X-Ray Photoelectron Spectroscopy of *p*-Benzoquinone, Hydroquinone and Their Halogen-Substituted Derivatives

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X-Ray photoelectron spectra of *p*-benzoquinone, chloranil, bromanil, iodanil, hydroquinone, tetrachlorohydroquinone and chloranilic acid were observed by using the samples freshly deposited in the high vacuum of the spectrometer. The chemical shifts of C 1s and O 1s levels determined from the XPS spectra are compared with the chemical shifts predicted according to the electrostatic potential model by use of the charge distributions calculated by CNDO/2 method. The charge distributions in the quinone derivatives are successfully estimated by using the observed binding energies of C 1s and O 1s levels.

X-Ray photoelectron spectroscopy (XPS) shows promise as a tool to investigate the electronic structures of molecules. From XPS spectra, we can determine the binding energies of core-electron levels, which are known to vary more or less depending on the chemical bonds. This chemical shift of a core-electron level exhibits a rather simple correlation with the charge distribution in the molecule. It was shown by Siegbahn and his collaborators[1] that the chemical shifts of C 1s levels determined from the gas-phase XPS spectra of simple organic molecules can be successfully predicted from the charge distributions obtained by CNDO calculations, by using the electrostatic potential model.

For investigating the electronic structure of molecule, it is naturally desirable to observe the gas-phase XPS spectrum. However, this is not easy to do in the case of the organic compound which is a solid of low vapor pressure at room temperature. In such a case, the XPS spectrum is usually measured with a powder specimen, but the C 1s and O 1s spectra thus obtained are often affected significantly by the presence of chemical species containing carbon and/or oxygen, adsorbed on the sample surface.

This paper reports the XPS spectra of *p*-benzoquinone, hydroquinone and their halogen-substituted derivatives, which were observed with the films freshly deposited in the high vacuum of the spectrometer to avoid the contamination effects. The purpose of this study is to elucidate the effect of halogen substitution on the binding energies of C 1s and O 1s levels.

Experimental

The XPS spectra were measured with McPherson ESCA 36 electron spectrometer by employing AlK_α (1486.6 eV). The sample was deposited on the surface of the variable-temperature sample holder which was kept at about -50 °C by using dry ice–acetone mixture, in the 10^{-6} Torr vacuum of the spectrometer. Only in the case of iodanil, we carried out both the preparation of the film and the measurement of XPS spectra at the room temperature, since its vapor pressure is sufficiently low. For calibrating binding energies, we deposited a small amount of gold onto the sample surface, and used Au $4f_{7/2}$ (84.0 eV) as the reference,[2] the core levels of halogen being used as subsidiary references. With this method, binding energies were obtained with the accuracy better than ± 0.2 eV.

All the compounds except bromanil and iodanil were commercially obtained and purified by sublimation *in vacuo*. The crystal of chloranilic acid usually contains water of crystallization but the powder which we obtained by sublimation, was found to be the water-free modification. Bromanil and iodanil were synthesized in our laboratory, and purified by sublimation.

Results

The C 1s spectra of chloranil, bromanil and iodanil are shown in Fig. 1. Each of them exhibits a C 1s spectrum with a shoulder in the high binding-energy side of the main peak, indicating clearly that the spectrum is composed of two bands, namely, a strong band at lower energy and a weak band at higher energy. In each case, we resolved the observed C 1s spectrum into two components by means of the following procedure. First, we determined the standard profile of a single band by examining the shape of Au $4f_{7/2}$ spectrum of an evaporated gold film and that of F 1s spectrum of Teflon. Then, assuming this standard profile for each constituent band, we adjusted the splitting and intensities so that the composite spectrum well reproduced the observed spectrum. The results are shown in Fig. 1 by solid lines. In these cases, we were able

