

$[\alpha]_D + 209 \rightarrow -45^\circ$ (c , 0.6 in methanol), and is probably α -*p*-toluidine-*N*-glucopyranoside. In the same way we have obtained evidence for the existence of an aniline-*N*-galactoside distinct from the previously known one. It appears to be general, where two isomers have been obtained from the same sugar and amine, that their specific rotations in methanol change to the same final equilibrium value.

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G. P. ELLIS
JOHN HONEYMAN

Department of Chemistry,
King's College,
Strand, London, W.C.2.
Oct. 11.

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The 'Turn Over' Transition of Suberic Acid

A LATTICE transition which is not induced by nuclei or boundaries but takes place simultaneously in the whole of a crystal by the jump of a whole lattice plane is termed 'turn over' (*Umklappen*). Such transitions are observed with certain metals (cobalt, thallium) and especially in the austenite-martensite transition. When, in 1941 in this laboratory¹, the phenomenon was discovered for the first time with an inorganic salt (potassium dichromate), we were informed by Prof. L. Kofler (Innsbruck) that a similar 'flashlike' transition can be observed with suberic acid crystals. The features of this 'turn over', as we have observed it, are described here.

Sufficiently pure suberic acid, molten between two cover glasses in a Leitz heating-stage of a polarizing microscope, crystallizes on cooling at 143° C. in the form shown schematically in Fig. 1 (right). On further cooling, at 90° C., the crystallites, every one separately, suddenly split up into a series of smaller crystallites, separated by striæ perpendicular to the longest dimension of the original crystal, as shown in Fig. 1 (left). The striated form remains unchanged down to room temperature. On reheating, at 90° C., the striæ disappear, again simultaneously and independently over the whole area of an original crystallite or a large part of it, and, by a number of such flashes,

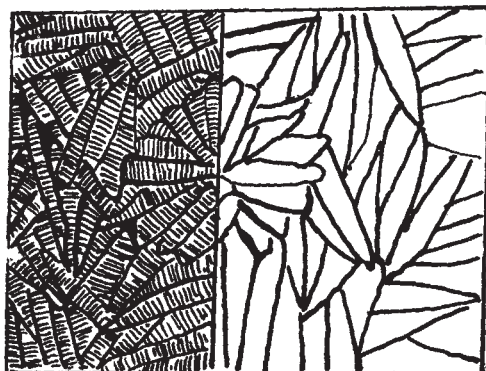


Fig. 1

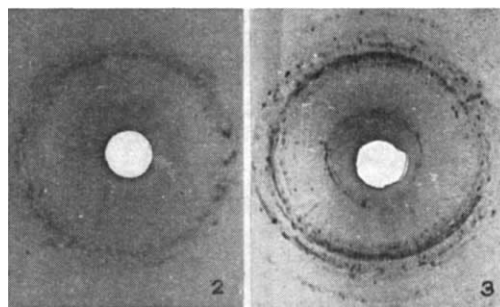


Fig. 2

Fig. 3

the high-temperature picture is restored. This can be repeated many times. This transition of the free acid does not occur with the amide, the ammonium or sodium salt.

X-ray photographs were taken both of the high- and low-temperature forms, with iron $K\alpha$ radiation and a camera diameter of 57.3 mm. Liquid suberic acid was sucked into a piece of Mark capillary surrounding an electrically heated axial platinum wire. The whole was rotated through 120° about the camera axis. The temperature-voltage characteristics of the arrangement being known, it was possible to keep the preparation at the temperature desired or to change its temperature quickly. The high-temperature form, crystallized from the melt between 143° and 90° C., in this arrangement forms large and orientated crystals so that only a few spots appeared on the film. In order to obtain measurable rings, it was necessary to melt the acid for 15 sec. and allow it to crystallize anew above 90° C. once a minute for one hour. Figs. 2 and 3 were obtained from the high- and low-temperature form respectively.

Suberic acid is reported² to crystallize in the monoclinic system with $a = 10.12$ Å., $b = 5.06$ Å., $c = 12.58$ Å., $\beta = 135^\circ$, two molecules lying parallel to c in a base-centred cell. The diagrams, after subtraction of faint platinum lines, were indexed on this basis, and indices, spacings and estimated intensities are given in the accompanying table for the calculated diagram, for the cold- and the hot-form.

X-RAY SPACINGS (d) AND INTENSITIES (I)

hkl	d (calc.)	d (cold)	I (cold)	d (hot)	I (hot)
001	8.88	8.55	5	—	—
002	4.44	4.33	3	—	—
011					
110	4.13	4.06	5	4.30	5
200	3.58	3.73	2	3.80	5
012	3.33	3.50	5	—	—
003	2.96	3.04	2	—	—
210	2.92	2.93	4	3.02	3
120	2.40	2.25	2	2.34	1
300					
202	2.14	2.16	2	—	—
221	1.85	1.84	2	—	—

The cold form corresponds to the calculation without systematic deviations. As for the hot form, it is characteristic that only the interferences $hk0$ appear. This can be seen directly in Fig. 2 where, at the position of the inner circle (001) of Fig. 3, only an 'amorphous ring' appears. This ring appears equally with liquid suberic acid and can be ascribed to the liquid state being present during a quarter of the exposure. Hence, the high-temperature modification shows lattice order only in the directions perpendicular to the c -axis, whereas in the c -direction it is 'liquid'.

