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The Formation of Diamond. I. Demonstration of Atomic Processes Involving Carbon

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Measurements of the mass ratio 45:44 in the combustion gases from graphite and laboratory-prepared diamond have confirmed that the metal catalyzed graphite–diamond reaction is not a diffusionless transition. Experiments with diamond prepared using different catalysts have shown a preliminary value of a factor of two difference for the isotope ratio gradient $\delta C^{13}:C^{12}/\delta r$ for diamond prepared using Ni and NiMn (1:1). Examination of the profile gradient shows that all the carbon incorporated in the diamond must have dissociated into atoms for the diffusion controlled step. Experiments involving natural diamond show that the isotope ratio profile is not similar to that in laboratory-prepared stones. The imputation is that natural stones grew in many steps or by a totally different mechanism.

Introduction

The reproducible preparation of diamond was first announced by a group of workers[1] in this Laboratory in 1955. The technique[2] involves the use of a liquid transition metal, or an alloy thereof, as a catalyst, and by applying pressure to a reaction mix of the molten metal and graphite, such that diamond is thermodynamically stable, small crystals of diamond are formed.

A simple overall representation of the structural rearrangement of carbon atoms in the reaction is shown (Fig. 1). No causal implication is intended, and it is unfortunate that such a picture has found widespread acceptance as a mechanistic representation. This is perhaps due to its great simplicity. From a chemist's point of view, of course, it raises the serious question of how the dehybridization of the carbon orbitals can occur while the same carbon is still held in the graphite lattice. An electronic rearrangement of the type $S^2p^2 \rightarrow sp^3$ must be permitted to occur for the reaction to go, and there is no indication at this time that the mere isothermal application of pressure is sufficient for this process to be spontaneous.[2a] In fact, a considerable repulsion between the antibonding π orbitals is to be expected if graphite is compressed in the c-direction, yet, in the simple atomic-structural picture, such compression is essential to the development of the correct interatomic distances and configurations. One is therefore led to seek for evidence of a dissociative step in the overall reconstructive transformation.

It should be realized that it is not possible to make direct observation of the reaction chamber during the graphite–diamond reaction, and we therefore are determined to search for evidence of atomic processes by other methods. This paper is concerned with the results of a mass-spectrometric investigation of the distribution of the isotope C^{13} in laboratory-prepared and natural diamond. The results demonstrate positively the action of the catalyst involves the excitation and transport of carbon as a monatomic species, in those reactions involving nickel and nickel–manganese and, presumably, for the transition-metal catalyzed reaction in general.

Experimental

Materials.—Diamond was either purchased, or prepared by the author in this Laboratory. Natural stones were obtained from the van Itallie Corporation, 70 W. 40th St., New York, N. Y.; we are grateful to Mr. John van Itallie for facilitating the hand-selection of particular grades of natural diamond. Samples of nickel and nickel–manganese catalyzed diamond were prepared in the following ways: the metal catalyst was introduced into the reaction volume either as a cylindrical tube round a cylindrical reaction mass of spectroscopic graphite, or as powder intimately mixed with spectroscopic graphite powder. In the second case, an inert liner such as "Vycor" glass or pure high density alumina was used to inhibit the entry of gaseous impurities from the cell wall into the reaction space. A suitably insulated graphite tube was placed around the sample, for use as a resistance heater.

Diamond Preparation.—The cylindrical sample holders were placed in a uniaxial press system, similar to the "Belt" design of Hall,[3] modified by Bovenkerk to permit a somewhat greater stability over extended periods of time. A calibrated current was passed through the graphite tube furnace so as to bring the metal catalyst into a molten condition, after the internal pressure had been raised to a value within the diamond-stable field (Fig. 2). After a given time had elapsed, the experiment was shut down and the diamond yield worked up by acid dissolution of the unwanted components. Particular care was taken that the last traces of work-up acid were removed from the yields by prolonged washing with boiling water. The yields from a given catalyst class were combined, then fractionated on a sieve deck, and finally quarter-sampled prior to the combustion procedure.

Combustion.—The diamond samples were burnt in refractory metal crucibles, usually platinum, in pure oxygen at temperatures between 800 and 1000°. This range of temperatures substantially excludes the possibility of interference by the one major competing reaction, namely, graphitization. A quartz vessel containing a molybdenum susceptor was used in conjunction with a small RF induction heater. Combustion gases were sampled on a manifold which had previously been evacuated to $\sim 10^{-7}$ mm. After the desired number of samples had been obtained and care had been taken to secure a sample of residual gas from the clean system, mass spectrometric determination of the $C^{13}O_2$: $C^{12}O_2$ ratio was performed. This involved a preliminary liquid air separation of the CO_2, which was usually present to the extent of several mm. partial pressure in ~ 100 mm. reagent oxygen. The determinations were replicated; mean results (with associated degrees of freedom ϕ, and standard deviation, σ) are shown in the following tabular paragraphs.

