

PREPARATION AND PROPERTIES OF PEROXY TITANIUM MALONATE

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Received December 14, 1962

(Communicated by Prof. M. R. A. Rao, F.A.Sc.)

ABSTRACT

The method of preparation and physicochemical properties of peroxy titanium malonate, $\text{TiO}_2(\text{OOC})_2\text{CH}_2 \cdot 3\text{H}_2\text{O}$ are given. The reasons for the poor complexing tendency of malonic acid are discussed. The nature of the bonds between titanium and the peroxy as well as malonate groups is assigned from spectrophotometric and infra-red absorption studies.

It has been noticed in this laboratory that peroxy titanium oxalate¹ forms a five-membered ring structure while the maleate² forms a seven-membered ring compound. The present study was undertaken to investigate the properties of a six-membered ring structure of the dicarboxylate group in peroxy titanium compounds. For this purpose peroxy titanium malonate was prepared as follows:—

Freshly prepared hydrated titanium peroxide in presence of excess of hydrogen peroxide (5%) was shaken in a glass-stoppered bottle with malonic acid (c.p.) in the ratio of Ti: acid as 1: 3 for about eight hours. The yellow peroxide dissolved comparatively very slowly, giving rise to an orange red solution of the malonato complex. The clear solution was separated from titanium peroxide using a sintered glass filter and the filtrate evaporated at room temperature by passing dry air for about 15 days. During the process of concentration of the solution, free malonic acid crystallized out and was filtered off at intervals. No crystals of the complex were obtained but just before solidification of the complex, a small portion of the viscous solution seemed to get hydrolysed, producing insoluble yellow hydrated titanium peroxide. The dried mass was extracted with 95% alcohol to remove free malonic acid while the hydrated titanium peroxide was removed by dissolution of the solid in 5% H_2O_2 and filtering off the insoluble titanium peroxide. This process of purification was repeated twice to obtain a rela-

tively pure complex. The molar composition of the representative samples as analysed by methods² described earlier was Ti: malonate: O_{peroxy}: H₂O as 23.3: 42.9: 6.0: 22.1, whereas the molar ratio of the compound with the formula TiO₂(OOC)₂CH₂.3H₂O was 20.3: 43.2: 6.8: 22.9. The solid compound prepared had always about 2.5% titanium in excess of what is required theoretically and could be removed from its solution by filtration. As in peroxy titanium oxalate¹ and maleate² the peroxy oxygen content is lower than the theoretical value.

Repeated attempts to prepare a pure peroxy titanium complex with malonic acid were not successful, owing to the reasons discussed later. Small impurity of hydrated titanium peroxide in the solid, however, does not much affect the physico-chemical properties of the complex investigated.

PROPERTIES OF THE COMPLEX

Like other peroxy titanium complexes,^{1,2} freshly prepared peroxy titanium malonate is orange red in colour, feebly hygroscopic and soluble in water. The Riesenfeld-Liebhafsky³ test indicates that the complex is a true peroxy compound and not a perhydrate. On keeping, the complex loses peroxy oxygen. The loss of peroxy oxygen from the complex, having the molar ratio of Ti: malonate: O_{peroxy}: H₂O as 1: 1: 0.83: 3, is given in Fig. 1. The loss is due to the presence of a strained triangular ring structure