For the cold form, the smaller angle at the centring chain in the plane perpendicular to c is calculated to be 71° . On transition to the hot form, within the accuracy of the few lines available, calculation indicates a dilatation of 4.5 per cent in the a -direction and a contraction of 3 per cent in the b -direction. This makes the above-mentioned angle decrease to 67° . The same tendency of the angle to approach 60° (hexagonal arrangement) has been observed by A. Müller³ on heating long-chain paraffins, and is explained by increasing rotation of the carbon chains about the c -axis. If we assume now that at the transition point this rotation begins to cover the full circle, it will eliminate in the hot form a considerable part of the dipole forces between the carboxyl groups of neighbouring parallel chains which, in the cold form, hold these groups in one plane. Thus, a parallel shift of the chains into disordered positions may be made possible.

As for the question why it is exactly that suberic acid shows this interesting type of transition, it is perhaps of interest that the high-temperature modification forms mixed crystals with adipic acid but not with sebacic acid, and that (001) is very weak in the former and strong in the latter. Perhaps the transition point, sharp or not, is situated below room temperature for adipic and above the melting point for sebacic acid, and observable only with suberic acid (only these two acids are comparable, as those with odd numbers of carbon atoms have double elementary cells, see ref. 2).

A flashlike transition has been described also by C. Weygand⁴ for "Tridekansäure"; however, we were unable to verify it, either with tridecylic (tridecanoic) or with myristic (tetradecanoic) acid.

GEORG-MARIA SCHWAB
MICHAEL DEFFNER

Departments of Inorganic and of
Organic Chemistry,
Nikolaos Kanellopoulos Institute,
Piræus.
Sept. 2.

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Molecular Interaction and its Relation to the Formation of Sodium Dodecylsulphate-Cetyltrimethylammonium Bromide Complex

It is well known that anionic and cationic detergents are not compatible in aqueous phase when they are present in equimolecular amounts. Compatibility is only observed for certain ratios which depend upon the molecular structure of both components. Precipitation of anionic by cationic detergents present in equimolar amounts constitutes the basis of one of the methods used for their estimation. The work carried out by Salton and Alexander¹ has shown this method to be applicable for determining small amounts of such pure detergents.

When the reagents are not well purified, the above method of titration is no longer valid, due to traces of polar compounds such as long-chain alcohols,

which are known to interact with the detergent to form a molecular association. Relatively high amounts of hexyl or heptyl alcohol are needed to prevent the precipitation, whereas the presence of octyl or nonyl-alcohol in equimolecular ratio will inhibit the formation of sodium dodecylsulphate-cetyltrimethylammonium bromide complex. For example, an $M/300$ solution of these substances with octyl alcohol will be completely clear when these reagents are in the molecular ratio 1:1:1; in the absence of the alcohol a marked flocculation of the sodium dodecylsulphate-cetyltrimethylammonium bromide complex is observed. It is clear that the alcohol-sodium dodecylsulphate complex is competing with the sodium dodecylsulphate-cetyltrimethylammonium bromide association, and that as a result of the presence of the long-chain alcohols (C_8 , C_9) the anionic detergent has lost certain of its properties. Schulman² has already shown that cholesterol will inhibit precipitation of sodium cetylsulphate by addition of silver nitrate. The results now obtained show that with octyl alcohol a strong molecular interaction occurs and demonstrate the existence of a 1:1 complex of sodium dodecylsulphate-octyl alcohol, a conclusion already reached by Matalon³.

The inhibition of precipitation of anionic by cationic detergents appears then to be due to competition between two types of molecular interaction.

R. MATALON
M. R. J. SALTON
M. COHEN

Department of Colloid Science,
Free School Lane,
Cambridge.
Oct. 12.

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Exchange of Carbon-13 Dioxide between Solid Carbonates and Gaseous Carbon Dioxide

IN connexion with a study of the reaction mechanism of the thermal decomposition of dolomite, we are investigating exchange between carbon-13 dioxide ($^{13}\text{CO}_2$) and solid carbonates at high temperatures. To our knowledge exchange reactions using isotopic tracers between gaseous and solid reactants have, so far, only been carried out^{1,2} on oxides and oxygen-18.

Depending on temperature and partial pressure of carbon dioxide, dolomite can be decomposed either partially to $\text{MgO} + \text{CaCO}_3$ or completely to $\text{MgO} + \text{CaO}$. (Experiments on the isobaric thermal decomposition of dolomite at various pressures of carbon dioxide have been carried out simultaneously and will be published elsewhere.) In order to obtain further information on the reaction mechanism involved, a detailed investigation, particularly on the first stage of decomposition, was thought appropriate. In this case two questions immediately arise: (a) Is calcium carbonate primarily formed from the original dolomite lattice?— $\text{CaMg}(\text{CO}_3)_2 \rightarrow \text{MgO} + \text{CaCO}_3 + \text{CO}_2$. (b) Is dolomite first decomposed to magnesium and calcium oxides, when, under sufficient partial pressure of carbon dioxide, the latter then recombines to form calcium carbonate?—(i) $\text{CaMg}(\text{CO}_3)_2 \rightarrow \text{MgO} + \text{CO}_2 + \text{CaO} + \text{CO}_2$. (ii) $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$.