

## X-RAY PHOTOELECTRON SPECTROSCOPIC (XPS) STUDIES OF IODINE OXOCOMPOUNDS

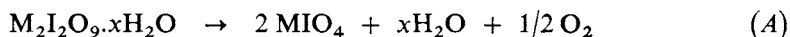
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The core electron binding energies of eighteen compounds containing iodine in different oxidation states ranging from (-I) to (VII) have been measured. The observed chemical shifts differ from the literature data. The anticipated existence of hexavalent iodine in certain compounds has not been demonstrated. The relative subshell photoemission intensities of iodine have been determined. Empirically derived atomic sensitivity factors and theoretical photoionization cross-sections have been used to calculate the surface stoichiometry. The concentration ratios obtained via the two methods are compared. In agreement with generally accepted view the results of this comparison imply that, for quantitative surface analysis, empirical values should be used rather than theoretical data.

Iodine forms many stable oxocompounds over a wide range of oxidation states. The most stable and the most usual oxidation states of iodine are (-I), (V), and (VII). Very little is known about the compounds of hexavalent iodine, the existence of which has been reported by several authors but has not been unambiguously proved. According to some literature data<sup>1-3</sup>, these compounds can be prepared by thermal decomposition of periodates  $M_2^I H_3 IO_6$  and  $M_2^{II} I_2 O_9 \cdot xH_2O$ :



or by oxidation of iodates in melts of alkali metal nitrates. With the exception of  $PbIO_4$ , the resulting products usually did not exhibit characteristic X-ray diffraction patterns<sup>4</sup>. The presence of I(VI) was deduced on the basis of the results of chemical analysis of samples and magnetic measurements<sup>3,4</sup>. For example the obtained value of the effective magnetic moment for  $PbIO_4$  was 1.54 BM (1 BM =  $9.2741 \cdot 10^{-24}$  J/T) which is close to the value expected for one unpaired electron (1.73 BM). However, it has been suggested<sup>5</sup> that the observed paramagnetism may be due to the presence of adsorbed oxygen and not a result of the paramagnetism of iodine.

The ability of X-ray photoelectron spectroscopy (XPS) to distinguish between various oxidation states of elements is now well documented in the literature. On the basis of the experimental binding energy data it was concluded by Fadley et al.<sup>6</sup> that, for iodine, the binding energy of the core levels changes by  $\sim 0.8$  eV (1 eV =

=  $1.60219 \cdot 10^{-19}$  J) per oxidation number unit. Consequently, it can be expected that the measurement of core-level shifts could help in identification of I(VI). In addition, because of the paramagnetism of I(VI), the iodine photoemission lines should be split or broadened by exchange interactions of core electrons with the unpaired valence electron spin density localized on iodine.

Inspection of the literature shows that the data on core level binding energies of iodine in different oxidation states are rather scarce<sup>6-9</sup> and inconsistent. This paper reports the XPS data for eighteen iodine-containing compounds, including compounds presumably containing hexavalent iodine. Most of the compounds were measured for the first time.

### EXPERIMENTAL

The X-ray photoelectron spectra were measured on a VG ESCA 3 MkII spectrometer using Al K $\alpha$  achromatic radiation ( $h\nu = 1486.6$  eV). The instrument was calibrated so that the difference between Au 4f<sub>7/2</sub> photoelectron peak and the Fermi level of Pd was 84.0 eV. The spectrometer was operated in fixed analyser transmission mode. The background pressure of residual gases during the spectra accumulation was typically  $\sim 10^{-6}$  Pa. The C 1s binding energy (258.0 eV) of adventitious carbon was used in calibration to compensate for charging effects. The XPS measurements were carried out at room temperature. Core level binding energies were determined with an accuracy  $\pm 0.2$  eV.

The commercially available compounds were used without further purification. The samples containing apparently hexavalent iodine were obtained from Department of Inorganic Chemistry, Charles University. The solid samples were crushed to fine powders and spread on adhesive tape attached to the sample probe. For thermal decomposition experiments, the samples were deposited onto a copper holder from an aqueous suspension. Most compounds examined in this study were stable; in several of them (K<sub>4</sub>I<sub>2</sub>O<sub>9</sub>, NaBa<sub>2</sub>IO<sub>6</sub>, and Ba<sub>5</sub>(IO<sub>6</sub>)<sub>2</sub>), photoreduction of iodine during spectral data collection has been observed.

