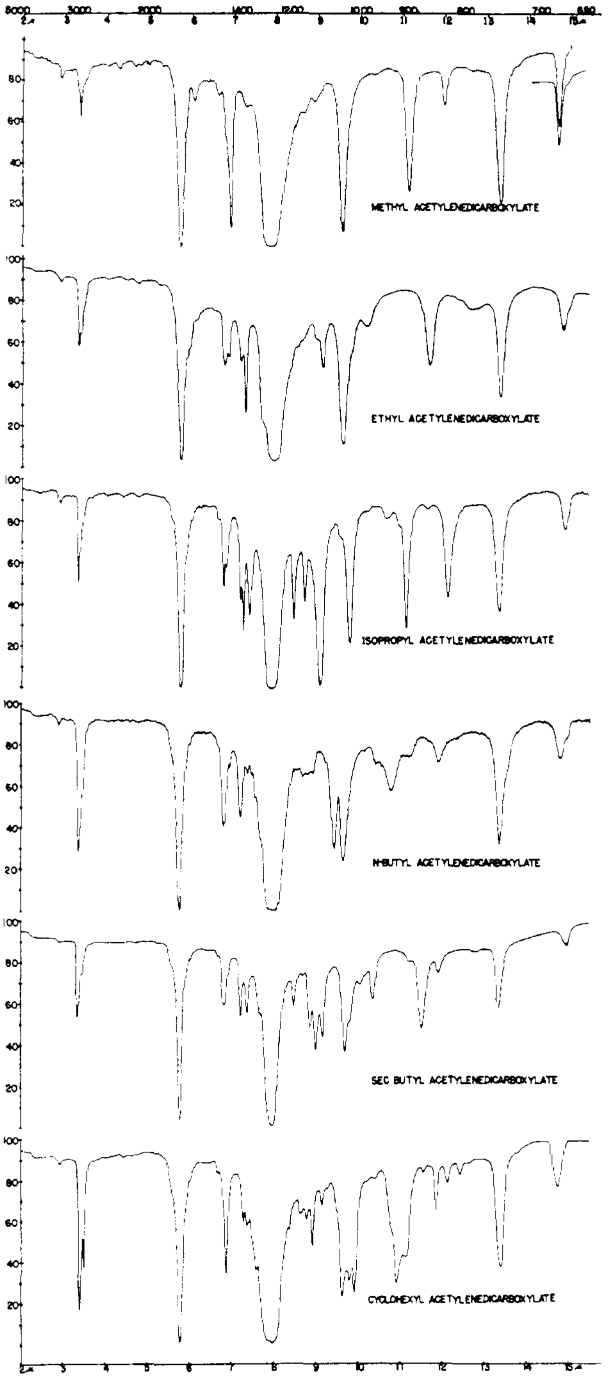

Fig. 4.

and 15.0 μ peaks of fumarates, it was at once apparent that the fumarate peaks were probably not due to hydrogen vibrations.

Figure 5 shows the spectra of cyclohexyl acetylenedicarboxylate run with polarized light. The solid curve is that in which the electric vector of the plane of polarization was parallel to the direction of crystal growth. The dotted curve had the plane of polarization 90° from the first position. Polarizations of the carbonyl stretching and of the complex C–O stretching absorptions are seen to be parallel to each other and at right angles to the 13.4 μ band.

As there obviously can be no steric restraint to free rotation of the ester groups about the linear axis of the four carbons in this compound, it is somewhat surprising to find any evidence of coplanarity of these ester groups. However, the fixation of these groups in coplanar positions is readily acceptable in the light of the reduced electrostatic repulsion (*versus* oxalates) and the predicted high degree of resonance stabilization.

Oxalates.—The literature provides no satisfactory evidence for the prediction of the relation between the planes of the ester groups. Crystalline sodium oxalate and ammonium oxalate have been studied by Jeffrey and Parry[12] using X-ray techniques. These ionic structures were found to be preferentially coplanar. However, these same authors point out that the expected effect of mutual repulsion of the carboxylate groups should generate a staggered structure (near 90° between planes of the carboxylate groups). Further, in liquid phase the non-ionic esters should have considerably more tendency to assume the staggered structure: their resonance interaction should be weaker. Four oxalate esters were examined, and it was found that there was no prominent fixed absorption in the 10–15.5 μ region.[13]