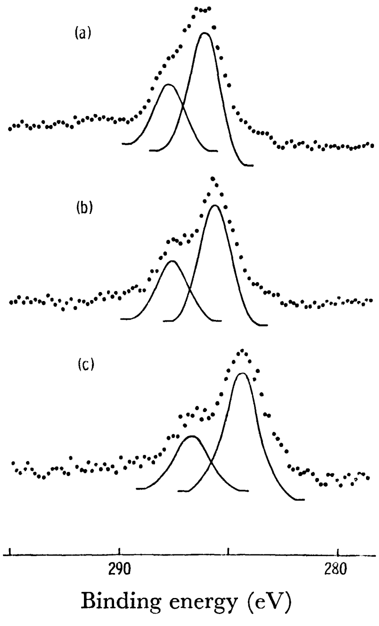


Fig. 1. Carbon 1s spectra.
(a): chloranil, (b): bromanil, (c): iodanil.

to resolve the observed C 1s spectrum into two components with the intensity ratio nearly 2: 1.

The situation was slightly complicated in the case of *p*-benzoquinone, where it was not possible to obtain the C 1s spectrum completely free from the contamination effect. Figure 2 shows the spectra measured respectively 10 and 20 min after preparation of the evaporated film. We can see that the profile of the spectrum appreciably changed with time. It is not clear why such phenomenon occurred only in the case of *p*-benzoquinone. Possibly it is connected in some way with the relatively high vapor pressure of this compound. As shown in Fig. 2, we can resolve the C 1s spectrum of *p*-benzoquinone into three components, of which binding energies are respectively 283.4, 284.3, and 286.0 eV. Among them, we can attribute the one at 284.3 eV to the C 1s band associated with the contamination carbon.

Like quinone derivatives, hydroquinone exhibited the C 1s spectrum with a shoulder, which was able to be resolved into two components with intensity ratio 2: 1 as shown in Fig. 3. However, the C 1s spectrum of tetrachlorohydroquinone exhibits no shoulder. Seemingly, the splitting is quite small in this case. It should be noted that there is an extra band separated by 6—7 eV from the main peak in the C 1s spectrum of hydroquinone as well as in that of tetrachlorohydroquinone. The corresponding extra bands were observed very weakly also in their O 1s spectra. It is most likely that these extra bands are the shake-up satellites associated with the excitations of valence electrons.[3]

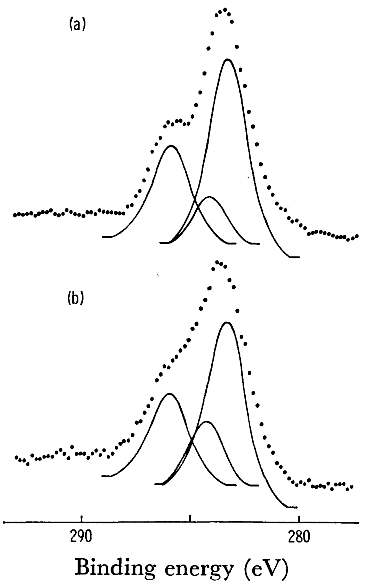


Fig. 2. Carbon 1s spectra of *p*-benzoquinone measured respectively (a) 10 min and (b) 20 min after preparation of the evaporated film.

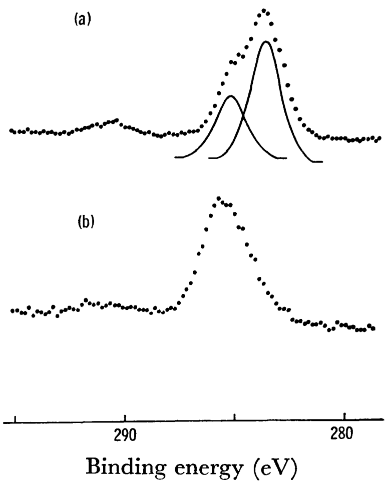


Fig. 3. Carbon 1s spectra.
(a): hydroquinone, (b): tetrachlorohydroquinone.

