324. *A Study of the Variations produced by Sublimation in the Infra-red Spectra of Some Substituted Succinic Acids.*

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Changes observed in the infra-red spectra of (±)-methylsuccinic acid, (+)-methylsuccinic acid and (±)-chlorosuccinic acid after sublimation are reported. These changes are best explained by assuming that the sublimates contain at least one other rotational isomer than is present in the original crystallised form. Confirmatory evidence for the existence of rotational isomers of (±)-methylsuccinic acid has been obtained from dipole-moment measurements.

WHILE establishing the identity of a sample of methylsuccinic acid by means of its infra-red spectrum, it was noticed that purification of the acid by sublimation produced specimens with low melting points and marked changes in their infra-red spectra when compared with those of samples purified by recrystallisation from solution (Grove, MacMillan, Mulholland, and Zealley, to be published). That the changes were not due to anhydride formation was ascertained by means of chemical analysis and by the fact that no characteristic anhydride bands were found in the spectra near 1800 cm.$^{-1}$. In addition, it has been reported by Adams and Anderson (*J. Amer. Chem. Soc.*, 1951, **73**, 136) that molecular distillation of dibasic and methyl-substituted dibasic acids at temperatures much higher than those used in the present work does not cause anhydride formation. These observations seemed to require investigation from the point of view of the characterisation of organic molecules by their infra-red spectra, if for no other reason, and the results of a qualitative study of the cause of such changes are now reported.

Similar changes were observed in the infra-red spectra of (±)- and racemic methylsuccinic acids and of (±)-chlorosuccinic acid after sublimation. Sublimation of *as*-dimethylsuccinic and *meso*-dichlorosuccinic acids caused their melting points to be lowered but no change was produced in their spectra, but malonic and glutaric acids showed no change in either melting point or spectra on sublimation.

EXPERIMENTAL

Spectroscopic Measurements.—The infra-red spectra were all obtained from solid samples of the acids which were ground to fine powders and suspended in thin films of " Nujol " between two rock-salt plates. The spectra of crystallised and sublimed samples of (±)-methylsuccinic acid in the regions of " Nujol " absorption (7μ and 3μ) were obtained by suspending the powdered acids in hexachlorobutadiene.

A modified Hilger D.209 spectrometer was used, working as a single-beam instrument and fitted with a 30° rock-salt prism on a Littrow mounting. Absorption due to atmospheric water vapour was reduced to a low level by enclosing the instrument in an air-tight " Perspex " case through which dry air was circulated. Hydrocarbon bands of known frequency, together with atmospheric carbon dioxide and residual water vapour bands, were used for frequency calibration. The calibration is considered to be accurate to $\pm$3 cm.$^{-1}$ in the region 750—1800 cm.$^{-1}$ and to $\pm$10 cm.$^{-1}$ at higher frequencies. During the recording of spectra from 750 cm.$^{-1}$ to 1800 cm.$^{-1}$ the spectrometer slit was closed in stages from a width of 0·6 mm. at the longer wave-length end of this range to 0·06 mm. at the shorter. The energy background was measured by replacing the samples by two rock-salt plates of the same thickness as those used for supporting the samples, and the absorption curves were then plotted in the usual way. No allowance was made for scattered radiation and therefore, although approximately equivalent sample thicknesses were used for each spectrum, it is not possible to compare the intensities of the bands in any one spectrum with those in another. However, as the slit widths were constant for approximately the same frequency ranges in each spectrum, it is possible to compare the relative intensities of the bands in any one spectrum with the relative intensities of those in others.

Preparation of Samples.—Commercial samples of malonic, succinic, glutaric, ($\pm$)-chlorosuccinic, and *meso*-dichlorosuccinic acids were recrystallised to constant m. p. from suitable solvents. ($\pm$)-Methylsuccinic acid was prepared as described in *Org. Synth.*, **26**, p. 54, and resolved through its strychnine salt (Ladenburg, *Ber.*, 1895, **28**, 1170). It had $[\alpha]_D^{19}$ +10°. *as*-Dimethylsuccinic acid was prepared by condensing acetone with cyanoacetic ester and addition of hydrogen cyanide to the resulting ethyl α-cyano-β-methylcrotonate, followed by hydrolysis and decarboxylation of the product in acid solution.

