

compared with known concentrations on a Beckman DU spectrophotometer at a wavelength of 437 nm.

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Stable Substoichiometric Cerium Oxide Formed in an Air Plasma

Abstract. Cerium dioxide was reduced to a stable, substoichiometric monophasic phase in an air plasma. This phase has been identified as $CeO_{1.94}$ by thermal gravimetric analysis. The existence of a stable, reduced phase of cerium oxide can be explained by interpretation of both theoretical and experimentally determined crystal data.

Cerium dioxide, CeO_2 , with a melting point of $2750^\circ C$, has attractive properties as a high-temperature refractory. It is stable in air but reduces to Ce_2O_3 when heated in reducing atmospheres for prolonged periods (1). The reduction of CeO_2 with hydrogen occurs appreciably at temperatures above $500^\circ C$ (2).

Ceria and oxides of many other heavy metals can be reduced to oxygen-deficient compounds by heating them in inert or reducing atmospheres. For example, CeO_2 is reduced to numerous substoichiometric forms by heating in a vacuum at elevated temperatures (3); ZrO_2 is reduced to $ZrO_{1.96}$ by heating at $900^\circ C$ at 10^{-3} torr for 1 hour (4); and ZrO_2 microspheres which are deficient in oxygen may be prepared in an argon plasma (5).

Stoichiometric CeO_2 particles were spheroidized by an inductively coupled plasma torch sustained by a 50-, 25-, and 10-kw induction heater modified to operate between 5 and 7 Mc/sec. The plasma gas employed with the 50-kw and 25-kw torches was air or O_2 ; the mixtures in the 10-kw system consisted of 50 percent Ar and 50 percent air or 50 percent Ar and 50 percent O_2 . The operation of these plasma torches and the mechanism used to feed particles into the plasma has been described (6). Blue-black microspheres were obtained in the high-powered plasma systems but only ivory-colored microspheres were obtained in the 10-kw system. The spheroidized product was collected in air at room temperature.

Thermal gravimetric analyses from ambient to $1000^\circ C$ were performed on representative samples of each of the cerium dioxide products. No weight increase was obtained on the ivory-colored microspheres. In duplicate samples a weight increase corresponding to an initial formula of $CeO_{1.940} \pm 0.005$ was obtained on the blue-black microspheres. The $CeO_{1.940}$ can be oxidized by heating in air at $500^\circ C$ for several hours; ivory-colored CeO_2 microspheres are produced.

Ceramographic cross sections of $CeO_{1.940}$ microspheres were optically examined at 200-power magnification. This examination showed that a homogeneous monophasic phase was present.

X-ray diffraction powder patterns of the blue-black microspheres indicate a single face-centered cubic phase with the fluorite structure having a lattice constant of 5.4098 ± 0.0007 Å. The ivory-colored microspheres, whether from the original material or from oxidation of the blue-black microspheres, show this same face-centered cubic monophasic phase with a lattice parameter of 5.404 ± 0.005 Å. These parameters were refined by the least-squares method (7) and the errors are given as standard deviations.

From x-ray diffraction studies on samples which varied between $CeO_{2.00}$ and $CeO_{1.82}$ in overall stoichiometry and which were variously quenched from 800° to $1200^\circ C$, Bevan (3, 8) found evidence of a face-centered cubic phase that had an unchanging lattice parameter (from a statistical viewpoint) down to an overall composition of $CeO_{1.83}$. The exact composition of this cubic phase is uncertain according to Bevan's data.

Our studies indicate that stable, monophasic $CeO_{1.94}$ microspheres can be produced in an induction-coupled plasma torch under oxidizing conditions and that these microspheres will retain their nonstoichiometric nature even at $250^\circ C$. [Oxygen-deficient CeO_2 prepared in an inert or reducing atmosphere or in a vacuum contained, in general, two phases (3).] The absence of the $CeO_{1.94}$ prepared in the 10-kw plasma system indicates that the reduction is energy-dependent.

This detectable change of stoichiometry (CeO_2 to $CeO_{1.94}$) in the 25- and 50-kw system without notable modification of the fluorite structure or even significant alteration in lattice parameter is crystallographically favorable because the radius ratio of Ce^{4+} to O^{2-} [1.01 and 1.40 Å, respectively

(9)] is below the ideal minimum for spherical ion contact of 0.73. Apparently, the gain from relief of anion-anion overlap by in-site reduction of a portion of Ce^{4+} ions to form larger Ce^{3+} ions (radius, 1.11 Å) and the concurrent oxidation of equivalent O^{2-} ions so nearly offsets the unfavorable energetics of Ce^{3+} relative to Ce^{4+} that in the higher-powered plasma environments, at least, a relatively stable, metastable, substoichiometric product can be obtained.

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Cholesterol: Treadmill Activity Accelerates Oxidation in Rats

Abstract. Cholesterol- $26-^{14}C$ was injected intravenously into male and female rats of two different strains. Recovery of radioactivity from the expired air was increased by treadmill activity.

When cholesterol- $26-^{14}C$ is injected intravenously into rats, 30 percent of the radioactivity can be recovered as $^{14}CO_2$ in the expired air within the first 24 hours (1). Oxidation of the side chain of cholesterol, similarly demonstrated in man (2), is implicated in the synthesis of bile acids (3), which play an important role in the elimination of cholesterol from the body (4). We have demonstrated that treadmill activity increases the rate of oxidation of cholesterol in rats.

Male and female rats of the Sprague-Dawley and Wistar strains were used. One milliliter of 0.9-percent solution of NaCl was added to 100 μ l of methanol containing 1 mg of Tween-80 (Atlas

Table 1. Body weights (grams) of rats injected with cholesterol-26-¹⁴C (means $\pm$ S.E.). Numbers of rats appear in parentheses. By *t*-test: Sprague-Dawley versus Wistar, *P* < .01; males versus females (Sprague-Dawley), *P* < .05.

