Surface Characterization of Activated Charcoal by X-Ray Photoelectron Spectroscopy (XPS): Correlation with Phenobarbital Adsorption Data

Gerald M. Burke,[1,2] Dale Eric Wurster,[1,3]
Mary J. Berg,[1] Peter Veng-Pedersen,[1] and
Dorothy D. Schottelius[1]

Received April 2, 1991; accepted July 30, 1991

X-ray photoelectron spectroscopy (XPS) was used to identify the functional states of carbon existing on the surfaces of various activated charcoals. The relative percentages of carbon, oxygen, and detectable trace elements comprising the activated charcoal surfaces were determined. Analysis of the carbon core-electron binding energy region revealed the existence of one hydrocarbon state (C–H, C–C are indistinguishable) and three oxygen-containing functional states. These states were hydroxyls or ethers (C–O), carbonyls (C=O), and carboxylic acids or esters (O–C=O). The C–O functional state contributed approximately 60–70% to the total percentage of oxygen-containing states. A very good correlation existed between the apparent areas occupied on the adsorbent surface per phenobarbital molecule and the relative percentages of the C–O functional state. Previously reported heat of displacement results for phenobarbital adsorption are now explained since the C–O state appears to be the primary site involved in the binding of phenobarbital by the activated charcoals.

KEY WORDS: X-ray photoelectron spectroscopy (XPS); activated charcoal; surface characterization; phenobarbital adsorption.

INTRODUCTION

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a technique for surface analysis. Experimentally, monochromatic X-ray radiation (typically from an Al Kα or Mg Kα source) is used to irradiate the sample. The X-ray radiation interacts with the sample and results in electrons being ejected from core orbitals of the atoms present on the surface. The binding energies of the photoelectrons, measured over a specified range, can be described mathematically by the following expression:

$$E_b = h\nu - E_k - \phi \qquad (1)$$

where E_b is the photoelectron binding energy, $h\nu$ is the characteristic photon energy of the X-ray source, E_k is the kinetic energy of the photoelectron, and ϕ is the spectrometer work function. The core-electron binding energies, of the atoms present in the sample, are used to obtain information on the chemical states of the atoms existing on the surface. There have been several review articles in the literature describing the basic principles of XPS (1–4).

Gai *et al.* (5) utilized XPS to determine the surface composition of activated coal chars (surface areas of 370 and 1024 m^2g^{-1}). The authors observed four carbon states: one hydrocarbon state and three oxygen-containing states. However, most of the research in XPS has been done with carbon fibers (6,7) and polymeric materials (8–10).

In other works, these investigators have examined the adsorption of phenobarbital from simulated gastric fluid, U.S.P. (without pepsin; SGF) and simulated intestinal fluid, U.S.P., (without pancreatin; SIF) (11,12) and, also, the heat of displacement for phenobarbital adsorption from solution by activated charcoals (13). The purpose of the present investigation is to relate the surface compositions of the same activated charcoals to the adsorption behavior observed in the aforementioned studies. In doing so, a better understanding of the adsorption of phenobarbital by activated charcoal is obtained.

MATERIALS AND METHODS

The XPS analysis was done at Perkin Elmer, Physical Electronics Division, Eden Prairie, MN, using a PHI Model 5500 ESCA system interfaced to an Apollo Domain Series 3000 Personal Workstation. The ESCA system was equipped with a dual-anode Al Kα X-ray source (Model 10-550, 1486.6 eV) operated at 400 W (15 kV and 26.7 mA) and calibrated with Ag $3d_{5/2}$, full-width half-maximum of 0.58 eV; a Model 10-410 PHI Toroidal X-ray Monochromator; a PHI OmniFocus II lens system; and a 180° Spherical Capacitor Analyzer (14). The activated charcoal samples, as obtained from the suppliers, were vacuum-dried (100°C, 25 μm Hg) for 24 hr prior to use. Immediately after vacuum drying, the charcoal sample was spread evenly over a piece of copper tape and mounted on a sample platen. The platen was inserted into an outer chamber and loaded into the analysis chamber. The chamber was maintained at approximately 1×10^{-9} Torr. The photoelectron takeoff angle was 65°. The analysis area on the sample was 800 μm in diameter and a pass energy of 11.75 eV was used. Three regions on each sample were analyzed. Survey scans were done from 1000 to 0 eV binding energy at 1-eV intervals (1001 total points per scan). The carbon (294–280 eV, C1s) core-electron binding region was analyzed by using a modified Gauss–Newton nonlinear least-squares optimization procedure. A function, $F(X_i,P)$, in the form of a Gaussian equation, where the X_i values contain the binding energy data and P is a parameter set containing those parameters that define the peak structure, was used to fit the data (15). The resulting curve fits for the individual carbon states comprising the C1s region were centered at binding energies specifically related to the carbon states present on the surface. These states were quantitated according to the relative areas under the curves for the individual carbon states comprising the C1s region. The XPS analyses were performed in triplicate.