Microanalyses for carbon and hydrogen, carried out by Mr. W. Brown on samples of methylsuccinic acid before and after sublimation, were found to be virtually identical (Found, for specimen crystallised from water and dried *in vacuo* at 20° over P_2O_5 : C, 45·5; H, 6·1. Found, for a specimen sublimed at 80—90°/10^{-3} mm. and dried as above : C, 45·3; H, 6·0. Calc. for $C_5H_8O_4$: C, 45·4; H, 6·1%).

The acids were sublimed as follows, small molecular stills being used consisting of two concentric glass tubes held vertically and closed at their lower ends. The tubes fitted together at their upper ends by means of a standard joint, the free space separating their lower ends being about 5 mm. A small amount of the acid to be sublimed was placed in the bottom of the outer tube, cold water was circulated through the inner tube and the annular space between the tubes evacuated by means of a mercury-diffusion pump. The lower end of the still was then placed in an oil-bath which was heated to, and kept at, the required temperature. The temperature of the oil-bath and the pressure inside the still in each case are given in Table 1, together with observed m. p.s of the acids. The melting points are uncorrected but the same thermometer was used for the comparison of melting points before and after sublimation.

TABLE 1.

Acid	Solvent for recrystn.	M. p.	Conditions of sublimation (°c/mm. Hg)	M. p. after sublimation
Malonic	Benzene–ether	134°	70—80/3 × 10^{-4}	134°
Succinic	Water	186	70—80/3 × 10^{-4}	181—182
Glutaric	Benzene–ether	96—98	55—60/5 × 10^{-5}	96—98
($\pm$)-Methylsuccinic	Chloroform–light petroleum	113—114	150/5 × 10^{-4}	110—111
	Water	113—114	70—80/5 × 10^{-4}	108—109
(+)-Methylsuccinic	Benzene	106—107	90/3 × 10^{-3}	105—106
as-Dimethylsuccinic	Water	141—142	70—75/5 × 10^{-4}	137—139
	Water	141—142	155/5 × 10^{-4}	141—142
($\pm$)-Chlorosuccinic	Ethyl acetate–light petroleum	152—153	65—70/3 × 10^{-4}	146—148
meso-Dichlorosuccinic	Ether–light petroleum	217 (d)	145/3 × 10^{-3}	204—206

Dipole-moment Measurements.—The dipole moments of the sublimed and crystallised forms of ($\pm$)-methylsuccinic acid in benzene solution were measured by Dr. R. G. Wilkins. All the measurements were made at 25° in an apparatus based on that of Hill and Sutton (*J.*, 1949, 2313). The use of very dilute solutions was necessitated by the low solubility of both forms of the acid in benzene, but this had the advantage of reducing intermolecular association. Complications arising from this last effect were minimised by using approximately the same concentration of the solutes for all the measurements. Even at the low concentrations used (0·006M) the solutions appear to be supersaturated, for gentle warming was necessary in their preparation, and after standing for a day in a stoppered flask at room temperature the solutes invariably crystallised out.

The moments were calculated in the usual way by using Jensen's approximate formula (*Acta Chem. Scand.*, 1949, **3**, 479) for the total polarisation (P_M) and the usual relationship $P_O = P_M - P_R$, for the orientation polarisation, where P_R is the refractivity of the solute calculated from the bond refractivities. Finally, the dipole moment was obtained in Debye units: $\mu = 0{\cdot}22\sqrt{P_O} = 0{\cdot}22\sqrt{P_M - P_R}$. Two measurements were made on each form of (±)-methylsuccinic acid, and the results are given below:

(i) (±)-Methylsuccinic acid (crystallised form)

10^3C	ε_s	P_M	P_R	P_O	μ, D
6·092	2·2735	26·3	28·35	0	0
6·169	2·2738	34·0	28·35	5·65	0·52

(ii) (±)-Methylsuccinic acid (sublimed form)

10^3C	ε_s	P_M	P_R	P_O	μ, D
6·212	2·2742	45·1	28·35	16·75	0·90
6·289	2·2745	52·5	28·35	24·15	1·08

RESULTS

The frequencies of the absorption bands in the spectra of (±)- and (+)-methylsuccinic acid, together with those of (±)-chlorosuccinic acid, throughout the region 750—1750 cm.$^{-1}$ are listed in Table 2, and some of the absorption spectra are presented in Figs. 1 and 2. In the following paragraphs some of the salient features of the various spectra are noted.