The specific ester, methyl oxalate, was found to be very interesting in that the crystalline material is clearly coplanar in the region bounded by the oxygen atoms. The polarized spectra of a single film are shown in Fig. 6. The high dichroic ratios shown for C═O st., C—O st. (at 8.2 μ) and C–O st. (at 8.6 μ) are evidence that the molecules are essentially flat and that their planes are normal to the direction of crystal growth in the film. The possibility that one carbonyl might be normal to the film plane and the other oriented to give absorption intensity as observed in the polarized spectrum can be disproved, since mull spectra show the same ratio of intensity for C═O st. and C–O st. as in the oriented films. Further, the high dichroic ratios for all three carbon-to-oxygen bond stretching vibrations, coupled with the knowledge of the near 120° angles involved in the ester groups, give additional proof.

Two strong sharp absorptions are observed at 10.81 and 12.81 μ. The former is believed to be out-of-plane deformation of the methyl group (it is not observed in sodium or calcium oxalate whereas the 12.8 μ peak is). The latter is probably a "double, out-of-plane Y-deformation" or essentially a motion of the two central carbon atoms simultaneously above and then below the plane of the oxygen atoms. This should be the only strongly infrared active vibration perpendicular to the plane and common to salts and methyl oxalate.

The methyl groups themselves are nearly in the plane of the molecules. This is clearly indicated by the very definite polarization of the 7.25 μ symmetrical deformation of the methyl groups.

Acrylates and Methacrylates.—In Fig. 7 are shown the spectra of several esters of each of the two series, the acrylates and the methacrylates. It is noteworthy that in both series only the methyl ester shows separation of the second C–O st. absorption into two bands paralleling the slight abnormality noted for the frequencies of the family peaks of these esters in Table II.

As can be seen from the data of Table II and the curves in Fig. 7, certain obvious features of the spectra are available for differentiation of the two families: with acrylates a doublet is resolvable in the 6.1 μ region and fairly constant peaks are noted at 9.4, 10.15 and 10.5 μ, whereas with methacrylates a peak at about 10.65 μ is characteristic and the other features are absent. The foregoing, together with

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[12] G. A. Jeffrey and G. S. Parry, THIS JOURNAL, **76**, 5283 (1954).

[13] The conclusion that an ester family does not have a characterizing absorption in a particular spectral range can be safe based on rather few esters; indeed, it could happen that no coincidence would occur in the first two examined and the conclusion would be valid even then. The reverse, proving that a peak is a constant one, also is readily established if the following logic be accepted. In the case of the 13.4 μ absorption of the acetylenedicarboxylates, all the esters have this peak falling within a range of 0.10 μ. A count of the peaks in the 10–15.5 range, which are one-tenth as intense as the 13.4 μ peak or stronger, shows that the peaks occur about one per 1.1 μ. Thus, the probability of a peak falling in a particular 0.10 μ wide range is only 0.1/1.1, and the probability that six such esters should all have peaks falling by accident in the same range is less than $^1/_{10^6}$. Two assumptions have been made: that each increment along the wave length scale is equally likely to find an absorption falling in it and that the absorption to be counted should have a certain minimum intensity. The first of these is probably fallacious but no doubt an arbitrary choice with order of magnitude accuracy when limited to the 10–15 μ range. The second is arbitrary and undoubtedly is conservative as to its effect on the answer.

