Although the chemical composition has not yet been determined, it is suggested that the glassy objects are microtektites and that they represent a portion of the tektite-strewn field of the Ivory Coast because of (i) their geographic location near the Ivory Coast strewn field; (ii) their apparent age of deposition which is similar to, but somewhat less than, the presently accepted K-Ar age determination of the Ivory Coast tektites; and (iii) their similarity in appearance and physical properties to both the Australasian microtektites and the Ivory Coast tektites. Preliminary chemical analyses, performed with the electron-microprobe at Goddard Space Flight Center, Greenbelt, Maryland, indicate that the glassy objects are also similar to the Ivory Coast tektites in composition.

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High-Pressure Polymorphism of Titanium Dioxide

Abstract. *X-ray diffraction studies made* in situ *under conditions of high pressure and high temperature revealed the direct transition of rutile to the alpha lead dioxide form in titanium dioxide. Compressibility studies of this alpha lead dioxide form at room temperature showed anomalous behavior in that its molar volume converges close to, but not equal to, that of the rutile form. Under this circumstance an unexpectedly large error appears in the calculations of the equilibrium pressure for the two forms at 298°K.*

Our present knowledge of transformations of the rutile form of TiO_2 (neglecting brookite, anastase, and other "low-pressure" forms) can be summed up very briefly as follows: On shock loading the rutile form undergoes a large volume discontinuity at 0.33 megabar and is recovered in the α-PbO_2 structure (*1*), some 2.8 percent denser, at 1 atm and room temperature. Thermochemical calculations (*2*), with the use of calorimetrically obtained data on the enthalpy of the conversion of α-PbO_2 to rutile, placed the equilibrium at 60 ± 20 kb. This is consistent with various reported syntheses (*3*) of the α-PbO_2 form. High-pressure, x-ray diffraction studies (*1*) showed no formation (to the limits of detection) of α-PbO_2 from rutile at pressures as high as 0.18 Mb at room temperature. In studies on rutile-type MnF_2, Vereshchagin *et al.* (*4*) found that the analogous α-PbO_2 type could be obtained only after the rutile type had been transformed to a third (tetragonal) modification. A similar succession of phases has been reported for ZnF_2 by Kabalkina *et al.* (*4*). This suggested that the shock-converted TiO_2, as well as that obtained in the quench studies (*3*), was derived from a third phase rather than by direct conversion from rutile. We tested this with the use of x-ray diffraction techniques carried out at high pressure and high temperature, as described elsewhere (*5*).

Runs were made with and without internal (pressure-measuring) standards. In the latter case the pressures were known only grossly, but a gain in pattern clarity was achieved. Patterns taken in several such runs showed the partial formation of the α-PbO_2 form from rutile at temperatures as low as 270°C, as indicated by the presence of its strongest diffraction line, 111. Explorations at 500°C revealed no further transformations. Because of the lack of internal standards, we can only describe our pressures as being within the area of pressure-temperature space delineated by Bendeliany *et al.* (*3*). To improve this situation, we made one run with NaF as an internal standard. The observed cubic cell edge of NaF was converted to that of NaCl by use of a room temperature correlation obtained earlier (*5*). Then, assuming this correlation to be temperature invariant, we entered the tabulation of Decker (*6*) for the compression of NaCl to obtain an estimate of the pressure. The first picture taken showed the α-PbO_2 form to be present under conditions of

