CRYSTALLOGRAPHY

Mixed Anthrone—Anthraquinone Crystals

A THREE-DIMENSIONAL refinement of anthrone, $C_{14}H_{10}O$ (recorded m.p. 154° C) by Srivastava[1] has shown that it is isostructural with anthraquinone, $C_{14}H_{10}O_2$ (recorded m.p. 286° C) (refs. 2 and 3). The unit-cell dimensions and other crystallographic data are:

$C_{14}H_{10}O$, m.w. 194·22, $P2_1/a$, $Z = 2$

$a = 15{\cdot}80$, $b = 3{\cdot}998$, $c = 7{\cdot}86$ Å $\beta = 101{\cdot}7°$

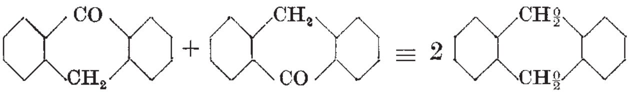
$D_x = 1{\cdot}326$ g cm^{-3} (using corrected value $N = 6{\cdot}02335{\cdot}10^{23}$ appropriate to the units used)

$C_{14}H_8O_2$, m.w. 208·20, $P2_1/a$, $Z = 2$

$a = 15{\cdot}83$, $b = 3{\cdot}97$, $c = 7{\cdot}89$ Å $\beta = 102{\cdot}5°$ (at 20° C)

$D_x = 1{\cdot}428$ g cm^{-3} (corrected)

The similarity between Weissenberg and other photographs of the two compounds is striking. There are small differences, of course, but they have to be looked for. The anthraquinone molecules are centrosymmetrical; the anthrone structure is disordered so that the two molecules in the unit cell each appear to be centrosymmetrical:



The disorder causes the appearance of diffuse layer lines interleaving the 3·998 Å layer lines in anthrone rotation photographs taken about the *b* axis. Both structures are markedly pseudo-orthorhombic.

In the course of a solid-state reaction being investigated by X-ray techniques in this laboratory it was found that the main decomposition product gave photographs corresponding with a somewhat fibrous crystal of anthraquinone. Mass spectrometry showed that some anthrone might also be present, although it was not at first certain whether the anthrone was only produced in the mass spectrometer. The fibrous nature of the decomposition product prevented small differences in intensity from being detected, and the presence of disorder and impurity in the final crystals made melting-point determinations a little uncertain. The question then arose as to whether, if anthraquinone and anthrone were both present, they would in any case form mixed crystals.

Attempts to form mixed crystals by recrystallization from solvents were unsuccessful, because anthrone is much more soluble than anthraquinone in all the following solvents: ethyl alcohol, acetone, acetic acid, benzene and chloroform. These were all tried, but acicular anthraquinone always came down first. It was found, however, that if anthraquinone and anthrone were melted together in known proportions in a sealed tube and the mixture allowed to cool slowly in a vacuum flask, acicular crystals formed which gave the melting-point/composition curve (Fig. 1). This implies that the crystals at any composition were formed by simple solid solution, no ordered structure appearing at any stage, except for pure anthraquinone.

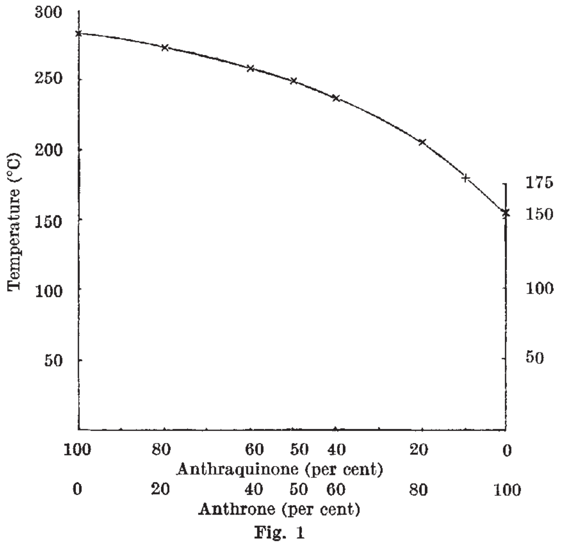


Fig. 1

Weissenberg photographs ([$h0l$] and [$h1l$]) were taken of a single crystal obtained from the 50 : 50 melt, the melting-point being checked on another crystal from the same batch. These Weissenberg photographs were compared with similar photographs of the two end members. The crystal in question proved to be a twin on the ($\bar{2}01$) plane, which is a pseudo-orthorhombic 'axial plane' of the anthraquinone/anthrone structure, and this twinning obscured even the small differences that exist between the two end members of the series. There is no doubt, however, that the structure does correspond closely with that of the end members, anthraquinone and anthrone, and that mixed crystals in any proportions can be formed.