The four activated charcoals studied were Darco KB-B, Norit, U.S.P. XX, Norit B Supra (all from American Norit Company, Inc., Jacksonville, FL), and SuperChar (Gulf Bio-Systems, Inc., Dallas, TX).

---

[1] College of Pharmacy, University of Iowa, Iowa City, Iowa 52242.

[2] Present address: McNeil Consumer Products Company, Fort Washington, Pennsylvania 19034.

[3] To whom correspondence should be addressed.

0724-8741/92/0100-0126$06.50/0

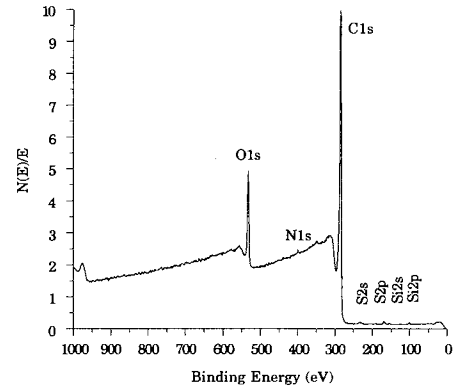

Fig. 1. Typical XPS survey scan of SuperChar.

RESULTS AND DISCUSSION

In XPS, only the top molecular layers of the surface of interest are analyzed. The mean sampling depth, D, can be determined from the following equation (10):

$$D = \lambda \sin\theta \qquad (2)$$

where λ is the mean free path of a photoelectron and θ is the photoelectron takeoff angle relative to the plane of the sample surface. There may be deep penetration of some of the X-rays into the sample. However, the photoelectrons produced in this case lose their energy in inelastic collisions. For this reason, only those photoelectrons in the top molecular layers of the surface escape and are analyzed (16). The mean free path of a C1s photoelectron can be calculated to be approximately 20–25 Å (17). Therefore, in this XPS study, where $\sin\theta$ was equal to 0.91, the approximate average depth of the activated charcoal surface analyzed was 18–23 Å.

Survey scans, from 1000- to 0-eV binding energies, of the four activated charcoals indicated that various trace elements were present, along with carbon and oxygen, on the surface. A typical survey scan is presented in Fig. 1. The percentage of carbon, oxygen, silicon, nitrogen, sulfur or phosphorus composing an activated charcoal surface was obtained by determining the contribution to the total area under the curve for all of the elements that was made by the area under the curve for each element. The results from these analyses are presented in the atomic concentration table (ACT; Table I). SuperChar was observed to have the highest percentage of oxygen, followed by Darco KB-B, Norit B Supra, and Norit, U.S.P. XX. The values for Darco KB-B and for Norit B Supra were quite similar.

