214. *On Monolayers of Isomeric Unsaturated Compounds.*

By J. Marsden and E. K. Rideal.

The properties of monolayers of a number of *cis*- and *trans*-unsaturated long-chain acids and alcohols have been examined. Their behaviour suggests that the *trans*-structure can form close-packed films by interlocking, which is impossible in the bent *cis*-form. This view is supported by the examination of mixed films, where it is found that *trans*-unsaturated chains can pack with saturated chains but that the *cis*-form causes expansion. Supplementary evidence is obtained from the oxidation rates of the two isomers in monolayers, which, for the *trans*-isomer, is shown to be very susceptible to compression. The properties of the " *cis* "- and " *trans* "-dihydroxy-acids are of interest in that the *trans*-form produces solid films which can be attributed to hydrogen bonding, suggestive in consideration of filamentous hydroxyl-containing macromolecules. The " *cis* "-dihydroxy-acid appears to be formed almost exclusively on oxidation at interfaces.

The fact that at corresponding temperatures and on the same substrate, monolayers of oleic acid are in the liquid-expanded and those of stearic acid in the condensed state (Langmuir, *J. Amer. Chem. Soc.*, 1917, **39**, 1848; Adam and Jessop, *Proc. Roy. Soc.*, 1922, *A*, **101**, 516), indicates that the insertion of a double bond in the chain of the fatty acid modifies the cohesion of the chains to one another. Adam concluded that the stereochemical configuration of the unsaturated chains was an important factor in influencing their cohesion, since he found, in the few cases examined, that the *cis*-isomers (oleic and erucic acids) possessed a half-expansion temperature some 25—30° lower than the corresponding *trans*-isomers (elaidic and brassidic acids). That oleic acid is the *cis*-isomer and elaidic the *trans*-form appears from the work of Hilditch (J., 1926, 1828) and Müller and Shearer (J., 1923, **123**, 3156).

In this communication the force–area and surface potential characteristics of a number of geometric isomers with the double bond in various positions along the chain are presented with the object of finding out how far the differences in the film characteristics of *cis*- and *trans*-modifications can be interpreted in terms of their molecular configurations.

FIG. 1.

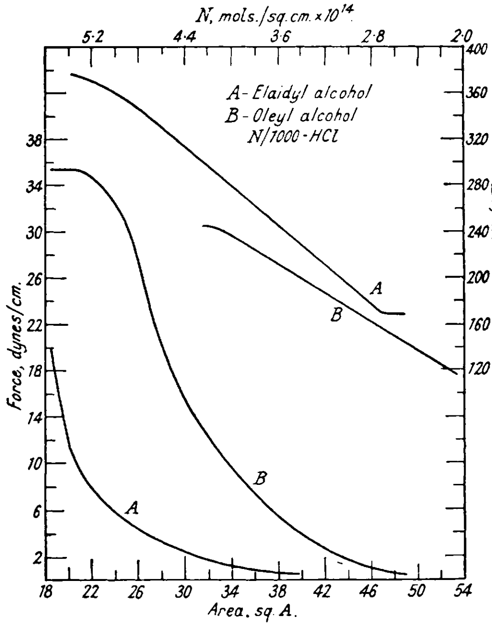


FIG. 2.

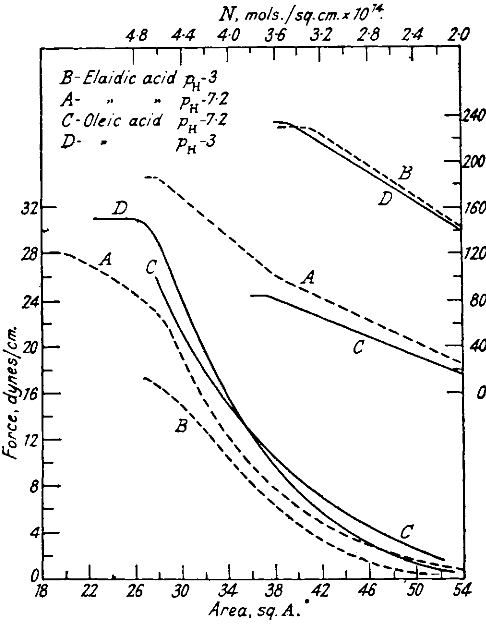


FIG. 3.

