The He(I) Photoelectron Spectrum of Cyclopentadienone

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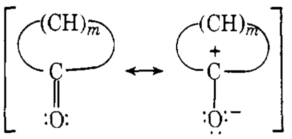
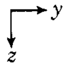
Abstract: The He(I) photoelectron spectrum of unsubstituted cyclopentadienone has been determined by flash vacuum pyrolysis of orthoquinone and pyrocatechol cyclic sulfite. The first three observed vertical ionization potentials are assigned as $^2A_2$ (Π_a, 9.49 eV), $^2B_2$ (n_O, 10.01 eV), and $^2B_1$ ($\Pi_s(-)$, 12.0 eV). The positions of the bands are discussed in terms of variation in carbonyl Π electron polarization and compared with tropone and cyclopropenone.

The properties of ketones, generally depicted as [**1a** ↔ **1b**], have been the subject of numerous investigations[2a] because of their relationship with Hückel's $4n + 2$ rule which applies to the carbon framework of the ionic representation (**1b**).



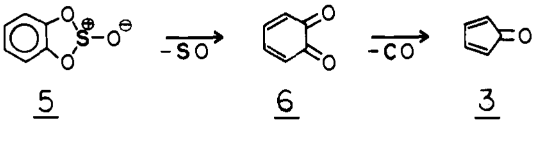
1a 1b



$m = 2$ cyclopropenone (**2**)
$m = 4$ cyclopentadienone (**3**)
$m = 6$ tropone (**4**)

Cyclopropenone (**2**) and tropone are expected to show "aromatic character" while cyclopentadienone is expected to show "antiaromatic character" according to this rule. Photoelectron spectra have been reported previously for cyclopropenone[3] and its di-*tert*-butyl derivative,[4] tropone,[5] and numerous derivatives,[6] and two di-*tert*-butylcyclopentadienone derivatives.[7] We presently wish to report our observation of the He(I) photoelectron spectrum of parent cyclopentadienone (**3**) which serves as a test of the several rationalizations and predictions which have been made concerning the electronic effects of the carbonyl group in this series of compounds.

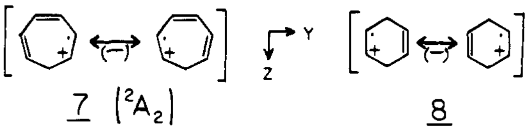
The kinetic instability of cyclopentadienone[8] (**3**) requires generation by a method such as flash vacuum pyrolysis[9] which has been used previously[2b] in infrared studies of the matrix isolated compound. Our adaptation of this method to a photoelectron spectrometer has been described previously.[10] The **3** generating reactions are shown below. Both the cyclic sulfite (**5**) and orthoquinone (**6**) have a PE band (Figure 1) at ca. 11 eV[11] which is not present with pyrolysis temperatures above 750 °C,[12] indicating their complete reaction. The spectrum of the sulfite at intermediate temperatures (Figure 2) shows the formation of CO[13] and SO[14] (which is itself a transient) although the latter is not evident in the spectra obtained at the temperatures needed for complete reaction of the sulfite precursor. The spectrum obtained starting with **6** and a pyrolysis temperature of 750 °C is nearly identical[15] with that obtained from the sulfite. The only organic product isolated after warming the condensate from these pyrolyses was the dimer which was clearly not present in the pyrolysis stream (Figure 4). We therefore believe that Figure 3 represents the PE spectrum of essentially pure cyclopentadienone.



We assign the first band in the observed spectrum as $^2A_2$ (Π_a) on the basis of its complex vibrational structure which is similar to that of cyclopentadiene.[16] The second observed band is assigned as $^2B_2$ (n_O) since its vibrational structure is less complex. We believe the third band to be associated with the $^2B_1$ (Π_s) state on the basis of the predictions of the structure representation (SR) model[17] and analogy with cyclopentadiene[18] (Figure 5).