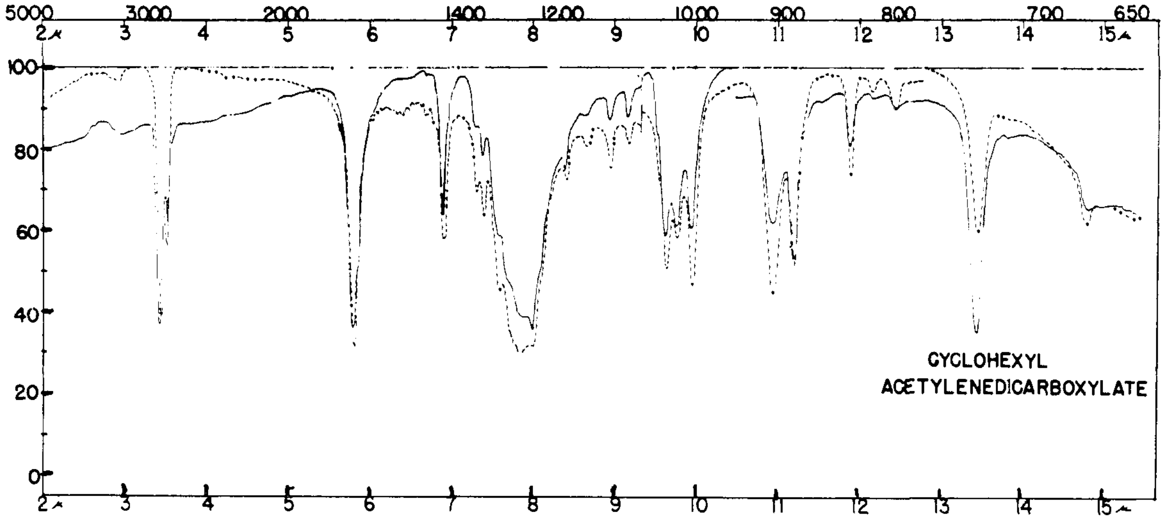

Fig. 5.

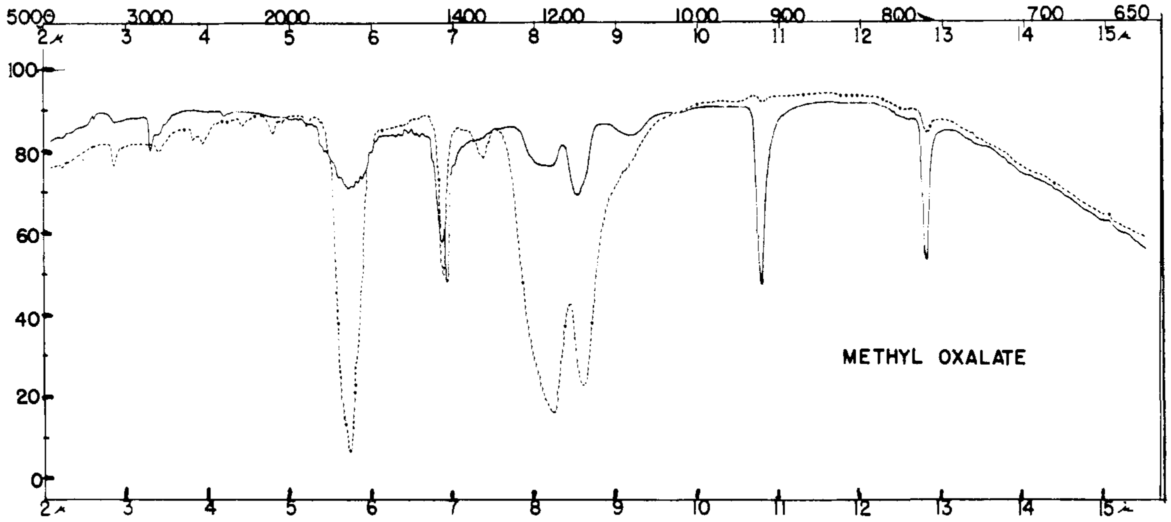

Fig. 6.

the information from an accurate measurement of the 12.3 μ absorption, can serve to distinguish the families rather conclusively. The moderately fixed absorption at around 15 μ is sometimes noted in the table and sometimes not. In general, this peak has offered less of analytical value—being somewhat weaker, less constant in a family and therefore not readily identified. It is probable that in some cases, not listed in the table, it will be found only if sufficiently thick samples are employed in searching for it.

The identification of the hydrogen vibrations has proved difficult. However, an interpretation which is marred by only one inconsistency has been developed: first, it is assumed that (1) vibrational coupling occurs between the hydrogen out-of-plane bending and the ester out-of-plane deformation, (2) coupling results in greater wave length shifts when the mass of two hydrogen atoms instead of one is vibrating and (3) the theoretical positions of the bands (without coupling effects) would have been only slightly different from the positions in the hydrocarbons. Now, since methacrylates have a structure $RR'C{=}CH_2$ for which in hydrocarbons a peak at 11.22 μ is assigned, it is proposed that this peak is shifted to 10.65 μ. A "pattern" has been assigned to α-alkyl acrylates,[14] namely, peaks at 10.6 and 12.2 μ. Thus, the present interpretation for methacrylates is probably applicable to the broader class on which empirical correlation is not new. The acrylates are compounds of the structure $R{-}HC{=}CH_2$ for which in hydrocarbons an absorption at 10.95 μ is assigned to the H_2 bending and an absorption at 10.05 μ is assigned to the H. (These are, of course, not presumed to be free of coupling in the hydrocarbon but rather must be spread to some extent already by the coupling effect.) The H_2 bending is then shifted to 10.5 μ and the H bending to 10.15 μ. The latter is in line with the small shifts observed as the result of both chemical-shift (variation between ester type and hydrocarbon) and coupling-shift in *trans*-crotonates, *trans*-cinnamates and fumarates. With the acrylates, however, it must be assumed that the chemical effect and coupling effect are in opposite directions and that the chemical effect is the greater.

