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Heats of Combustion and Electron Spin Resonance of Ultrafine Graphite*

N. J. MAMMANO

Department of Chemistry, State University of New York,
Plattsburgh, New York 12901

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Heats of combustion, (ΔH_c) and ESR measurements on ultrafine graphite, an amorphous "degraphitized" form, depended on prior exposure of the material to air. Air-free samples: ΔH_c increased from 18 to 35% over the literature value for polycrystalline graphite; the ESR signal was a symmetrical Lorentzian line centered at $g = 2.0034$. Air-exposed samples; ΔH_c was about 4% higher than the literature value; the ESR signal was reversibly and asymmetrically broadened to 4 times the air free value and was nearly Gaussian. The different reactivities of edge and planar carbon atoms in the finely divided material are invoked to explain the combustion data. The asymmetric broadening of the ESR signal on exposure to air is accounted for by postulating anisotropic dipolar coupling between physisorbed molecular oxygen and the unpaired spins. The linewidth data support a model of thin graphite platelets roughly 10 Å thick and 30 Å in diameter.

Introduction

This paper presents the results of a study of heats of combustion and electron spin resonance of an unusual form of graphite powder called "wear dust" or "ultrafine graphite." The material may be prepared by rubbing together two pieces of graphite, or a graphite rod against a rotating copper disc, at high velocity (1200 cm/sec) in an inert atmosphere or vacuum. Savage and Brown (*1*) measured adsorption isotherms of H_2 and N_2 and calculated surface areas of 390–435 m^2/g concluding also that about 5 m^2/g is "chemically active" with respect to chemisorption by H_2. Chemisorption of nitrogen is only about 1/10 that for hydrogen but is appreciable in view of the nonreactivity of molecular nitrogen with charcoal. The active surface was postulated as resulting from edge atoms exposed by the fracture of the graphite structure perpendicular to the cleavage planes; most of the total surface area consists of face atoms. Other surface area determinations from N_2 adsorption isotherms yielded values ranging from 200–800 m^2/g (*2, 3*). Electron micrograph and powder X-ray data (*2*) reveal that ultrafine graphite comprises thin plates with a range of diameters extending from 10,000 down to 100 Å or less; the very broad 002 X-ray reflection indicates an amorphous material with particles on the order of 20 Å, or about 6 layers, in thickness. A sharp 002 reflection is observed superimposed on the broad pattern indicating the presence of crystalline graphite particles in the samples.

O_2 uptake is difficult to estimate. Freshly prepared ultrafine graphite surfaces react

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spontaneously and occasionally pyrophorically with air with the loss of CO and CO_2 at room temperature, presumably from the more reactive edge sites. Residual oxygen is chemisorbed as carbon–oxygen complexes (*4*), although physisorption occurs at temperatures below about −45° (*5*). Elemental analysis and oxygen determination by titration with diphenyl guanidine on samples which have been exposed to the atmosphere indicate that oxygen adsorption may vary from 4–10% by weight (*6*). The range of values and reactivities observed is consistent with the powder X-ray and electron micrograph data which show that the material is quite heterogeneous with respect to crystallite size, surface area, and relative number of planar and edge sites. Moreover, the presence of larger crystalline graphite chips in the ground samples tends to lower the observed gas uptake and surface area calculated per unit weight; the higher values are probably more representative of ultrafine graphite. Zarifyanz and co-workers conclude from ESR and magnetic susceptibility measurements on ball-milled samples that "most of the active centers on the graphite fresh surface are not free radicals" (*5*). Singer and Wagoner reviewed the dependence of the ESR on the size and structure of graphite crystallites (*7*). Bobka and Singer have determined the effects of heat and chemical treatment on the magnetic susceptibility, ESR, and powder X-ray patterns of ultrafine graphite (*8*). Their ESR observations reveal a symmetric absorption, closely Lorentzian, with a peak to peak linewidth ~9 G at room temperature which decreased by one-half at 100 K; they report a *g* value of 2.0023 ± 0.0001 and a Curie law dependence of spin susceptibility. Chemical treatment with acetyl chloride, HCl, and NaOH had no effect on the ESR; exposure to air on pyrophoric samples produced a dull red glow indicating partial combustion but reevacuation resulted in an ESR signal identical to that observed originally. In general when samples were exposed to air the line broadened by a factor of two; reevacuation regenerated the original ESR signal. A calculation of the spin density (10^{20} spins/g) suggests that spin–spin dipole interactions between the conduction electrons responsible for the resonance determine the linewidth. Powder X-ray patterns confirm that the material is highly amorphous; the 002 reflection is very broad and asymmetric and "indicates average crystallite thicknesses of, perhaps, two or three layers." Other reflections point to layer diameters of, perhaps 10–20 Å. The disordered material may be annealed or "regraphitized" by heating above 3000°C as evidenced by the return of the powder X-ray pattern and ESR signal characteristic of the polycrystalline form.