### RESULTS AND DISCUSSION

Our experimental binding energies obtained for potassium iodide used as a reference compound do not agree with those published by Fadley et al.<sup>6</sup> (see Table I). The differences between our and Fadley's data are not identical for all the measured lines and therefore cannot be explained by different calibration of the spectrometer or by charging effects. This finding has prompted us to verify the conclusion<sup>6</sup> concerning the increase in the binding energy by  $\sim 0.8$  eV per unit increase in the iodine oxidation number. Table I gives the shifts in the individual core level binding energies in K<sub>4</sub>I<sub>2</sub>O<sub>9</sub> relative to KI. It can be seen from this table that the shifts obtained for different levels are of comparable magnitude. The average shift amounts  $4.6 \pm 0.3$  eV, which gives  $\sim 0.6$  eV per unit change of iodine oxidation number, assuming that the dependence of the magnitude of the shift on the oxidation number is linear. In fact this is not the case, as can be seen from Table II. It follows from this table

that the change in the I  $3d_{5/2}$  core level binding energy value when going from pentavalent to heptavalent iodine is rather small, 0.15 eV. From the point of view of identification of I(VI), this situation is, of course, not favorable. The question arises why the  $E_B$  shift between I(V) and I(VII) is rather small. There are three electronegative oxygen atoms bonded to iodine in  $\text{IO}_3^-$  ion, four in  $\text{IO}_4^-$ , and five in  $\text{I}_2\text{O}_9^{4-}$ . The two effects may contribute to the observed low values of  $E_B$  shifts

TABLE I  
Experimental core-level binding energies for KI and  $\text{K}_4\text{I}_2\text{O}_9$

Level	$E_B$ , eV			$\Delta E_B^a$ eV
	KI <sup>b</sup>	KI (ref. <sup>6</sup> )	$\text{K}_4\text{I}_2\text{O}_9^b$	
I 4d	50.10(3.4)	54.4	54.7(3.6)	4.6
I 4p	122.60(4.0)	123.0	127.7(4.1)	5.1
I 4s	186.65(3.6)	190.5	191.3(4.0)	4.7
I $3d_{5/2}$	619.25(2.4)	623.9	623.9(2.6)	4.7
I $3d_{3/2}$	630.75(2.4)	635.5	635.5(2.4)	4.8
I $3p_{3/2}$	874.50(4.4)	880.7	878.8(5.3)	4.3
I $3p_{1/2}$	930.20(4.5)	937.0	934.9(4.3)	4.7
I 3s	1 071.30(3.1)	1 072.0	1 075.5(—)	4.2
K 2p	293.25(2.3)	—	292.5(3.0)	—0.7
K 2s	377.80(3.4)	—	377.0(3.8)	—0.8
O 1s	531.20(2.9)	—	530.4(3.0)	—0.8

<sup>a</sup> Binding energy shifts in  $\text{K}_4\text{I}_2\text{O}_9$  relative to KI; <sup>b</sup> figures in parentheses are the peak widths at half heights.

TABLE II  
Experimental binding energies  $E_B$ (eV) for iodine  $3d_{5/2}$  level in potassium iodide, potassium iodate, and potassium periodate

Compound	$E_B^a$	$E_B^b$	$E_B^c$	$E_B^d$
KI	619.25(2.4)	623.5	619.1	618.8
$\text{KIO}_3$	623.75(2.9)	628.8	—	623.5
$\text{KIO}_4$	623.90(3.2)	629.8	624.5	624.0

<sup>a</sup> Figures in parentheses are the peak widths at half-maxima (FWHM); <sup>b</sup> values published by Fadley et al.<sup>6</sup>; <sup>c</sup> values published by Wagner<sup>8</sup> corrected to  $E_B(\text{C } 1s) = 285.0$  eV; <sup>d</sup> values published by Sherwood<sup>7</sup> for sodium compounds.

