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Preliminary communication

ON THE ELECTRONIC STRUCTURES OF CYCLOBUTADIENE AND TRIMETHYLENEMETHANE

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Summary

The photoelectron spectra of eight 4 π-electron hydrocarbons and their tricarbonyl complexes have been measured. From these spectra the perturbation energies of the π orbitals introduced by the tricarbonyliron moiety have been determined. These perturbation energies are 0.89 ± 0.07 and 0.22 ± 0.06 eV for the first and second π orbitals, respectively. Given these perturbation energies and the photoelectron spectra of the tricarbonyliron complexes of cyclobutadiene and trimethylenemethane, π-ionization energies for the two transients, cyclobutadiene (8.29 and 11.95 eV) and trimethylenemethane (8.36 and 11.79 eV), have been predicted.

Certainly one of the most promising current frontiers of ultraviolet photoelectron spectroscopy (UPS) is the investigation of the electronic structures of radicals and other transient species [1]. In order to study such transients, one must employ either sophisticated home-built or extensively modified commercial instrumentation. For this reason few photoelectron spectroscopists have been, or are, working in this important area. Cyclobutadiene and trimethylenemethane are two transient organic molecules which have received a vast amount of attention from theoretical chemists as to their geometric and electronic structures [2]. However, experimental studies of the structures of these molecules have necessarily been limited to spectroscopic observations of the transients in low-temperature matrices [3]. While it may well prove possible to eventually study these two transients by gas-phase UPS*, the experimental difficulties will be immense due to the short lifetimes of the species and overlapping bands in the spectra caused by precursors and other contaminants. For this reason it would seem helpful to know the approximate positions of the critical transient

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*An effort has been made already to study the photoelectron spectrum of trimethylenemethane [4].

bands in the complex photoelectron spectra. This communication reports the approximate π-ionization potentials for cyclobutadiene and trimethylenemethane obtained by an indirect means from the photoelectron spectra of the tricarbonyliron complexes of these two transients. We shall not presume to claim that we have definitely determined the electronic structures of the two, but rather we feel that our conclusions will help those photoelectron spectroscopists who eventually study the species directly to make accurate band assignments.

Actually work similar to that in this study was done by Dewar and Worley some years ago [5—8]. The photoelectron spectra of 1,3-butadiene [5], butadieneiron tricarbonyl [6,7], cyclobutadieneiron tricarbonyl [6,7], and trimethylenemethaneiron tricarbonyl [8] were reported. A comparison of the spectra for the first two stable molecules, after applying a small correction for the *trans/cis* conformation change, provided estimates of the magnitude of perturbation introduced by complexation of the π-MO's of butadiene by the tricarbonyliron moiety. Using the perturbation energies estimated by this procedure and the spectra of the complexes of the two transients, the π-ionization energies of cyclobutadiene [6,7] and trimethylenemethane [8] were predicted. However, there were some shortcomings in this early work. First, the spectra were all measured using a cylindrical-grid-type analyzer and were consequently poorly resolved; thus the ionization potentials obtained from them were of questionable accuracy. Second, 1,3-butadiene was the only model compound employed. It was uncertain whether the perturbation-energy correction would remain constant over a wide series of related compounds. In the current work we have attempted to circumvent the possible shortcomings of the early work by using a high-resolution analyzer (ca. 30 meV)* and studying a wide range of 4π electron ligands and their tricarbonyliron derivatives**.

It should be noted that high-quality photoelectron spectra of butadieneiron tricarbonyl [9] and cyclobutadieneiron tricarbonyl [10] have been reported, but these works did not address the transient cyclobutadiene. Also, Green and coworkers [11] have discussed the photoelectron spectra of several tricarbonyliron and tricarbonylruthenium complexes of cyclic 4π-electron systems. The high-resolution UPS of trimethylenemethaneiron tricarbonyl has not been reported, however, and it is shown in Fig. 1. The appearance of the spectra for the tricarbonyliron complexes is usually similar to that in Fig. 1 [9—11]. The first broad complex band must be assigned to ionization of orbitals primarily confined to the tricarbonyliron moiety [5—8, 9—11]. The second and third band systems correspond to ionization of the two perturbed π-MO's [5—8, 9—11]. It is these two bands that are of primary interest to us in evaluating the appropriate perturbation energies, and Table 1 lists the vertical ionization potentials corresponding to the two π-ionization processes for all of the molecules included in this study. Also listed in Table 1 are available data from other laboratories. A detailed discussion of the complete spectra of these compounds will be presented at a later date.

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*The photoelectron spectra described in this work were measured on a Perkin—Elmer PS 18 spectrometer equipped with a heated inlet probe. The data in Table 1 represent an average of at least four runs for each compound. Xenon and Argon were always employed as internal calibrants.

**The complexes used in this work were prepared and purified by standard literature methods. The dienes were obtained from Aldrich Chemical Co. or Chemical Samples Co. and used directly.

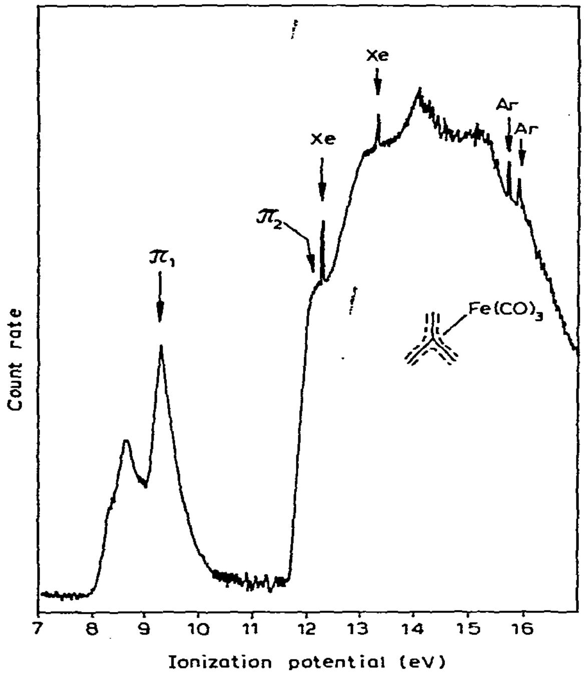

Fig. 1. The photoelectron spectrum of trimethylenemethaneiron tricarbonyl. The excitation source was the He(I) resonance line.