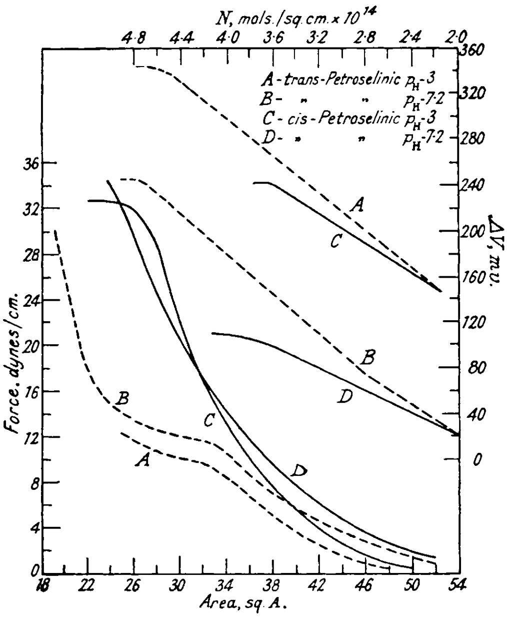
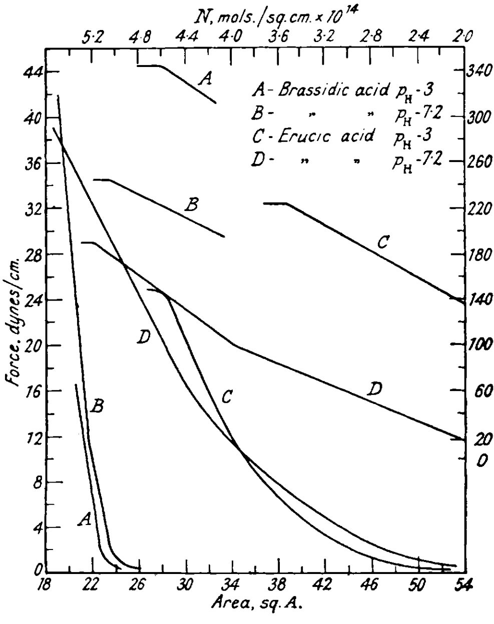


FIG. 4.



EXPERIMENTAL.

The structures and m. p.'s of the substances employed are shown in Table I. No sharp m. p. could be obtained for oleyl alcohol; monolayers from two different specimens were identical. The measurements of the force–area characteristics were made in a Langmuir trough sensitive to 0·12 dyne/cm. and so constructed as to eliminate metallic impurities. The phase-boundary potentials were measured simultaneously with the force–area determinations by the method previously described (Schulman and Rideal, *Proc. Roy. Soc.*, 1931, *A*, **130**, 259; Gee and Rideal, *ibid.*, 1935, *A*, **153**, 116). All measurements were carried out at 21°. The monolayers were spread from light petroleum solution with an Agla micro-syringe. Potassium dihydrogen phosphate–sodium hydroxide buffer was employed for p_H 7·2 substrates (Clark, "Determination of Hydrogen Ions," p. 200); for p_H 3 substrates, unbuffered hydrochloric acid was used.

TABLE I.

Compound.	Structure.	M. p.
Oleyl alcohol	*cis*-$CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot CH_2\cdot OH$	—
Elaidyl alcohol	*trans*- ,, ,,	24·7° ± 0·3°
Oleic acid	*cis*-$CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$	11·0
Elaidic acid	*trans*- ,, ,,	43·6 ± 0·2
Petroselinic acid	*cis*-$CH_3\cdot[CH_2]_{10}\cdot CH{:}CH\cdot[CH_2]_4\cdot CO_2H$	29·5 ± 0·2
Petroselinic acid	*trans*- ,, ,,	52·9 ± 0·1
Erucic acid	*cis*-$CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_{11}\cdot CO_2H$	32·7 ± 0·2
Brassidic acid	*trans*- ,, ,,	59·6 ± 0·2

