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He I and He II Photoelectron Spectral Studies of Alkyluranocenes

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Photoelectron spectra of a series of alkyl-substituted uranocenes, obtained with both He I and He II radiation, are presented. Intensity measurements confirm an ionization energy ordering $e_{2u} < e_{2g}$ and are consistent with relativistic SCF $X\alpha$ scattered-wave calculations, indicating a contribution from both metal 5f and 6d orbitals to ring-metal bonding. Analysis of ionization energy trends suggests that metal-ring bonding interactions increase in strength with increasing alkylation of the cyclooctatetraene rings.

Introduction

Until recently, the extensive chemical and physical studies of uranocenes¹ had only indicated substantial metal-ring covalency and had not provided specific evidence for the involvement of 5f orbitals as originally proposed by Streitwieser and Müller-Westerhoff.² Photoelectron (PE) spectral studies by Clark and Green,³ which compared He I and He II intensity patterns, lead to an MO ordering $e_{2g} < e_{2u}$, indicating a significant contribution of the metal 6d orbitals to metal-ring bonding. A covalent interaction was also identified between the e_{2u} combination of ring π orbitals and the metal 5f orbitals. These conclusions have been supported by nonrelativistic SCF $X\alpha$ scattered-wave calculations and more recently by relativistic calculations by Rösch and Streitwieser,⁴ which included 6d orbitals in the basis set. Good agreement was found between transition-state energies and experimental ionization potentials. The calculations also indicated

mixing between ring e_{1g} and metal 6d orbitals.

In order to obtain further experimental support for these conclusions, we have examined a series of alkyl-substituted uranocenes by He I and He II PE spectroscopy.

Experimental Data and Results

The compounds have been described previously.⁵ Purified samples were sealed under helium or argon for shipment to Oxford.

The photoelectron spectra were recorded on a Perkin-Elmer PS 16/18 spectrometer fitted with a heated inlet probe and a Helectros helium discharge lamp emitting both He I and He II radiation. The spectra were calibrated by introducing a small pressure of a mixture of xenon and nitrogen into the target chamber immediately after the spectrum was run. The separation of the Xe and N₂ peaks was used to provide the scaling factor for the calibration, and the position of the bands was measured relative to the He self-ionization band which was recorded with each spectrum run. The ionization energies quoted are in most cases average values obtained from several spectra. The estimated error for the absolute ionization energy of a typical band is approximately ± 0.05 eV, though separations of neighboring bands are accurate to ± 0.02 eV.

The intensities of bands were calculated by dividing band areas by the electron kinetic energy. This is necessary because the sensitivity of the analyzer decreases linearly with decreasing

(1) A summary of these investigations may be found in various reviews. (a) T. J. Marks, *Prog. Inorg. Chem.*, **25** (1979). (b) K. O. Warren, *Struct. Bonding (Berlin)*, **33**, 98 (1977). (c) H.-D. Amberger, R. D. Fischer, and B. Kanellakopoulos, *Theor. Chim. Acta*, **37**, 105 (1975). (d) E. C. Baker, G. W. Halstead, and K. N. Raymond, *Struct. Bonding (Berlin)*, **25**, 33 (1976).

(2) A. Streitwieser, Jr., and U. Müller-Westerhoff, *J. Am. Chem. Soc.*, **90**, 7364 (1968).

(3) J. P. Clark and J. C. Green, *J. Chem. Soc., Dalton Trans.*, 305 (1977).