A melting-point determination for the decomposition product mentioned here, carried out in a sealed tube under conditions similar to those used for obtaining the results in Fig. 1, gave 257 ± 1° C. This confirmed that the product was not pure anthraquinone (or anthrone) but that it may have contained up to about 45 per cent anthrone or a lesser amount of anthrone together with other impurities.

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CHEMISTRY

Gamma-ray-induced Polymerization of some Vinyltin Compounds

ALTHOUGH much work has recently been carried out on the syntheses of vinylmetallic compounds[1], work on their polymerization has been surprisingly scarce, especially radiation polymerization. Moreover, these compounds seem to be regarded as substances scarcely polymerizable in general. For example, with triethylvinyltin, one of the compounds treated in this communication, Korshak *et al.*[2] observed the formation of the oligomer, when they heated it with di-*t*-butylperoxide to 120° C under pressure as high as 6,000 atm. (ref. 2).

We have irradiated triethylvinyltin and triphenylvinyltin by γ-rays from cobalt-60 in the ordinary state and observed the formation of the polymeric substances from both compounds.

Triethylvinyltin (b.p. 58°–59° C/13 mm mercury) and triphenylvinyltin (m.p. 38·5°–39·5° C) were synthesized by the reaction of triethyltin chloride and triphenyltin chloride respectively with vinyl Grignard[3]. The monomers were sealed under 10^{-5} mm mercury after vigorous degassing.

When triethylvinyltin was irradiated by γ-rays from cobalt-60 *in vacuo*, it became turbid, and the mixture of the slightly yellowish viscous product, which occupied the major part, and an insoluble white powder was left behind after pumping out the remaining monomer at room temperature. Yields of the polymeric substances are shown in Table 1.

Fig. 1 shows the infra-red spectra of triethylvinyltin and its soluble polymer. In the 1,100 ~ 3,000 cm^{-1} region many of the vibrational frequencies of vinyl- and ethyl-substituted organometallic compounds were well

Table 1. γ-IRRADIATION OF TRIETHYLVINYLTIN AND TRIPHENYLVINYLTIN

Monomer	Dose-rate (r./h)	Irradiation temperature (° C)	Irradiation time (h)	Percentage of conversion	*G*-value (overall) of conversion	Weight fraction of soluble polymer* (%)	Molecular weight of soluble polymer†	Remarks
Triethylvinyltin	27×10^4	27	25	7·54	50	75	460	Liquid
	$4·5 \times 10^4$	45	90	8·02	90	83	540	Liquid
	$4·5 \times 10^4$	80	50	7·22	140	99	500	Liquid
Triphenylvinyltin	27×10^4	27	110	1·44	1·4	100	850	Solid
	$4·5 \times 10^4$	80	16	5·42	220	100	690	Liquid

* Separated from the mixture by the extraction with benzene.
† Measured cryoscopically and ebulliometrically.

brought out by the work of Kaesz and Stone[4], and found to be almost independent of the nature of the metal. It can easily be seen that the vinyl group which existed in the monomer decreased considerably in the oily product although some fractions of it seemed to remain unchanged. Such an unsaturated bond has also been proved by the bromine absorption of the product. From these observations and from Table 1 it may be concluded that the viscous oily product is a dimer or a trimer which contains the unsaturated bond.

We have not obtained enough satisfactory results on the insoluble product to report here. By prolonged irradiation the insoluble part changed its colour to grey, and from analysis of ash it was revealed that the powder was fairly rich in tin (content 65 per cent). It seems probable that a fraction of triethylvinyltin decomposed to form such an insoluble product by the side-reaction during irradiation. The behaviour of triethylvinyltin against the radiation was apparently very complicated. The yield of the insoluble product decreased with increasing irradiation temperature.