Results

The first experiments involved the determination of $C^{13}:C^{12}$ in (crushed) spectroscopically pure graphite rod and the outside layers of diamond prepared from this graphite, using C.P. nickel as the catalyst. The combustion was run for 5 min. only at 800°: thus the above results refer to a homogeneous graphite sample but only to the

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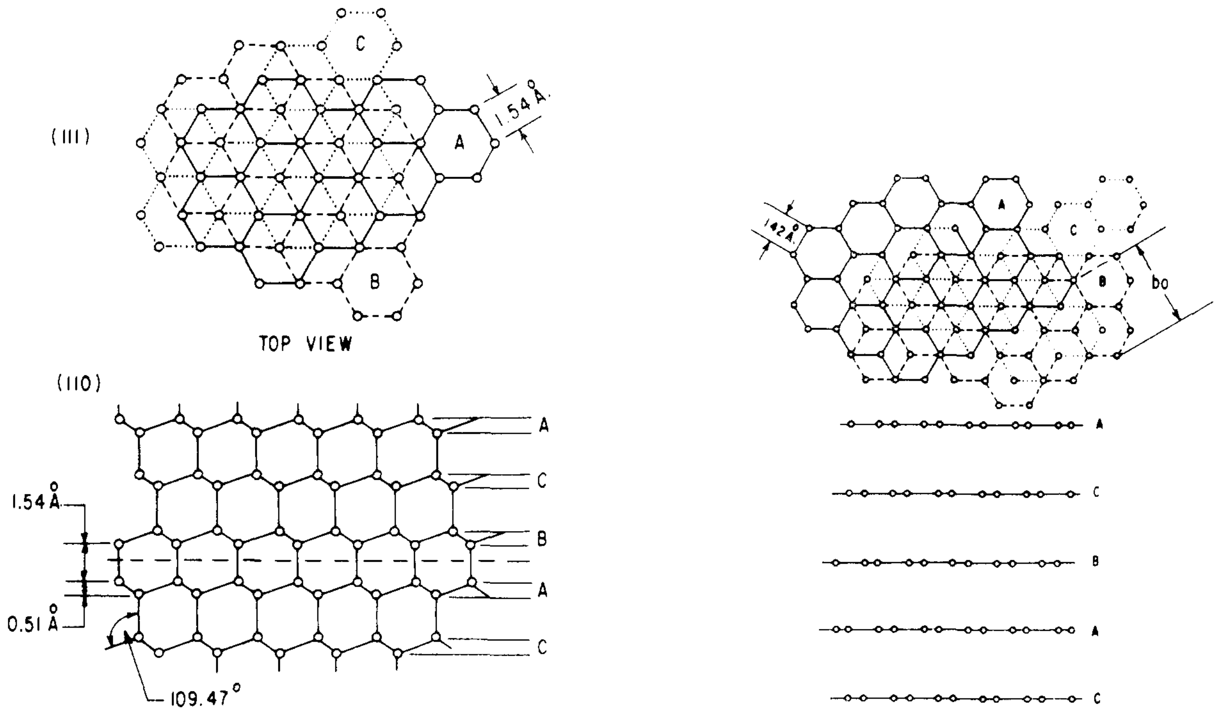
(1) F. P. Bundy, H. T. Hall, H. M. Strong and R. H. Wentorf, Jr., *Nature*, **176**, 51 (1955).

(2) H. P. Bovenkerk, F. P. Bundy, H. T. Hall, H. M. Strong and R. H. Wentorf, Jr., *ibid.*, **184**, 1094 (1959).

(2a) ADDED IN PROOF.—F. P. Bundy of this Laboratory recently has achieved the uncatalyzed reaction at $\tau \gtrsim 3300°K$, $p > 120$ Kb.

(3) H. T. Hall, *Rev. Sci. Instr.*, **31**, 125 (1960).



(a) (b)

Fig. 1.—Steric relationships between (a) diamond and (b) rhombohedral graphite: the projections are of equivalent planes in the two lattices.