Results.—The force–area and surface–potential curves of the unsaturated compounds are shown in Figs. 1—4. The *cis*-isomers form homogeneous liquid-expanded films at areas per molecule greater than 50 A.^{2}. These isomers on acid substrates form oil lenses at low areas, as indicated by a constant pressure during compression in this region. On p_H 7·2 substrates the *cis*-compounds do not form oil lenses, but rather liquid films which undergo collapse by a process of cracking, as testified by a rise in pressure on compression which decreases with time. Of the *cis*-isomers, erucic acid is the only exception; this acid forms an unstable liquid film on p_H 3 substrates and a weak solid on neutral substrates. The *trans*-acids, petroselinic and elaidic, form liquid-expanded films at low pressures. In the case of *trans*-petroselinic acid at $\simeq$ 34 A.^{2}, the pressure changes only slightly on compression, indicating a transition region and the formation of micelles. Contrary to the results found by Schulman and Hughes (*Proc. Roy. Soc.*, 1932, *A*, **138**, 430) for myristic acid, *trans*-petroselinic acid films are homogeneous in the transition region, as indicated by a constant potential (5 mv.) over different parts of the surface. Elaidic acid does not exhibit the phenomenon of micelle formation. These *trans*-acids on p_H 3 substrates form unstable liquid films at high pressures. On p_H 7·2 substrates, *trans*-petroselinic acid becomes a stable solid at areas below 19·8 A.^{2}; elaidic acid is converted into a fragile solid in this area region. As in the saturated acids, the expansion temperature rises with increasing chain length; thus, since the expansion temperature of brassidic acid is above 21°, condensed films are formed at this temperature. On p_H 3 substrates this acid forms homogeneous films at 24 A.^{2}, becoming a solid at $\simeq$ 21 A.^{2}; on p_H 7·2 substrates the film is a strong solid which is stable at high pressures ($<$40 dynes/cm.). The force–area curves (Fig. 4) for erucic and brassidic acid furnish the most evident examples of the difference in the film properties of the *cis*- and the *trans*-compounds and the similarity of the latter to the saturated compounds.

DISCUSSION.

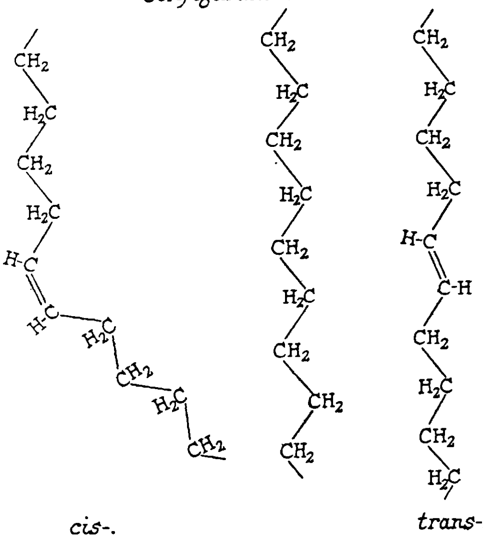
Although the *X*-ray data on the *cis*- and *trans*-modifications (Müller and Shearer, *loc. cit.*) are in themselves not sufficiently complete to enable definite molecular configurations to be assigned to the acids examined, yet it is reasonably certain that the chain configurations are as depicted in Fig. 5. The configuration of the saturated chain is included for comparison.

Lyons and Rideal (*Proc. Roy. Soc.*, 1929, *A*, **124**, 333) suggested that molecular areas in the close-packed solid-condensed monolayers of saturated fatty acids were identical with the areas occupied in the crystalline state, and that in consequence the chain axis in the monolayer was inclined at 26·5° to the vertical with the chains interlocking. Subsequent investigation revealed that the solidity of the film was not the sole criterion for this structure, since such films may be liquid unless there is both interaction between the head groups and interlocking along the chains. We note that the *trans*-configuration should permit of such an interlocking process more readily than the *cis*-form, in which the hydrocarbon chain is bent. We also observe that, in agreement with this view the *cis*-isomers form more highly expanded monolayers than the *trans*-modification, and that the *cis*-isomers on collapse always form oil lenses, which are never formed with the *trans*-compounds where chain adlineation can take place with formation of solids or smectic liquids. Erucic acid (*cis*) is the only exception, but here the length of the chain between the polar group and the double bond is sufficiently long to impart the properties of a *trans*- or saturated chain derivative to this compound.

