

The Reaction of Oxygen with Carbonaceous Compounds
in the Electrodeless Ring Discharge

Chester E. Gleit

Department of Chemistry, North Carolina State University, Raleigh, North Carolina, 27607

Abstract

The electrodeless ring discharge has recently found use in chemical analysis as a means of removing carbon from graphitic and organic compounds preceding elemental analysis and determination of microstructure. To determine appropriate reaction conditions, the relationship between oxidation rate and sample temperature was studied. Samples were immersed in a plasma produced by passing molecular oxygen through a radiofrequency field. An inductively coupled, 13.56-MHz generator producing 95 watts was utilized. Gas pressure was 1.2 torr, and flow 150 cc/min. The apparent activation energy of pure graphite was found to be 6.5 Kcal/mol in the temperature range 100 to 300°C, and zero at higher temperatures. The activation energy of both impure graphite and sucrose were slightly lower. These values are consistent with those of atomic oxygen. The reaction of graphite with CO₂ did not occur below 120°C and yielded an apparent activation energy of 3.2 Kcal/mol in the temperature range 150 to 300°C. Oxidation rate was observed to depend on electrical field configuration. Increasing the temperature of the reaction tube's walls decreased the rate of carbon oxidation. Trace ions, such as Fe(II), Se(IV), Os(IV), and iodide, were converted to higher oxidation states. Neither oxidation nor volatility was observed to be strongly temperature dependent.

Introduction

In 1962 a method was reported for the decomposition of organic substances based on reaction with an oxygen plasma, produced by passing molecular gas through a radiofrequency electrodeless discharge (5). This method has found use in a variety of chemical studies. Loss of trace elements through volatilization and diffusion is less than that in conventional dry ashing. Destruction of mineral structure is reduced. As a small quantity of purified oxygen is the only reagent, the possibility of chemical contamination is diminished. Applications of this method include: microincineration of biological specimens (13), the ashing of coal (6) and filter paper (4), and the recovery of mineral fibers from tissue (1). Several reviews of analytical applications have been published (9)(14).

In conventional ashing both reaction rate and retention of volatile components are strongly temperature dependent. However, disagreement exists as to the effect of temperature in plasma ashing. In part, this is due to difficulty in applying conventional temperature measuring techniques to solids immersed in a strong radiofrequency field. The question is further complicated by the fact that a single temperature cannot be assigned to the system. Electrons in the low pressure plasma are not in thermal equilibrium with the ions and neutral species. Furthermore, the temperature of the specimen and the surrounding vessel may differ considerably. In this study the effects of temperature on oxidation rate, recombination of active gaseous species, and volatility of inorganic reaction products are considered.

Experimental

The reaction system employed in these studies (figure 1) consisted of a 100-cm long, 3.5-cm I.D., borosilicate cylinder (Pyrex No. 7740). Specimens were placed on

the principal axis 43 cm from the gas inlet. A 0.6-cm tube, C, passed diametrically through the cylinder and held the specimen on a central projection. Sample temperature was regulated, in part, by circulating liquids between this tube and a constant temperature bath. Radiofrequency excitation was supplied from a 250-watt, crystal controlled 13.56-MHz generator, described previously (3). Except as otherwise noted, an output of 115 watts was employed. Power was transferred to the gas by means of an impedance matching network terminating in a 10-turn coil of $\frac{1}{4}$ -inch O.D. copper tubing tapped 2 turns from ground. The coil, B, which had an inside diameter of 4.5 cm and was 12.5 cm long, was coaxial with the reaction tube and placed 10 cm from the gas inlet.

After passage through a rotometer, molecular gas entered the reaction system through a capillary orifice, A. Pressure was monitored by a McCloud gauge attached to side arm E, located 50 cm beyond the gas inlet. Pressure was maintained at 1.2 torr; and flow rates at 150 cc per minute, S.T.P. U.S.P. grade oxygen and instrument grade carbon dioxide were used.