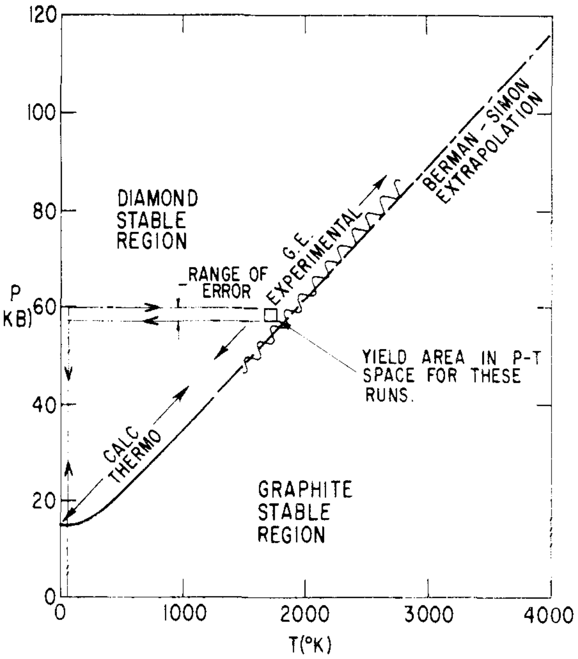


Fig. 2.—Program of experimental conditions in pressure-temperature space for preparation of diamond in these experiments.

outside layers of the diamond involved. The differences between the two sets of mean 45:44 values observed are statistically significant.

Having established that some isotope separation of carbon had taken place during the reaction, an attempt was made to determine the profile of the distribution of C^{13} across the diamond crystals.

TABLE I

RESULTS FROM GRAPHITE AND DIAMOND PREPARED THEREFROM

	Graphite rod sample		Diamond from rod sample	
	1	2	1	2
Mass 45:44	0.0112_5	0.0113_3	0.0114_9	0.0116_1
ϕ	9	9	9	9
σ	0.00004	0.00010	0.00009	0.00007

TABLE II

RESULTS OF COMBUSTION OF Ni-BASED DIAMOND

	Elapsed combustion time at 1000°, min.			
	30	60	90	120
Mass 45:44	0.0114_5	0.0114_3	0.0114_0	0.0113_5
ϕ	9	9	9	9
σ	0.00005	0.00003	0.00003	0.00005

$\Delta C^{13}:C^{12}/\Delta r \simeq 3 \times 10^{-4}$ mm.$^{-1}$, σ 7×10^{-5} mm.$^{-1}$.

Carefully determined size fractions of Ni and Ni–Mn catalyzed materials were burned according to an interrupted schedule. Separate runs were made in which the combustion gases were not sampled, but the residual material was subjected to size determination by careful microscopic and sieve analysis. This was done in order to evaluate the differential $\Delta C^{13}:C^{12}/\Delta r$, r being the equivalent of a radial parameter.

Thus, for the nickel-based material the combustion intervals were 30 min. at 1000°, and in 2 hr. total combustion time about one-half of the 400 mg. original sample was destroyed. The residuum consisted of slightly blackened particles of smaller size than initially.

A 150 mg. sample of −150/+200 mesh diamond prepared using a 50 Ni–50Mn catalyst at 50 kb.

and 1330°, was burned for four consecutive 10 min. periods at 1000°. The residue consisted of 9.2 mg. of very fine diamond powder.

TABLE III

RESULTS OF COMBUSTION OF Ni–Mn BASED DIAMOND

	Elapsed combustion time at 1000°, min.		
	10	20	30
Mass 45:44	0.01179	0.01177	0.01170
ϕ	9	9	9
σ	0.00003	0.00003	0.00003

$\Delta C^{13}:C^{12}/\Delta r \simeq 7 \times 10^{-1}$ mm.$^{-1}$, σ 7×10^{-2} mm.$^{-1}$

An experiment similar to the last was made using 1 k. of selected DM 1 natural drill stones. These were roughly uniform in size, octahedral, and numbered ~40 individual crystals. Only a very small residue of diamond was present after 2 hr. burning.

TABLE IV

RESULTS OF COMBUSTION OF NATURAL DIAMOND "DM 1"

	Elapsed combustion time at 1000°, min.			
	30	60	90	120
45:44	0.01102	0.01153	0.01169	0.01160
ϕ	9	9	9	9
σ	0.00012	0.00005	0.00004	0.00008

In view of the non-monotonic nature of the last set of results, an attempt was made to repeat the experiment using a selected 1/10 k. natural octahedron of excellent quality. Only two samples of CO_2 in O_2 were obtained from this experiment, since this diamond burnt more rapidly than was expected. The values of $C^{13}:C^{12}$ thus obtained were 0.01207 (1st mm. of depth) and 0.01203 (center), standard deviations 0.00004 and 0.00002, respectively, $\phi = 9$.