Band 1. Assignment $^2A_2$ (Π_a). Previous studies[7] of alkyl-substituted cyclopentadienones led to the prediction that the $^2A_2$ (Π_a) band should occur near 9.3 eV and the observed position of this band (in our assignment)[18] is in fair agreement with this prediction. A second method of estimating the position of the $^2A_2$ (Π_a) state of cyclopentadienone is by perturbation of the corresponding state of cyclopentadiene. Differences in the position of this band, according to Hückel models, should give a direct measure of the "inductive" effect of the substituent (CH_2 or CO) lying on the C_2 axis. The parameter derived for this effect from one study of tropone,[5b] compared to *hypothetical* planar cycloheptatriene, predicts[19] the position of the $^2A_2$ band in **3** at 10.8 eV. No band is observed near this predicted value.

The discrepancy in predictions could be removed by a reduction in the magnitude of the "inductive" parameter from 3.14 eV[5b] to 1.20 eV. The position of the $^2A_2$ band in planar cycloheptatriene (**7**) would then be estimated at 10.25 eV instead of the 9.57 eV of ref 5b. The former value (10.25 eV) is very near that estimated for **7** by Miller, Schweig, and Vermeier[5] in their reports on the tropone PE spectrum using **7** as a reference point. It is also very close to that predicted by the structure representation model[17] comparing hypothetical planar cycloheptatriene (**7**) with 1,4-cyclohexadiene (**8**).[20] The ionic states (**7** and **8**) corresponding to $^2A_2$ of this discussion, are subject solely to the direct (through space) interaction of the ene ions as shown below. For 1,4-cyclohexadiene the interaction constant is +0.74 eV.[20] For **7**, this interaction constant should have a value of ca. +0.4 giving the $^2A_2$ state at 10.1 eV above the neutral polyene starting material. The reduced value of the interaction for **7** compared with **8** simply arises from the change in the geometrical relationship of the interacting ene ion units. The inductive parameter suggested by Frost, Bünzli, and Weiler[5b] appears to us to be too large to be applied to planar, fully conjugated, cyclic ketones.



While an inductive parameter for carbons α to the carbonyl group of ca. $\alpha + 1.2$ eV would appear to rationalize the positions of the $^2A_2$ ionic states for both **3** and **4** compared with their hydrocarbon counterparts, the arguments in this rationalization are slightly inconsistent. We wish to point out

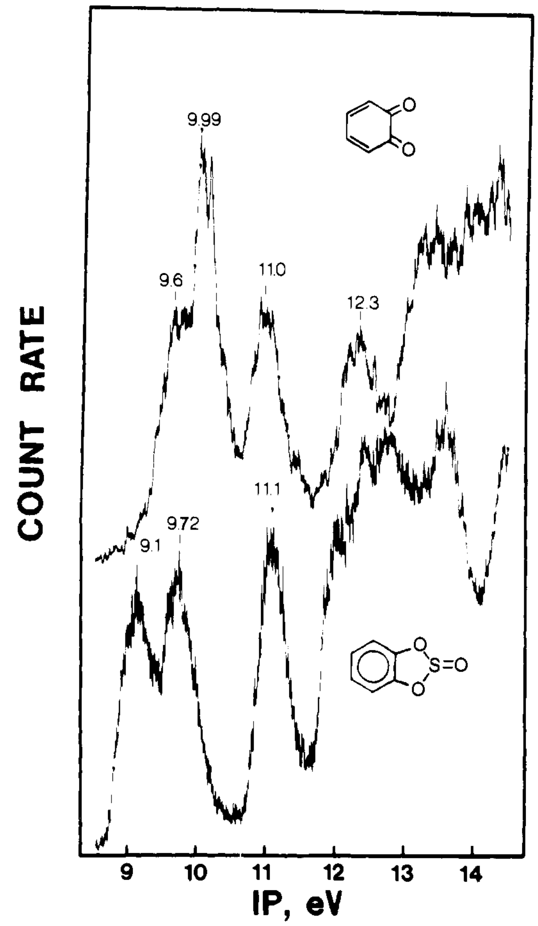


Figure 1. He(I) photoelectron spectra of orthoquinone (**6**) and pyrocatechol cyclic sulfite (**5**) at temperatures below 150 °C.