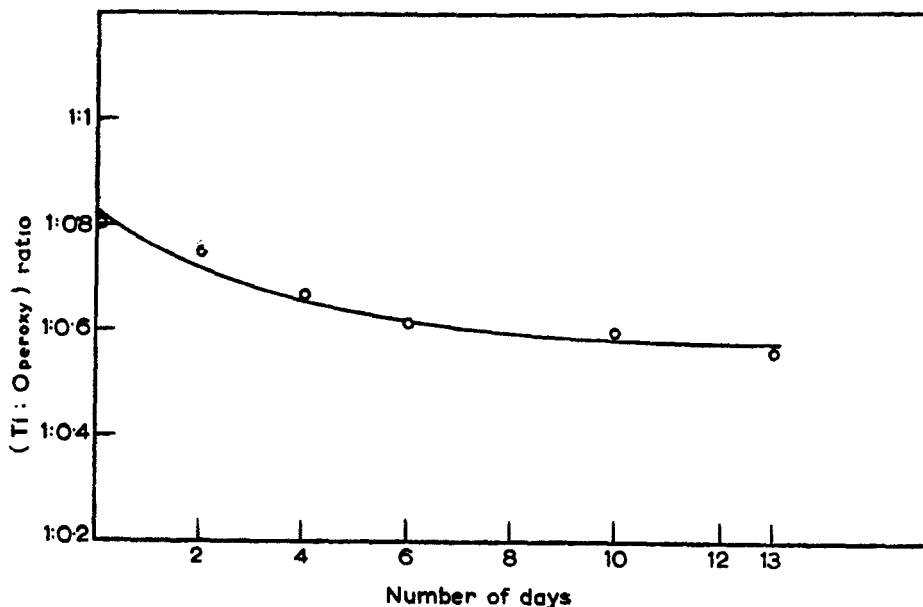


Fig. 1. Effect of storage on peroxy titanium malonate.

of the peroxy titanyl group of the complex.⁴ It may be pointed out that a sample of the complex kept in a sealed tube lost all its peroxy oxygen in about a year, giving white titanyl malonate. This also shows that the colour is due to the peroxy group in the complex.

Thermal and X-ray Diffraction Studies

The thermal behaviour of peroxy titanium malonate was studied both by thermogravimetry (TGA) and differential thermal analysis (DTA). The DTA results obtained with a manual apparatus⁵ are given in Fig. 2, which shows a small endothermic peak at 75° C. due to the loss of loosely held water outside the co-ordination sphere. This is followed by a sharp exothermic peak at 100° C. due to the decomposition of the peroxy group yielding titanyl malonate. The DTA gives an endothermic peak at 150° C. in the temperature range 130–90° C. with a shoulder in the range 190–275° C. This transition corresponds mainly to the loss of co-ordinated water together with some carbon dioxide. The endothermic peak at 310° C. in the range of 275–375° C. is due to the decomposition of the malonate group giving rise to TiO₂ and carbon as solid products. The exothermic peak at 475° C. in the range 400–525° C. is due to the crystallisation of the amorphous TiO₂ into anatase as revealed by X-ray diffraction studies. The exothermic peak at 600° C. in the range 575–650° C. is due to the oxidation of carbon.

It has been observed in TGA that the transitions involving losses in weight are not sharp till 350° C., probably due to the overlapping of the consecutive reactions. But the small inflections in the thermogram except at 475° C. are almost at the same temperatures as observed in the DTA.

Peroxy titanium malonate and its thermally degraded products up to 350° C. are amorphous. Anatase is obtained around 450° C. and remains in this form till about 900° C. It gets converted into rutile at about 1000° C.

Nature of Water associated with the Complex

The nature of water associated with the complex was investigated by vacuum dehydration over P₂O₅ at laboratory temperature and by vapour pressure method. The vacuum dehydration of the complex shows that out of the three moles of water, only one mole is lost, while the other two are firmly bonded to the complex. The heat of dissociation (ΔH) of the loosely held water calculated from vapour pressure studies at different temperatures, using the apparatus described by Kharkar and Patel,¹ is 11.8 K.cal./mole of H₂O.