(±)-*Methylsuccinic acid.* In Fig. 1 are shown the spectra of (±)-methylsuccinic acid when (*a*) crystallised from water, (*b*) sublimed at 70—80°/5 × 10^{-4} mm., (*c*) sublimed at 150°/5 × 10^{-4} mm. It can be seen that sublimation causes an increase in the number of absorption bands in the spectrum, the changes produced being summarised as follows. The band at 850 cm.$^{-1}$ is replaced by one at 830 cm.$^{-1}$. There is marked weakening of the band at 903 cm.$^{-1}$ and slight lowering in frequency of the 950 cm.$^{-1}$ band, a slight shoulder appearing on the side of the latter at about 970 cm.$^{-1}$. Two new weak bands appear at 1050 and 1150 cm.$^{-1}$ and a strong band appears at 1230 cm.$^{-1}$. The strong band at 1330 cm.$^{-1}$ with a shoulder at about 1300 cm.$^{-1}$ is replaced by three bands of lower intensity at 1264, 1296, and 1340 cm.$^{-1}$, and the band at 1435 cm.$^{-1}$ moves to a slightly higher frequency (1441 cm.$^{-1}$) revealing a slight shoulder

TABLE 2. *Frequencies (in cm.$^{-1}$) of absorption bands of some substituted succinic acids before and after sublimation.*

(Figures in parentheses denote shoulders on the sides of other bands. The letters denote band intensities as follows: vw = very weak, w = weak, *m* = *medium*, s = strong, vs = very strong.)

(±)-Methylsuccinic acid		(+)-Methylsuccinic acid		(±)-Chlorosuccinic acid	
Crystallised	Sublimed	Crystallised	Sublimed	Crystallised	Sublimed
—	—	—	785 vw	—	780 m
—	—	—	812 vw	809 m	(810)
—	833 w	—	835 *m*	—	—
852 w	—	855 w	—	—	—
—	(880)	—	—	(870)	(890)
903 m	(900)	903 w	—	—	—
951 s	942 s	938 s	952 s	932 s	945 s
—	(970)	—	—	—	(965)
1048 vw	(1060)	(1055)	(1044)	—	—
1073 m	1081 m	1070 m	1087 m	—	1085 w
—	—	1098 vw	1108 w	—	—
1136 m	(1135)	1137 m	1140 w	—	—
—	1149 w	—	—	—	—
—	—	—	—	—	1192 m
1205 s	1210 s	1205 s	1210 s	1201 s	1208 s
—	1232 s	—	1233 s	1238 vw	—
1254 vw	—	(1255)	—	—	(1255)
—	1267 m	—	1261 s	—	—
(1300)	1297 m	—	1301 s	1307 s	(1295)
1331 s	—	1322 s	—	—	1315 s
—	1342 m	—	1347 m	—	—
1380 vw	(1380)	—	—	—	—
—	(1418)	—	(1417)	—	—
1435 s	1441 s	1430 s	1443 s	1437 s	1438 s
1475 m	(1470)	—	—	—	—
1701 vs	1701 vs	1705 vs	1705 vs	1723 vs	1723 vs

at about 1420 cm.$^{-1}$. However, no change can be detected in the frequency of the very strong band at 1700 cm.$^{-1}$, within the limits of experimental accuracy. At higher frequencies (2000—3500 cm.$^{-1}$), it is not easy to analyse differences between the spectra of crystallised and sublimed samples owing to the poor resolving power of the rock-salt prism in this region, but it appears that sublimation causes the absorption beginning at about 2400 cm.$^{-1}$ to get broader and less intense compared with the absorption maximum at 2900 cm.$^{-1}$.

Comparison of the three curves in Fig. 1 reveals that sublimation of the acid at 150° causes less strongly marked changes in its spectrum than does sublimation at 80—90°. This is shown, for example, by the strengths of the bands at 900, 1135, and 1230 cm.$^{-1}$ relative to those at 950—940, 1150, and 1205 cm.$^{-1}$, respectively.

FIG. 1.