(4) (a) N. Rösch and A. Streitwieser, Jr., *J. Organomet. Chem.*, **145**, 195 (1978). (b) N. Rösch and A. Streitwieser, Jr., submitted for publication in *J. Am. Chem. Soc.*

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Table I. Vertical Ionization Energies (eV) of Alkyl-Substituted Uranocenes

Band	$U(\eta\text{-C}_8\text{H}_7\text{Me})_2$	$U(\eta\text{-C}_8\text{H}_7\text{Et})_2$	$U(\eta\text{-C}_8\text{H}_7\text{-}n\text{-Bu})_2$	$U(\eta\text{-C}_8\text{H}_7\text{-}t\text{-Bu})_2$	$U(\eta\text{-C}_8\text{H}_6(\text{CH}_2)_2)_2$	$U(\eta\text{-C}_8\text{H}_4\text{Me}_4)_2$	$U(\eta\text{-C}_8\text{H}_8)_2^a$
A	6.08	6.03	6.05	6.03	6.02	5.73	6.20
B ₁	6.76	6.70	6.71	6.70	6.69	6.48	6.90
B ₂	7.67	7.61	7.62	7.61	7.52	7.33	7.85
C ₁	9.67	9.60	9.61	9.62	9.51	9.14	9.95
	9.94	9.92	9.99	9.94	9.82	9.34	10.28
C ₂	10.31	10.28				9.80	10.56
	11.4	11.1	11.5		10.6	11.3	
	12.1	11.9	12.0	11.8	12.1	12.1	11.5
	13.2	13.4			13.5	12.9	12.4
	14.0	14.0	14.1	14.1		13.8	14.1
	14.9	14.6	14.7	14.7	14.9		14.7
						15.8	
	17.7	17.3	17.7	17.4	16.9	17.9	17.9
		19.4	18.8	18.2	18.1	19.3	
	21.1	20.9		20.8		21.7	

^a IE taken from ref 3 included for purposes of comparison.

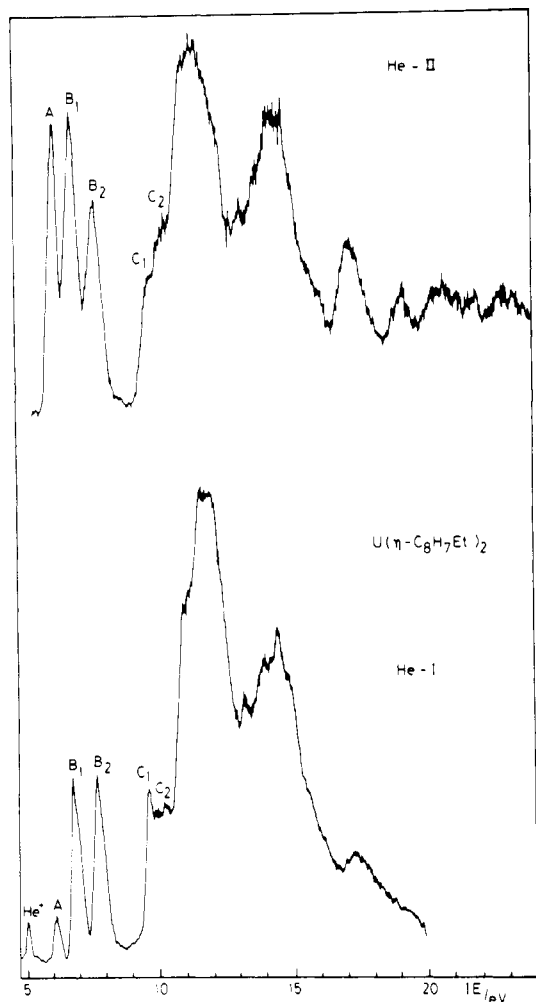


Figure 1. He I and He II spectra of 1,1'-diethyluranocene.

electron energy.⁶ Intensity values quoted are the average of results obtained for several spectra, estimated errors being of the order of $\pm 5\%$. In the He II spectra, resolution of the first three bands is generally poor (because of the high kinetic energy of the evicted electrons) and the bands were broadened considerably from their natural widths by this factor, introducing uncertainty into the values obtained for relative intensities. For this reason band heights were also measured to provide a check on relative band intensities.

Conditions used for running the various samples are given in Table I. Vertical ionization energies (IE) and band intensity data

(6) O. Klemperer, "Electron Optics", Cambridge University Press, London, 1953.