Discussion

A reasonable interpretation of the above results is that the catalyzed graphite–diamond reaction involves a selective excitation and diffusion step. The difference in the $C^{13}:C^{12}$ ratios between the parent graphite and product diamond in Table I is sufficient to establish this fact. The existence of the determined profiles of this ratio permit extension of this remark to the statement that all the carbon incorporated in the growing diamond has in fact passed through a mono-atomic state. Thus, the profiles presented in the case of the catalyzed reaction product are monotonic with the radial parameter: were the parent graphite not all dissociated into atoms, one would expect a maximum in the $C^{13}:C^{12}$ ratio at a value of the radial parameter intermediate between maximum and crystal center positions. This is obviously so, since having established the existence of a diffusion-controlled step, any hypothetical fragments C_n would be expected to arrive at a growing diamond crystal later than either C_1^{12} or C_1^{13}, and, in addition, any such fragment C_n will have a lower $C^{13}:C^{12}$ ratio than a surrounding equilibrium bath of $C^{12} + C^{13}$ atoms, because of the slightly lower strength of a C^{13}–C^{12} bond compared with C^{12}–C^{12}.

The observation that the profile gradients are different for Ni and Ni–Mn catalyzed diamond indicates that the barrier heights involved in the diffusion of the atoms in the two reactions are significantly different. Because of the nature of the observed gradient, which consists of a concentration gradient in space, frozen into the diamond at different points in time, it is not possible to write an exact equation in only one variable covering these observations. The variation, incidentally, establishes the direct involvement of the molten metal (rather than the carbon alone) in the nucleation of diamond by this technique. It is to be hoped that further studies of this variation in gradient will be useful in determining diffusion coefficients at this range of pressure–temperature conditions.

In the case of the natural diamond samples, it is evident that the results are not similar. This may arise from the possibility that the 40 or so DM 1 stones do not constitute a homogeneous sample, but the results from the single 1/10k. crystal indicate that the profile of $C^{13}:C^{12}$ is in fact not of the same kind as that seen in the synthetic stones. The value of the profile gradient, $\Delta C^{13}:C^{12}/\Delta r$, $\simeq 1 \times 10^{-2}$ mm.$^{-1}$, is not distinguishable from zero on the basis of the statistics of the observations. This implies that the growth mechanism may be different, or that this particular diamond was derived by the same growth mechanism over geological periods of time. Further speculation is idle; the fact is that the profile is not the same as that seen in the laboratory-prepared material.

It is necessary to comment on the possibility of a relationship between these results and the approximate thermodynamic and rate data given by Bundy, *et al.*[4] The activation energy for the *reverse* reaction was found to be approximately the same as the heat of vaporization of carbon, provided an activation volume of 170 cc./mole is admitted. This value is rather large for the range of values anticipated in a solid state transformation, but is consistent with the present results, provided the reaction involves states of the type $2s^22p3s$ or $2s^22p3d$ for the carbon atoms. Slater equivalent orbital radius calculations give atomic volumes of approximate size 170 cc./mole ($2s^22p3s$), 300 cc./mole ($2s^22p3d$) and 70 cc./mole ($2s3p^3$). It is justifiable to invoke such states in the course of transitions between $2s2p^3$ and $2s^22p^2$, which are strictly disallowed in the L–S coupling scheme. Thus, the two sets of data are consistent with an atomic dissociation step, especially one involving a large atomic dipole. It should be possible to study this situation further using various impurities which are acceptors or donors with respect to carbon, acting as co-catalysts or poisons for the reaction.

We may conclude that the reaction graphite → diamond, catalyzed by Ni or Ni–Mn (and presumably for all transition metals) contains a diffusion-limited step involving C atoms, and that this result is consistent with pre-existing data concerning the intermediate state in the reverse reaction. It seems likely that the intermediate state is closely related to the first excited state of C atoms, and

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(4) F. P. Bundy, H. P. Bovenkerk, H. M. Strong and R. H. Wentorf, Jr., *J. Chem. Phys.*, **35**, 383 (1961).

that the molten transition metal is involved in the excitation and the transport of carbon. No extension of these remarks to the formation of natural diamond is possible at present.

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Complex Ion Formation between Cations. Spectra and Identification of a Np(V)–Cr(III) Complex[1,2]

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A complex ion $Cr(H_2O)_5{}^{+3}(NpO_2{}^+)$ has been separated by use of an inorganic ion exchanger. Identity of the species was determined by the analytical ratio of Np/Cr in solution. Spectra are presented. Specific rate for decomposition of the complex is $(2.32 \pm 0.08) \times 10^{-6}$ sec.$^{-1}$ at 25° in 1.0 M $HClO_4$. From spectrophotometric observations the relative strength of interaction between Np(V) and M(III) perchlorates in 2.0 M $HClO_4$ is Fe > In > Sc > Ga > Al.