The temperature of solid specimens in the plasma was determined by means of an infrared radiation thermometer (Infrascopes Model 3-1000, Huggins Laboratories Inc., Sunnyvale, Calif.) attached to a chart recorder. This device employs a lead sulfide detector and suitable filters to permit remote measurement of 1.2 to 2.5 μ radiation emitted by the specimen. To compensate for variations in emissivity and inhomogeneity in the optical field, empirical calibration curves were constructed. Thermocouples were employed to determine cylinder-wall temperatures. To eliminate interaction with the radiofrequency field, the transmitter was inactivated during the latter measurements.

High purity graphite rods (National Carbon Co., Grade AGKSP) were employed as standard specimens. These rods were 0.61 cm in diameter and had a cavity machined into their base to affix them to the cooling tube. Pellets of sucrose and carbon containing small quantities of cupric acetate were also employed. The latter were produced by heating and then pressing a slurry of the salt solution and 200-mesh graphite powder.

Results and Discussion

Sample Temperature: The temperature variation of oxidation rate of graphite exposed to the oxygen plasma is shown in figure 2. Over the range 120 to 300°C, the Arrhenius equation, $K = Ce^{-E_a/RT}$, fits the data well and yields a value of 6.5 Kcal/mol for the apparent activation energy, E_a . Between 300 and 450°C, the highest temperature studied, oxidation rate is not dependent on temperature. The oxidation of graphite by molecular oxygen at high temperature is strongly dependent on the purity of the graphite. To determine if a similar effect occurs in plasma oxidation, pellets composed of pure graphite powder and inorganic salts were utilized. The results of the addition of 0.01 M cupric acetate are shown in figure 2. At low temperature the change in oxidation rate of pure and impure graphite with temperature is similar. However, the rate of oxidation of the impure graphite becomes independent of temperature at a lower temperature. Measurements performed with specimens containing lower concentrations of cupric acetate led to results which fell between the illustrated curves.

The gas in the low pressure electrodeless discharge is chemically similar to that in the positive column of a low pressure arc. Molecule-molecule and ion-molecule collisions are frequent. The ions and neutral species are, therefore, nearly in thermal equilibrium. Elastic collisions between these species and electrons are less frequent. At low pressure electron temperatures are quite high. In the oxygen discharge atomic oxygen (O^2P) is believed to be the most abundant active species. Higher energy states of atomic oxygen, positive and negative ions, and electronically excited

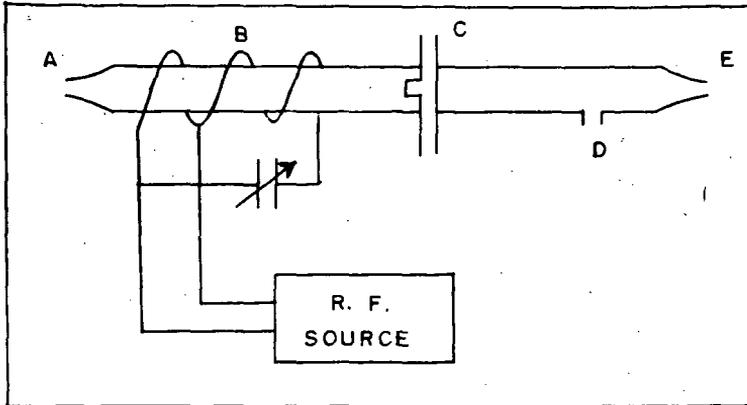


Fig. 1. Experimental apparatus: capillary inlet, A; power coil, B; specimen mounting tube, C; sidearm to manometer, D; outlet to vacuum pump, E.