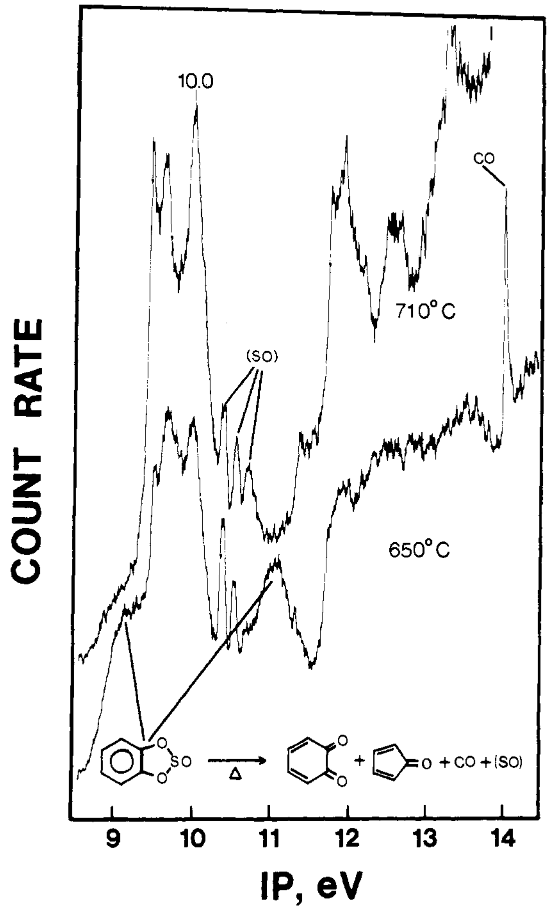


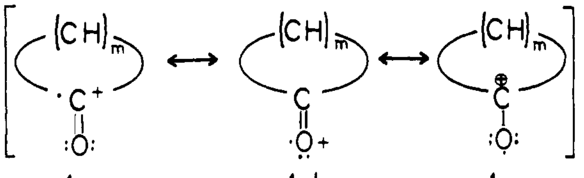
Figure 2. He(I) photoelectron spectra from pyrocatechol cyclic sulfite at 650 and 710 °C.

what we believe to be a better physical interpretation of the shift in the position of the $^2A_2$ state of **3** compared with cyclopentadiene (+0.8 eV). It is the loss of the stabilization energy associated with the Π electron polarization of the carbonyl group. That is, the $^2A_2$ (Π_a) ionic state should contain less dipolar (C^+-O^-) character than the ground state. This follows, in a qualitative sense, simply from the fact that the dipolar (C^+-O^-) form of the carbonyl group will be much (~3 eV) higher in energy with respect to the covalent (>C=O) form *in the ions* (where it is neighboring the positively charged ene units) than in the ground state. The stabilization of the molecular ground state due to this (C^+-O^-) polarization will thus be larger than that for the ionic states and the ionization potential will be increased. A qualitative picture of this argument is shown as Figure 5.

Results of INDO[21] calculations (Table I) support this argument in that the Π electron density of the oxygen atom of **3** goes from 1.15 in the neutral ketone to 1.02 in the $^2A_2$ SCF configuration. Though the Koopmans' theorem value (12.55 eV) and the $E^{+\cdot} - E^0$ value (11.31 eV) are both far too high compared with the observed (9.49 eV) ionization potential in the INDO parameterization, the wave functions were the basis of the INDO parameter choice and are thus still suggestive.

The shift in the $^2A_2$ state of **4** compared with the hydrocarbon (**7**) is only +0.6 eV. The above argument alone would indicate either that neutral tropone (**4**) had less dipolar (C^+-O^-) character than cyclopentadienone or that the amount of C-O polarization was relatively constant in **4** and its $^2A_2$ ionic state. The INDO method suggests the latter in that the Π electron density on oxygen is 1.30 in the neutral ketone and 1.28 in the $^2A_2$ ionic SCF configuration. This could be taken as an indication of the expected $4n + 2$ effect, i.e., the position of the $^2A_2$ ionic state of **4** (10.67 eV) is low in energy in comparison with that expected from **3** owing to the increased ability of the seven-carbon framework to accommodate positive charge. There are of course other rationalizations possible.

