# Variable-Temperature Ultraviolet Photoelectron Spectroscopy of the Keto–Enol Tautomers of Pentane-2,4-dione

*Noel S. Hush,*[A] *Michelle K. Livett,*[B] *J. Barrie Peel*[C] *and Gary D. Willett*[D]

[A] Department of Theoretical Chemistry, University of Sydney, N.S.W. 2006.
[B] Chemistry and Physics Department, Melbourne College of Advanced Education, Carlton, Vic. 3053.
[C] Department of Chemistry, La Trobe University, Bundoora, Vic. 3083.
[D] School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033.

*Abstract*

The He I photoelectron spectra of pentane-2,4-dione measured at various temperatures have been subjected to a spectrum-stripping technique to enable isolation of the complete He I photoelectron spectra of the keto and enol tautomers. The resulting spectrum-stripping coefficients allow evaluation of the enolization equilibrium constant at each temperature and subsequently the enthalpy of enolization. Interpretation of the photoelectron spectra is achieved with the use of *ab initio* molecular orbital calculations. Photoionization of non-bonding oxygen, and $\pi$-type electrons, contribute to the low ionization energy region of the spectrum, with a $\pi_{CC} < n_O^- < \pi_{CO}$ ordering for the enol tautomer, and $n_O^- < n_O^+ < \pi_{CO}^+$ for the keto tautomer. Because of different electronic relaxation effects, $\Delta$SCF calculations are required to predict correctly the observed $\pi_{CC}/n_O^-$ spacing for the enol tautomer.

## Introduction

Early determinations of the equilibrium between keto and enol tautomers which relied on chemical methods, notably bromine titration,[1] have now been superseded by spectroscopic measurements which have the advantage of not interfering with the equilibrium mixture of tautomers. Infrared, Raman and ultraviolet spectroscopic measurements have used the extinction coefficients of bands assigned to the individual tautomers in evaluation of the tautomeric equilibrium constant.[2-6] The nuclear magnetic resonance technique has found the most widespread application in mainly liquid and solution studies,[6] whereas gas-phase structural investigations have employed the electron diffraction technique.[7] Recently, mass spectrometry[8] and photoelectron spectroscopy[9] have been added to the selection of tools available for gas-phase

[1] Meyer, K. H., *Justus Liebigs Ann. Chem.*, 1911, **380**, 212; *Ber. Dtsch. Chem. Ges.*, 1912, **45**, 2843.
[2] Mines, G. W., and Thomas, H., *Proc. R. Soc. London, Ser. A*, 1975, **342**, 327.
[3] Kohlrausch, K. W. F., and Pongratz, A., *Ber. Dtsch. Chem. Ges.*, 1934, **67**, 976, 1465.
[4] Kahovec, L., and Kohlrausch, K. W. F., *Ber. Dtsch. Chem. Ges.*, 1940, **73**, 1304.
[5] Nakanishi, H., Morita, H., and Nagakura, S., *Bull. Chem. Soc. Jpn*, 1977, **50**, 2255.
[6] Duus, F., *J. Am. Chem. Soc.*, 1986, **108**, 630.
[7] Lowrey, A. H., George, C., D'Antonio, P., and Karle, J., *J. Am. Chem. Soc.*, 1971, **93**, 6399.
[8] Holmes, J. L., Lossing, F. P., and Terlouw, J. K., *J. Am. Chem. Soc.*, 1986, **108**, 1086.
[9] Schweitzer, G. K., *Appl. Spectrosc. Rev.*, 1975, **10**, 257.

tautomerization studies.   A comprehensive discussion of the development of the concept of tautomerism is given by Ingold,[10] while an extensive review of enolization investigations is provided by Forsen and Nilsson[11] and supplemented by Hart.[12]

A comprehensive review of variable-temperature photoelectron spectroscopy has been provided by Schweitzer.[9]  Besides providing for the measurements on involatile compounds, the wider potential of variable-temperature photoelectron spectroscopy now includes (i) pyrolysis techniques to produce transient species formed by thermal decomposition[13,14] which have been utilized by Bock and coworkers to optimize chemical reactions;[15] (ii) considerably reduced temperatures obtained with supersonic expansions in specially designed instruments for high resolution[16] and cluster studies;[17] (iii) conformational equilibria such as the rotational isomerism of the dihalo-substituted ethanes[18-20] and tetramethyldiphosphine;[21] (iv) tautomerization of pentane-2,4-dione and its methyl- and fluoro-substituted derivatives[2,22] and more recently that of thioacetylacetone and related compounds.[23]  Honegger and Heilbronner have drawn attention to erroneous conclusions that may be drawn in some cases when the variable temperature photoelectron technique is applied to systems where conformers differ only slightly in relative stabilities and are separated by low energy barriers.[24]