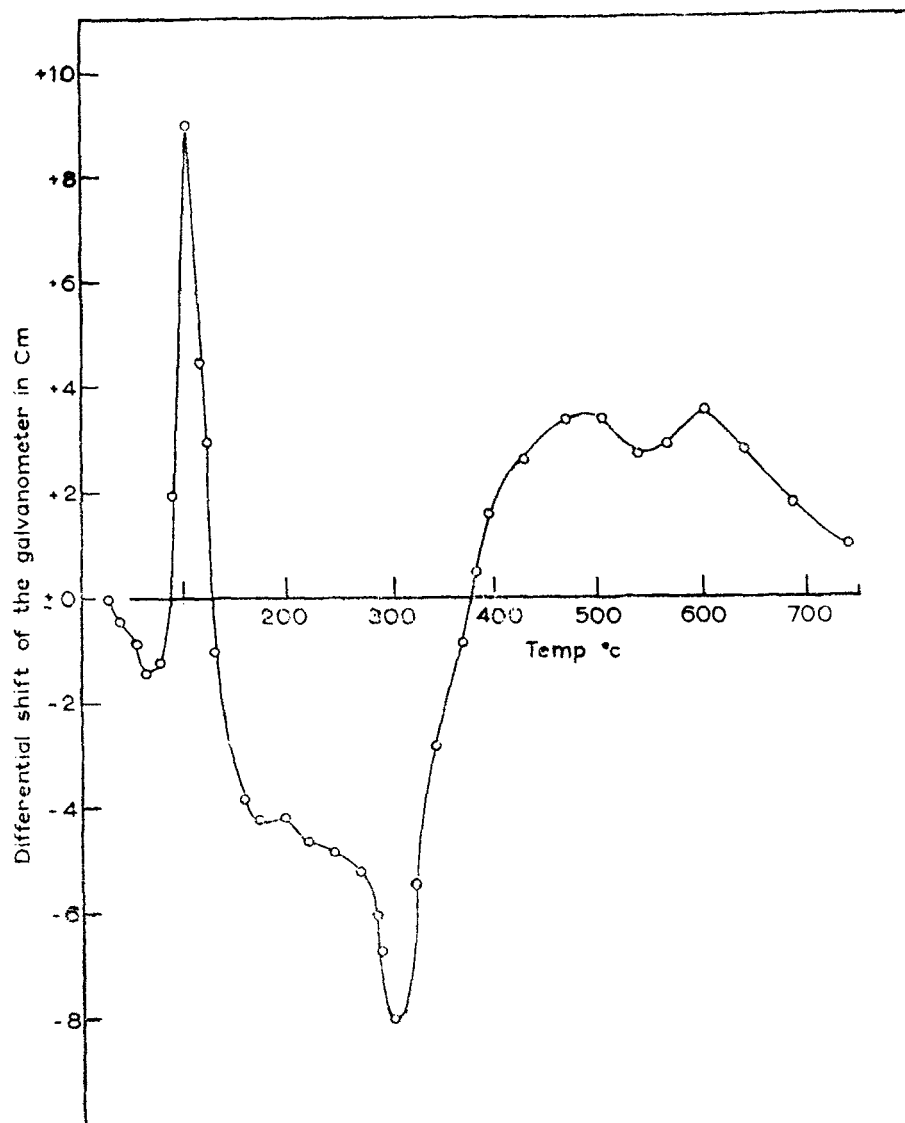


FIG. 2. Differential thermal curve of peroxy titanium malonate.

Electrical Conductivity

The conductivity of clear aqueous solutions of peroxy titanium malonate was determined at various dilutions, using circular bright platinum electrodes and a glass cell having a cell constant of 0.360 cm.^{-1} . The results given in Table I show that the molecular conductivity increases with dilution. The

molecular conductivity at infinite dilution is 201. The average dissociation constant K of the complex, as calculated according to the following mode of dissociation, is 2.34×10^{-3}

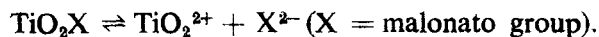


TABLE I

Conductivity of peroxy titanium malonate

Molar composition of the complex, Ti: malonate: O_{peroxy} : H_2O as 1: 1: 0.9: 3.
 Molecular weight of the complex = 236.
 Temperature = $25^\circ \pm 0.1^\circ \text{C}$.

Concentration of the complex, moles/litre. $C \times 10^3$	Molecular conductivity λC	Degree of dissociation a	Dissociation constant $K = (a^2 C / (1-a)) \times 10^3$
3.25	113.2	0.56	2.36
2.60	122.6	0.61	2.42
1.94	130.6	0.65	2.33
1.30	142.1	0.71	2.21
			Average = 2.34



Molecular and Electronic Spectra

The infrared spectrum of peroxy titanium malonate was taken with Perkin-Elmer infracord spectrophotometer, model 137, in the rock-salt region from 2 to 15μ . The observed frequencies with group assignments are given in Table II. The malonate bands are assigned after Schmelz and co-workers.⁶ The absorption bands, corresponding to the water molecules and also the

peroxy titanyl group, $= \text{Ti} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$, are assigned according to our previous work.^{7,8}

The electronic absorption spectrum of peroxy titanium malonate was studied with Hilger UV-speck spectrophotometer, model H 700. The aqueous solution of peroxy titanium malonate gives a broad absorption maximum at $378 \text{ m}\mu$ ($\epsilon = 814$) due to the peroxy group. The Beer's law is obeyed up to 35 ppm. of titanium.