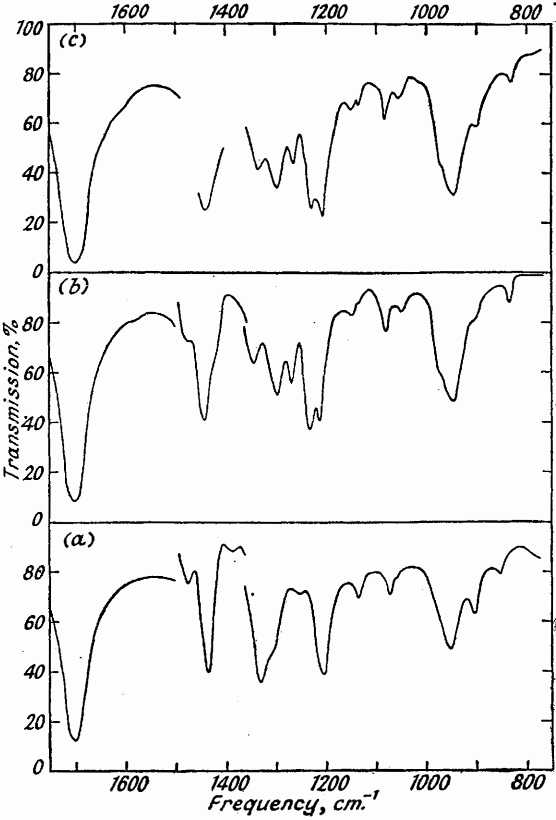


FIG. 2.

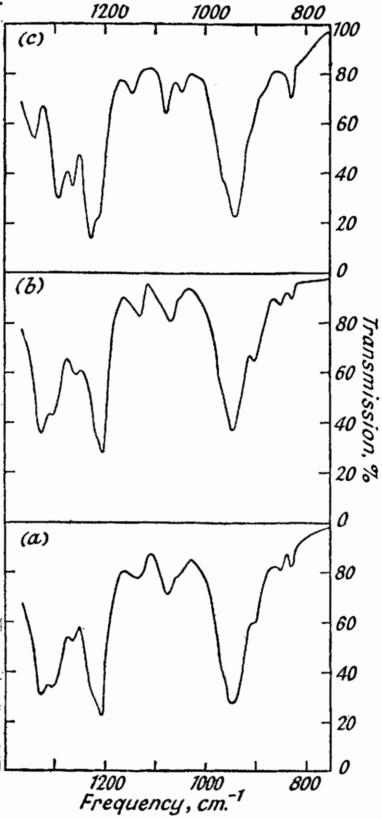


FIG. 1. *Infra-red spectra of* (±)*-methylsuccinic acid :* (a) *crystallised from water ;* (b) *sublimed at* 70—80°/5 × 10^{-4} *mm. ;* (c) *sublimed at* 150°/5 × 10^{-4} *mm.*

FIG. 2. *Infra-red spectra of sublimed* (±)*-methylsuccinic acid obtained after :* (a) *recrystallisation from aqueous solution at room temperature ;* (b) *recovery from the sodium salt at room temperature ;* (c) *refluxing its aqueous solution for* 30 *minutes.*

Some experiments were performed to investigate the reconversion of the sublimed form of (±)-methylsuccinic acid into the crystallised form, and absorption curves between 750 and 1350 cm.$^{-1}$, obtained from the samples of the sublimed acid after various treatments in solution, are given in Fig. 2. Fig. 2*c* is the spectrum of the sublimed acid after it had been heated under reflux in aqueous solution for 30 minutes, and the solvent then completely removed at room temperature and reduced pressure over phosphoric oxide. The spectrum is little changed from that of the sublimed acid, the only significant difference being the relative intensities of the bands at 1230 and 1210 cm.$^{-1}$. Some of the solution used in this experiment was refluxed for a further 2 hours and the solvent then completely removed by standing in a desiccator over phosphoric oxide. The resulting acid had a spectrum (not shown) identical with that of the normal crystallised acid. A more dilute solution of the sublimed acid was then evaporated at room temperature over phosphoric oxide and the recovered acid was found to have a spectrum in between those of the sublimed and the crystallised form (Fig. 2*a*). The reconversion seems therefore to be facilitated by using dilute solutions and this probably has two causes: (i) that the time taken to remove the solvent is increased, and (ii) that in aqueous solutions reconversion into the crystallised form proceeds more rapidly through the anion than through the acid itself. Both the 830 and the 850 cm.$^{-1}$ band were present, the 900 cm.$^{-1}$ band had begun to reappear, the 1230 cm.$^{-1}$ band was only apparent as a shoulder on the side of the 1205 cm.$^{-1}$ band, and the bands near 1300 cm.$^{-1}$ were nearly restored to those of the crystallised form. A similar result was found when some of the sublimed acid was converted into its sodium salt and then recovered, all the necessary operations being carried out at room temperature (Fig. 2*b*). Lastly, it was found that the sublimed acid could be recovered with an unchanged spectrum when recrystallised from non-polar solvents such as benzene and toluene.