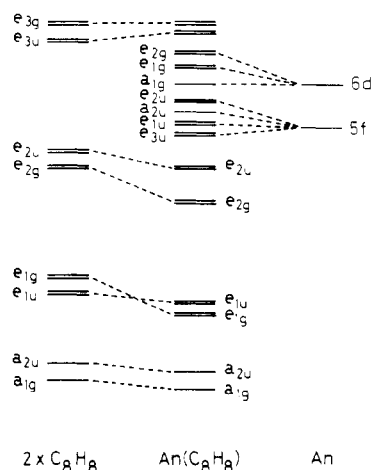


Figure 2. MO scheme for bis(η -cyclooctatetraenyl)actinides.

are given in Table II and a representative spectrum, that of diethyluranocene, is shown in Figure 1.

Discussion

A MO scheme of the bonding in uranocene is presented in Figure 2 as a guide to the symmetry of the component orbitals and their interactions.

The spectra of the alkyl-substituted uranocenes closely resemble in main outline that of uranocene itself.^{3,7,8} The gross features are assigned in accord with previous work,³ namely, the first band A to ionization of the f electrons, bands B₁ and B₂ to ionization from the e_{2u} and e_{2g} orbitals, and bands C₁ and C₂ from ionization of the e_{1u} and e_{1g} orbitals and higher ionization bands to ionization of the lowest ring π levels and the σ structure of the cyclooctatetraenyl rings. For the alkyl-substituted uranocenes, in the ionization region above 10 eV, variation is seen due to the additional ionization of alkyl C-C and C-H orbitals. In particular, the octamethyl compound displays a prominent band at 11.3 eV, which may, by analogy with the spectra of polyalkylated metalocenes⁹ and of a wide variety of methyl compounds in general,¹⁰ be assigned to ionization of the nonaromatic C-H₃ σ orbitals. In certain

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(8) I. L. Fragala, E. Ciliberto, R. D. Fischer, G. R. Sienel, and P. Zahella, *J. Organomet. Chem.*, 120, C9 (1976).

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(10) I. L. Fragala, in "Organometallics of the f-Elements", H. D. Fischer and T. J. Marks, Eds., D. Reidel Publishing Co., North Holland, 1979.

Table II. He I and He II Intensities, He II/He I Intensity Ratios, and Half-Width Values ($w_{1,2}$) for the A, B₁, and B₂ Bands in the PE Spectra of the Alkyl-Substituted Uranocenes

		U(η -C ₈ H ₇ Me) ₂	U(η -C ₈ H ₇ Et) ₂	U(η -C ₈ H ₇ <i>n</i> -Bu) ₂	U(η -C ₈ H ₇ <i>t</i> -Bu) ₂	U(η -C ₈ H ₆ (CH ₂) ₂) ₂	U(η -C ₈ H ₃ Me ₄) ₂
HeI	A	0.52	0.55	0.45	0.55	0.54	0.48
	B ₁	3.25	3.25	3.25	3.57	3.42	3.10
	B ₂	4.00	4.00	4.00	4.00	4.00	4.00
HeII	A	2.90	3.47	3.50	2.81	3.43	2.63
	B ₁	4.65	4.81	5.01	4.85	4.48	5.23
	B ₂	4.00	4.00	4.00	4.00	4.00	4.00
HeII/HeI	A	5.6	6.3	7.8	5.1	6.4	5.5
	B ₁	1.43	1.48	1.54	1.36	1.31	1.69
	B ₂	1.00	1.00	1.00	1.00	1.00	1.00
$w_{1,2}$, eV	A	0.32	0.30	0.31	0.37	0.29	0.33
	B ₁	0.49	0.43	0.47	0.50	0.43	0.51
	B ₂	0.52	0.47	0.60	0.51	0.45	0.64

cases this alkyl structure overlaps with bands C₁ and C₂.

The results complement those recently published for 1,1'-bis(trimethylsilyl)- and 1,1'-bis(di-*tert*-butylphosphino)uranocenes.¹¹ The alkyl substituents generally produce a somewhat greater perturbation of the uranocene system, particularly compared to the phosphino compound.