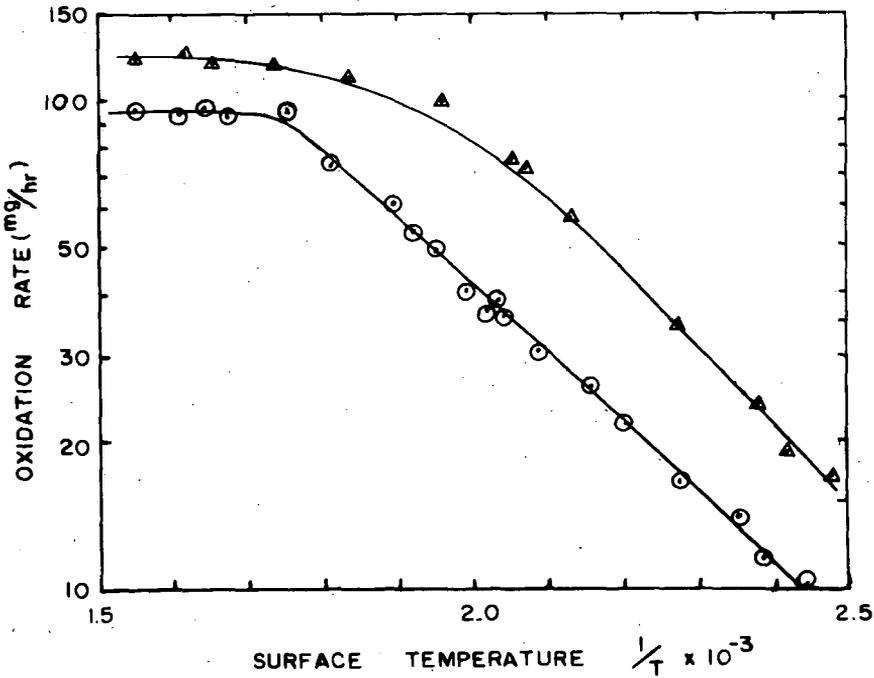


Fig. 2. Rate of oxidation vs. surface temperature for graphite rods, ○, and graphite pellets containing 0.01 M cupric acetate, △.

states of molecular oxygen are also present.

It is instructive to compare these results with measurements of the activation energy of graphite with atomic oxygen removed from the luminous discharge. In several early studies a value of zero was reported (2) (16). Hennig (8) observed no dependence on temperature at a pressure of 1.0 torr and a value of 7 Kcal/mol at 10 torr. This difference was attributed to ozone formation. In a recent detailed study of the atomic oxygen-graphite reaction, Marsh et al. (11) reported an activation energy of 10 Kcal/mol between 14 and 200°C, which approached zero at 350°C. Although the rate of oxidation in these studies was considerably lower than that obtained in the plasma, their values are consistent with the belief that atomic oxygen is a major reactant within the discharge.

Of a variety of specimens, only graphite exhibited an abrupt change in activation energy near 300°C. For example, the apparent activation energy in the decomposition of sucrose is approximately 4 Kcal/mol over the entire measurement range. The independence of oxidation rate for graphite at high temperatures is ascribed to the formation of surface oxides. Numerous studies of graphite combustion have shown that such surface compounds control rate at elevated temperatures in excess oxygen. As anticipated, increasing radiofrequency power to the discharge does not measurably increase the rate of graphite oxidation at high sample temperature.

The exhaust gas of the oxygen-graphite reaction contains both carbon monoxide and carbon dioxide, with the latter predominating. In the luminous discharge region these gases react with graphite. The results of measurements in which carbon dioxide was passed through the radiofrequency field and then exposed to graphite rods activated are shown in figure 3. Between 150 and 400°C the Arrhenius equation fits well, yielding an apparent activation energy of 3.2 Kcal/mol. Below 120°C less than one mg per hour of carbon was removed. This small weight loss is attributed to ion and electron bombardment.

Wall Conditions: In a number of experiments, increasing power beyond an optimum value led to the anomolous result of reducing ashing rate. Earlier it was noted that placing a dry ice-acetone trap in the exhaust stream extended the length of the luminous discharge (5). To study this effect, wall temperatures were varied while the carbon rod was maintained at 200°C. The results of a series of measurements are shown in figure 4. Assuming that the decrease in oxidation rate at increased wall temperature is due to recombination of active species at the wall, the overall activation energy at low temperatures for this process is approximately 2 Kcal/mol.

The major sources leading to loss of active oxygen species are recombination of atomic oxygen and ions at the walls of the vessel. The recombination of discharged oxygen on glass surfaces has been investigated. Linnett and Marsden (10) reported that the recombination coefficient of atomic oxygen on clean borosilicate glass (Pyrex) was independent of temperature. However, positive values were observed on contaminated surfaces. In a later series of papers Greaves and Linnett (7) studied a number of oxide surfaces, in all cases the recombination coefficient was temperature dependent. For silica apparent activation energies were 1 to 13 Kcal/mol over the temperature range 15 to 300°C. The exceptional nature of Pyrex was noted.