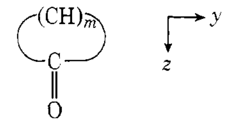
Band 2. Assignment $^2B_2$ (n_O). Previous workers[7] also predicted the position of the $^2B_2$ (n_O) band for **3** to be near 9.3 eV (accidentally degenerate with $^2A_2$) while it is observed at 10.01 eV. This prediction was made on the basis of the observed spectrum of the sterically stabilized di-*tert*-butyl derivatives of **3** and the expected effect of removal of the *tert*-butyl substituents. The factor not considered in making this prediction is just the converse of the CO depolarization described above for the $^2A_2$ (Π_a) ionic states. The effect of removing one lone pair electron should increase the C-O Π electron polarization relative to the ground state, transmitting the formal (σ) positive charge on oxygen (**1d**) into the carbon Π electron system (**1e**).



1c 1d 1e

The $^2B_2$ (n_O) ions should thus be sensitive to Π carbonium ion stabilization effects such as ring size ($4n + 2$ effect) and alkylation. The observed shift in the $^2B_2$ band for **3** with alkylation is about the same as that for the $^2A_2$ ionic state while the prediction of near degeneracy of the two in the PE spectrum of **3** assumed that the n_O band would not respond to the alkyl-

Table I. Observed and Calculated Ionization Potentials[a]



Compd	Band	Assignment	Obsd	Δ alkyl[b]	$E^{+\cdot} - E_0$[c]	KT[d]	SR[e]
Cyclopropenone[i]	①	$^2B_2$ (n_0)	9.57[3]	−1.23[f]	8.91	10.55	
	②	$^2B_1$ (Π_S)	11.19[3]	−0.55[f]	11.43	13.11	
Cyclopentadienone[j]	①	$^2A_2$ (Π_a)	9.49	−1.0[g]	11.31	12.55	8.6
	②	$^2B_2$ (n_0)	10.01	−0.85[g]	10.09	12.18	10.4[25]
	③	$^2B_1$ (Π_S)	12.0		13.75	15.25	11.2
Tropone[k]	①	$^2B_1$ (Π_S)	8.89[6]	−0.18[h]	9.71	11.05[l]	8.4
	②	$^2B_2$ (n_0)	9.25[6]	−0.16[h]	8.30	11.52[l]	10.5[25]
	③	$^2A_2$ (Π_a)	10.64[6]	−0.38[h]	15.82	16.41[l]	10.1

[a] Electron volts. [b] Shift in observed vertical ionization potential with alkylation. [c] Difference in INDO configurational energies of the ion of stated symmetry and the neutral ground state. [d] INDO Koopmans theorem estimates ($-\epsilon_{\mathrm{INDO}}$). [e] Structure representation values assuming that the ions are derived from the purely covalent (**1a**) form of the ketone. [f] 2,3-Di-*tert*-butyl: ref 3 vs. ref 4. [g] 2,5-Di-*tert*-butyl: this work vs. ref 7. [h] 2-Methyl: ref 6. [i] The geometry of Flygare.[22] [j] Fulvene geometry[23] with a C–O bond length of 1.22 Å. [k] The geometry of Flygare,[24] with H atoms bisecting interior angles. [l] The values given in ref 5a are $-\epsilon_{b_1}$, 10.98; $-\epsilon_{b_2}$, 10.38; $-\epsilon_{a_2}$, 16.74. The descrepancies between these values and those which we obtain are presumably due to differences in C–C–H bond angles.