In the case of chloranilic acid, the O 1s spectrum appeared as a very broad band with a width of about 3 eV. This spectrum was able to be resolved into two components of equal intensity. Although we can expect that the C 1s spectrum of this compound is composed of three components, we could not resolve the observed C 1s spectrum to the corresponding bands.

The binding energies of core levels determined from the XPS spectra are summarized in Table 1.

Table 1. Binding energies of core levels (unit; eV)

Compound	C 1s		O 1s	
	C_1	C_2		
Chloranil	287.7	286.1	531.5	
Bromanil	287.5	285.6	531.4	
Iodanil	286.7	284.4	531.0	
p-Benzoquinone	286.0	283.4	530.8	
Hydroquinone	285.1	283.5	532.2	
Tetrachlorohydroquinone	285.5		532.5	
Chloranilic acid	286.2		533.1	531.7

Compound	Cl 2p	Cl 2s	Br $3p_{3/2}$	Br 3d	I $3d_{5/2}$	I 4s	I 4p	I 4d
Chloranil	200.2	270.9						
Tetrachlorohydroquinone	200.0	270.7						
Chloranilic acid	200.1	271.2						
Bromanil			183.4	70.1				
Iodanil					619.8	187.2	123.0	50.1

Discussion

Chemical Shifts in C 1s and O 1s Levels. According to the electrostatic potential model, the binding energy of a core level can be correlated with the charge distribution in the molecule by Eq. (1);

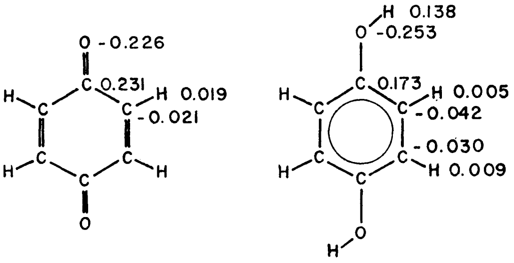
$$E_i = E_A{}^0 + k_A q_i + \sum_j q_j/R_{ij} \qquad (1)$$

where q_i is the charge on the i-th atom, q_j is that on the j-th atom, R_{ij} is the interatomic distance given in atomic units, and $E_A{}^0$ and k_A are the empirical constants characteristic of the kind of atom. This relation was originally proposed by Siegbahn *et al.*[4] on the basis of classical electrostatic theory. For the charge densities calculated by CNDO method, they gave the k_A values as follows; $k_C=21.9$ for C 1s and $k_O=25.8$ for O 1s (unit; eV/unit charge).[1] The quantum mechanical meaning of Eq. (1) was critically discussed by Schwartz, Switalski, and Stronski,[5] who gave theoretically the following k_A values; $k_C=22.108$ and $k_O=30.951$ (eV/unit charge).

When we are interested only in the chemical shift, we can use the energy change expression given as follows;

$$\Delta E_i = k_A q_i + \sum_j q_j/R_{ij} \qquad (2)$$

We carried out CNDO/2 calculations on *p*-benzoquinone, hydroquinone, chloranil, tetrachlorohydroquinone and chloranilic acid, assuming the molecular geometries based on the crystal structure data.[6] Figure 4 shows the charge densities of the first two compounds. Due to the molecular symmetry, we can classify the six carbon atoms into two groups, namely the two carbon atoms forming bond with oxygen and the other four carbon atoms. We will denote these two types of carbon atom as C_1 and C_2, respectively. Since the charge density is considerably different between these two kinds of carbon atom, we can expect a splitting between their C 1s levels.



(a) *p*-Benzoquinone (b) Hydroquinone

Fig. 4. Charge densities obtained from CNDO/2 calculations.