The conversion of the monomer was almost linear with the irradiation time in the initial stage, and the overall activation energy of the monomer conversion was about 3 kcal/mole in the range 25°–80° C.

It was much the same with triphenylvinyltin, but without the formation of the insoluble product. The polymer was precipitated by pouring the irradiated monomer into methyl alcohol, and separated by filtering. It was soluble in aromatic solvents and considered also to be a oligomer, which possessed the rest of the unsaturation, with monomer units of about three.

The conversion of the monomer increased almost linearly with the irradiation time with a slight acceleration of the rate at higher conversion. Triphenylvinyltin polymerized both in the liquid and solid states (Table 1); but the polymers obtained in both phases did not seem to differ much from each other, to judge from the infra-red observation.

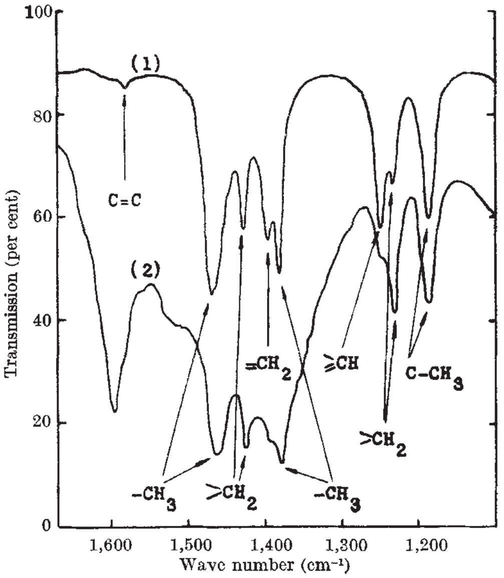

Fig. 1. Infra-red spectra of triethylvinyltin and its polymer. (1) Triethylvinyltin; (2) the soluble polymer, the main product (27° C)

Fig. 2 shows the dependence of the overall *G*-value of monomer consumption on the temperature of irradiation. The activation energy was 9 kcal/mole for liquid-phase polymerization and 3 kcal/mole for solid-phase polymerization. We did not observe any abnormal augmentation of the rate of polymerization around the melting-point of monomer crystal. The *G*-value of conversion in the solid phase was very small, and it seemed probable that a different kind of reaction from that of the liquid phase occurred in triphenylvinyltin, although the products from both phases looked alike in appearance. The rate of conversion in the solid phase showed approximately 0·7 power dependence on the dose rate in the range of $3 \times 10^4 - 27 \times 10^4$ r./h at 27° C.

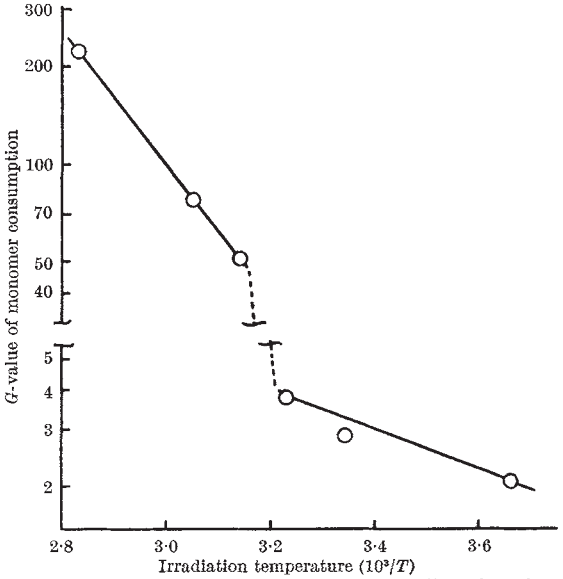

Fig. 2. Arrhenius plot of the apparent *G*-value of the polymerization of triphenylvinyltin initiated by γ-ray

We are far from knowing what kind of kinetics are involved in the polymerizations of both compounds. But, as for the formation of extremely short-length polymer, we are inclined to consider it to be the result of steric hindrance by the bulky group. The comparatively high *G*-value of monomer consumption, in spite of the low molecular weight of polymer, would be due to the frequent occurrence of the chain transfer process.

We have also been investigating the γ-ray-induced polymerization of vinylsilicon compounds and have observed the formation of the oligomer from triethylvinylsilane which was also stated to be unpolymerizable without applying high pressure[5].

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