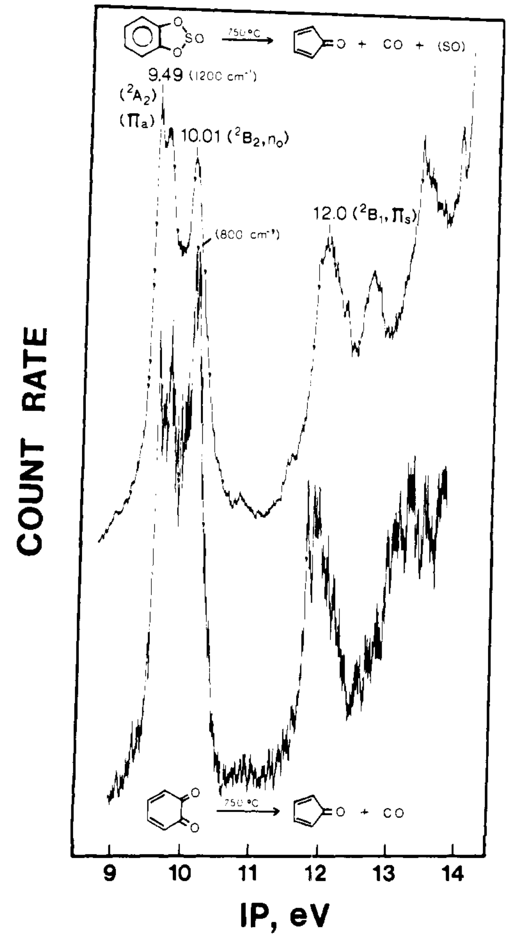


Figure 3. He(I) photoelectron spectra of cyclopentadienone at 750 °C. The instrumental resolution for the spectrum from orthoquinone (**6**) was 30 meV while that starting with the sulfite (**5**) was 60 meV.

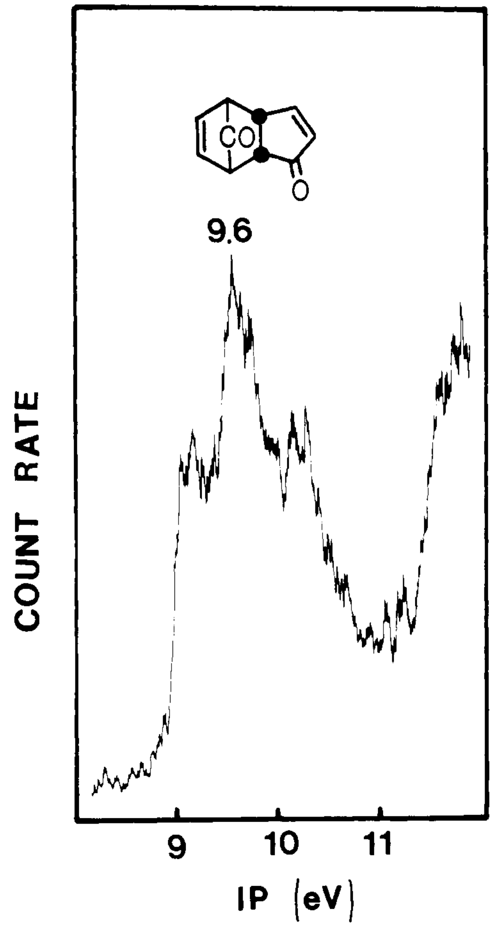


Figure 4. The He(I) photoelectron spectrum of cyclopentadienone dimer.

ation. A similarly large shift is observed in the n_0 ($^2B_2$) ionization potential of cyclopropenone with di-*tert*-butylation (Table I). The INDO (Table I) wave functions for cyclopentadienone support this notion in that the Π electron density on oxygen goes from 1.15 in the neutral ketone to 1.54 for the $^2B_2$ SCF configuration.

The position of this $^2B_2$ band is also sensitive to the hyperconjugative interaction with the σ framework (depicted as **1c**) and the SR model indicates that this effect is virtually the same for **3** and **4** giving the calculated[25] band position at 10.4–10.5 eV if only **1c** and **1d** are considered for each compound. Taking 10.4 eV as a reference point, the effect of **1e** lowers the energy of the $^2B_2$ (n_0) state of the five-ring system by 0.4 eV and the seven-ring system by 1.5 eV. The larger shift for the tropone