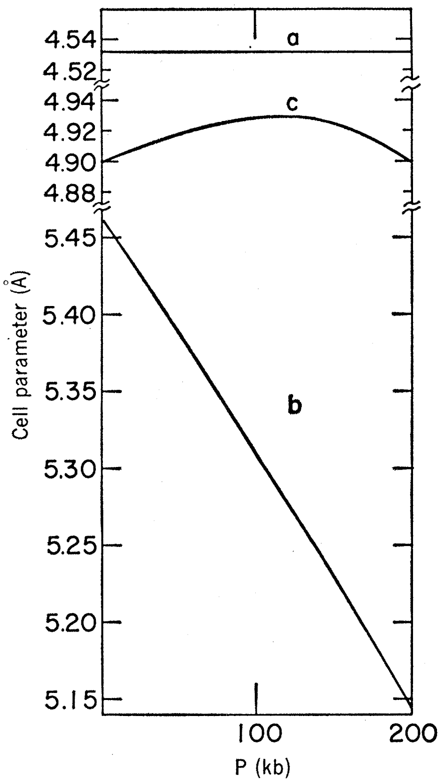

Fig. 1. The variation in the cell parameters of the orthorhombic α-PbO_2 form of TiO_2 as a function of pressure at room temperature. Vertical scales for all three parameters are identical in order to display aberrant behavior of the axes *a* and *c*. This structure may be regarded as a linkage of distorted octahedra, and its pressure behavior is probably a function of the distortion of those chains. However, one parameter is needed to determine titanium positions and three are needed for oxygen positions. Intensity measurements at high pressures are too insensitive to obtain these parameters; therefore, any detailed discussion of atomic movement to explain the lattice parameter behavior would be speculative at this time.

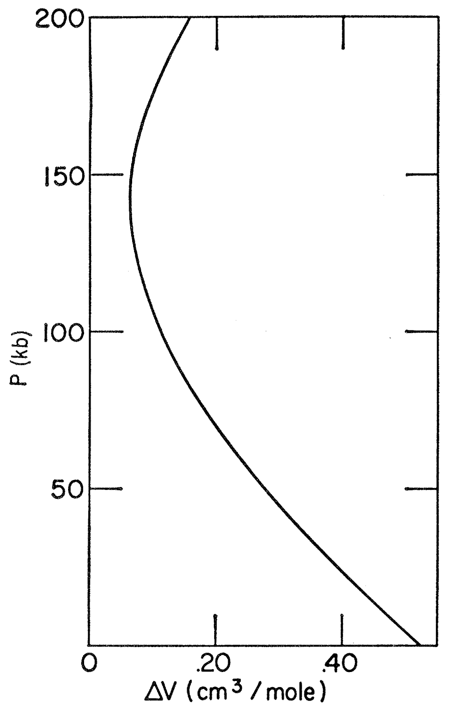

Fig. 2. The difference in molar volumes, ΔV, of the rutile and α-PbO_2 forms of TiO_2.

400°C and 106 kb. A second film taken at 500°C and 86 kb showed essentially no change. Since reactions were sluggish, this was not pursued further. Upon release of temperature and pressure, a film taken of the recovered sample showed a definite amount of the α-PbO_2 form. This had also been true of the runs made without standards. We believe this is the first definite proof that the α-PbO_2 phase may form from a rutile type without any intermediate phase, as occurs in MnF_2 and ZnF_2. Careful reexamination of earlier x-ray films of samples that had been exposed to elevated pressure (only at room temperature) showed that the most intense reflection of the α-PbO_2 type can occasionally be found at room temperature, but its appearance is erratic and may be related to slight variations in sample preparation.

We also determined the compressibility of the α-PbO_2 form with the use of material recovered from shock-loading experiments (*1*). Again NaF was used as an internal standard to measure pressure. For consistency with previously published work (*1, 5*), we used the Drickamer-Christian volumes for NaCl as a function of pressure. To calibrate the camera, lattice parameters of McQueen *et al.* (*1*) at a pressure of 1 bar were used for the α-PbO_2 form of TiO_2 and the value a_0 = 5.347 Å for the NaF internal standard (*7*). Twelve diffraction lines of the α-PbO_2 form of TiO_2 were measured from three different samples at 18 different pressures. Because of interference from either the NaF standard or the minor amount of rutile present in these samples (*1*), all but five diffraction lines were used only as qualitative evidence of the degree of fit to values calculated from the remaining five unobstructed lines—110, 111, 021, 220, and 311. The cell parameters were calculated from smoothed values of the abovementioned five lines as a function of pressure and are displayed in Fig. 1. Note that the *a*-axis is almost independent of pressure and the *c*-axis rises to a maximum, about 120 kb. Until after this maximum in *c* is surpassed, the compressibility of the α-PbO_2 form is much less than that of rutile. Hence the earlier calculation (*2*) of the equilibrium pressure (P_e), 60 ± 20 kb, must be revised although it was based on the very plausible assumption that $P_e \simeq \Delta H^\circ_{298}/\Delta V^\circ_{298}$, where ΔH_{298} is the change in enthalpy and V is volume. In Fig. 2 we show $\Delta V(P)$ as determined from the present work and from McQueen *et al.* (*1*). We could solve graphically