The second major source of loss of active species results from electron-ion recombination at the chamber walls. The electric field restricts the drift of ions to the chamber walls. Rate of recombination is controlled by ambipolar diffusion, but is limited by the presence of negatively charged oxygen ions in the discharge (15). Although diffusion is not dependent on wall temperature, a distortion of the axially symmetric electrical field will enhance wall recombination, producing an increase in wall temperature and a reduction of oxidation rate. This effect is noted in table I. The presence of a 6-cm long metallic ring on the exterior wall of the reaction vessel reduced oxidation rate by more than ten per cent. Grounding the ring in common with

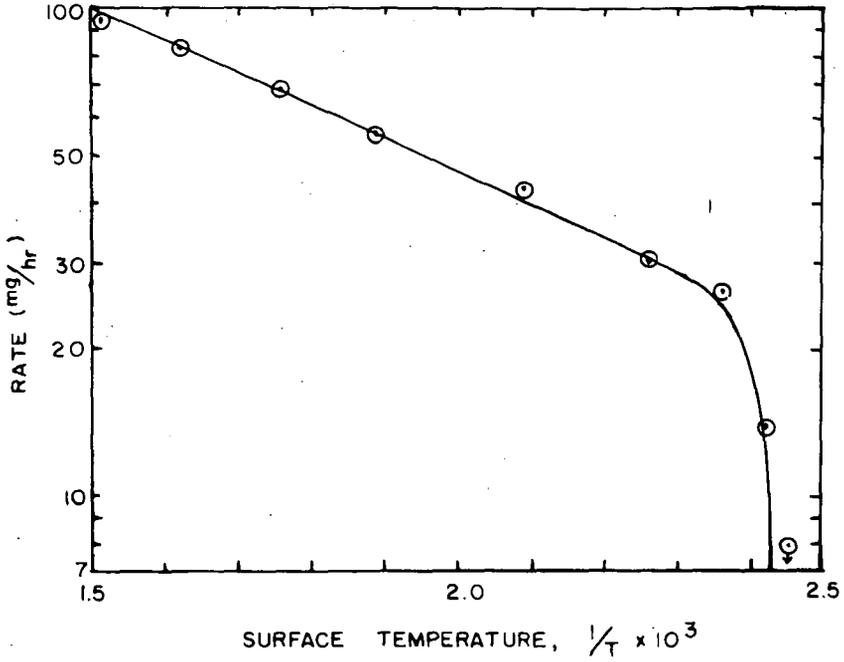


Fig. 3. Rate of gassification vs. temperature for graphite rods exposed to carbon dioxide discharge.

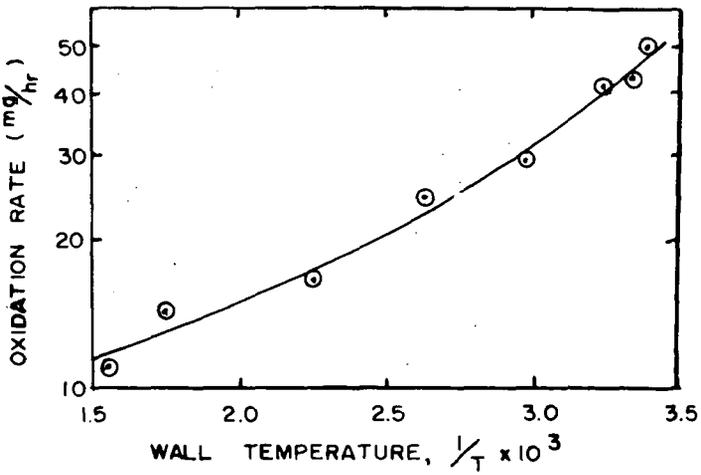


Fig. 4. Effect of wall temperature on the oxidation rate of graphite.

the output coil further reduced the oxidation rate. This is a local effect, in that oxidation rate beyond the ring was not greatly reduced. Distortion of the field can also be introduced by changing the angle between the end of the output coil and the reaction tube. Variations from axial symmetry led to reduced rates and decreased the length of the luminous discharge. Similar effects have been observed in electrodeless discharges at higher pressure (12).