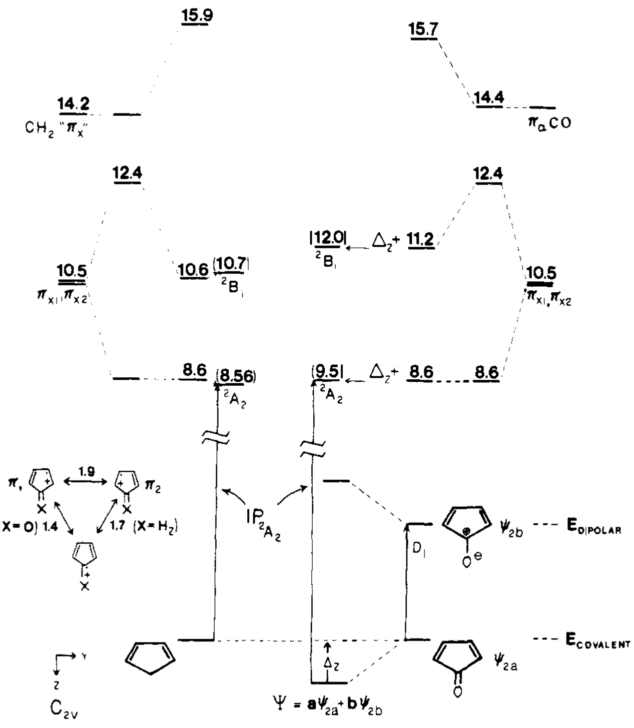


Figure 5. Comparison of the Π states of cyclopentadiene and cyclopentadienone using the structure representation model. The diagonal elements of the energy matrix are the bond ionization potential of an olefin ($W_{\Pi_{CC}}$, 10.5 eV, ethylene), a pseudo Π methylene ($W_{``\Pi"_{CH_2}}$, 14.2 eV, methane), or a $\Pi$ carbonyl ($W_{\Pi_{CO}}$, 14.4 eV, formaldehyde). The off-diagonal elements of the energy matrix are the interaction constant between the two $\Pi_{CC}$ ions ($S_{\Pi,\Pi}{}^{cis}$, +1.9 eV) and that for a $\Pi_{CC}$ ion and the "$\Pi$"$_{CH_2}$ ion ($S_{``\Pi",\Pi}$, 1.74 eV, 1.4-cyclohexadiene) or Π_{CO} ion ($S_{\Pi,\Pi}{}^{trans}$, 1.4 eV, 1,3-butadiene). The ionization potential for the ketone estimated in this manner is corrected for the stabilization of the ground state due to the polarization of the carbonyl (Δ_z) which is lost in the ion. The C^+–O^- structures for the ions are above and off the energy scale shown in this figure.

system could again be an indication of the $4n + 2$ effect. This interference is strengthened by the INDO calculated reorganization energy (defined as the difference in the Koopmans' theorem and $E^{+\cdot} - E^0$ estimates of the ionization potential). For the five-ring (**3**) system this value is 2.09 eV while for tropone ($^2B_2$) it is 3.22 eV. Even though the $E^{+\cdot} - E^0$ difference gives a low estimated ionization potential for $^2B_2$ of **4**, an unusually large reorganization energy for the seven-ring system seems apparent. We therefore suggest that the low $^2B_2$ band position of **4** does reflect the "aromatic character" of the tropone system or that the relatively high position of this band for **3** reflects its "antiaromatic character".

Band 3. Assignment $^2B_1$ (Π_S). The ground state stabilization of **3**, due to the C^+–O^- polarization, should affect the observed ionization to this state to a similar extent as it does the $^2A_2$ (Π_a) state. Indeed, the correction to the SR calculation, shown in Figure 5, is almost the same. The INDO wave functions do not give a clear indication of the C–O Π electron depolarization in this case because of the symmetry difference. The C–O group directly shares the radical cation character and the oxygen atom Π electron density change is not simple to interpret. This band is apparently not resolved from the σ continuum in the di-*tert*-butyl compounds studied previously[7] but should be in methylated or fluorinated derivatives. We hope to confirm the assignments suggested here through studies of such derivatives.

Summary

As is well known, the INDO parameterization and Koopmans' theorem approach to the assignment of photoelectron bands is of doubtful value (Table I). This parameterization and the difference in SCF configurational energies of the cation and substrate ($E^{+\cdot} - E^0$) give values usually within 1 eV for the n_O states of ketones (including a much larger number of examples than shown in Table I). However, it gives extremely poor values for the Π ionic states of ketones and their hydrocarbon analogues (errors greater than +2 eV in most cases). If the present assignments for **3** and those agreed upon[5,6] for tropone are both correct then the high $^2B_2$ (n_O) ionization potential of **3** (10.01 eV) compared with the low value for **4** (9.25 eV)[6] is most indicative of the "antiaromatic" vs. "aromatic" feature of the two ketones.

Our choice of interpretation in terms of the SR model demonstrates how it may point to distinctions between ground state effects vs. ionic state effects. In this regard, the microwave structure[24] and dipole moment of tropone give no particular indication of a large dipolar (**1b**) contribution whereas the energetic position of the $^2B_2$ (n_O) ionic state is considerably lower for **4** compared to **3**. We have interpreted this difference in terms of ionic state effects. The adoption of the Koopmans' theorem concept removes all chance of making such distinctions which is one of the principal reasons why we believe that the widespread use of this conceptualization is so regrettable. It is our hope that the arguments presented above may stimulate the application of better theories than semiempirical or single determinant models to these molecules and their ions.