$$\int_1^{P_e} \Delta V(P)\,dP = \Delta H^\circ_{298} \qquad (1)$$

and obtain P_e for 298°K. However, it is much more instructive to insert the various errors involved into Eq. 1. According to Navrotsky *et al.* (*2*), ΔH°_{298} may be written as 31.80 ± 7.12 kb-cm³, because of the calorimetric error. In addition there are the experimental errors in the determination of the molar volumes of rutile and the α-PbO_2 form. A value of 18.80 ± 0.02 cm³/mole has been published (*8*) for the molar volume of rutile, based on the work of Swanson and Tatge (*7*) and that of Cromer and Herrington (*9*). The former claim an error leading to ± 0.06 cm³/mole at 25° ± 1°C, while the latter claim much greater precision which would lead to an uncertainty in the molar volume of ±0.005 cm³/mole. A similar situation exists for the α-PbO_2 form. A value of 18.27 cm³/mole was obtained by McQueen *et al.* (*1*) on highly strained material, but no real precision could be quoted. Bendeliany *et al.* (*3*) give a precision leading to a value for a molar volume of the α-PbO_2 form of 18.37 ± 0.01 cm³/mole. Thus, from the above, ΔV could not be better known than ± 0.03 cm³/mole. Accepting this value and including the calorimetric error, we rewrite Eq. 1 as

$$\int_1^{P_e} \Delta V(P)\,dP = (31.80 \pm 7.12 \pm 0.03\,P_e)\ \text{kb-cm}^3 \qquad (2)$$

This is solved implicitly in Fig. 3. If only calorimetric error is considered, then limits of 70 kb $\leqslant P_e \leqslant$ 200 kb can be placed about the equilibrium pressure. If the ΔV uncertainty is added to these calorimetric errors, a lower bound of 60 kb is found with no upper bound from available data. This inability to calculate an equilibrium pressure from thermochemical data and compressibilities is due entirely to the peculiar volume behavior of these two

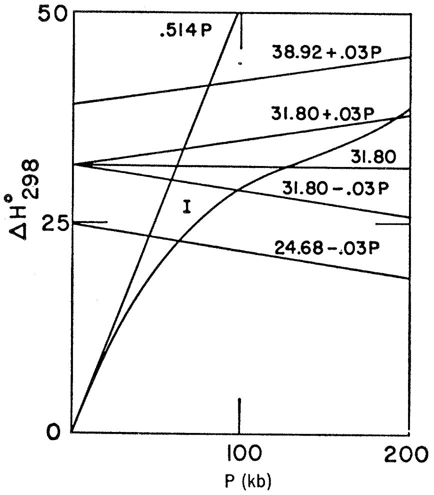

Fig. 3. Plotted value of left side of Eq. 2 with $\Delta V(P)$ values from Fig. 2 superimposed on several plotted error values derived from the right side of Eq. 2. The horizontal line, 31.80 kb cm³/mole, represents the mean enthalpy value from Navrotsky *et al.* (*2*) by calorimetric methods. If the ΔV uncertainty is added to the mean enthalpy, the resulting values plot as the lines, 31.80 ± 0.03 *P*. Lines 38.92 + 0.03 *P* and 24.68 − 0.03 *P* are the extreme upper and lower bounds of uncertainty, including calorimetric error and ΔV uncertainty. The equilibrium pressure for the two forms of TiO_2 for a particular value of enthalpy can be found from the intersection of the error value lines with the curve of

$$I = \int_1^{P} \Delta V(P)\,dP$$

As can be seen, an extreme lower limit of 60 kb can be set for the equilibrium pressure, but no extreme upper limit can be derived because of the restricted range of data to higher pressures. Also shown is the *I* value for ΔV = 0.514 cm³/mole, independent of pressure (*2*).

phases. However, if the volumes were "normal," for example if ΔV is constant, the situation would improve greatly, as the line $\Delta V = 0.514$ cm^3 shows in Fig. 3. For larger ΔV's in different transitions this type of absolute volume error would play a less significant role. It is only in cases such as this, with a comparatively small ΔV at 1 atm, that anomalous volume behavior at high pressure may lead to gross inaccuracies in phase predictions.

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8 April 1968

Juvenile Hormone: Activity of Natural and Synthetic Synergists

Abstract. *A group of nonsesquiterpenoid compounds currently used commercially as insecticide synergists possesses a high order of juvenile hormone activity and species specificity.*

Certain compounds not in themselves appreciably toxic to insects increase the toxicity of such insecticides as pyrethrins and carbamates. Such compounds are commonly referred to as adjuvants or synergists.

