somewhat more stable thermodynamically than their unbranched isomers. This could play a role in their stability to attack by the $TiCl_n^+$ ions.

Thermochemistry. As indicated in Tables I-IV the observed reactions generally have rates within an order of magnitude of the reactant collision frequencies[14] and hence are thermoneutral or exothermic. The reactions therefore imply lower limits on the binding energies between various hydrocarbons and the $TiCl_n^+$ ions. Several of these limits are listed in Table V. In determining the limits it is necessary to assign structures to the hydrocarbon ligand in the metal complex product ion and to the neutral products. The structures assigned are those of the most stable hydrocarbon consistent with all the chemistry observed and reasonably simple mechanisms. In general, choosing other structures gives greater lower limits. The possibility of using competitive ligand substitution[12,13] reactions to obtain relative metal ligand bond strengths in these systems is under investigation in our laboratory.

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Negative Activation Enthalpy in the Dimerization of Anthracene at Very High Pressure

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Abstract: Solid polycrystalline anthracene polymerizes more readily at 80 K (liquid nitrogen cooling) than at room temperature when subjected to 58 000 bars of quasihydrostatic pressure in a piston-cylinder device. The products appear to be four dimers. Three of the four show accelerated rate effects if the anthracene was previously irradiated with ^{60}Co γ radiation. It is postulated that the negative temperature coefficient can be rationalized if the compressionally derived activation energy $P\Delta V^{\ddagger}$ exceeds the thermal activation energy $\Delta E^{\ddagger}$.

Polycyclic aromatic hydrocarbons are in general strongly affected by very high pressures in excess of 10 kbars. Shifts in band maxima may be observed in the ultraviolet, visible, and fluorescent spectra of such materials under these extreme conditions. The magnitude of this effect indicates that the application of high pressure results in a significant perturbation of the intramolecular potential function. The variation in electrical resistivity with pressure of many such semiconducting organic solids has been investigated in order to attempt to quantitate this phenomena. In particular Drickamer et al.,[1-4] Vaidya and Kennedy,[5] and others[6-8] have measured the physical effects of compressing organic materials to pressures as high as 500 kbars.

We report here a study of the chemical effects of very high pressures upon the polycyclic aromatic hydrocarbon anthracene. Previously little attention has been paid to the chemical reactions which are greatly accelerated by such conditions. This area is of critical importance as the variations in physical properties which are measured will be significantly modified by even a small total amount of self-reaction. In addition the composition and quantity of the products provides information as to the general mechanism of reaction in the organic solid state and indirectly may shed some light on the nature of the intermolecular forces which are responsible for the many unique properties of these materials.

Experimental Section

Anthracene (zone refined, 99.9+%, Aldrich Chemical Co.) was transferred in a nitrogen or argon filled glove box to a cylindrical sample capsule of either tantalum or Teflon of outside dimensions 1.00 in. by 0.250 in. The filled capsule was placed inside a graphite and talc sleeve which could be wrapped in lead foil and fitted into a cylindrical high-pressure vessel of tungsten carbide compact (Carmet Grade CA-4). The open end of the sample vessel was closed with a carbide end plug, separated by a thin steel shim. All carbide components were massively supported (along the horizontal axis) with tool steel interference fitted binding rings. The general design of the press and sample assembly is described in detail elsewhere[9] and is similar to that of Kennedy and LaMori[10] and Katzman.[11]

Sample temperatures were monitored with the aid of a platinum: platinum, 10% iridium thermocouple which was inserted through a capillary hole in the carbide end plug. Pressure was calculated from the master ram Heise gauge reading using area and frictional corrections. Cooling to 80 K was effected by an external liquid nitrogen jacket placed about the steel support rings of the sample vessel.

Analysis of the sample after removal of pressure was carried out using both conventional and chemical ionization mass spectrometry.[12,13] Unpressurized starting material was used as an internal control. Inlet temperature and pressure were standardized from analysis to analysis in order to eliminate possible interferences from contaminants which might be formed in situ.