Although the vibronic transitions of the Np(V) ion in aqueous media are not markedly influenced by anions such as sulfate or chloride they are strongly affected by some cations. We have demonstrated[3] that the association quotient for the reaction between Np(V) and U(VI) obtained from spectrophotometric data is in excellent agreement with the value obtained from potentiometric measurements carried out in acidic perchlorate media with the weighted mean value at 25° and ionic strength of three; $K = 0.690 \pm 0.013$ l./mole.

To provide additional information on the structure of such complex species a Np(V)–Cr(III) complex has been prepared, separated from the reaction mixture and its spectrum characterized. In an effort to determine the importance of the factors which influence association between Np(V) and cations in perchloric acid–perchlorate solutions, spectrophotometric observations have been made on solutions of a number of di-, tri- and tetravalent salts.

Experimental

Solution.—The preparation and standardization of stock solutions of perchloric acid, sodium, Np(V), yttrium, lanthanum, thorium,[4] mercurous and mercuric[5] perchlorates have been described elsewhere. Solutions of aluminum, scandium, gallium, indium, silver, lead and bismuth perchlorates were prepared by the dissolution of the appropriate oxide in reagent grade perchloric acid followed by recrystallization if feasible. Solutions of ferric perchlorate were prepared from G. F. Smith Co. ferric perchlorate that had been twice recrystallized from concentrated perchloric acid. Prior to the first recrystallization a small amount of hydrogen peroxide was added to the solution to insure that the iron was fully oxidized.[6] Chromic perchlorate solutions prepared by the double recrystallization of G. F. Smith material and by the method of Postmus and King[7] gave identical results in kinetic studies. On the basis of the criteria presented by Altman and King[8] both preparations were relatively free of polymeric Cr(III) species with values for $\epsilon_{230}/\epsilon_{260}$ of 0.55 and 0.20, respectively.

Conventional methods of analysis were used by the analytical division of this laboratory to standardize the above stock solutions. Np(V) concentrations were determined by radiometric assay.

Ion Exchange Separations.—Initial runs were made at room temperature using columns of 1 cm. diameter and *ca.* 10 cm. length of Dowex 50 cation exchanger (AG 50W-X 12) 200–400 mesh in the hydrogen ion form. The resin used had been previously treated with perchloric acid then washed extensively with triple distilled water. Final separations were achieved by use of an inorganic exchanger Bio-Rad ZP-1, 100–200 mesh (Bio-Rad Laboratories). This zirconium phosphate type of cation exchange crystal was washed with perchloric acid and triple distilled water prior to use. The separation was carried out in a jacketed column with the temperature maintained at 0–1°.

Spectrophotometric Procedures.—A Carey Model 14 MR Recording Spectrophotometer, with cell compartment thermostated at 25°, was used for all spectral studies. 1, 2 and 5 cm. quartz absorption cells were used. Detailed procedures used in the spectrophotometric studies have been previously described.[3] For the Np(V)–Cr(III) complex perchloric acid of the appropriate molarity was used to determine necessary blank corrections. With the exception of the chromic perchlorate solutions the spectra obtained as soon as possible after mixing did not change over a period of weeks.

Analysis of Np(V)/Cr(III).—Standard radiochemical assay procedures were used to determine the Np(V) concentration. Chromium concentrations were determined using the method described by Gates and King[9] after destruction of the complex by zinc amalgam.

Results

A solution originally 2.0 M in chromic perchlorate, 1.0 M perchloric acid and *ca.* 10^{-3} M in neptunium(V) perchlorate when examined spectrophotometrically shows a slow decrease in the optical density at 9800 Å. and concomitant increase at 9937.5 Å. At 25° the spectrum ceases to change after several days and remains constant over a period of months.

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(1) Work performed under the auspices of the United States Atomic Energy Commission.

(2) A preliminary account of this work presented at the 7th International Conference on Coördination Chemistry, Stockholm, June 1962.

(3) J. C. Sullivan, J. C. Hindman and A. J. Zielen, *J. Am. Chem. Soc.*, **83**, 3373 (1961).

(4) J. C. Sullivan, A. J. Zielen and J. C. Hindman, *ibid.*, **82**, 5288 (1960).

(5) A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, in press.

(6) G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953).

(7) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1209 (1955).

(8) C. Altman and E. L. King, *J. Am. Chem. Soc.*, **83**, 2826 (1961).

(9) H. S. Gates and E. L. King, *ibid.*, **80**, 5012 (1958).