The C1s regions of the survey scans were then analyzed, utilizing the aforementioned nonlinear least-squares optimization procedure (15), to determine the functional states present on the activated charcoal surfaces. Typical C1s spectra are presented in Figs. 2–5. Analyses of the C1s regions indicated that there were four carbon states present for all of the activated charcoals studied. These analyses were performed by fitting the raw data with four individual Gaussian curves. These individual curves sum to the final curve fit, indicated by the line drawn through the raw data. The functional states present are hydrocarbons (C−H and C−C, which are indistinguishable), hydroxyls or ethers (C−O), carbonyls (C=O), and carboxylic acids or esters (O−C=O). The peak positions of these chemical states have been well documented in the literature (18). However, the peak positions may shift slightly, compared to those reported in the literature, due to the chemical nature of the neighboring atoms on an individual surface. The Gaussian distribution for each functional state was varied to obtain the optimum final curve fit. The percentages of C−C or C−H, C−O, C=O, and O−C=O composing the activated char-

Table I. Atomic Concentration Table from the Analysis of the Survey Scans: Average of Relative Percentages of the Elements Comprising the Surface of the Activated Charcoals

Sample	Average percentage[a] of C, O, Si, N, S and P present (n = 3)					
	C1s	O1s	Si2p	N1s	S2p	P2p
SuperChar	86.6	12.4	0.3	0.5	0.2	—
Darco KB-B	92.3	7.4	0.1	—	—	0.2
Norit B Supra	91.9	7.1	0.9	0.1	—	—
Norit, U.S.P. XX	93.6	6.0	0.3	—	0.1	—

[a] Average of three determinations.

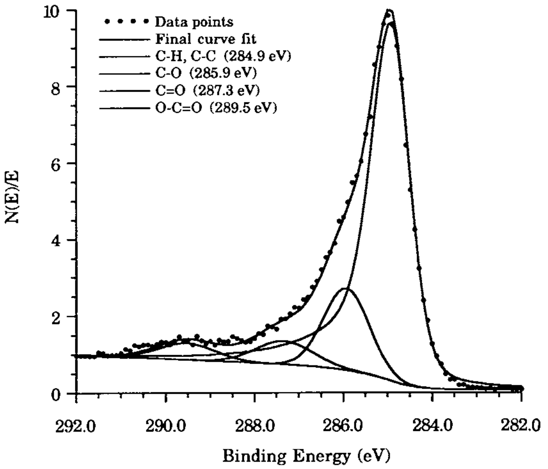

Fig. 2. Typical C1s spectrum of SuperChar.

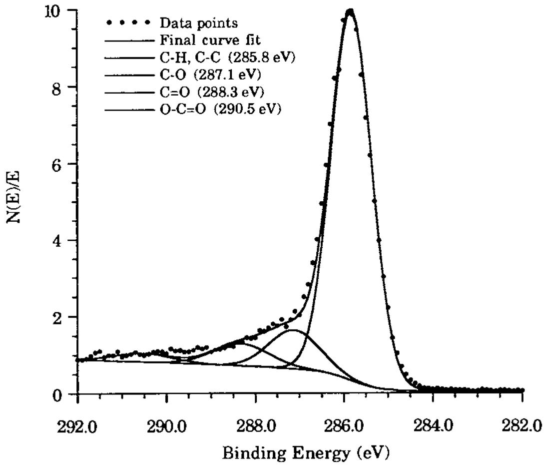

Fig. 3. Typical C1s spectrum of Darco KB-B.

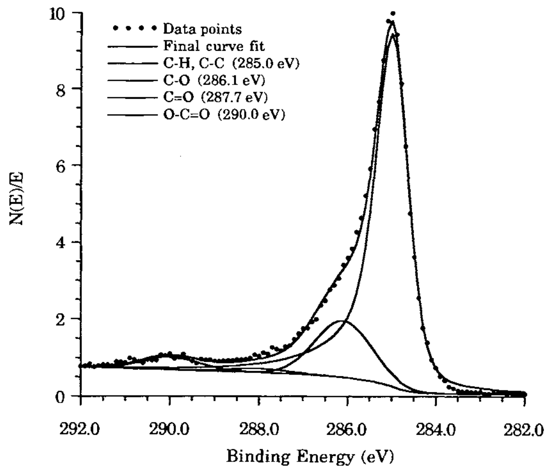

Fig. 4. Typical C1s spectrum of Norit B Supra.