The model proposed (*8*) to explain these intriguing properties is one in which the graphite structure is fractured by rubbing to produce a "degraphitized" form. The resistance to strong chemical treatment and the reversible oxygen effects suggest that the conduction electrons responsible for the spin resonance are "an integral part of the carbon skeleton and not localized at surface sites." The graphite particles are viewed as buckled or strained crystallites which may then be annealed by heat treatment to "regraphitize" carbon.

The ultrafine graphite used in these studies was prepared from the same lampblack-base graphite and in the identical apparatus "G" employed by Bobka and Singer in their study of magnetic and X-ray properties and consists essentially of a spring-loaded rod of carbon rubbing against a rotating wheel of the same material in a sealed, nitrogen-filled chamber (*8*). The fine particles of ultrafine graphite are then collected in a small Pyrex tube connected via an aperture at the bottom of the chamber.

Results

Heats of combustion (ΔH_c). Visual observation of the product revealed that the material is produced in a variety of particle sizes ranging from a relatively coarse powder to an exceedingly fine dust. All the combustion studies were performed in a Parr oxygen bomb calorimeter routinely used in the physical chemistry laboratory. These thermodynamic studies were originally planned as an exploratory first step in a broader systematic study of ΔH_c vs surface area. However, segregation by particle size was not feasible so that the data obtained are representative of a broad range of particle sizes. A quantitative interpretation of the experimental results is also complicated by the exceedingly huge surface areas and the related uncertainty in sample weights due to adsorbed oxygen. One set of measurements, Series A, was performed on samples which were exposed to the atmosphere prior to combustion; these samples, including several which were 15–20 years old, yielded ΔH_c of 409.2 ± 2.9 kJ/mole or about 4% above the literature value for pure graphite, 393.5 kJ/mole. The agreement within ±0.7% suggests that the prepared samples are relatively homogeneous. If for these air-exposed samples, appropriate corrections are made to sample weights to reflect probable saturation with oxygen (approx. 10% oxygen by weight (*6*)), then heats of combustion for Series A may be appreciably higher, on the order of 450 kJ/mole, or about 15% above the literature value.

In the second set of measurements, Series B, samples were sealed in nitrogen in polyethylene bags and not exposed to the atmosphere before ignition; ΔH_c of the polyethylene used was determined separately and corrected for. The unexposed samples of Series B yielded widely divergent values of ΔH_c of 468, 472, 481, 518, and 531 kJ/mole, increases from 18 to 35% above the literature value.

ESR. The ESR was measured at 9 GHz at room temperature. For oxygen-free samples sealed in nitrogen-filled sample tubes, our results are virtually identical with earlier ESR work (*8*): we observe a symmetric Lorentzian line with a peak to peak width of 8 G and a g value of 2.0034. Our results differ significantly for air exposed samples; ESR signals for samples exposed to air and then resealed were reversibly and inhomogeneously broadened to 31 G and the lineshape changed to nearly Gaussian.

Discussion

The increase in heat of combustion may be regarded as the return on the investment in mechanical energy when graphite is partially "atomized" to ultrafine graphite; i.e., if the combustion of graphite (Eq. (3)) is expressed as a stepwise process

$$\mathrm{C(gr)} \rightarrow \mathrm{C(ufg)} \qquad (1)$$

$$\mathrm{C(ufg)} + \mathrm{O_2} \rightarrow \mathrm{CO_2} \qquad (2)$$

$$\mathrm{C(gr)} + \mathrm{O_2} \rightarrow \mathrm{CO_2} \qquad (3)$$

then the enthalpy adsorbed endothermically when the graphite lattice is mechanically shattered to smaller fragments, (Eq. (1)), is released as an increase in the heat of combustion (Eq. (2)) so that the net change is that of Eq. (3), which represents the combustion of pure crystalline graphite, i.e., −393.5 kJ/mole. Thus Eq. (1) represents in effect a portion of the lattice or atomization energy of graphite, estimated to be approximately 717 kJ/mole (*9*). The largest heat of combustion observed in this study 531 kJ/mole for Series B samples represent an increase of 137 kJ/mole over the value for pure graphite suggesting that up to about 20% of the energy of atomization has been breached by grinding.