(+)-*Methylsuccinic acid.* The spectrum of this acid, crystallised from benzene, is very similar to that of the (±)-modification crystallised from water, the main difference being that the band occurring at 950 cm.$^{-1}$ in the latter occurs at a slightly lower frequency in the former. The changes produced in the spectrum of the active form by sublimation are closely parallel to those found for the racemic form. The principal differences between the two cases are that with the active form the 950 cm.$^{-1}$ band is raised in frequency by sublimation, and although it is broad it shows no shoulders, that weak new bands occur at 785, 821, and 1108 cm.$^{-1}$, and that the relative intensities of the bands between 1200 and 1350 cm.$^{-1}$ are altered. Small differences in frequency of some of the bands also occur.

(±)-*Chlorosuccinic acid.* The spectrum of the crystallised acid is similar in form to that of crystallised methylsuccinic acid, as are some of the changes caused by sublimation; *e.g.*, strong bands occur at 932, 1201, 1307, 1437, and 1724 cm.$^{-1}$, together with a band of medium intensity at 810 cm.$^{-1}$. Sublimation causes the 810 cm.$^{-1}$ band to shift to a lower frequency, the 932 cm.$^{-1}$ band to shift to a higher frequency and to develop shoulders, a new band to appear near 1080 cm.$^{-1}$, the 1201 cm.$^{-1}$ band to split into two components, and lastly, the 1307 cm.$^{-1}$ band to become just resolvable into two components at 1290 and 1315 cm.$^{-1}$. As with (±)-methylsuccinic acid, the changes are less marked when the sublimation temperature is raised.

Other dibasic acids. Of the spectra of other dibasic acids which were measured during the present work, only the salient features will be mentioned here. They all show broad absorption bands in the region of 2600 cm.$^{-1}$ and very strong bands near 1700 cm.$^{-1}$. The acids with α-chloro-substituents have this band at slightly higher frequency than the others. Strong bands occur in all the spectra at 920—950, 1200—1230, 1300—1320, and near 1430 cm.$^{-1}$. Malonic and succinic acids both show two bands in the neighbourhood of 1700 cm.$^{-1}$, presumably owing to symmetrical and antisymmetrical modes of vibration involving C=O stretching. Substitution of comparatively heavy groups, such as methyl or chlorine, at the α-carbon atom seems to weaken the coupling between these two vibrations, for only one C=O band was observed in each of the spectra of dimethylmalonic, methylsuccinic, and chlorosuccinic acid.

DISCUSSION

The bands near 2600 and 1700 cm.$^{-1}$ in the spectra of substituted succinic acids can be assigned quite definitely to vibrational modes involving the stretching of carboxylic O–H and C=O bonds respectively, the low frequency and broadness of the O–H stretching band compared with the O–H band of alcohols being indicative of strong hydrogen bonding between two carboxyl groups, as is well known (Davies and Sutherland, *J. Chem. Phys.*, 1938, **6**, 755).

Assignments of other strong bands characteristic of carboxylic acids to vibrations involving the carboxyl group are less certain. Davies and Sutherland (*loc. cit.*) have assumed from a variety of evidence that the vibration of acetic acid which involves the stretching of the C–O bond causes the absorption band in its spectrum near 1430 cm.$^{-1}$, an assignment in agreement with that of Gillette and Daniels (*J. Amer. Chem. Soc.*, 1936, **58**, 1139). It has also been suggested by Davies and Sutherland that the bands near 1250 and 930 cm.$^{-1}$ are probably due to in-plane and out-of-plane deformation modes of the hydroxyl group. However, Flett (*J.*, 1951, 962) found that many carboxylic acids do not show a strong band in their spectra near 1400 cm.$^{-1}$ and concluded that it is not a good diagnostic band for this type of compound.