Table I

Effect of Field Distortion on Carbon Oxidation Rate

	Angle	Oxidation Rate mg/hr
Pyrex tube	0°	79
Pyrex tube and ungrounded copper ring	0°	70
Pyrex tube and grounded copper ring	0°	62
Pyrex tube	1.°	71
Pyrex tube	3.°	63

Effect on Mineral Constituents: It has been reported that there is no appreciable loss of a number of metal ions in plasma oxidation (4,5). Nonvolatile species include: Na(I), Cs(II), Cu(II), Zn(II), Mn(II), Pb(II), Cd(II), Co(II), Ho(III), Er(III), Fe(III), Cr(III), As(III), Sb(III), and Mo(VI). The effect of ashing temperature, the reason for the surprisingly low volatility, and the final oxidation state of the product were not previously explored. As part of the present study, 20 to 100 mg of compounds containing radioactive tracers were deposited on Whatman cellulose filters. After exposure to ashing for a sufficient period to remove the filter paper, generally 30 minutes, the activity of the ash was measured and the oxidation state of the element determined. Specimen temperature was adjusted during ashing by altering input power.

These measurements are summarized in table II. In general, temperature has little effect on retention. These results and earlier observations indicating complete retention of metals in compounds such as arsenic chloride and metalloporphyrins (5) are believed to be due to competition between volatilization and oxidation to less volatile compounds. Unlike the other elements studied, the highest valence oxide of osmium, OsO₄, is the most volatile. Therefore, this element is volatilized in the plasma oxidation process.

The volatility of iodide, shown in figure 5, is also consistent with the hypothesis of competition between volatilization and oxidation. During these measurements, ashing was stopped at 5 minute intervals. It is seen that loss of I¹³¹ closely follows the curve for filter paper gassification. No loss of I¹³¹ occurs after the filter paper is removed. Loss of I¹³¹ varied between 15 and 35 per cent. However, none of the residual I¹³¹ could be precipitated with silver nitrate, indicating that the iodide had been oxidized. When the I¹³¹ tracer was converted to NaIO₃ before ashing all of the iodine activity was retained.

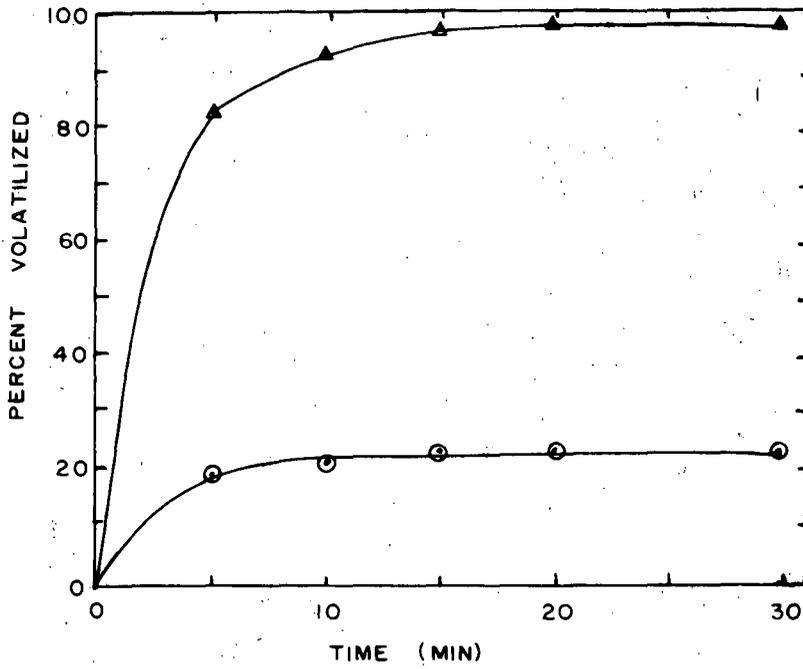


Fig. 5. Loss of sample weight, Δ ; and loss of I^{131} tracer, \odot , during ashing of filter paper in an oxygen plasma.