The ability of the chains to interlock in the case of the *trans*-compounds is dependent on the distance of the double bond from the polar group. The transition region present in *trans*-petroselinic acid (Fig. 3) is absent in elaidic acid, where the double bond is three CH_2 units further removed from the carboxyl group. Thus the ease of micelle formation is increased by shortening the distance between the double bond and the polar group, the limiting case being that of αβ-*iso*oleic acid, which forms condensed films as shown by Hughes (J., 1933, 338).

FIG. 5.

Configurations.



The formation of expanded films of the *trans*-acids (petroselinic and elaidic) at *low pressures* must be attributed to some factor other than structural configuration, since the saturated acid of the same chain length forms condensed films. In view of the evidence that unsaturated hydrocarbons are more soluble than the saturated, it has been suggested that the double bond is attracted to the water surface, thereby causing expanded films. However, the weak hydrophilic nature of the double bond is shown by the fact that the limiting areas of the *cis*-acids are the same and independent of the position of the double bond. It seems doubtful whether this weak attraction is sufficient to account fully for the expanded films of the *trans*-acids at low pressures.

The Effect of Hydrogen-ion Concentration.—The effect of a change in hydrogen-ion concentration of the substrate from p_H 3 to p_H 7·2 is shown in Figs. 1—4. When the substrate is rendered more alkaline, the films undergo a relative expansion at large areas and a contraction at high pressures. Harkins and Myers (*J. Chem. Physics*, 1936, **4**, 716) showed that the same phenomenon of expansion followed by contraction occurs with myristic acid on ionisation, and attributed the expansion to a repulsion of the ionised head groups, but did not attempt to explain the subsequent condensation effect. Although on these substrates there is undoubtedly increased hydration and the long-range forces are electrical repulsive ones, yet it seems possible that on compression of the film the number of " free " ions becomes smaller owing to the accumulation of the " bound " ions, and in many cases, as for example on acid soaps, actual association might well occur. The experimental evidence for this hypothesis, however, is admittedly very incomplete.

The *cis*-unsaturated acids which form oil lenses when undissociated do not exhibit this property on ionisation, but rather form unstable liquid films at high pressures. The non-formation of oil lenses may be attributed both to the increased hydration and to the attractive forces between polar groups being greater than the negative spreading force of the hydrocarbon chains, the instability of these films being due to the non-packing of the asymmetric chains. The formation of stable solid films of the *trans*-unsaturated acids on p_H 7·2 substrates is dependent on the interlocking of the chains and also on the attractive forces between polar groups.

Surface Potential Characteristics.—The values of μ, the vertical component of the dipole moment, calculated from the Helmholtz equation ($\Delta V = 4\pi n\mu$) at different values of n (mols. $\times$ 10^{14}/sq. cm.) are given in Table II. The values of μ, calculated from the ΔV–N curve determined by Hughes (*loc. cit.*), are included for the purpose of comparison.

TABLE II.

		Values of $\mu \times 10^{-19}$ (e.s.u.) at $n \times 10^{14}$ (mols./sq. cm.).				
Compound.	p_H.	2·0.	2·8.	3·6.	4·0.	4·6.
cis-Petroselinic acid	3	—	1·79	1·78	—	—
Oleic acid	3	1·85	1·81	1·80	—	—
Erucic acid	3	1·80	1·73	1·70	—	—
cis-Petroselinic acid	7·2	0·27	0·57	0·74	0·73	—
Oleic acid	7·2	0·21	0·46	0·60	—	—
Erucic acid	7·2	0·24	—	0·62	0·66	0·92
trans-Petroselinic acid	3	—	1·92	1·96	1·98	—
Elaidic acid	3	1·89	1·86	1·86	—	—
Brassidic acid	3	—	—	—	2·0	1·99
Myristic acid	3	1·7	1·9	2·0	2·1	—
trans-Petroselinic acid	7·2	0·27	0·72	1·08	1·19	1·35
Elaidic acid	7·2	0·33	0·60	0·74	0·90	1·07
Brassidic acid	7·2	—	—	—	—	1·28
Stearic acid *	7·2	—	—	—	—	1·23
Oleyl alcohol	3	—	1·53	1·55	1·57	—
Elaidyl alcohol	3	—	1·68	1·75	1·85	1·90

* Schulman and Marsden (*loc. cit.*).