between I(V) and I(VII). First, the oxygen-iodine distance<sup>7</sup> in  $\text{IO}_4^-$  is smaller than in  $\text{IO}_3^-$ , resulting in the increased Madelung potential contribution to  $E_B$  in  $\text{IO}_4^-$ . The second effect follows from relaxation energy calculations<sup>7</sup>, showing that, for iodine, these energies increase in the order  $\text{HIO}_3 < \text{I}_2\text{O}_5 < \text{H}_5\text{IO}_6 < \text{NaIO}_4$ . In addition, the calculations show<sup>10</sup> that the effective positive charge localized on iodine does not increase with increasing number of coordinated oxygen atoms — it amounts to 1.8 for  $\text{KIO}_4$  and 2.2 for  $\text{KIO}_3$ . These facts seem to explain why the binding energy shifts are not a simple function of the number of oxygen atoms coordinated to I. The average I—O distance also depends on the kind of cation. Consequently, the binding energy differences between different periodates, differing in the number of oxygen atoms bonded to iodine and in the cation, are even larger than the binding energy differences between penta- and heptavalent iodine in  $\text{KIO}_3$  and  $\text{KIO}_4$ , respectively (see Table III).

The hexavalent iodine in some compounds, if present, may be unstable and may be oxidized to I(VII) (or reduced to I(V)) in the surface layer probed by XPS (approx. 5 nm), because the samples were prepared and stored under ambient atmosphere. For this reason, we have also prepared a compound with expected composition  $\text{PbIO}_4$  directly in the preparation chamber of the spectrometer by the method described in the literature<sup>4</sup>, i.e. by thermal decomposition (500 or 650 K, 20 min) of  $\text{Pb}_2\text{I}_2\text{O}_9 \cdot 3\text{H}_2\text{O}$  in vacuo. The product was transferred to the measuring chamber

TABLE III

Experimental binding energies of  $3d_{5/2}$  photoelectron peak for compounds containing iodine in different oxidation states

Compound	$E_B$ , eV	Compound	$E_B$ , eV
iodine (V)		iodine (VII)	
$\text{KIO}_3$	623.8(2.9)	$\text{Li}_2\text{H}_3\text{IO}_6$	624.6(2.5)
$\text{Sr}(\text{IO}_3)_2$	623.7(2.8)	$\text{NaBa}_2\text{IO}_6$	623.5(2.7)
$\text{Pb}(\text{IO}_3)_2$	623.8(2.8)	$\text{KIO}_4$	623.9(3.2)
$\langle E_B \rangle$	$623.8 \pm 0.1$	$\text{K}_4\text{I}_2\text{O}_9$	623.9(2.6)
iodine(VI) <sup>a</sup>		$\text{Ba}(\text{IO}_4)_2$	623.4(3.4)
$\text{Be}_3\text{I}_2\text{O}_9$	624.6(2.9)	$\text{Na}_5(\text{IO}_6)_2$	623.5(2.9)
$\text{Na}_2\text{IO}_4$	624.0(2.5)	$\text{Pb}_2\text{I}_2\text{O}_9$	624.2(2.6)
$\text{MgIO}_4$	624.4(3.2)	$\text{Pb}_3(\text{IO}_5)_2$	624.2(2.6)
$\text{K}_2\text{IO}_4$	624.3(2.7)	$\langle E_B \rangle$	$623.9 \pm 0.4$
$\text{CaIO}_4$	623.8(3.0)	iodine(-I)	
$\text{PbIO}_4$	624.1(3.3)	$\text{KI}$	619.3(2.4)
$\langle E_B \rangle$	$624.2 \pm 0.3$		

<sup>a</sup> Assumed.

without exposing it to the ambient air. On the basis of the measured I  $3d_{5/2}$  binding energy and the width of the line, the existence of I(VI) in the prepared compound cannot be unambiguously excluded. However, the obtained data can alternatively be explained as resulting from the presence of roughly equimolar amounts of hepta and pentavalent iodine.

It was also interesting to determine the surface composition of the studied samples and compare it with their nominal stoichiometry. For this purpose, it was instructive to verify the adequacy of the published subshell photoionization crosssections<sup>11</sup> and sensitivity factors used to convert relative photoelectron peak intensity data into data on the elemental composition. Relative intensity measurements were carried out on all discernible iodine photoemission lines. A simple linear background was used for peak area determination in the present work. This procedure is likely to underestimate the peak area except for those transitions for which the probability of energy loss processes is particularly low. Experimental and theoretical relative photoemission peak intensities are compared in Table IV and Fig. 1, in which the relative empirical sensitivity factors published by Szajman<sup>11</sup> and Wagner<sup>12</sup> are also included. The theoretical data are taken from the most commonly used tabulation by Scofield<sup>13</sup>. With the exception of the  $4d$  and  $3d_{3/2}$  levels, all the measured relative intensities are lower than the ratio of corresponding theoretical photoionization cross-sections.