The case of the unsymmetrically substituted succinic acids is somewhat different in that two vibrations involving the stretching of C–O bonds should be observed, and the author considers it at least as likely that these modes are responsible for the bands near 1200 cm.$^{-1}$ as that one of them is the cause of the band near 1430 cm.$^{-1}$. Support for this assignment is given later.

Having considered some of the probable causes of absorption in the spectra of the dibasic acids it now becomes of interest to discuss the changes produced by sublimation. This requires some enquiry into the process of sublimation which, for convenience, we can divide into three stages, namely, evaporation, passage through a vapour phase, and condensation. It is well known from spectroscopic and other data that carboxylic acids in the solid state are associated through their carboxyl groups, and that at low pressures and high temperatures the vapour consists to a large extent of the monomeric form. It can therefore be assumed that the first stage of sublimation in a high vacuum causes considerable dissociation of an acid from the dimeric (or possibly with dibasic acids, polymeric) form to the monomeric form. The values of the hydroxyl and carbonyl stretching frequencies of the sublimed acids show that the reverse occurs on condensation, *viz.*, association by hydrogen-bond formation between the carboxyl groups.

Changes in the vibrational spectra of the acids after sublimation might be expected on the grounds that the molecular environment had changed owing to the rapidity of condensation having prevented the formation of the most stable crystalline form, the intermolecular forces thereby being altered. However, this alone does not explain the following points. First, not all the acids investigated showed changes in their spectra after sublimation under identical conditions; secondly, it was found possible to recrystallise the sublimed form of (±)-methylsuccinic acid without causing any significant change in its spectrum, and lastly, the changes produced by sublimation are considered to be too great to be solely attributable to such a cause. However, imperfect crystal formation may well account for the lowering of the m. p.s of the acids after sublimation.

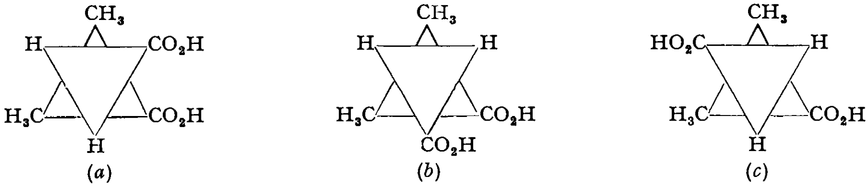
The spectra of crystallised and sublimed forms might also be expected to be different for the same reason as was put forward by Lecomte to explain the differences between the infra-red spectra of the salts of optically active and racemic tartaric acids (" Contribution à l'Étude de la Structure Moleculaire," p. 137, Maison Desoer, Liége, 1947—48). He suggested that crystals of the racemate consist of D- and L-molecules arranged in pairs in such a way that every pair has a centre of symmetry, thereby rendering some of the molecular vibrations inactive towards infra-red absorption. Such an arrangement, necessitating the presence of both optical antipodes in the crystal, cannot take place with either one or other of the active forms, and this explanation was put forward for the occurrence of considerably fewer bands in the spectra of the racemic salts than in those of the optically active ones. It was found in the present work that, although the only two acids which showed changes in their spectra after sublimation contained asymmetric carbon atoms and sublimation might be expected to destroy to some extent the " pairing " of (+)- and (—)- molecules, yet this explanation does not accommodate the fact that the dextrorotatory form of methylsuccinic acid shows parallel changes on sublimation to those found with the (±)-acid. Furthermore, if molecules of this type tended to attain the most symmetrical arrangement by " pairing " in the solid state, *as*-dimethylsuccinic acid would be expected to do so. In fact, no changes were produced in the spectrum of the latter compound by sublimation, and it is concluded that this, in conjunction with the behaviour of (+)-methylsuccinic acid, rules out any explanation of the above type for the phenomena described in this paper. However, the differences between the spectra of (±)- and (+)-methylsuccinic acids may be due to this cause.