The one seriously discordant observation is that acrylic acid in liquid form shows three broad peaks at 10.2, 10.8 and 12.3 μ. Possibly the identity of the peaks is in the same order except that for some reason their frequencies are not as true.

There is a basis for believing that the vibrations in question are all directed normal to the plane in the planar molecules, namely, that their structures are essentially similar to that of acrylamide.

Acrylamide.—Figure 8 shows the spectra of acrylamide (in oriented crystals) run on the same film but with two settings of the polarizer. The CH stretching vibrations and the carbonyl stretching vibration show their strong absorption at the same position of the plane of polarization. Thus these absorptions, and therefore most of the atoms of

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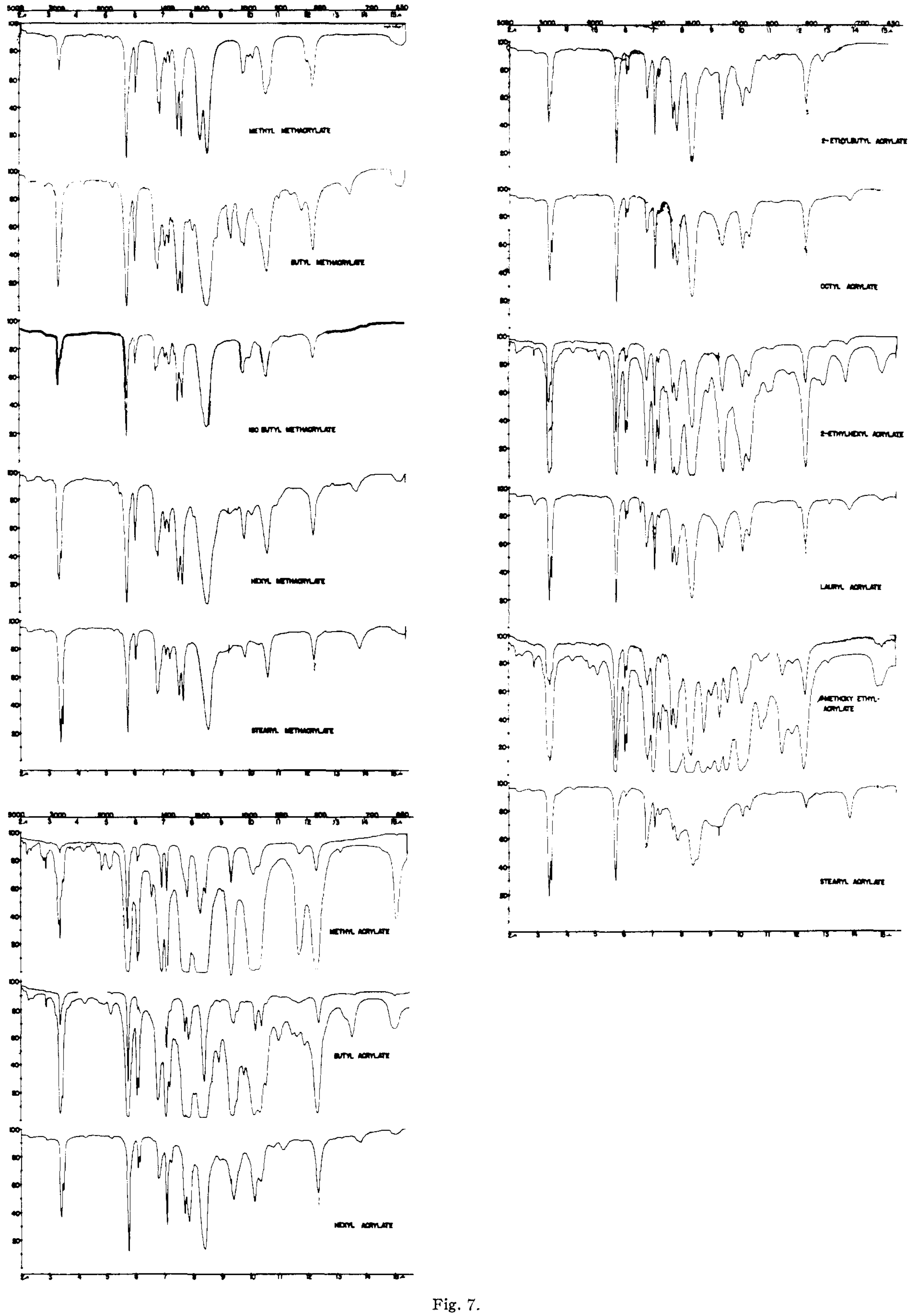
[14] C. J. Albisetti, D. C. England, M. J. Hogsed and R. M. Joyce, THIS JOURNAL, **78**, 472 (1956) (acknowledgment to J. R. Downing).