The measured intensities are modified by the dependence of the electron mean free path  $\lambda$  and spectrometer transmission on the kinetic energy of the photoelectrons,  $E_K$ , by anisotropy of photoemission and by the presence of surface contamination. The dependence of  $\lambda$  on  $E_K$  for KI has been experimentally determined by Szajman et al.<sup>11</sup> These authors obtained the equation:

$$\lambda = 3.2 \cdot 10^{-3} E_K + 2, \quad (1)$$

where  $\lambda$  is in nm and  $E_K$  in eV.

For inorganic compounds, Seah and Dench<sup>14</sup> have recommended the empirical relationship:

$$\lambda_m = 2170/E_K^2 + 0.72(aE_K)^{1/2}, \quad (2)$$

where  $\lambda_m$  is now given in units of monolayers and  $a$  is the monolayer thickness in nm.

According to literature<sup>15,16</sup> the transmission of the spectrometer varies as a function of  $E_K^{-1}$  at high energies,  $E_K^{-1/2}$  at intermediate energies and becomes constant at low energies. The break points between each regime depend on many parameters, the most important being instrument type, manufacturing tolerances, slit width, pass energy, and specimen size. The angular intensity distribution of the emitted electrons was described by Reilman et al.<sup>17</sup>. The experimental data were corrected using the values of the asymmetry parameters tabulated by these authors.

We have applied all these corrections and their combinations to our experimental data but no improvement in the agreement between experiment and theory was achieved. The differences between experimental and theoretical values do not change systematically with the  $E_K$  value of the peak and they can therefore hardly be explained as a consequence of the presence of a contamination layer on the surface of the samples. We suggest that the reason for the observed differences lies in underestima-

TABLE IV  
Experimental and theoretical relative photoemission peak intensities  $i_r = i(I nI)/i(I 3d_{5/2})$

Level	$i_r$		$i_r^a$	$i_r^b$	$i_r^c$
	KI	$K_4I_2O_9$			
4d	0.25	0.24	0.208	0.227	0.24
4p	0.032	0.047	0.168	0.051	—
4s	0.029	0.030	0.0483	0.024	—
3d <sub>5/2</sub>	1.00	1.00	1.00	1.00	1.00
3d <sub>3/2</sub>	0.69	0.66	0.693	0.762	0.60
3p <sub>3/2</sub>	0.32	0.35	0.534	0.311	—
3p <sub>1/2</sub>	0.19	0.15	0.255	0.190	—
3s	0.13	0.07	0.178	0.095	—

<sup>a</sup> Data derived from Scofield's tabulation<sup>11</sup>; <sup>b</sup> empirical values taken from ref.<sup>9</sup>; <sup>c</sup> empirical sensitivity factors recommended by Wagner<sup>10</sup>.

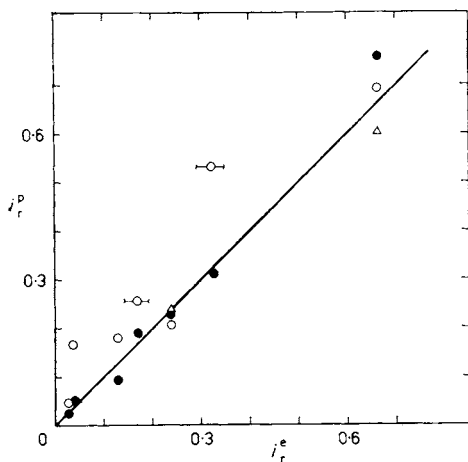


FIG. 1

The published ( $i_r^p$ ) vs obtained experimental relative photoemission peak intensities of iodine, normalized to the intensity of the I 3d<sub>5/2</sub> line. A straight line with slope equal to unity is drawn through the data. ○ Scofield's theoretical data, ● data published by Szajman<sup>11</sup>, △ empirical sensitivity factors recommended by Wagner<sup>12</sup>

tion of the peak areas due to neglecting of the shake-up and shake-off intensities. In fact, we have noticed the presence of satellites in the iodine XPS spectra separated by approx  $\sim 13$  eV from the parent peaks. The observed satellites were weak and their intensities could not be determined accurately. Our estimates show that the satellite area is about 20% of the parent line. It therefore seems likely that the differences between the experimental and theoretical relative intensities are primarily due to inaccuracies in background determination and the presence of energy-loss satellites. This conclusion is consistent with finding that the relative uncorrected experimental iodine peak intensities agree rather well with the relative empirical sensitivity data (Fig. 1). The use of empirical sensitivity factors has also led to good agreement between the determined and actual stoichiometry of the studied compounds (Table V). For example, the atomic ratios obtained by careful chemical analysis of  $\text{MgIO}_4$  are