It is in the vapour stage of the sublimation process that a state of affairs can be postulated which accounts qualitatively for all the effects produced by sublimation. It has already been assumed that the vapour stage consists, to some unspecified extent, of single molecules of the acid being sublimed and these molecules are presumably able to undergo internal rotation about one or more of their single bonds. If it is assumed that, under the conditions used, the rate of rotational isomerisation is sufficiently high compared with the average rate of passage through the vapour to the condensed phase, then the sublimate should consist of more than one rotational isomer. A considerable amount of evidence has been accumulated which demonstrates the occurrence of rotational isomerism in liquid disubstituted ethanes, such as 1 : 2-dihalogenoethanes, and in *n*-propyl bromide (see Mizushima *et al.*, *J. Chem. Phys.*, 1949, **17**, 591; Brown and Sheppard, *Discuss. Faraday Soc.*, 1950, No. 9, 148; Beach, *Ann. Rev. Phys. Chem.*, 1950, **1**, 196), but so far it has not been possible to obtain more than one rotational isomer of this type in the solid state. However, rotational isomerism in the solid state is well known in the case of heavily *o*-substituted diphenyls and has been reported for tin and lead tetraethyls (Staveley *et al.*, *J.*, 1950, 2290). With succinic acids the position is complicated by the fact that rotation can occur about the bonds connecting the carboxyl carbon atoms to the hydrocarbon nucleus in addition to rotation about the central carbon–carbon bond.

The changes produced in the spectra by sublimation are consistent with the occurrence of rotational isomers. In the first place, the changes are so marked that they must be due to some considerable change in the molecular configuration. Also, it can be seen that one of the most characteristic changes is the splitting of the band which occurs near 1200 cm.$^{-1}$ in all the spectra into two components. It has already been suggested that bands near 1200 cm.$^{-1}$ can be attributed to modes involving the stretching of carboxylic C–O bonds, and that in monosubstituted succinic acids there should be two such modes. If the crystallised forms of the acids have the carboxyl groups situated *trans* to each other (as is probable), one of these modes will produce only a weak infra-red absorption which could well be masked by the strong absorption due to the other. The rotational isomers which are possible would have the carboxyl groups less symmetrically situated and then both C–O stretching modes would cause strong absorption and two bands should be observed.

The behaviour of the disubstituted and unsubstituted succinic acids can be understood if the interpretation of the behaviour of the monosubstituted acids as due to rotational isomerisation is correct. The case of the disubstituted acids being taken first, there are three possible reasons why they show no changes in their spectra after sublimation, *viz.*, (i) that the hindrance to internal rotation is large enough to prevent any appreciable isomerisation during the passage of molecules through the vapour phase; (ii) that the energy difference between the isomers is so great that even at the temperature of sublimation the equilibrium strongly favours the most stable isomer; (iii) that the energy difference between permissible isomers is so small that the equilibrium between them is fairly independent of temperature. Neglecting rotation of the methyl and carboxyl groups and assuming that staggered configurations are the most stable (Beach, *loc. cit.*), we can see that there are three possible rotational isomers of, say, *as*-dimethylsuccinic acid. Of these, two [Fig. 3, (*a*) and (*b*)] are equivalent and an equilibrium involving them alone would not be temperature-variable. In addition, these two isomers, being mirror images, would be indistinguishable by their infra-red spectra. If such an equilibrium is present during sublimation, then the formation of the third isomer [Fig. 3 (*c*)] must be prevented either by a high activation energy for rotation of a carboxyl group past a β-methyl group or else by the third isomer being very unstable. Alternatively, the third isomer is the most stable one and the transition to either of the other two is not achieved under the conditions of sublimation. Similar considerations apply to the case of *meso*-dichlorosuccinic acid.

FIG. 3.



(*a*) (*b*) (*c*)

Two factors provide explanations for the difference in behaviour between succinic acid and its monosubstituted derivatives. First, the rate of isomerisation must be greater in the former than in the latter case as there is one less bulky substituent to hinder internal rotation; *i.e.*, the potential energies of the " eclipsed " configurations of succinic acid are less than those of the corresponding configurations of the monosubstituted acids. The activation energy for isomerisation thus being lower for succinic acid than for, say, methylsuccinic acid makes it more difficult to " freeze " the equilibrium present in the vapour by condensation on a cold surface. The second factor is that the difference in energy between the two most probable rotational isomers of methylsuccinic acid (Fig. 4) is expected to be less than that between the isomers of succinic acid. An analogous pair of molecules for which the equilibrium between rotational isomers has been compared consists of propylene dichloride and ethylene dichloride. Morino, Miyagowa, and Haga (*J. Chem. Phys.*, 1951, **19**, 791) have pointed out that the former has a smaller energy difference between two of its isomers than has ethylene dichloride because of the repulsion between the methyl group and a chlorine atom, which occurs in its low-temperature form, but not in its next most stable isomer.