From Table 1 it can be seen that the perturbation correction to the highest lying π-MO generally falls in the range 0.8—1.0 eV; the average value, in fact, is 0.89 ± 0.07 eV. Applying this average perturbation to the data for cyclobutadieneiron tricarbonyl and trimethylenemethaneiron tricarbonyl, we predict that the first π-ionization energies of the transients cyclobutadiene and trimethylene-

TABLE 1

THE π IONIZATION ENERGIES OF SOME 4π-ELECTRON HYDROCARBONS AND THEIR TRICARBONYLIRON COMPLEXES[a]

Compound	Ligand	Complex		Ligand	Complex	
	π_1	π_1	$\Delta\pi_1$	π_2	π_2	$\Delta\pi_2$
1,3-Butadiene	9.08[b]	9.88[c]	0.80	11.34[b]	11.48[c]	0.14
2-Methyl-1,3-butadiene	8.87	9.68	0.81	10.89	11.05	0.16
trans-1,3-Pentadiene	8.60	9.62	1.02	11.11	11.30	0.19
2,3-Dimethyl-1,3-butadiene	8.72	9.47	0.75	10.41	10.67	0.26
2-Methyl-*trans*-1,3-pentadiene	8.47	9.46	0.99	10.57	10.88	0.31
Ethyl-*trans,trans*-2,4-hexadienoate[d]	8.85	9.75	0.90	11.13	11.47	0.34
1,3-Cyclohexadiene	8.32[e]	9.24[f]	0.92	10.84[e]	11.01[f]	0.17
Bicyclo[2.2.1]heptadiene	8.73[g]	9.63	0.90	9.59[g]	9.80	0.21
Cyclobutadiene		9.18[h]			12.17[h]	
Trimethylenemethane		9.25			12.01	

[a] All values are in electron volts and represent vertical ionization potentials. [b] Ref. 16. [c] Previous values are 9.93 and 11.52 eV [9]; 9.82 and 11.43 eV [11]. [d] Two bands at (ligand/complex: 9.96/9.98, 10.53/10.63) have been assigned to ionization of MO's which are primarily carbonyl- and ester-oxygen lone pairs, respectively. [e] Literature values are 8.25 and 10.75 eV [17]. [f] Literature values are 9.33 and 11.04 eV for these two ionization potentials [11]. [g] Literature values are 8.69 and 9.55 eV [18]. [h] Lit. [10] 9.21 and 11.78 eV (adiabatic).

methane should be 8.29 and 8.36 eV, respectively. These predicted values are several tenths of an eV lower than those obtained in the early, low-resolution work [5—8]*. Furthermore, the 8.29 eV value for cyclobutadiene is in excellent accord with an electron-impact measurement (8.2—8.6 eV) [13] made by Hedaya et al., on a pyrolysis product of photo-α-pyrone. Thus Hedaya and coworkers [13] probably succeeded in measuring the first ionization potential of cyclobutadiene rather than some other isomer such as vinylacetylene. Table 1 also shows that the perturbation correction for the lower lying π-MO for these systems is ca. 0.22 ± 0.06 eV. Therefore, we predict that the second π-ionization potentials of cyclobutadiene and trimethylenemethane should lie near 11.95 and 11.79 eV, respectively.

One might question the validity of using the perturbation correction derived for cyclobutadieneiron tricarbonyl in predicting the π-electronic structure of cyclobutadiene given that the ring is square in the former and probably rectangular in the latter [14]. In addition the geometries of trimethylenemethane and cyclobutadiene are certainly quite different, thus rendering a constant perturbation correction for these two transients seemingly unsound. However, Table 1 shows that the corrections for non-conjugated bicycloheptadieneiron tricarbonyl which has a geometry differing drastically from any of the conjugated complexes are of the same magnitude as those for all of the conjugated 4π-electron systems studied. Furthermore, in a recent ESCA study of the core levels of trimethylenemethaneiron tricarbonyl and butadieneiron tricarbonyl, Jolly and coworkers [15] have concluded that the overall donor and acceptor characters of the two ligands are similar. Thus although our approach may not be truly "theoretically rigorous", we do feel that the estimated ionization potentials for the two transients are accurate to within 0.1 eV, and as such, will be of use to experimentalists studying the electronic structures of the species directly**.

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*While Dewar and Worley [12] made a 0.14 eV correction to their perturbation energy based on a theoretical computation which placed the first ionization energy of *cis*-1,3-butadiene 0.14 eV above *trans*-1,3-butadiene, we have not done this in this work. It is certain that the *IP* of the *cis* isomer is at least 9.08 eV [5] but whether it is above 9.08 eV is speculative and dependent upon the theoretical computational method chosen. In any case the error introduced in assuming equal *IP*'s for the two isomers would be small, for *cis*/*trans* isomers rarily differ in *IP* by more than 0.03 eV.

**It should be noted that trimethylenemethane has a triplet ground state while the tricarbonyliron complex is a singlet. Thus our estimate of the π-ionization potentials for trimethylenemethane may better refer to the excited singlet. Again, drastic differences in geometry do not seem to affect the perturbation correction appreciably (Table 1).

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