5000
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METHYL METHACRYLATE
BUTYL METHACRYLATE
ISO BUTYL METHACRYLATE
HEXYL METHACRYLATE
STEARYL METHACRYLATE
METHYL ACRYLATE
BUTYL ACRYLATE
HEXYL ACRYLATE
2-ETHYLBUTYL ACRYLATE
OCTYL ACRYLATE
2-ETHYLHEXYL ACRYLATE
LAURYL ACRYLATE
β-METHOXY ETHYL-ACRYLATE
STEARYL ACRYLATE

Fig. 7.

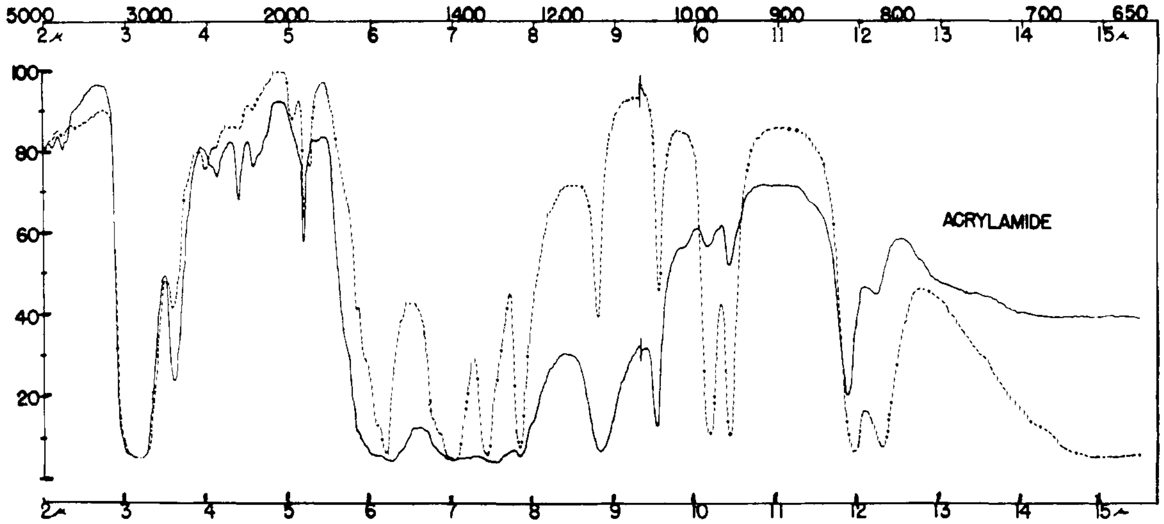

Fig. 8.

the molecule, lie in a plane which incidentally is normal to the direction of crystal growth. The three absorptions at 10.17, 10.42 and 12.30 µ are shown to be due to out-of-plane vibrations in accordance with the interpretation that they are, respectively, the α-hydrogen out-of-plane bending, the β-out-of-plane bending and the Y out-of-plane deformation.