For the same number of molecules per sq. cm., the values of μ are very nearly constant for the *cis*-unsaturated acids, *i.e.*, they are independent of the position of the double bond in the hydrocarbon chain. Furthermore, the values of μ for the *trans*-unsaturated acids are equal to those for the saturated acid (myristic). These facts indicate that the double bond, when removed by at least four CH_2 groups from the carboxyl group, does not contribute to the vertical moment of the dipole. This conclusion is not in agreement with that of Hughes (*loc. cit.*), since he found the values of μ for oleic and *cis*-petroselinic acids ($2{\cdot}1 \times 10^{-19}$ e.s.u.) to be slightly greater than that for myristic acid ($1{\cdot}8 \times 10^{-19}$ e.s.u.). The effect of the double bond when adjacent to the carboxyl group has, however, been clearly demonstrated by Hughes, who found the electric moment ($4{\cdot}2 \times 10^{-19}$ e.s.u.) of $\alpha\beta$-*iso*oleic acid to be approximately double that of the saturated acid (stearic) in the corresponding state. As indicated above, the double bond itself does not contribute to the vertical dipole moment of unsaturated acids, but when adjacent to the carboxyl group it causes an induction in the polar group.

The slope of the surface-potential curves of a *trans*-unsaturated compound is slightly greater than that for the corresponding *cis*-isomer (seen graphically in Fig. 1—4). This results from the more symmetrical structure of the chains in the *trans*-compounds, which allows the whole molecule to orientate in a more nearly vertical position than in the *cis*-isomers. Since the values of μ for the *trans*-unsaturated acids are equal to those for myristic acid, the average orientation of the polar groups must be the same; this provides further evidence of the similarity of the *trans*-isomeric acids and saturated acids.

There is an abrupt change of slope of the surface-potential curves in those films which are transformed by compression from the liquid-expanded state to the solid-condensed state (Figs. 1—4). This change must be associated with a reorientation of the polar group.

It is worthy of mention that the extrapolated surface-potential curves of the unsaturated acids (p_H 3) intercept the ordinate axis at small values of ΔV (largest value found, 30 mv.—for *trans*-petroselinic acid). According to the views expressed by Schulman and Hughes (*Proc. Roy. Soc.*, 1932, *A*, **138**, 430), this indicates negligible contribution of the ions in the substrate to the surface potential of the acid films, a zero effect of the substrate being fulfilled when the extrapolated curve passes through the origin. On ionisation of the films (p_H 7·2) the intercept values of the surface potential of the films in the expanded state are much larger (> 80 mv.), indicating, among other effects, the absorption of ions by the monolayer from the underlying solution.

Langmuir (*J. Chem. Physics*, 1933, **1**, 756) has shown that the conception of a duplex film for monolayers in the liquid-expanded state leads to the following equation of state:

$$(F - F_0)\,(a - a_0) = kT$$

where F = force in dynes/cm. exerted by the monolayer on a movable barrier, F_0 = negative spreading force of the hydrocarbon chains, a = area (sq. A.) occupied per molecule, and a_0 = empirical constant. If F and a are considered as variables, the above is a rectangular hyperbolic equation, with asymptotes at $F = F_0$ and $a = a_0$.

The force–area curves calculated by using the values of a_0 and F_0, shown in the Table III, agree remarkably well with the experimental curves, except at high pressures. The calculated erucic acid curve (p_H 7·2) does not agree as well as those of the other liquid-expanded films.

TABLE III.

p_H of substrate.	Compound.	a_0, A.^{2}.	$-F_0$, dynes/cm.
2	Oleyl alcohol	15·76	12·63
2	Oleic acid	19·5 (19·9)	11·9 (11·2)
7·2	,,	18·0	10·0
2	*cis*-Petroselinic acid	18·5	13·25
7·2	,, ,,	17·7	10·7
2	Erucic acid	18·5	13·75
7·2	,,	15·7	11·0
2	Elaidic acid	15·95	12·1
7·2	,,	16·15	10·85
2	*trans*-Petroselinic acid	15·5	12·66
7·2	,, ,,	14·2	10·0

The values of a_0 and F_0 for oleic acid calculated by Langmuir from the experimental curve as given by Adam and Jessop (*Proc. Roy. Soc.*, 1928, *A*, **120**, **473**), and shown in parentheses in the above table, agree very well with those determined in this investigation.