γ irradiation was performed with a kilocurie ^{60}Co source at the U.C.L.A. Laboratory for Radiobiology and Nuclear Medicine. This

Table I. Mass Spectrometric Analysis of Pressurized Anthracene

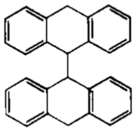
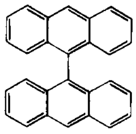
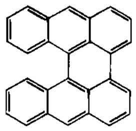
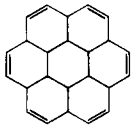
		Percent of parent m/e 178			
m/e	Structure	Background	Cooled to 80° K then compressed to 58 000 atm and held 2 h	Compressed to 58 000 Atm at 25 °C for 2 days	Irradiated with 7 Mrads, cooled to 80 K, compressed to 58 000 atm, and held 2 days
356		3.7×10^{-5}	2.1×10^{-3}	1.1×10^{-3}	0.206
354		9.4×10^{-5}	5.0×10^{-3}	1.1×10^{-3}	0.420
352		5.6×10^{-4}	1.4×10^{-2}	0.8×10^{-3}	0.250
302		1.0×10^{-4}	1.3×10^{-2}	0.5×10^{-3}	0.018

Table II. Rates of Reaction at High-Pressure, Unirradiated Anthracene

	Rate in percent m/e 178/min (58 kbars)	
m/e	80 K	300 K
356	1.8×10^{-5}	3.6×10^{-7}
354	4.2×10^{-5}	3.6×10^{-7}
352	1.2×10^{-4}	2.8×10^{-7}
302	1.1×10^{-4}	1.7×10^{-7}

Table III. Activation Enthalpies

Dimer	Rate ratio (80 K/308 K)	$\Delta H^\ddagger$(58 kbars), cal/mol	$\Delta V^\ddagger$, cm^3/mol
356	50	-728	-5.2
354	116	-884	-6.4
352	429	-1128	-8.1
302	647	-1204	-8.7

was carried out at room temperature under argon in sealed glass ampules.

Results and Discussion

The products of the high-pressure-induced self-reaction of anthracene appear to be four dimers as shown in Table I. Although the yields are low it is seen that the influence of reduced temperatures and γ irradiation result in respective increases in the extent of reaction. Table II gives the reaction rates for the formation of the various dimers at both room temperature and 80 K. Clearly the rates are very much increased with the corresponding decrease in temperature, a most unexpected result.

Although the analysis of this system is based almost totally on mass spectral evidence mass to charge ratios represent definite compounds formed by the action of high pressure rather than those degradation products which are created within the mass spectrometer. Mass spectra obtained using the chemical ionization technique (isobutane reactant gas) gave the same distribution ratios for the dimers within error as were observed in the conventional instrument run at the usual hard vacuum. The conditions of chemical ionization would not be expected to fragment anthracene telomers if present, as would be the case in conventional mass spectrometry. This allows one to distinguish between native dimers and fragmentation products of similar mass to charge ratios.

As is shown in Table I several different dimers are formed under the influence of high pressure. The m/e 356 may be a face to face doubly cross-bonded entity, which can be thought of as four aromatic rings which are attached to a four-carbon rectangular structure. It corresponds to the anthracene photodimer.[14] This species is however not the predominant product at low temperatures, as this distinction is reserved for the fully aromatic m/e 352 dimer. This is not surprising as loss of resonance energy is not involved in the formation of this or the m/e 354 molecule. The latter dimer is probably not more abundant because it represents only a very localized inflection upon the anthracene–anthracene potential energy surface, while the m/e 352 corresponds rather more nearly to a minima.

The specificity for the formation of the various dimers is seen much more clearly at 80 K than at 298 K. We thus see that thermal motion in the solid state at high pressures appears to govern product distribution.