The lattice energy may be regarded as consisting of two parts reflecting the anisotropic character of graphite: (1) a Van der Waals contribution parallel to the cleavage planes and (2) a larger "covalent" contribution resulting from the fracture of the chemical bonds within the carbon framework perpendicular to the cleavage planes. The difference between the combustion data of Series A and B probably reflects different contributions from these two sources. The higher values observed for Series B samples (those which were not exposed to air before combustion) imply a contribution to the combustion heats from the more reactive edge atoms exposed by the breaking of covalent bonds. If the samples are exposed to air before combustion, as in Series A, these more energetic sites spontaneously combine with oxygen, presumably with some loss of CO and CO_2 so that the "covalent" contribution will not be reflected upon subsequent combustion. The residual increase in ΔH_c, as observed in the air-exposed samples, would then be due to the van der Waals contribution to the lattice energy, resulting from the combustion of face atoms. However, even this contribution is uncertain since some of the face carbon atoms will have been partially oxidized to CO_2 in the form of chemisorbed carbon oxygen complexes, so that a quantitative accounting would be speculative at best.

The good agreement for the Series A data contrasts with the scatter observed for Series B but is not unexpected in view of the observed heterogeneity of ultrafine graphite samples with respect to crystallite size and thickness and the relative reactivities of edge atoms compared to planar atoms. Since the residual lattice energy associated with the edge atoms is considerable, relatively small variations in their number would be reflected in large scatter in the resulting heats of combustion.

Our ESR data are consistent in most respects with other work on this material with the significant exception that in this study, on exposure to air, the ESR signal is reversibly and asymmetrically broadened, and the lineshape changes from Lorentzian to nearly Gaussian. The fact that the signal is reversible with respect to strong chemical attack and oxygen exposure indicates that the electron spins are not at vulnerable surface sites but at protected locations, possibly stabilized in smaller delocalized networks. The X-ray, electron microscope, and ESR data point to a tentative model (*8*) in which the ultrafine graphite consists of thin plates of varying diameters with some evidently as small as three layers thick (10 Å) and perhaps 15 Å in diameter.

An independent estimate of the platelet size may be approximated from the experimental linewidth using the Van Vleck expression for isotropic dipolar broadening (*10*):

$$H_d = 4.72 \times 10^4[(S)(S + 1)]^{1/2}(d/m)$$

Where the last term is the density divided by the molecular weight of the paramagnetic moiety, i.e., the ultrafine graphite platelet. Using the observed linewidth of 8 G, and a density of 2 g/cc, we calculate a "molecular weight" of 10,000 g mole^{-1} or 1.6×10^{-20} g platelet^{-1} corresponding to a volume of roughly 8000 Å^3 per platelet, in agreement with a model of thin plates 10 Å thick and 30 Å in diameter. The calculated planar surface area of ultrafine graphite would then be 900 m^2 g^{-1} which is in reasonable correspondence with surface areas determined from nitrogen adsorption isotherms ranging from 200–800 m^2 g^{-1}. Since each platelet comprises approximately 800 carbon atoms and the upper limit of O_2 uptake is estimated at 10% by weight then there is a maximum of about 60 oxygen atoms per crystallite. While most of this oxygen is presumably chemisorbed in the form of carbon–carbon complexes, the reversible oxygen effects on the ESR signal strongly support a model in which at least some of the oxygen is reversibly physisorbed as O_2.

Asymmetric broadening of the ESR signal on exposure to air could result from anisotropic dipolar coupling between physisorbed molecular oxygen and the unpaired spins on the carbon skeleton. The ESR envelope would then be a systematic superposition of the individual absorptions whose field positions differ as a result of the g value anisotropy of molecular oxygen. The observed signal would be broadened inhomogeneously and reversibly and the attendant lineshape nearly Gaussian. A crude approximation of the average dipolar broadening resulting from the interaction between the unpaired spin and molecular oxygen is possible. A reasonable estimate of the field arising at one electron from another at a distance of 10 Å is about 10 G (*10, 11*). Since for O_2, $S = 1$, the $[S(S + 1)]^{1/2}$ factor requires that the estimated field developed by a single O_2 molecule be scaled up by about 2, to 20 G, and this should further broaden the oxygen-free signal to roughly 28 G. This is in plausible agreement with the observed value of 31 G for air-exposed samples and not inconsistent with electron–O_2 distances which may be inferred from considerations of platelet size.

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