TABLE II

INFRARED ABSORPTIONS OF ESTERS

Esters	Family[e] peak, µ	Second peak, µ	Other peaks, µ	Other peak assignment	Technique
		Fumarates			
	12.94	14.98		⊥Bending of hydrogen on ethylene	c
Methyl	12.92	15.03	10.22		b
Ethyl	12.90	14.99	10.21		b
Propyl	12.90	14.96	10.21		b
Isopropyl	12.84	14.96	10.20		b
Butyl	12.88	14.92	10.23		b
Isobutyl	12.92	14.98	10.21		a
	12.89	15.00			b
sec-Butyl	12.90	14.98	10.20	⊥Bending of hydrogen on ethylene	a
Cyclohexyl	12.89	14.90[b]	10.21		a
Nonyl	12.90	14.91[b]	10.23		a
Lauryl	12.93	14.94	10.20		a
Tetrahydrofurfuryl	12.94	15.02	10.20		a
β-Methoxyethyl	12.93	14.91	10.24		b
Polydipropylene[i]	12.94	14.98	10.19		a
Allyl	12.94	...	...		
		Acetylenedicarboxylates			
Methyl	13.37	14.77			a
Ethyl	13.38	14.87			a
Isopropyl	13.36	14.91			a
Butyl	13.38	14.83			a
sec-Butyl	13.37	15.00			a
Cyclohexyl	13.37	14.76	round ±0.05		a
	13.36				a ?
		Acrylates			
Methyl	12.301[f]	15.14	10.12 10.34 9.36	⊥α-H ⊥β-H$_2$?	
Butyl	12.34[b] 12.37[a]	15.5[b]	10.19 10.40 9.43	⊥α-H ⊥β-H$_2$?	a
Hexyl	12.326[f]	15.08	10.16 10.39 9.43	⊥α-H ⊥β-H$_2$?	a
2-Ethylbutyl	12.329[f]		10.15 10.40 9.44	⊥α-H ⊥β-H$_2$?	a
Octyl	12.326[f]		10.16 10.40 9.45	⊥α-H ⊥β-H$_2$?	a
2-Ethylhexyl	12.326[f]	15.05	10.16 10.39 9.42	⊥α-H ⊥β-H$_2$?	b
Lauryl	12.34	15.07	10.15 10.40 9.44	⊥α-H ⊥β-H$_2$?	a
β-Methoxyethyl	12.35	14.88	10.14 10.40 9.37	⊥α-H ⊥β-H$_2$?	a
Stearyl	12.38	15.00	10.17 10.42 9.41	⊥α-H ⊥β-H$_2$?	a
		Methacrylates			
Methyl	12.247[f]		10.65	⊥β-H$_2$	a
Butyl	12.28	15.2–15.4	10.66	⊥β-H$_2$	a
Isobutyl	12.29		10.65	⊥β-H$_2$	a
Hexyl	12.262[f]	15.2–15.35	10.69	⊥β-H$_2$	a
Stearyl	12.269[f]	15.45	10.68	⊥β-H$_2$	a
β-Vinyloxyethyl[g]	12.3		10.6	⊥β-H$_2$	
β-Polyvinyloxyethyl[g]	12.3		10.6	⊥β-H$_2$	
Glycidil[h]	12.3		10.6	⊥β-H$_2$	
		Crotonates[h]			
Ethyl	11.90	14.40	10.30	*trans*-Hydrogen ⊥ bending	
Vinyl	12.00	14.80	10.18		
Butyl	11.88	14.60	10.30		
Glycidil	12.00	14.60	10.30		
		trans-Cinnamates			
Methyl	13.03	14.05 14.64	10.17	*trans*-Hydrogen ⊥ bending	d
Butyl	13.02	14.10 14.65	10.20		a
		Propionates			
Methyl	12.40				c, j
Ethyl	12.46 weak				c
	12.41				b
Butyl	12.39 weak				a, k
Cyclohexyl	12.40 weak				a

[a] Sandwich cell, pure liquid. [b] Std. cell, pure liquid. [c] Std. cell, solution in CS_2. [d] Crystal film. [e] Ester out-of-plane deformation. [f] These measurements were carried out with maximum precision in comparison with ammonia vapor peaks at 12.381 and 12.684 µ. Wave lengths are probably more accurate than ±0.005 µ. It is noted that wave lengths ranges are specific for the ester family except that the methyl esters are both about 0.02 µ lower wave length than the rest of the family (as far as explored). [g] H. C. Haas and M. S. Simon, *J. Polymer Sci.*, **17**, 422 (1955). [h] W. A. Patterson, *Anal. Chem.*, **26**, 830 (1954). [i] Polyester based on commercial dipropylene glycol and fumaric acid. [j] In benzene. [k] Benzene present.