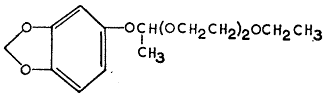
Recent interest in the use of insect hormones, particularly juvenile hormones, as insect control agents prompted me to examine the effects of several well-known synergists with 10, 11-epoxyfarnesenic acid methyl ester (*1*), an analog of the cecropia juvenile hormones, to see whether its activity could be augmented.

In preliminary tests, juvenile hormone activity was increased somewhat by the combination of hormone and synergist, but control insects treated with the synergist alone also manifested the unmistakable morphogenetic effects associated with juvenile hormone activity. The biological activity of several synergists and related analogs have now been examined.

The activities of all compounds were determined in *Tenebrio* and milkweed bug assays (*2*, *3*). Juvenile hormone activity is measured by treating the penultimate stage of the insect with the test compound and examining it after its last molt toward the adult form for the retention of immature features. Freshly molted pupae of the yellow mealworm, *Tenebrio molitor* (L.), and last instar nymphs of the milkweed bug *Oncopeltus fasciatus* (Dallas), are treated topically on the venter of the abdomen with the test compounds in 1 μl of acetone and held until the following molt when juvenile hormone activity is signaled by the presence of immature characters (Figs. 1 and 2).

Initial studies were made with technical products; but, any which were active at 100 μg were purified by column chromatography to a purity greater than 99 percent so that specific activity could be determined more accurately. Purity was ascertained by a combination of thin-layer and gas-liquid chromatography. Sesamin and sesamolin were isolated from sesame oil by chromatography over Florisil (*4*) and recrystallization; they were judged pure on the basis of melting point, ultraviolet and infrared spectra, and gas-liquid chromatography. Because sesamin and sesamolin are insoluble in acetone, they were tested by application in 0.25 μl of Carbowax 200.

The specific activity of representative compounds is presented in Table 1. In the *Tenebrio* test, the most active synergist was sesoxane (I) which produced second pupae at each dose. Subsequent tests at 0.75, 0.5, and 0.25 μg gave 4, 4, and 3 degrees of activity, respectively. The Niagara synergist, propyl 2-propynyl phenyl phosphonate (Niagara 16388) (II), was nearly as active as sesoxane and somewhat more active than piperonyl butoxide (III). Of the remaining synthetic synergists, MGK 264 [*N*-(2-ethylhexyl)-5-norbornene-2,3-dicarboximide] and bucarpolate [2-(2-butoxyethoxy) ethyl piperonylate] caused only nominal activity. In contrast, the naturally occurring synergists sesamin (IV) and sesamolin (V) were nearly inactive (sesamin had slight activity at 100 μg).



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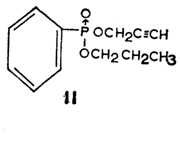

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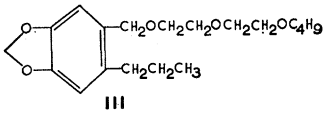

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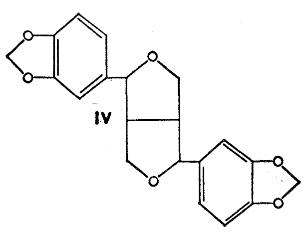
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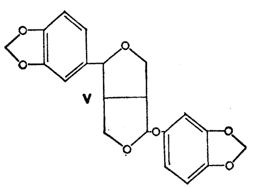
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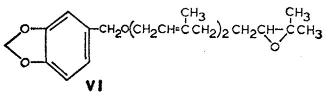

VI

The milkweed bug assays provided interesting information on species specificity reminiscent of results obtained with the monocylic sesquiterpenoid ester juvabione (*3*, *5*). Metamorphosis was inhibited in the milkweed bug by each of the compounds active on *Tenebrio* except NIA-16388, and by several compounds which were ineffective on *Tenebrio*, that is, MGK 264, tropital, piperonal bis [2-(2-butoxyethoxy)ethyl] acetal, and sesamolin. With the exception of MGK 264 and NIA-16388, all of the compounds active on *Tenebrio* and the milkweed bug were derivatives of methylenedioxyphenyl (MDP) which differ principally with respect to the side chain substituents. Derivatives of MDP lacking a side chain (safrole, piperonyl alcohol, piperonal) were ineffective. Derivatives of MDP without