Langmuir has indicated that a_0 will be equal to the area per molecule (18·6 A.^{2}) for close-packed chains on the basis of the existence of only repulsive forces of very short range, but since there is evidence of short-range attractive forces between polar groups, then such forces will tend to decrease the apparent value of a_0. As the results in Table III indicate, the values of a_0 for the films on a neutral substrate (p_H 7·2) are smaller than the values of a_0 for the films spread on an acid substrate. This decrease in a_0 is to be expected as a consequence of the ionisation of the film molecules and a subsequent increase in attractive forces between head groups.

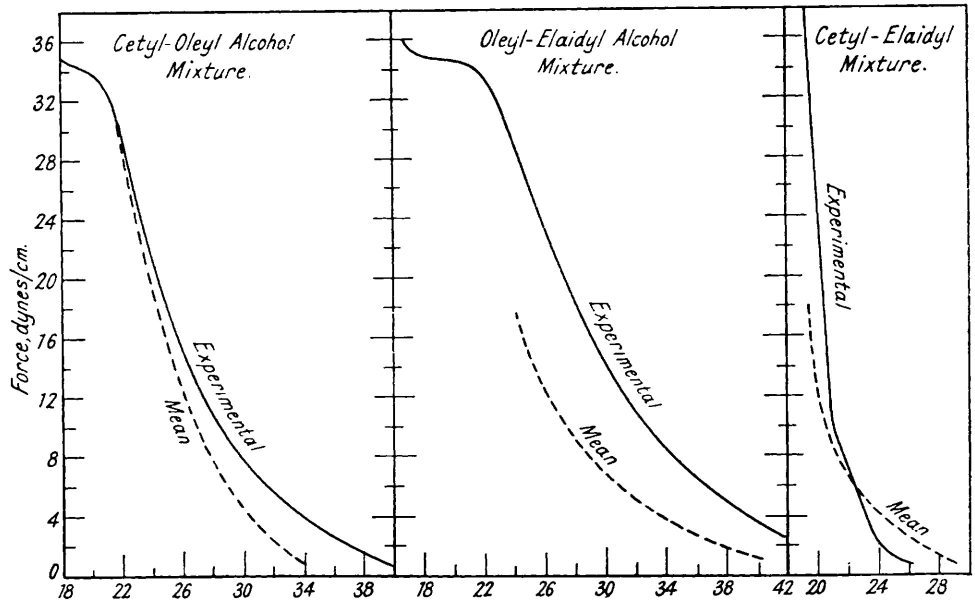
Owing to the closer packing possible for their more symmetrical structures, the values of a_0 for the *trans*-compounds are less than those for the *cis*-isomers by approximately 3 A.^{2}.

The smaller values of $-F_0$ on neutral substrates may be ascribed to an increased hydration of the terminal head groups causing a reduction in the van der Waals forces between the lower portions of the hydrocarbon chains.

Equimolecular Mixed Monolayers.—The foregoing experimental data suggest that the configuration of the *trans*-unsaturated acids is similar to that of the saturated acids, and that in both these compounds interlocking of the chains occurs. In the case of the *cis*-compounds, not only is there no interlock, but a greater expansion and the formation of an oil lens distinguishes these from the first two classes of compound. These views are confirmed by examining the characteristics of equimolecular mixed films of the saturated cetyl alcohol with elaidyl (*trans*) and oleyl (*cis*) alcohols severally. These are shown in Fig. 6.

The " calculated " curves depicted show the mean molecular area on the assumption that the component molecules have no effect upon each other. We note that in the cetyl–elaidyl mixed film condensation takes place at high areas; this is followed by a slight expansion at lower areas, forming a stable, very incompressible solid film at 20 A.^{2}, which is homogeneous to the collapse point at areas below 19 A.^{2}. The cetyl–oleyl alcohol mixed film, on the other hand, shows no evidence of such interlock but reveals an initial expansion of 5 A.^{2}. This diminishes with increasing pressure, and at 20 A.^{2} and a pressure of 35 dynes/cm. the oleyl alcohol is forced out of the mixed film under conditions where this component forms an oil lens ($F = 35{\cdot}6$ dynes/cm., $A = 21$ A.^{2}). A mixed film of oleyl and elaidyl alcohols behaves in a similar manner to the *cis*-unsaturated–saturated alcohol mixture.