TABLE III

"Y" CONFIGURATION COMPOUNDS OTHER THAN ESTERS

Ester family	Family peak, μ	Compound	Family peak, μ
Fumarates	12.84–12.94	Fumaric acid	12.88
		Fumaryl chloride	12.62, 12.59
		Fumaryl benzylamide	12.4[a]
Crotonates	11.9–12.0	Crotonic acid	11.88
		trans-1-Ethyl-2-nitroethylene[b]	11.85
Acrylates	12.34–12.38	Acrylic acid	12.24, 12.29
		t-Butylacrylamide	12.34
		Nitroethylene	12.48
		Acrylamide	12.22 (12.30 cryst.)
Methacrylates	12.26–12.29	Methacrylic acid	12.24–12.39
Acetylenedicarboxylates	13.36–13.42	Acetylenedicarboxylic acid	13.42
Cinnamates	13.00–13.10	Cinnamic acid	13.04
		trans-β-Nitrostyrene	13.00

[a] R. W. Stafford, R. J. Francel and J. F. Shay, *Anal. Chem.*, 21, 1455 (1949). [b] This is a near comparison, in the light of both compounds being *trans*-1,2-disubstituted ethylenes.

Polarized Spectra of Other Esters.—Cyclohexyl maleate was examined in oriented crystal film; it showed rather high dichroic ratios for the C–O stretching absorptions. Further, those absorptions were strong at the same setting of polarizer that gave strong absorption by the C═C stretching vibration. Thus, a high degree of coplanarity for the ester group and the ethylene exists. Significantly, the absorption at 8.2 μ which was shown to be characteristic of maleates[1] was absent. Thus, this molecule is preferentially oriented in crystallization and could be substantially unlike *normal* maleates. Another point of abnormality recorded in the earlier paper is that the melting point of the maleate is in this case higher than the fumarate: 86° *vs.* 35–36°.

Methyl cinnamate was studied; it yielded only moderate dichroic ratios in any assigned peaks. However, such ratios as were noted were again qualitatively in accord with expectations based on our generalization.

Tabulated Spectral Data.—Table II shows the wave lengths of the family-constant peak for the various ester families. Other peaks of interest also are shown.

Several ester families were examined to see if constant peaks were present in the 10–15 μ region and none were found. These included succinates, acetates and oxalates. However, the propionates have a peak that is remarkably constant at 12.4 μ as had been noted by Tompson and Torkington in 1945.[2] This absorption is very near the wave length of the peaks of the acrylates and the methacrylates. It is, however, much less prominent than that in the unsaturated esters. Possibly the explanation of this absorption could be that a low degree of double bond character exists at the C–C bond between the carbonyl and α-carbons and that some portion of the molecules at a given instant assume the conformation that most nearly matches that of the acrylates.

Types Other Than Esters.—It was noted early in this investigation that the corresponding acids have peaks which match the family-constant ester peak. As the study progressed more compounds of related types were examined and confidence increased in the greater breadth of the generalization. Table III lists other types in comparison with the esters.

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Light Induced Spectral Shift of the Thiazine Dyes in the Bound State[1]

BY NEIL WOTHERSPOON AND GERALD OSTER

RECEIVED MARCH 8, 1957

We have found that thiazine dyes in the presence of polymethacrylic acid or polyacrylic acid undergo a spectral shift when irradiated with visible light. A combined recording spectrophotometer and irradiation apparatus was used to follow the reaction either at a fixed wave length or by scanning the spectrum repetitively. Two photo products are formed, one in the absence of oxygen and the second by the photoöxidation of the first. The rate of formation of the second product is retarded by small amounts of paraphenylenediamine or by potassium iodide suggesting that long-lived excited states are involved. The final photoproduct is the same for all the thiazine dyes studied and is identical to thionine. The reaction requires a polyacrylic acid but does not take place in the presence of other high polymeric acids or of dibasic acids.

Introduction

During the course of our studies on the photochemical properties of methylene blue, we observed that a purple species having a bright red fluorescence was formed when a solution of the dye containing polymethacrylic acid was illuminated. It is the purpose of the present study to investigate the nature of this photochemical reaction. In particular, we are concerned with determining which dye and high polymer combinations exhibit this phenomenon.

The photochemical properties of many dyes

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(1) (a) This paper represents a part of the dissertation to be submitted by Neil Wotherspoon to the faculty of the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)1182.