Table II. Functional States Present in the C1s Spectra

	Average percentage of functional state present (n = 3)			
Sample	C−H, C−C hydrocarbon	C−O hydroxyl, ether	C=O carbonyl	O−C=O carboxylic acid, ester
SuperChar	73.4	15.7	5.7	5.1
Darco KB-B	78.1	12.8	6.2	2.9
Norit B Supra	78.6	15.1	2.6	3.7
Norit, U.S.P. XX	84.9	8.8	3.2	3.1

coal surfaces were obtained by determining the contribution to the total area under the C1s curve made by the area under the curve for each carbon state. The results from these analyses are presented in Table II.

In previous studies (11,12), the apparent areas occupied per phenobarbital molecule, A_0, were calculated according to the following equation:

$$A_0 = \frac{A_{sp}}{N_0 k_2 / MW} \tag{3}$$

where A_{sp} is the specific surface area, N_0 is Avogadro's number, k_2 is the Langmuir capacity constant of the activated charcoal for phenobarbital, and MW is the molecular weight of phenobarbital. The specific surface areas were obtained from a BET analysis of nitrogen vapor adsorption data. The capacity constants were obtained by using nonlinear least-squares regression analysis to fit the Langmuir model to the adsorption from solution data for phenobarbital. The values calculated for the apparent area occupied per adsorbed phenobarbital molecule are presented in Table III. The active adsorption site spacings on SuperChar and on Norit B Supra are probably optimal for phenobarbital based upon the estimated projected area that a single phenobarbital molecule should occupy on the adsorbent surface. The latter figure was obtained from group contributions and found to be 100–120 Å^2/molecule (11,19,20). This value assumes that the orientation of the phenobarbital molecule is parallel to the surface with neither overlap of functional groups nor open spaces. The active adsorption site spacing is not optimal for phenobarbital on Darco KB-B and on Norit, U.S.P. XX.

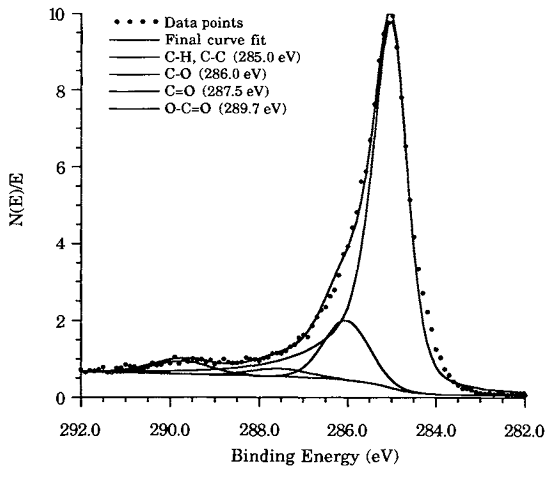

Fig. 5. Typical C1s spectrum of Norit, U.S.P. XX.

The initial assumption was that all of the oxygen-containing functional states could be sites for phenobarbital adsorption. On this basis, correlation plots were developed in which the apparent areas occupied per phenobarbital molecule on the surfaces of the activated charcoals were plotted against the relative percentages of the various oxygen-containing functional states present on the same surfaces. The coefficients of determination for the plots of mean apparent area versus mean relative percentage of either C=O or O−C=O were quite poor (r^2 = 0.04 and 0.60, respectively). The t tests for significance of correlation indicated that neither plot exhibited significant correlation at the 80% confidence level. However, a very good correlation, r^2 = 0.98, was obtained between the mean apparent areas occupied per phenobarbital molecule and the mean percentages of the C−O functional state present (Fig. 6). This correlation was significant at the 98% confidence level. This relationship suggests that the C−O functionality, probably in the form of hydroxyl groups, is the primary functional state involved in the binding of phenobarbital.

This finding helps explain several aspects of the previous adsorption studies. The surface areas of the various charcoals (13) are presented in Table IV. Analysis of variance followed by a Newman–Keuls comparison of means

Table III. Apparent Areas Occupied per Phenobarbital Molecule (12)

Activated charcoal	Apparent area occupied per phenobarbital molecule[a] (Å^2 ± SD)
SuperChar	110 ± 6
Norit B Supra	120 ± 1
Darco KB-B	152 ± 3
Norit, U.S.P. XX	185 ± 15

[a] Averaged from results obtained in SGF and SIF.