FIG. 6.



Oxidation of the Isomeric Unsaturated Acids.—The oxidation of erucic and brassidic acids in bulk phase yields two dihydroxy-isomers (Hilditch, J., 1926, 1828). In acid solutions, erucic acid yields dihydroxybehenic acid, m. p. 100°, and brassidic acid forms the isomer with m. p. 130° : these will be referred to as the " *cis* "- and the " *trans* "-dihydroxy-acid respectively. According to Hilditch (*loc. cit.*), an inversion occurs in alkaline solution, erucic and brassidic acids forming respectively the " *trans* "- and the " *cis* "-dihydroxy-acid.

In an earlier investigation (Hughes and Rideal, *Proc. Roy. Soc.*, 1933, *A*, **140**, 253) the oxidation rates of monolayers of oleic and *cis*-petroselinic acids by dilute permanganate were followed at constant area, and it was found that the pseudo-unimolecular constant decreased on compression. Examination of the force–area characteristics, however, reveals the fact that in the area region where these acids form homogeneous liquid-expanded films, the oxidation products form unstable vapour-expanded monolayers. Changes in reaction velocity at different areas under these conditions cannot be interpreted as solely due to changes in molecular orientation. In this investigation, accordingly, the reaction kinetics were followed by measuring the rate of change of area at constant pressure, such pressures being employed that the reaction product formed a stable film.

Erucic acid was spread on 0·005% potassium permanganate + N/100-sulphuric acid substrate at $F = 2$ and $F = 8$ dynes/cm. The film expands rapidly at first, then more slowly, followed by eventual contraction, and solution of the products of oxidation. It is interesting to note that the dihydroxy-acids themselves are stable when spread on this substrate. The ΔA–time curves are shown in Fig. 7.

FIG. 7.

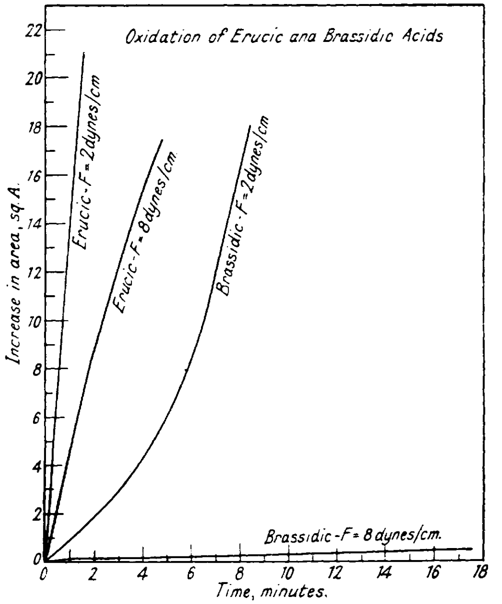
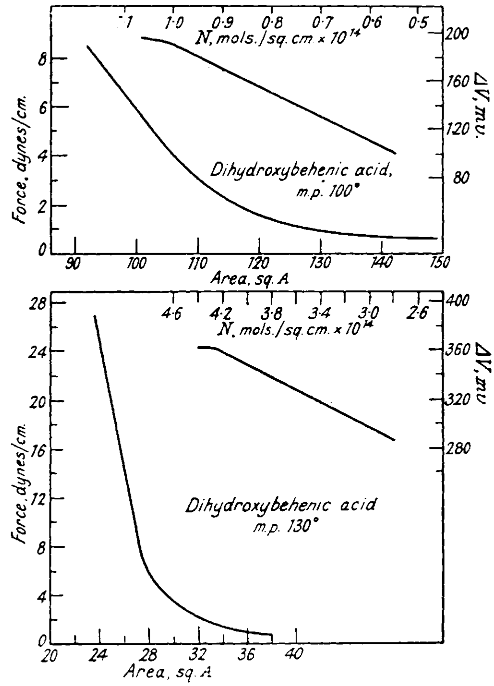


FIG. 8.