The f Band (A). The lowest energy band is assigned to ionization of the f² configuration on the basis of its absence in the spectrum of thoracene. Since, for the actinide elements, ligand field effects are considerably weaker than those of interelectronic repulsion and spin-orbit coupling,^{1a} we may obtain a prediction of the band pattern expected from ionization of this configuration by consideration of the ³H₄ ground state predicted by the Russell-Saunders coupling scheme. This ground state gives rise to two ion states, ²F_{5/2} and ²F_{7/2}, associated with the 5f¹ configuration, separated by $\frac{7}{2}\zeta$, i.e., ~0.8 eV. Using a fractional parentage scheme, Cox¹² calculated a cross section ratio of approximately 6:1 (²F_{5/2}:²F_{7/2}); inclusion of relativistic effects¹³ gives, for an intermediate coupling situation, a much smaller cross section for ionization to the ²F_{7/2} ion state, which becomes zero in the *j-j* coupling limit. For the case of U⁴⁺, a cross section ratio of ~40:1 (²F_{5/2}:²F_{7/2}) is predicted. This accounts for the observation of only a single band assignable to a f orbital ionization in the PE spectra of all 5f² systems so far examined,^{11,14} the second f orbital band being too weak to be observed. For the uranocenes the second band is predicted to fall beneath the first e₂ orbital band, but its contribution to the He I/He II intensity of this band should be negligibly small and may therefore safely be ignored.

The e₂ Orbital Bands (B₁ and B₂). After the f electrons, the next two highest occupied orbitals in uranocenes are of e_{2u} and e_{2g} symmetry. Clark and Green's assignment of the second (B₁) and third (B₂) bands in uranocene, as arising from ionization of the e_{2u} and e_{2g} orbitals, respectively, is based on the observation in the He II spectrum of a substantial (~50%) intensity increase of the former band relative to the latter compared with the He I spectrum. Use of the Gelius model for ionization cross sections¹⁵ and consideration of the very large intensity increase observed for 5f electron ionizations in the He II spectrum relative to the He I spectrum leads to the pro-

posal that the first e₂ band has considerable 5f character and is therefore of e_{2u} symmetry.

Similar intensity changes have been observed in the π orbital bands of other organometallic uranium compounds.^{11,16} The alkyl-substituted uranocenes display the same pattern of He II/He I intensity variation, and an analogous assignment is proposed. On the basis of the observed trend of He II/He I intensity ratio for metal d orbitals 3d > 4d > 5d \approx 1 (relative to carbon 2p) the 6d He II/He I intensity ratio was estimated to be 1, or slightly less than unity. This is consistent with the above assignment since, in all cases, the second e₂ band shows only a small intensity increase in the He II spectra relative to the main σ orbital band, which is in accordance with previous observations of higher He II/He I cross sections for carbon p π than carbon p σ orbitals. The second e₂ orbital band is broader than the first for all the alkyl-substituted uranocenes, as is observed in uranocene (and thoracene) itself. This lends support to the view that the e_{2g} orbital has greater bonding character than the e_{2u} orbital. The alkyl-substituted uranocenes also resemble the parent molecule in the smaller He I intensity of the e_{2u} orbital band compared with that of the e_{2g} orbital band, which may be explained by the 6d orbital He I ionization cross section being much larger than that of the 5f orbitals.

These deductions as to the ordering and characters of the e_{2u} and e_{2g} orbitals are supported by relativistic X α scattered-wave calculations carried out by Rösch and Streitwieser.¹⁶ In particular, they find the level ordering e_{2u} > e_{2g} and relatively large admixture of metal and carbon orbitals in both MOs. The sphere populations in the MOs is analogous to orbital populations in LCAO treatments but is not completely straightforward because of "outersphere" and intersphere regions; nevertheless, it seems significant that the total carbon sphere populations in both MOs in the relativistic X α -SW treatment for uranocene are approximately equal (0.4).