Experimental Section

The photoelectron spectra were obtained using a Perkin-Elmer PS-18 photoelectron spectrometer modified as described previously.[10] The band positions were fixed using the 15.76 eV line of argon and the 12.13 eV line of xenon as calibrants which were present during the pyrolysis. The product of the pyrolysis was isolated from a liquid nitrogen cooled trap after warming to room temperature in a nitrogen atmosphere. The methylene chloride soluble material showed infrared ($CHCl_3$ solution, C=O stretch 1795, 1700 cm^{-1}, lit.[26] 1800, 1700 cm^{-1}) and ^1H NMR ($CDCl_3$ solution, δ ~7.32 (1 H), ~6.12 (3 H, vinyl), ~3.30 (3 H), ~3.15 (1 H), ~2.85 ppm (1 H)) spectra identical with those of an authentic sample of the cyclopentadienone dimer which was prepared by the method of Eaton.[26] Pyrocatechol cyclic sulfite (**5**) was prepared in good yield from pyrocathechol and thionyl chloride.[27] Orthoquinone was prepared in low (1–10%) and irreproducible yields by silver oxide oxidation of pyrocatechol.[28] The cyclic carbonate of pyrocatechol[29] failed to react in our flow systems at all temperatures up to 900 °C and was reisolated without change from the cold trap after attempted pyrolysis. Photoelectron spectra were recorded with the cyclopentadienone dimer passing through the pyrolysis system under the conditions used to obtain the spectra shown as Figure 2. These spectra showed no similarities to the features which we assign to **3**.

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(1) National Science Foundation Undergraduate Research Participant, 1975.

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(11) The interpretation of the spectra of **5** and **6** are unimportant for the present purposes and will be discussed in a future publication.

(12) The temperatures required for complete reaction of **5** or **6** are ca. 200 °C higher in our system than those reported in ref 2b. The pyrocatechol carbonate was unreactive in our system.

(13) Sharp bands for CO at 14.01 ($^2\Sigma_g^+$), 16.54 (ν 1600 cm^{-1}, $^2\Pi_u$), and 19.69 eV ($^2\Sigma_u$) were present starting with either **5** or **6**. D. Turner, C. Baker, A. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1970, p 49.

(14) (a) Sharp bands for SO at 10.38 eV (lit.[14b] 10.34 μ) (ν 1210 cm^{-1}, $^2\Pi$) and 14.96 eV (lit.[14a] 14.96 eV) (ν 970 cm^{-1}) were present in the spectra of **5** at intermediate temperatures. (b) N. Jonathan, D. J. Smith, and K. J. Ross, *Chem. Phys. Lett.*, **9**, 217 (1971).

(15) The resolution during the pyrolysis of **6** (30 meV) was better than that during the pyrolysis of **5** (60 meV), which gives some differences in the appearance of the peak shapes.

(16) P. J. Derrick, L. Åsbrink, O. Edquist, and B.-Ö. Jonsson, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 203 (1971); *Spectrochim. Acta, Part A*, **27**, 2525 (1971). The main vibrational spacing in the first band of **3** is ~1400 cm^{-1}, like that of cyclopentadiene. There are also lower frequency spacings present in this band which have not been completely resolved for **3** though they have been for cyclopentadiene. The main vibrational spacing of the second band in the spectrum of **3** is ~800 cm^{-1}, like that observed for the n_0 band of most ketones. Our criterion of assignment is like that used[5a,6] make the difficult choice of the ground state of the tropone radical cation as Π ($^2B_1$, $\bar{\nu}$ ~1530 cm^{-1}, IP_{obsd} 8.89 eV) under n_0 ($^2B_2$, $\bar{\nu}$ ~830 cm^{-1}, IP_{obsd} 9.25 eV). See ref 18.