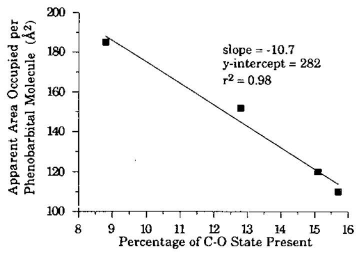

Fig. 6. Correlation plot of the apparent areas occupied per phenobarbital molecule to the percentages of the C – O functional state present.

indicated that SuperChar has a significantly larger surface area ($P < 0.05$) than any of the other charcoals. Norit B Supra was equal in surface area to Darco KB-B ($P > 0.05$) and Norit, U.S.P. XX, had a significantly smaller surface area than any other activated charcoal ($P < 0.05$). Upon comparison of the capacities for phenobarbital adsorption, obtained using the Langmuir model (Table IV), a different statistical result was found for both SGF (12) and SIF (13). The calculated capacities exhibited the following order: SuperChar > Norit B Supra > Darco KB-B > Norit, U.S.P. XX. All comparisons were significant ($P < 0.05$) in both SGF and SIF. The same statistical procedure was employed as for the analysis of the surface area data. The comparison between Darco KB-B and Norit B Supra is interesting. While they have statistically equal surface areas, Norit B Supra adsorbed 25–30% more phenobarbital. The XPS results reveal that, while Darco KB-B and Norit B Supra have equal surface areas and quite similar percentages of total oxygen, Norit B Supra has a higher percentage of the functional state, C – O, that is, apparently, the site for phenobarbital interaction.

Also, in previous work (13), heat of displacement studies, employing isoperibol solution calorimetry, were performed to verify that the Langmuir model was the appropriate model to describe the adsorption of phenobarbital by activated charcoal from SIF. The results of this work indicated that all of the sites available for adsorption were energetically equivalent. This study also showed that the differential heats of displacement for phenobarbital differed, at most, by 8% among the four activated charcoals. There were no significant differences between the differential heats of displacement, even at confidence levels as low as 50% (Table V). These conclusions were surprising considering that activated charcoal surfaces are generally regarded to be heterogeneous (21). This heterogeneity was, of course, shown by the XPS data. However, the conclusion that phenobarbital interacts predominantly with the surface hydroxyl groups readily explains these results.

Table IV. Surface Areas and Capacities of the Activated Charcoals

Activated charcoal	Surface area (13) (m^2/g)	Langmuir capacity for phenobarbital adsorption (mg/g) SGF (13)	SIF (12)
SuperChar	2900	1052	980
Norit B Supra	1510	487	483
Darco KB-B	1490	374	383
Norit, U.S.P. XX	940	207	184

Table V. Differential Heats of Displacement for the Replacement of Water by Phenobarbital on the Charcoal Surface (Medium is Simulated Intestinal Fluid, U.S.P.) (13)

System	Heat of displacement, $\overline{Q}_2$ (kcal/mol of phenobarbital adsorbed)
Darco KB-B	−9.6
SuperChar	−9.7
Norit B Supra	−10.1
Norit, U.S.P. XX	−10.4

CONCLUSIONS

This study has identified the functional states of carbon present on the four activated charcoal surfaces and has also provided the relative percentages of these states. The XPS spectra obtained clearly showed that differences existed in the surface compositions of these adsorbents. The correlations between the apparent areas occupied per phenobarbital molecule, based upon surface area and adsorption from solution studies (11,12) and the relative percentages of the various functional states present have given greater insight into the binding of phenobarbital by pharmaceutical-grade activated charcoals.

ACKNOWLEDGMENTS

This work was supported by National Institute on Drug Abuse Grant DA04083 and Biomedical Research Support Grant RR05877.