From the charge densities obtained by CNDO/2 calculations, we calculated ΔE according to Eq. (2) with the assumption that $k_C=21.9$ eV/(unit charge). The results are given in Table 2. These results suggest that, in the cases of *p*-benzoquinone, hydroquinone and chloranil, the C 1s spectrum will split into two bands separated by 1—2 eV. Since the intensity of each band is to be proportional to the number of atoms responsible for it, the intensity of the low-energy band will be twice of that of the high-energy band. This is in accord with the observations, consequently, we can assign without ambiguity the two bands obtained by resolving the C 1s spectrum of each of these compounds to the two levels predicted by the above calculations. In the case of chloranilic acid, the calculation predicts the presence of three C 1s bands of equal intensity, but we were not able to resolve its C 1s spectrum to the components corresponding to these predicted bands.

TABLE 2. CALCULATED CHEMICAL SHIFTS, ΔE (UNIT; eV)

Compound	C 1s		O 1s
	C_1	C_2	
p-Benzoquinone	2.5	0.9	−3.0
Chloranil	4.1	2.6	−1.6
Hydroquinone[a]	1.5	0.1, 0.2	−3.0
Tetrachlorohydroquinone	3.3	2.1, 2.1	−1.6

Compound	C 1s			O 1s	
	C_1	C_2	C_3	O_1	O_2
Chloranilic acid[b]	3.4	3.5	1.2	−2.4	−1.1

a) The C 1s levels of C_2 carbons split into two depending on the orientation of OH group. b) C_1, C_2, and C_3 correspond to C(O), C(OH), C(–Cl) respectively, and O_1 and O_2 to (C)O, O(H) respectively.

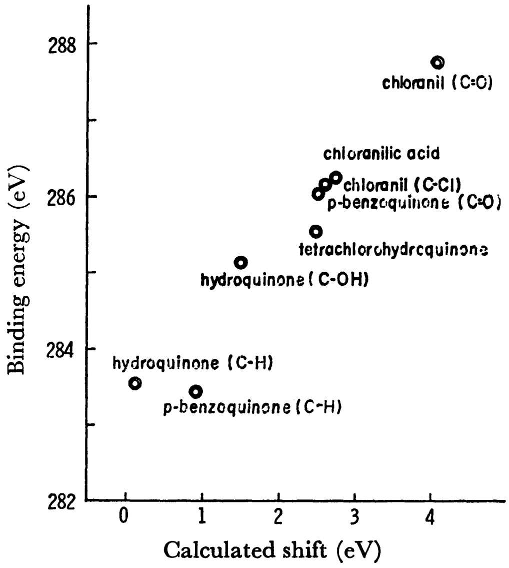


Fig. 5. Measured binding energy shifts of carbon 1s electrons versus shifts calculated with the electrostatic potential model.

Figure 5 demonstrates the good correlation between the observed binding energies of C 1s level and the calculated values of ΔE. The data well fit on a straight line which makes an angle of 45 degree with the abscissa.

The correlation between the observed and calculated chemical shifts of O 1s level is shown in Fig. 6, where we assumed that $k_O=25.8$ eV/(unit charge). The correlation is less satisfactory in this case as compared with the case of C 1s level.

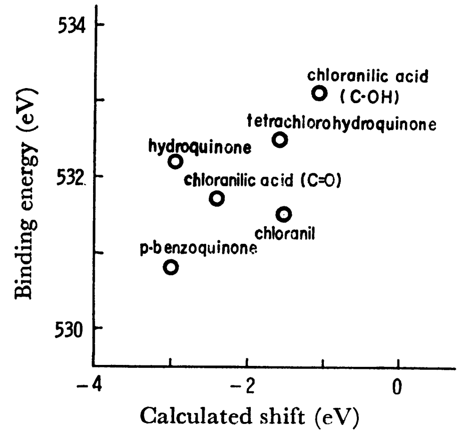


Fig. 6. Measured binding energy shifts of oxygen 1s electrons *versus* shifts calculated with the electrostatic potential model.