The e₁ Orbital Bands (C₁ and C₂). The e₁ orbital ionizations may be assigned, as in uranocene, to the series of poorly resolved bands (C) on the low ionization energy side of the large C-C/C-H orbital band. In the spectra of the *n*-butyl-, *tert*-butyl-, and dicyclobutenouranocenes, a large portion of the e₁ ionizations are obscured by bands due to C-C σ orbital ionizations, while for the octamethyl-, diethyl-, and dimethyluranocenes, the e₁ band structure is clearer and is similar in profile to that observed in uranocene and thoracene.³ Band C₁ has a sharp leading edge and a shoulder on the high ionization energy side, which may be attributed to Jahn-Teller distortion of the ion state, a feature commonly found for ionization bands of complexed aromatic e ionizations.¹⁷ The second e₁ band,

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(12) P. A. Cox, *Struct. Bonding (Berlin)*, **24**, (1975).

(13) R. G. Egdel, A. F. Orchard, D. R. Lloyd, and N. V. Richardson, *J. Electron Spectrosc. Relat. Phenom.*, **12**, 415 (1977).

(14) The spectrum of U(η -C₅H₄Me)₂BH₄⁸ is reported to give two f orbital ionizations; however, considerable doubt is cast on this result by the fact that the unmethylated compound U(η -C₅H₅)₂BH₄ shows only a single f orbital band.

(15) U. Gelius, "Electron Spectroscopy", D. A. Shirley, Ed., D. Reidel Publishing Co., North Holland, Amsterdam, 1972, p 311. U. Gelius and K. Siegbahn, *Farad. Diss. Chem. Soc.*, **54**, 257 (1972).

(16) J. C. Green, M. R. Kelly, J. A. Long, B. Kanellakopoulos, and P. I. Yarrow, *J. Organomet. Chem.*, **212**, 329 (1981).

C_2 , is separated from the first, which overlaps it on the low ionization energy side, by ca. 0.66 eV, and merges on the high ionization energy side with the leading edge of the main band. It is thus not possible to obtain reliable intensity measurements of these bands. However, a consistent feature of the spectral profile in this region, on changing from He I to He II radiation, is an increase in the peak height of C_2 relative to C_1 . Whether this represents a genuine increase in band intensity is difficult to say; the increase in photon energy brings about a decrease in resolution and broadening of the main band and might well cause an apparent intensity increase in C_2 . It therefore seems unreasonable to draw any conclusions as to assignment of the e_1 bands, on the basis of the changes of spectral profile with photon energy, until further studies over a wider range of photon energies have been made.

The recent $X\alpha$ -SW calculations of Rösch and Streitwieser^{4b} give a level ordering $e_{1g} > e_{1u}$ for the interaction of two [8]annulene rings but a reverse assignment, $e_{1g} < e_{1u}$, for uranocene. The absolute difference in calculated ionization potentials for uranocene, 0.51 eV, is in good agreement with the experimental value of 0.61 eV.

Ionization Energy Trends. As is well documented,¹⁹ alkylation of an aromatic system lowers the ionization energies of the π orbitals. Studies on cyclopentadienyl-metal tricarbonyls indicate that in the case of the coordinated cyclopentadienyl ring this is mainly a result of hyperconjugative interaction between the methyl group and the ring orbitals.²⁰ This result is also found in the alkyl-substituted uranocenes. The band C_1 shows an IE decrease relative to uranocene, on alkyl substitution, as follows: ~ 0.28 eV in dimethyluranocene, ~ 0.36 eV in diethyl-, di-*n*-butyl-, and di-*tert*-butyluranocenes, ~ 0.43 eV in dicyclobutenouranocene, and ~ 0.8 eV in octamethyluranocene. The slightly smaller effect of the methyl group compared with the other alkyl groups is comparable to relative ionization potentials of alkylbenzenes.²⁰ The IE shift of band C_1 of octamethyluranocene is smaller than that expected based on the assumption of additivity of the effect of methyl substituents. A similar saturation phenomenon is observed in the PE spectra of alkylated bis-(arene) compounds.²¹

The f band, A, shows a similar, but less marked, variation on substitution: the variations are approximately half that observed for the C_1 band.