REFERENCES

1. J. A. Gardella Jr. Recent developments in instrumentation for X-ray photoelectron spectroscopy. *Anal. Chem.* **61**:589A–600A (1989).
2. L. E. Davis. Modern surface analysis. Metallurgical applications of auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). TMS-AIME Short Course; Las Vegas, NV, 1980, pp. 1–12.
3. R. Holm and S. Storp. Surface and interface analysis in polymer technology: A review. *Surf. Inter. Anal.* **2**:96–106 (1980).
4. D. Litchman. A comparison of the methods of surface analysis and their application in methods of surface analysis. In A. W. Czanderna (ed.), *Methods of Surface Analysis,* Elsevier Scientific Publishing Company, New York, 1975, pp. 39–73.
5. P. L. Gai, B. H. M. Billinge, and A. M. Brown. Microstructure of carbons. *Carbon* **27**:41–53 (1989).
6. Y. Xie and P. M. A. Sherwood. X-ray photoelectron-spectroscopic studies of carbon fibre surfaces. IX. The effect of microwave plasma treatment on carbon fibre surfaces. *Appl. Spectr.* **43**:1153–1158 (1989).
7. D. Youxian, W. Dianxun, S. Mujin, C. Chuanzheng, and Y. Jin. A study of the surface of carbon fiber by means of X-ray photoelectron spectroscopy. III. *Comp. Sci. Tech.* **30**:119–126 (1987).
8. L. Salvati Jr., G. L. Grobe III, and J. F. Moulder. Surface characterization of polymer based biomaterials: A combined XPS/Static SIMS approach. *PHI Interface* **12**:1,3–7 (1990).
9. M. C. Burrell, Y. S. Liu, and H. S. Cole. An X-ray photoelectron spectroscopy study of poly(methylmethacrylate) and poly-

(alpha-methylstyrene) surfaces irradiated by excimer lasers. *J. Vac. Sci. Technol. A* 4:2459–2462 (1986).

10. PHI Applications Note 8401. Plasma modified polymers: Angle resolved ESCA analysis, Eden Prairie, MN, 1984.
11. D. E. Wurster, G. M. Burke, M. J. Berg, P. Veng-Pedersen, and D. D. Schottelius. Phenobarbital adsorption from simulated intestinal fluid, U.S.P., and simulated gastric fluid, U.S.P., by two activated charcoals. *Pharm. Res.* 5:183–186 (1988).
12. G. M. Burke. *Adsorptivity and Surface Characterization of Activated Charcoals,* Ph.D. thesis, University of Iowa, Iowa City, 1991.
13. G. M. Burke, D. E. Wurster, V. Buraphacheep, M. J. Berg, P. Veng-Pedersen, and D. D. Schottelius. Model selection for the adsorption of phenobarbital by activated charcoal. *Pharm. Res.* 8:183–186 (1991).
14. Perkin-Elmer. Performance, Engineering, and Environmental Specifications, PHI 5500 Multi-Technique System, Eden Prairie, MN, 1990.
15. Perkin-Elmer. V3.0 Multi-Technique Software Manual, Eden Prairie, MN, 1990.
16. L. I. Yin. Electron spectroscopy. In G. D. Christian and J. E. O'Reilly (eds.), *Instrumental Analysis,* Allyn and Bacon, Boston, 1986, pp. 451–457.
17. S. Tanuma, C. J. Powell, and D. R. Penn. Material dependence of electron inelastic mean free paths at low energies. *J. Vac. Sci. Technol. A* 8:2213–2216 (1990).
18. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg. *Handbook of X-Ray Photoelectron Spectroscopy,* Perkin-Elmer, Eden Prairie, MN, 1979.
19. A. W. Adamson. *Physical Chemistry of Surfaces,* 4th ed., John Wiley and Sons, New York, 1982, p. 537.
20. P. C. Hiemenz. *Principles of Colloid and Surface Chemistry,* 1st ed., Marcel Dekker, New York, 1977, p. 291.
21. R. D. Vold and M. J. Vold. *Colloid and Interface Chemistry,* Addison-Wesley, Reading, MA, 1983, pp. 322–323.