We can rewrite Eq. (1) in the following form:

$$E_i - \sum_j (q_j/R_{ij}) = E_A{}^0 + k_A q_i \qquad (3)$$

Thus, if we plot $E_i - \sum_j (q_j/R_{ij})$ against q_i, we will obtain a straight line, and we can determine k_A from its inclination and $E_A{}^0$ by extrapolating it to $q_i=0$. Since the data were limited, we were not able to determine the k_A value with sufficient accuracy. Therefore, we assumed the k_A values proposed by Siegbahn *et al.*, and determined $E_A{}^0$ by the extrapolation. By this way, we found the $E_C{}^0=283.3\pm0.2$ eV for $k_C=21.9$ eV/(unit charge) and $E_O{}^0=534.0\pm0.5$ eV for $k_O=25.8$ eV/(unit charge).[7]

Charge Distributions in the Quinone Derivatives. As we can see in Table 1, the C 1s and O 1s levels of the halogen-substituted quinones are systematically shifted with the electronegativity of halogen. In these molecules, we need to know only four quantities in order to specify the charge distribution. Those are the charge densities on oxygen, halogen and two non-equivalent carbon atoms, C_1 and C_2, which we will denote as q_O, q_X, q_{C_1}, and q_{C_2}, respectively. These quantities must satisfy the condition of the electrical neutrality of molecule, consequently, one of them can be derived from other three quantities. By using the relation given by Eq. (1) for the O 1s level and the C 1s levels of the two kinds of carbon atom, we obtain three equations relating the observed binding energies to the charge densities. We solved such equations for the E_A and k_A values which we have determined in the preceeding section. The results are given in Table 3.

Table 3. Charge densities estimated from XPS spectra of quinone derivatives

Compound	C_1	C_2	O	X
Chloranil	0.29_5	0.05_3	-0.24_4	-0.07_9
Bromanil	0.29_8	0.02_8	-0.24_3	-0.05_6
Iodanil	0.29_2	-0.02_0	-0.24_6	-0.00_2
p-Benzoquinone	0.28_7	-0.08_4	-0.24_5	0.06_3

The validity of the above procedure could be questioned when we consider the approximate nature of Eq. (1), and the limited reliability of the empirical values of $E_A{}^0$ and k_A. Nevertheless, the results given in Table 3 seem to be quite satisfactory. The charge densities on carbon and oxygen atoms in C=O group are little affected by the substituted halogen. The charge density on the carbon atom directly bounded with halogen and that on the halogen atom systematically change with the electronegativity of the substituted halogen. These are in accord with the chemical intuitions.

References

1) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA applied to free molecules," North-Holland, Amsterdam, (1969).

2) This method of calibration could not be used in the case of *p*-benzoquinone, where the C 1s peak of the contamination carbon (284.3 eV) was used as a subsidiary standard.

3) See for example, I. Ikemoto, J. M. Thomas, and H. Kuroda, *Faraday Discuss. Chem. Soc.*, **54**, 208 (1972).

4) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA-Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Uppsala, (1967).

5) M. E. Schwartz, J. D. Switalski, and R. E. Stronski, "Electron Spectroscopy," ed. by D. A. Shirley, North-Holland, Amsterdam (1972), p. 605.

6) The literatures for the crystal structure data of these molecules are as follows: *p*-benzoquinone: J. Trotter, *Acta Crystallogr.*, **13**, 86 (1960); hydroquinone: K. Maartmann-Moe, *ibid.*, **21**, 979 (1966); chloranil: S.S.C. Chu, G. A. Jeffrey, and T. Sakurai, *ibid.*, **15**, 661 (1962); tetrachlorohydroquinone: S. K. Sikka and R. Chidambaram, *ibid.*, **23**, 107 (1967); chloranilic acid: E. K. Andersen, *ibid.*, **22**, 188 (1967).

7) It is to be noted that $E_C{}^0$ and $E_O{}^0$ for the solid XPS spectra are different from the values for the gas-phase XPS spectra.