Kinetic data were determined on the basis of ambient and low-temperature experiments terminated at 1, 2, 4, and 6 days, respectively. For all the molecules represented in Table I the kinetics of self-reaction are first order. Excellent linearity for the rate law was observed graphically, without exception. From Table II these rates are seen to vary over two and one-half orders of magnitude in the most extreme case upon reducing the temperature from ambient to 80 K. Such rate ratios allow the calculation of activation enthalpies, and these are shown in Table III. The activation volumes, albeit estimated since the reaction could not be run at a wide range of pressures, are also given. In comparison with typical cycloaddition reactions the

Table IV. Effect of 7 Mrad Exposure to ^{60}Co on 80 K Dimerization Rates for Anthracene at 58 kbars

Dimer	80 K + 7 Mrads	Rate unirradiated	Rate irradiated	Ratio
356	1.7×10^{-3}	1.8×10^{-5}	1.2×10^{-5}	94
354	3.5×10^{-3}	1.8×10^{-5}	3.5×10^{-3}	83
352	2.1×10^{-3}	1.2×10^{-4}	2.1×10^{-3}	18
302	1.5×10^{-4}	1.1×10^{-4}	1.5×10^{-4}	1.4

activation volume for the anthracene dimerization is only about half as large and negative.[15,16] Clearly very high pressure conditions are required to promote this reaction.

The concept of a negative temperature coefficient for a reaction rate is not at all new. It is implicit in the Eyring theory that the $P\Delta V^{\ddagger}$ term can at least formally exceed the thermal activation energy $\Delta E^{\ddagger}$ so $\Delta H^{\ddagger}$ can be negative. In our case the relative change in bulk volume V/V_0 has been measured for anthracene[5] and is 21.4% or 30.5 cm^3/mol. This corresponds to 42 kcal/mol of compressive work, so the dominance of the $P\Delta V^{\ddagger}$ term is reasonable.

The negative activation enthalpy is only observed as a result of the externally applied high pressure. Normally this type of reaction would have a substantial activation energy barrier, and thus the use of the transition state theory is justified, as an indicator of the $P\Delta V^{\ddagger}$ term upon the barrier height. It is the only coherent approach available for the study of such data. It is clear that the transmission coefficient remains relatively small in spite of the favorable activation enthalpy. This may well be due to a quasistable potential minimum which lies in the anthracene–anthracene potential surface.

Tunneling through the barrier is not expected to be significant in the reaction of normal anthracene, as a net electron transfer does not appear to be involved.

From a structural standpoint the more substantial the rearrangement the larger becomes the influence of high pressure.

The effect of irradiation prior to compression upon reactivity is shown in detail in Table IV. There is no yield without compression, the face to face dimer (*m/e* 356) and edge to edge products (354 and 352) all are promoted by the irradiation, while the *m/e* 302 is not. We imagine that catalysis is promoted by a small number of trapped electrons which are tightly bound to the anthracene, possibly in the form of a radical ion. The doses of radiation delivered to the anthracene caused no change in the mass spectrum of the material. This is expected as it is well known that similar aromatic compounds are virtually unaffected by massive doses of ionizing radiation. That physical change which was brought about can be readily seen as the irradiated anthracene is dark brown in color due to the formation of color centers. Support for a tightly bound electron model is found by simply heating the irradiated material to its melting point (under argon) for a few hours. Rather surprisingly this treatment does not remove all of the color centers, as measured by laser induced (argon line) fluorescence spectroscopy.

It is therefore clear that tunneling may play an important role in the observed rate acceleration for the irradiated anthracene.

Our results indicate that the propinquity required for dimerization is possible only at high compressions, and that under these conditions temperature is an inhibiting factor. This without doubt is sufficiently general to apply to any high-pressure reaction provided that the density of the products is greater than the density of the reactants. Only under these conditions can the $P\Delta V^{\ddagger}$ term predominate as we have demonstrated. In the present case the density of anthracene is 1.283, while the density of the face to face dimer is estimated to be about 1.37. We would also expect alkenes with a smaller positive free energy of formation (and correspondingly a decreased density assuming a homologous sequence) to experience the same types of effects toward dimerization but at somewhat lower pressures. This is of course the case for familiar examples such as ethylene and 1-butene. Studies on such simple systems may allow correlation with theory in order to understand the forces which characterize organic molecular crystals.

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