Strain	Control	Experimental	Males	Females
Sprague-Dawley	217.5 $\pm$ 16.5 (6)	207.5 $\pm$ 12.8 (12)	231.1 $\pm$ 15.6 (9)	190.6 $\pm$ 8.6 (9)
Wistar	150.5 $\pm$ 7.2 (10)	149.5 $\pm$ 4.7 (10)	156.0 $\pm$ 7.0 (10)	144.0 $\pm$ 4.1 (10)

Powder Co.) and 2.5 μ C of cholesterol-26-¹⁴C (Nuclear-Chicago, Chicago, Ill.; specific activity, 24.0 mc/mmole). The optically clear preparation was injected into the tail vein. The rats were immediately placed in a specially designed airtight drum having a diameter of 30 cm and a total volume of 7.2 liters. Air free of CO₂ was admitted

to the drum and then aspirated at a rate of 1.2 liter/min and bubbled into 15 ml of a 1:2 (by volume) mixture of ethanolamine and ethylene glycol monomethyl ether (5).

Fifteen minutes after the injection, expired CO₂ was collected for four to nine 20-minute periods; every third period the rat was exercised by rotation of the treadmill at a rate of 15 to 17 rev/min. Control animals were immobilized and suspended on the axis of the drum; the treadmill was rotated and CO₂ was collected as before. Fifteen milliliters of a scintillation solution (5) was added to 3 ml of collecting fluid, and the radioactivity was assayed in a Packard Tri-Carb liquid-scintillation spectrometer (model 3003).

Body weights and sex distribution (Table 1) were similar in control and experimental animals. Since the response to treadmill activity was the same in males and females, the results for both sexes are reported together for each strain. Results of typical experiments are shown in Fig. 1. Figure 2 shows the ¹⁴C radioactivity in the expired air from six control and 12 experimental Sprague-Dawley rats. So that all animals could be compared, the disintegrations per minute for the period immediately preceding rotation of the treadmill have been taken to equal 100.

One sees that rotation of the treadmill caused no significant changes in the controls. In the experimental animals, however, treadmill activity led to increased oxidation of cholesterol, which persisted into the period immediately following activity. Oxidation was consistently increased in each animal during the three activity periods. Results with Wistar rats were essentially similar (Fig. 1).

Despite the indications that disturbed metabolism of cholesterol may be implicated in the genesis of atherosclerosis (6), we do not know what mechanisms influence the possible inverse relation between occupational activity and occlusive arterial disease (7). Our results clearly demonstrate accelerated oxidation of cholesterol,

induced by treadmill activity in rats. If our findings prove to be true for other species, one may speculate that physical exercise may retard development of atherosclerosis by increasing the removal of cholesterol by oxidation.

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Secretory Immunoglobulin A: Autoantibody Activity in Gastric Juice

Abstract. An immunoglobulin A of the secretory variety, present in the gastric juice of a patient with pernicious anemia, was shown to have specificity for intrinsic factor. This is the first demonstration in gastric juice of antibody activity restricted to secretory IgA; further, this is the first example of an exocrine (gastric) immune system producing an autoantibody specifically directed toward a product synthesized by that same exocrine organ.

Immunoglobulin A (IgA) of exocrine origin (saliva, gastrointestinal fluids) differs from serum IgA in that it contains an additional nonimmunoglobulin component, the so-called secretory piece (1, 2). As shown by Tomasi *et al.*, the complex of IgA and secretory piece, referred to as secretory IgA, is unique to exocrine fluids (1). Isoagglutinin antibody activity has been demonstrated in secretory IgA of salivary secretions (1), but an autoantibody of this variety has hitherto not been reported. This paper describes a secretory IgA autoantibody to intrinsic

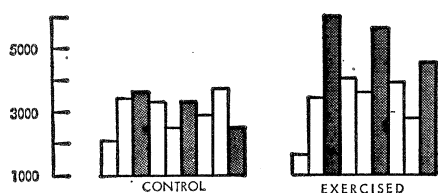


Fig. 1. Typical results showing ¹⁴C (disintegrations per minute) in the expired air from two Sprague-Dawley rats. Columns correspond to consecutive 20-minute collection periods starting 15 minutes after intravenous injection of 2.5 μ C of cholesterol-26-¹⁴C. Stippled columns, rotation of the treadmill; open columns, rest periods.

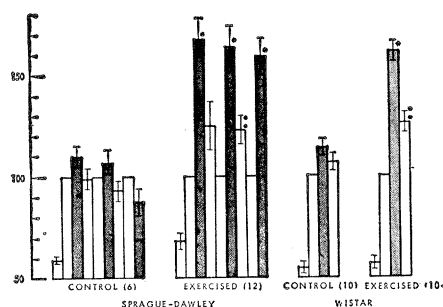


Fig. 2. Average ¹⁴C (arbitrary units) in the expired air from rats. Collection of CO₂ was started 15 minutes after intravenous injection of 2.5 μ C of cholesterol-26-¹⁴C. Columns correspond to consecutive 20-minute collection periods; bars, standard errors of the means. Stippled columns, rotation of the treadmill; open columns, rest periods. The period immediately preceding rotation of the treadmill is taken to equal 100 for the initial as well as for the following two periods. Numbers of animals appear in parentheses. For the Sprague-Dawley rats the number of determinations for each period equals the number of animals; for the Wistar rats there were 16 rotation and 14 postrotation periods for the controls, and 16 activity and 12 post-activity periods for the exercised animals. Differences (*t*-test) between corresponding periods for control and experimental animals: *P* < .001 (*), *P* < .01 (**).