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(18) (a) The entire assignment scheme proposed here should be regarded as tentative and is certainly not rigorously established by the experimental information available. Indeed, a referee has suggested that the assignments of the first and second bands be reversed. The primary basis of his argument is that the spacing of the two Π bands of the spectrum of **3** should be the same as observed for cyclopentadiene (2.0 eV). Taking the 12 eV band of **3** as Π_s ($^2B_1$) would then put the Π_a ($^2A_2$) band at 10.0 eV. We strongly disagree with the postulate. The spacing of the two Π bands of **3** could only *fortuitously* be the same as cyclopentadiene. The interaction constant for the CH_2 pseudo Π group and a neighboring olefinic group is +1.74 eV[20] while that between an exocyclic Π ion (like the carbonyl) and an adjacent transoid Π group should be +1.44 eV (e.g., butadiene). The bond ionization potential of a carbonyl can be taken directly from the observed spectrum of formaldehyde, 14.4 eV. This difference in interaction parameters for a CH_2 vs. C=O group with an olefin should be magnified by a factor of ca. $\sqrt{2}$ (~0.4 eV) in the observed splitting between the Π_a and Π_s bands. To be sure, the polar character of the CO group is problematical, but there is no good reason to expect that this effect would just reduce the split back to the value of the hydrocarbon. Similar additivity arguments have been used in a recent review[18b] where the Π band position of acetone is placed at 13.4 eV (vertical). This assignment may be correct but the argument made for it[18b] is highly questionable. Additivity would certainly not be expected of a hyperconjugative origin of the shifts with methylation. The Π bond ionization potential of the *localized* carbonyl group of **3** should certainly be closer to that of formaldehyde (14.4 eV) than that of acetone. (b) J. L. Meeks, H. J. Maria, P. Brint, and S. P. McGlynn, *Chem. Rev.*, **75**, 603 (1975).

(19) Following the arguments of ref 5b the appropriate HMO coefficients for the diene unit are 0.602 and the inductive shift is given as $2C_{ij}^2$ (3.14 eV) = 2.27 eV. This increment is added to the observed first ionization potential of cyclopentadiene (8.56 eV).

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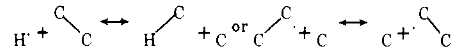
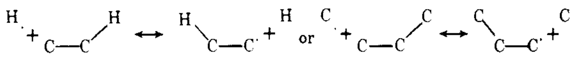


+2.31 and +2.62 eV. The vicinal interaction constants were $S_{CH,CC}$ =



$S_{CH,CH} = S_{CC,CC} = 0.25 + 0.75 \cos \Theta$, where Θ is the dihedral angle between the interacting bonds. The hyperconjugative interaction constant between the oxygen vacancy structure (**1d**) and that with the vacancy in an adjacent C–C bond (**1c**) was +2.5 eV. These values arise from the SR analysis of smaller molecules such as ethylene and formaldehyde.

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Addition of Nitronic Esters to Alkynes. Formation under Kinetic Control of Aziridine Invertomers. Study of the Transposition of 4-Isoxazolines to Acylaziridines

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Abstract: The addition of nitronic esters **1** and **2** to alkynes has been studied. This reaction which leads to *N*-methoxyaziridines is stereospecific for the nitrogen atom; the *Z* nitronic esters give only two aziridines which differ in the configuration of the ring carbon atoms. The *E* isomers give quantitatively two other aziridines, which are invertomers of the two *Z* nitronic esters products. A two step mechanism is suggested for this reaction. Each of the isomeric 1,3 dipoles leads under kinetic control to only one of the two diastereoisomeric 4-isoxazolines which in turn isomerize stereospecifically to aziridines. In these examples, a study of the transposition of 4-isoxazolines to acylaziridines has been realized stereochemically for the first time. The various possible mechanisms are discussed. 1,3-Sigmatropic shifts with retention of configuration at the migrating nitrogen atom seems most probable. However, a mechanism involving the intermediacy of biradicals may not be completely ruled out.

Baldwin et al.[2] have shown that 1,3-dipolar cycloadditions of nitrones to alkynes lead to 4-isoxazolines which rearrange easily to acylaziridines. Very few additional reports have dealt specifically with this reaction[3] and in particular its stereochemistry has never been studied. The major complication is that 4-isoxazolines generally exhibit only one asymmetric center owing to fast nitrogen inversion under the conditions of rearrangement.

We have previously shown[4] that 1,3-dipolar addition of nitronic esters to alkenes takes place with formation under kinetic