Table II

Recovery of Trace Elements from Ashed Filter Paper

<u>Tracer</u>	<u>Compound</u>	<u>Max. sample Temperature</u>	<u>Percent Recovered</u>	<u>Highest Oxidation State</u>	<u>Percent in Highest Oxidation State</u>
Fe ⁵⁹	Fe(OH) ₂	120	100	III	95
Fe ⁵⁹	Fe(OH) ₃	120	100	III	100
Se ⁷⁵	Na ₂ SeO ₃	110	99	V	91
Se ⁷⁵	Na ₂ SeO ₃	250	100	V	93
Se ⁷⁵	Na ₂ SeO ₄	110	100	V	100
Se ⁷⁵	Na ₂ SeO ₄	250	100	V	100
Ag ^{110m}	AgCl	110	89(99)*	I	--
Ag ^{110m}	AgCl	250	79(100)*	I	--
Os ¹⁹¹	OsO ₂	120	<1	VIII	--
Os ¹⁹¹	Na ₂ OsO ₄	150	<1	VIII	--

* Recovered after rinsing tube with HF-HNO₃

The behavior of silver ion represents a different type of ashing loss. As opposed to the other metals in this study, only 75 to 90 per cent of the Ag^{110m} could be recovered from the borosilicate sample holder by rinsing with dilute nitric acid. To recover the remainder of the Ag^{110m}, the glassware had to be repeatedly rinsed with a warm mixture of nitric and hydrofluoric acids. By maintaining the system at low temperature this difficulty was ameliorated, but not eliminated.

Conclusion: A number of active species are known to be present in the luminous electrodeless discharge. Although a similarity between reactions in the plasma and those of discharged oxygen is noted, it cannot be concluded that within the plasma only the reactions of atomic oxygen are significant. The present study indicates appropriate conditions for the application of the electrodeless discharge to decompose carbonaceous materials prior to elemental analysis. Specifically, increasing sample temperature to 200-300°C leads to an improvement in ashing rate without appreciably increasing volatility losses.

Acknowledgement

The electrical apparatus used in this study was constructed by James Breitmeier. The assistance of Juan Wong and Daniel Silvers is appreciated. Walter Holland, Harvey Beaudry and Robert Reinhart assisted in preliminary studies performed under a contract between Union Carbide Chemical Corporation and the Laboratory for Electronics. This study was supported by grants from the North Carolina Engineering Foundation and North Carolina State University Professional Development Fund.

Literature Cited

1. Berkley, C., Churg, J., Selikoff, I. J., and Smith, W. E., Ann. New York Acad. Sci., 132, 48 (1965).
2. Blackwood, J. D., and McTaggart, F. K., Austral. J. Chem., 12, 114 (1959).
3. Gleit, C. E., Microchem. J., 10, 7 (1966).
4. Gleit, C. E., Benson, P. A., Holland, W. D., and Russell, I. J., Anal. Chem., 36, 2067 (1964).
5. Gleit, C. E., and Holland, W. D., Anal. Chem., 34, 1454 (1962).
6. Gluskoter, H. J., Fuel, 44, 285 (1965).
7. Greaves, J. C., and Linnett, J. W., Trans. Farad. Soc., 54, 1355 (1958).
8. Hennig, G. R., Dienes, G. J., and Kosiba, W., Proc. Second Intern. Conf. Peaceful Uses At. Energy, Geneva, 7, 301 (1958).
9. Hollahan, J. R., J. Chem. Educ., 43, A401, A497, 392 (1966).
10. Linnett, J. W., and Marsden, D. G. H., Proc. Roy. Soc. (London) Ser. A, 234, 489 (1956).
11. Marsh, H., O'Hair, T. E., and Wynne-Jones, W.F.K., Trans. Farad. Soc., 61, 274 (1965).
12. Mitin, R. V., and Pryadkin, K. K., Zh. Tekhn. Fiz., 35, 1205 (1965).
13. Thomas, R. S., J. Cell Biol., 23, 113 (1964).
14. Thomas, R. S., "Techniques of Electron Microscopy: Microincineration for the Fine Localization of Mineral Constituents" in "Subcellular Pathology" ed. by Steiner, J. W., Morat, H. Z., and Ritchie, A. C., Harper and Row, New York (in press).
15. Thompson, J. B., Proc. Phys. Soc. (London), 73, 818 (1959).
16. Turkevich, J., and Streznewski, T., Revue L'Inst. Fran. du Petrole, 13, 686 (1958).