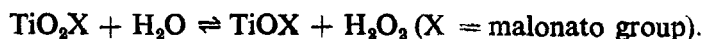
TABLE II
Assignment of observed frequencies of peroxy titanium malonate complex

Frequency, cm. ⁻¹	Intensity	Assignment
3175 (broad)	.. Vs	ν (H ₂ O)
1667	.. Vs	ν_a (O—C—O)*
1610	.. Vs	δ (H ₂ O)
1443	<i>m</i>	ν_s (O—C—O)
1342 (shoulder)	.. <i>m</i>	ν_s (O—C—O)
1290	<i>w</i>	CH ₂ wagging
1167	.. <i>w</i>	Ti—O—C
1041	.. <i>m</i>	ν_a TiO of Ti 
909	.. <i>s</i>	(C—C) overlapping with background Ti—O absorption
891	.. <i>w</i>	ν_s (TiO) of Ti 
869	.. <i>w</i>	H ₂ O rocking
810	.. <i>m</i>	δ (O—C—O)

(1) Vs = very strong; *s* = strong; *m* = medium; *w* = weak; *b* = broad; ν = stretching; ν_a = antisymmetric stretching; ν_s = symmetric stretching; δ = bending.

* (2) The usage of O—C—O for C=O and C—O is in accordance with the earlier work of Schmelz and co-workers.⁶

Employing equimolar concentrations of titanium (in excess of malonic acid) and hydrogen peroxide (1.7×10^{-4} moles of Ti or H₂O₂/litre), the Job's method gave a ratio Ti:H₂O₂ as 1:1 in the complex. The dissociation constant *K* by the molar ratio method⁹ for the peroxy titanyl group, according to the following equation is 2.8×10^{-5} :



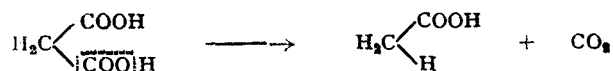
DISCUSSION

Poor Complexing Tendency of Malonic Acid

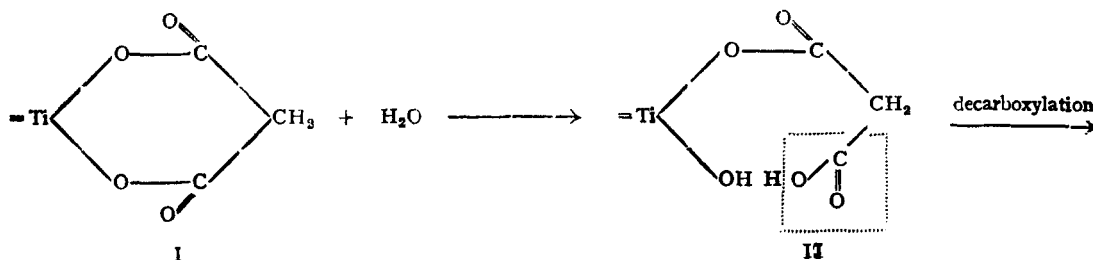
It is noticed that the reaction of hydrated titanium peroxide, $\text{TiO}_2(\text{OH})_2$, with malonic acid, is much slower than that with oxalic or maleic acid. In oxalic¹⁰ and maleic¹¹ acids, the carboxylic groups are planar and in maleic acid they are also in *cis*-position.¹¹ Such an arrangement of the carboxylate groups is responsible for the ease of chelate formation by oxalic and maleic acids. In malonic acid, only one of the carboxylic groups is nearly coplanar with the methylene carbon atom and the other is turned perpendicular to it.¹² Such an arrangement of the carboxylic groups cannot facilitate the chelation process, since a certain amount of rearrangement of the carboxylic groups has to occur to enable the malonic acid to form a chelate ring occupying two co-ordination positions of titanium. This explains the low reactivity of malonic acid to form a chelate.