The B bands are less sensitive to alkyl substitution than C_1 ; for example, in octamethyluranocene the e_{2g} and e_{2u} have respective IE 0.52 and 0.42 eV lower than those of unsubstituted uranocene. Since e_1 and e_2 ring orbitals would be expected to show IE variations of a similar magnitude in the absence of involvement in ring-metal bonding, the considerably smaller variations of the e_2 orbital IE must result from interactions with uranium 5f (e_{2u}) and 6d (e_{2g}) orbitals, which increase in strength on ring alkylation due to the decreased separation of the energies of ring and metal orbitals. The data (Table I) show the IE of the e_{2u} orbital (band B_1) to be less sensitive to substitution than the e_{2g} orbital (band B_2), and as a result the separation of bands B_1 and B_2 decreases from 0.95 ± 0.02

eV in uranocene to 0.85 ± 0.02 eV in octamethyluranocene. Dialkyluranocenes have intermediate values (0.91 ± 0.02 eV) while the value obtained for dicyclobutenouranocene (0.83 ± 0.02 eV) is anomalously low (considerable distortion of the eight-membered rings from D_{8h} symmetry is found for this compound.²² This suggests that the increase in metal-ring bonding contribution of the e_{2u} orbital on alkyl substitution is greater than for the e_{2g} orbitals. A likely explanation of this observation lies in the lower energy of the 5f orbitals compared with the 6d orbitals. The changes induced in the energy separation between the ring and metal orbitals will therefore be greater for the 5f orbitals.

The foregoing discussion makes use of the symmetry of the parent molecule. This symmetry is broken in the substituted compounds. The effect on the two degenerate levels of the parent will depend on the relative conformations of the substituents on the opposite rings. In some conformations both levels will be affected equally, and in others one level will be more strongly perturbed while the second is unchanged. If the rings are effectively freely rotating, the result will be a general lowering of the peak energy and a spreading of the bands. Both e_2 bands of the alkyl-substituted uranocenes are indeed generally broader than for the parent.

The proposal of more extensive metal-ring bonding in octamethyluranocene is supported by the fact that the e_{2u} orbital band has a significantly larger He II intensity (relative to the e_{2g} orbital band) in octamethyluranocene than in other uranocenes, indicating the largest proportion of f orbital character in this band.

From the well-resolved He I spectra of dimethyl-, diethyl-, and octamethyluranocenes the C_1 - C_2 band separation is demonstrated to be approximately constant at 0.66 eV and little different from the value found for uranocene (0.61 eV). This observation, together with the large substituent shifts found for the e_1 bands, suggests smaller metal-ring bonding involvement of the e_1 orbitals than the e_2 orbitals. The relativistic $X\alpha$ -SW calculations of Rösch and Streitwieser^{4b} show only a small metal sphere population in the e_1 MOs.

Summary

The photoelectron spectra of the alkyl-substituted uranocenes support the assignment of Clark and Green and indicate that the extent of 6d and particularly 5f orbital involvement in metal-ring bonding increases on alkylation of the ring. Bonding between the metal and ring e_2 orbitals is more extensive than that between metal and ring e_1 orbitals. Increase in the band widths on alkylation is probably due to the presence of several conformers in the vapor phase.

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Registry No. $U(\eta\text{-C}_8\text{H}_7\text{Me})_2$, 41367-67-3; $U(\eta\text{-C}_8\text{H}_7\text{Et})_2$, 37274-10-5; $U(\eta\text{-C}_8\text{H}_7\text{-}n\text{-Bu})_2$, 37274-12-7; $U(\eta\text{-C}_8\text{H}_7\text{-}t\text{-Bu})_2$, 63230-70-6; $U(\eta\text{-C}_8\text{H}_6(\text{CH}_2)_2)_2$, 70377-87-6; $U(\eta\text{-C}_8\text{H}_4\text{Me}_4)_2$, 12715-87-6.

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