TABLE V

The surface stoichiometry of iodine compounds (K 2*p*, Sr 3*d*, Pb 4*f*, Be 1*s*, Mg 2*s*, Ca 2*p*, Na 1*s*, Ba 3*d*<sub>5/2</sub>, I 3*d*<sub>5/2</sub>, and O 1*s* lines and elemental sensitivity factors published by Wagner were used)

Compound	X : I : O
KI	0.98 : 1.00 : 0.4 <sup>a</sup>
KIO <sub>3</sub>	1.11 : 1.00 : 3.04
Sr(IO <sub>3</sub> ) <sub>2</sub>	0.64 : 1.00 : 3.25
Pb(IO <sub>3</sub> ) <sub>2</sub>	0.55 : 1.00 : 3.18
Be <sub>3</sub> I <sub>2</sub> O <sub>9</sub> (4 H <sub>2</sub> O) <sup>b</sup>	2.85 : 1.00 : 9.10
MgIO <sub>4</sub> (1/2 H <sub>2</sub> O) <sup>b</sup>	1.10 : 1.00 : 4.80
CaIO <sub>4</sub> (H <sub>2</sub> O) <sup>b</sup>	0.92 : 1.00 : 4.50
PbIO <sub>4</sub> <sup>c</sup>	0.61 : 1.00 : 3.43
PbIO <sub>4</sub> <sup>d</sup>	0.90 : 1.00 : 3.64
PbIO <sub>4</sub> <sup>e</sup>	1.02 : 1.00 : 3.60
PbIO <sub>4</sub> <sup>f</sup>	1.18 : 1.00 : 3.96
NaBa <sub>2</sub> IO <sub>6</sub>	0.89 : 1.55 : 1.00 : 5.64
KIO <sub>4</sub>	1.09 : 1.00 : 3.55
K <sub>4</sub> I <sub>2</sub> O <sub>9</sub> (9 H <sub>2</sub> O) <sup>b</sup>	2.27 : 1.00 : 4.35
Ba(IO <sub>4</sub> ) <sub>2</sub>	0.44 : 1.00 : 3.30
Ba <sub>5</sub> (IO <sub>6</sub> ) <sub>2</sub>	1.85 : 1.00 : 6.35
Pb <sub>2</sub> I <sub>2</sub> O <sub>9</sub> (3 H <sub>2</sub> O) <sup>b</sup>	0.90 : 1.00 : 4.89
Pb <sub>3</sub> (IO <sub>5</sub> ) <sub>2</sub>	1.52 : 1.00 : 6.85

<sup>a</sup> Oxygen is present in amounts varying from sample to sample; <sup>b</sup> the samples were inserted into the spectrometer in the form of hydrates but they have apparently lost the most of the water by vacuum treatment; <sup>c</sup> the sample prepared by heating Pb<sub>2</sub>I<sub>2</sub>O<sub>9</sub> in spectrometer to 500 K; <sup>d</sup> dtto with exception of temperature which was 650 K; <sup>e,f</sup> the samples prepared by heating Pb<sub>2</sub>I<sub>2</sub>O<sub>9</sub> outside the spectrometer to 500 K and 650 K, respectively.

1:14 : 1:00 : 4:8 which agree quite well with the ratios calculated from XPS intensities. The actual stoichiometry of lead compounds containing formally hexavalent iodine does not correspond to the nominal stoichiometry, and seems rather to correspond to a compound with composition  $\text{Pb}_2\text{I}_2\text{O}_7$ .

### CONCLUSIONS

The X-ray photoelectron spectra of eighteen iodine-containing compounds including the compounds of presumably hexavalent iodine have been measured. The  $\text{I } 3d_{5/2}$  binding energy appears to be only slightly dependent on the number of oxygen atoms coordinated to iodine. The existence of hexavalent iodine in certain compounds could not be unambiguously proven on the basis of the measured binding energies and photoemission peak widths. The results obtained show, that for determination of the surface stoichiometry of compounds, empirically derived atomic sensitivity factors should be used in preference to theoretical photoionization cross-sections.

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