The initial portions of the curves are of unimolecular form, and the velocity constant calculated from the usual expression, $(A_t - A_\infty)/(A_0 - A_\infty) = e^{-kt}$, gave the following values :

Force, dynes/cm.	Area, A.².	k_{uni} (min.⁻¹).	Force, dynes/cm.	Area, A.².	k_{uni} (min.⁻¹).
2	44·0	0·4	8	36·8	0·3

The decrease in k_{uni} on compression indicates a decrease of the accessibility of the double bond to the oxidising agent.

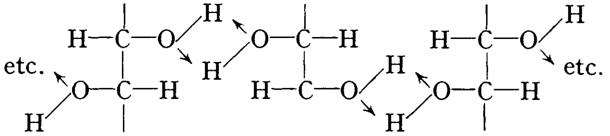
It was found that in the case of brassidic acid, permanganate solution between the chains was picked up mechanically during the process of spreading; consequently, the monolayer was spread on the acid substrate, compressed to $F = 8$ dynes/cm., and permanganate subsequently injected to give a concentration of 0·005%. At $F = 8$ dynes/cm. the oxidation rate of brassidic acid is negligible, the film expanding by only 0·5 A.² in 20 minutes. On decreasing the pressure to 2 dynes/cm., a rapid expansion takes place. The curve is shown in Fig. 7, and is not unimolecular. This is due to the fact that there is a marked interaction in mixed films of brassidic acid and its oxidation product. In the early stages the brassidic acid causes a condensation of the oxidised acid; an expansion of the brassidic acid by the vapour-expanded dihydroxy-acid follows during the latter part of the reaction.

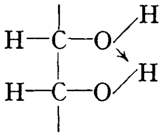
The alteration in velocity of oxidation of the two unsaturated acids on compression is very different. The *trans*-compound is more sensitive to compression, since the film is converted on release of the pressure, from $F = 8$ to $F = 2$ dynes/cm., from a solid into a liquid, whilst in erucic acid compression of the liquid film causes a smaller decrease in the reaction velocity. The complete inhibition of the oxidation of the brassidic acid in the solid state provides further evidence of the close-packed structure of the *trans*-acids.

Dihydroxy-acids.—In Fig. 8 are shown the *F–A* and ΔV–n curves for the two dihydroxy-acids; the " *cis* "-acid forms films of the vapour-expanded type, as would be anticipated for molecules which have two possible points of attachment to the substrate, *viz.*, the carboxyl and the two hydroxyl groups. The value of μ for this dihydroxy-acid is $5{\cdot}0 \times 10^{-19}$ e.s.u. Compared with the value to be expected ($\Delta\mu \simeq 4{\cdot}0 \times 10^{-19}$ e.s.u.) on the assumption that the dipole moments are additive, the observed increase in μ ($\Delta\mu \simeq 3{\cdot}0 \times 10^{-19}$ e.s.u.) on addition of the two hydroxyl groups indicates appreciable interaction between these adjacent groups.

The " *trans* "-acid, on the other hand, forms homogeneous condensed films at 34 A.^{2}, and behaves as an elastic solid up to 26 A.^{2}, beyond which it is converted into a strong solid film. The value of μ is $2{\cdot}3 \times 10^{-19}$ e.s.u. ($n = 4 \times 10^{14}$ mols./cm.^{2}), which is approximately the same as for the corresponding unsaturated acid (brassidic). The non-hydrophilic character of the two hydroxyl groups in the *trans*-position, the formation of a solid film, and the disappearance of any dipole contribution from these groups suggest that there is hydrogen bonding between adjacent molecules forming a polymeric linkage (I), as may possibly occur in other laterally adhering chain systems such as cellulose. In the case of the " *cis* "-dihydroxy-acid the formation of polymeric molecules is prevented, since interaction occurs between adjacent hydroxyl groups in the single molecule of the type (II). Such interaction between these groups has been clearly demonstrated by Pauling from the infra-red measurements on catechol (*J. Amer. Chem. Soc.*, 1936, **58**, 94).

(I.)





(II.)

It is interesting to note that the oxidation products of both erucic and brassidic acids in the form of monolayers on the dilute acid permanganate appear to be identical, and to correspond most closely with the properties of the " *cis* "-dihydroxy-acid as described by Hilditch: the limiting areas indicated a loss of as much as 20% of the " *cis* "-dihydroxy-acid from the surface. There is thus some evidence for a directive oxidation due to orientation at an interface.

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