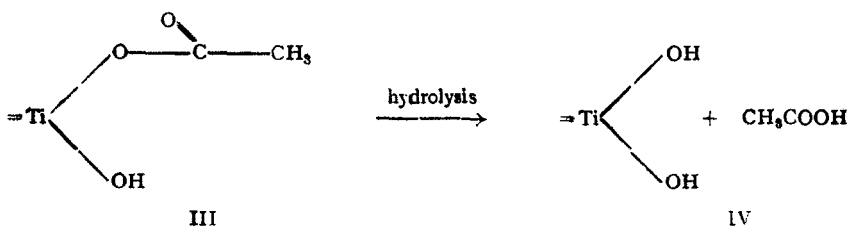
During the preparation of the complex, a small portion of the complex undergoes hydrolysis before solidification, producing insoluble hydrated titanium peroxide and acetic acid. This behaviour could be explained by considering the nature of both the malonic acid and the resulting complex.

In malonic acid, the two carboxylic acid groups are attached to the same carbon. Such a structure, although stable enough to exist as an independent chemical entity, is always susceptible to decarboxylation as shown below:



According to the mechanism proposed for decarboxylation of malonic acid,¹³ a transition complex is first formed by the co-ordination of the polarized electrophilic carboxyl carbon atom of the malonic acid with the unshared pair of electrons of the solvent molecule. This intermediate complex splits into acetic acid and carbon dioxide. The formation of a small amount of titanium peroxide and acetic acid, before solidification of the complex, can similarly be explained by the mechanism represented below:





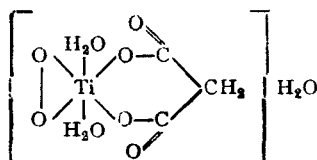
The formation of complex II in presence of water is likely to take place because of the internal strain in the non-rigid malonato group of the complex. The complex II may then undergo decarboxylation forming the acetate complex III by the same mechanism as proposed for the decarboxylation of malonic acid.¹³ The acetate complex being mono-dentate hydrolyses giving rise to dihydroxy titanium peroxide and free acetic acid, which is lost from the complex during the process of evaporation.

The DTA gives a sharp exothermic peak at 100° C. for the decomposition of the peroxy group in the complex, while the peroxide gives a very small peak at 88° C.,¹⁴ showing some increased stability of the peroxy group on introduction of a chelate ring in the other part of the molecule.

The weak band at 869 cm^{-1} in the IR spectrum is attributed to the rocking mode of vibration of water. This band arises when the water molecules are co-ordinated to the metal atom.¹⁵ The co-ordinated water is not lost even in vacuum at room temperature, but is lost only around 130° C. at atmospheric pressure. This shows that the bond between titanium and the co-ordinated water is fairly strong.

The infra-red spectrum gives the characteristic carboxyl stretching frequency at 1667 cm^{-1} . This shows that the bond between titanium and oxygen of the malonato group has certain degree of covalent character. However, the covalent character in malonato complex is lower than that in the corresponding oxalato and malonato complexes since the carbonyl anti-symmetrical stretching frequency is higher in the latter complexes. The lower covalent character of malonato complex than that of oxalato metal complexes finds support from the work of Schmelz *et al.*⁶ The development of colour on introduction of the peroxy group in the titanium malonato complex indicates covalent nature of the bond between titanium and the peroxy group. This is in accordance with the observations of Pitzer and Hildebrand.¹⁶ The absorption maximum at 378 $\text{m}\mu$ is due to the $n \rightarrow \sigma^*$ transitions¹⁷ of the non-bonded p electrons on the O-O group. The amorphous nature of the complex may be due to the random hydrogen bonding in the molecules.

As in other peroxy titanium complexes,^{1,2} titanium exhibits co-ordination number 6 with d^2sp^3 hybridization. All the properties given above can be explained by assigning the following structure to the complex.



ACKNOWLEDGMENT

The authors are thankful to Prof. M. R. A. Rao for his keen interest in the work.

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