It is thought that the reason for the changes in the spectra of monosubstituted succinic acids being less pronounced when the sublimation temperature is raised is that the temperature of the condensing surface is also raised, particularly when it becomes coated with a fairly thick layer of poorly heat-conducting sublimate. Then condensation at a higher temperature enables more molecules to orient themselves in the configuration stable in the solid state, *i.e.*, the " freezing " of the high-temperature equilibrium between the isomers is less complete.

The factors affecting the reconversion of the sublimed into the crystallised form can also be explained on the basis of rotational isomerisation. Of the conditions used in the present work, reconversion seems to take place most readily by way of the sodium salt in water. The acid itself in water presumably isomerises to its stable form most rapidly through its anion, and for this reason the reconversion takes place more easily in dilute than in concentrated solutions. Prevention of ionisation by the use of non-polar solvents allows the sublimed form to be heated in solution for comparatively long periods without changing its spectrum.

FIG. 4.

(R = CH_3 or Cl.)

The stability of the two forms of methylsuccinic acid in benzene solution suggested a confirmatory test of the theory that rotational isomerisation takes place during sublimation, because it is apparent that a *gauche* isomer must have a significantly larger dipole moment than one in which the carboxyl groups are situated *trans* to each other. It is difficult to calculate with any degree of certainty how large this difference should be, as it appears from dipole measurements (Pohl, Hobbs, and Gross, *Ann. N.Y. Acad. Sci.*, 1940, **40**, 389) that even in dilute solutions such as were used in the present work, carboxylic acids are considerably associated in non-polar solvents. However, it can be expected that if one form of methylsuccinic acid has its carboxyl groups arranged *trans* to each other, its moment should be very small or zero, while a *gauche* form should, from an approximate calculation, have a dipole moment between 1·5 and 2·7 D depending upon the degree of association. The observed moments of 0·25 ± 0·25 D for crystallised and 1·00 ± 0·10 D for sublimed methylsuccinic acid are in qualitative agreement with those expected. Little significance is attached to the discrepancy between the measured dipole moment of the sublimed acid and that calculated for a *gauche* isomer, since the calculation takes no account of dipole interaction, and in addition the sublimed form must contain some of the isomer of lower moment as is indicated by its spectrum (*e.g.*, at 900 cm.$^{-1}$).

Having postulated that the presence of at least two rotational isomers is responsible for the changes produced in the infra-red spectra of methyl- and chloro-succinic acids by sublimation, we can now say something about the configurations which are present. *X*-Ray diffraction has shown that succinic acid crystallises in long chains of centrosymmetrical molecules, the four carbon atoms of each molecule being coplanar, and the carboxyl groups being twisted out of this plane by an angle of about 10° (Morrison and Robertson, *J.*, 1949, 980; Verweel and MacGillavry, *Z. Krist.*, 1939, **102**, 60). Rieck (*Rec. Trav. chim.*, 1949, **63**, 170) found that the high-temperature form of succinic acid has the same molecular configuration but different packing of the chains. It must be concluded that the selection rules for infra-red absorption by succinic acid are considerably modified in the solid state, if the assignments of the bands at 1705 and 1720 cm.$^{-1}$ in its spectrum to symmetrical and antisymmetrical vibrations involving C=O stretching is correct. If, as the dipole measurements and infra-red spectra suggest, crystallised methyl- and chloro-succinic acids have configurations that are analogous to that of succinic acid [represented by the projection formula in Fig. 4 (*a*)] then, it being borne in mind that disubstituted succinic acids seem to show a fairly strong resistance of a carboxyl group to rotation past a β-methyl or chloro-group, the probable configuration of the unstable isomers is given in Fig. 4 (*b*). Consideration of the angles which the planes of the carboxyl groups make with say a plane perpendicular to the $C_{(2)}$–$C_{(3)}$ bond is beyond the scope of the present work.

In conclusion, it is pointed out that, when using infra-red spectra to identify compounds of this type, care must be used in preparing samples for examination if the method is not to produce confusion.

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