Theoretical approaches to tautomerism have varied from semiempirical INDO and CNDO/2 molecular orbital calculations to extensive *ab initio* studies.[25]   Interest has mainly centred on the relative stability of the keto and enol species.[26,27]   The intramolecular hydrogen bonding available to the enol tautomer of such $2\beta$-diketones as pentane-2,4-dione enhances the stability of these species and gives rise to their special interest for the theoretical chemist. Inevitably, attention has been concentrated on the least complex of the series, propanedial (malonaldehyde). Calculations of the total molecular energy as a function of molecular geometry have provided information about the stability and geometry of its keto and enol tautomers.   The question of whether hydrogen bonding in the enol form, $\beta$-hydroxyacrolein, is sufficiently

[10] Ingold, C. K., 'Structure and Mechanism in Organic Chemistry' p. 530 (Cornell University Press: Ithaca, New York, 1953).

[11] Forsen, S., and Nilsson, M., in 'The Chemistry of the Carbonyl Group' (Eds J. Zabicky and S. Patai) Vol. 2 (John Wiley: London 1970).

[12] Hart, H., *Chem. Rev.*, 1979, **79**, 515.

[13] Dyke, J. M., Jonathan, N., and Morris, A., in 'Electron Spectroscopy: Theory, Techniques and Applications' (Eds C. R. Brundle and A. D. Baker) Vol. 3, pp. 189–229 (Academic Press: London 1979).

[14] Westwood, N. P. C., and Werstiuk, N. H., *J. Am. Chem. Soc.*, 1986, **108**, 891.

[15] Bock, H., Hirabayashi, T., and Mohmand, S., *Chem. Ber.*, 1982, **115**, 492.

[16] Pollard, J. E., Trevor, D. J., Lee, Y. T., and Shirley, D. A., *Rev. Sci. Instrum.*, 1981, **52**, 1837.

[17] Carnovale, F., Peel, J. B., and Rothwell, R. G., *Aust. J. Phys.*, in press.

[18] Ames, D. L., and Turner, D. W., *J. Chem. Soc., Chem. Commun.*, 1975, 179.

[19] Gan, T. H., Peel, J. B., and Willett, G. D., *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 965; Gan, T. H., Peel, J. B., and Willett, G. D., *J. Mol. Struct.*, 1978, **44**, 211.

[20] Carnovale, F., Gan, T. H., and Peel, J. B., *J. Electron Spectrosc. Relat. Phenom.*, 1979, **16**, 87.

[21] Schweig, A., Thon, N., and Vermeer, H., *J. Am. Chem. Soc.*, 1979, **101**, 80.

[22] Schweig, A., Vermeer, H., and Weidner, U., *Chem. Phys. Lett.*, 1974, **26**, 229.

[23] Jorgensen, F. S., Carlsen, L., and Duus, F., *J. Am. Chem. Soc.*, 1981, **103**, 1350.

[24] Honegger, E., and Heilbronner, E., *Chem. Phys. Lett.*, 1981, **81**, 615.

[25] Binkley, J. S., Frisch, M. J., and Schaeffer, H. F., *Chem. Phys. Lett.*, 1986, **126**, 1.

[26] Bouma, W. J., and Radom, L., *Aust. J. Chem.*, 1978, **31**, 1167; 1978, **31**, 1649.

[27] Noack, W.-E., *Theor. Chim. Acta*, 1979, **53**, 101.

strong to locate the bridging hydrogen symmetrically between the two oxygen atoms is answered inconsistently by calculations differing in their choice of basis set and geometry optimization procedure.[28] The resulting $O \cdots O$ distance is found to be critical in determining the preferred symmetry of the molecule. This issue has been resolved in favour of the asymmetric structure by X-ray photoelectron spectroscopy,[29] with a similar result for pentane-2,4-dione[30] confirmed by $^{13}C$ n.m.r. results.[31,32] Theoretical investigations of other keto–enol systems are less complete, perhaps due to the paucity of experimental data. While the MINDO/1 method has been used to calculate the heat of enolization of a collection of ketones and esters[33] and a CNDO/2 investigation of pentane-2,4-dione undertaken,[34] detailed calculations of electronic structure are not generally available. In particular, a *trans* arrangement of the keto tautomer of $\beta$-diketones is generally assumed with little consideration given to other possible conformations involving rotation of the carbonyl groups.

Variable-temperature photoelectron spectroscopy has been used by Mines and Thompson[9] and Schweig *et al.*[22] to distinguish the photoelectron bands due to the keto and enol tautomers of pentane-2,4-dione in the 8–11 eV region. Assignment was achieved by correlation with the photoelectron spectra of its methyl and fluoro derivatives. Both groups used intensity data deduced from overlapping bands in the photoelectron spectra to evaluate the tautomerization equilibrium constant at various temperatures, and thus the enthalpy of enolization of pentane-2,4-dione. The results obtained by Schweig *et al.* and Mines and Thompson are $-7 \cdot 9$ kJ mol$^{-1}$ and $-16 \cdot 6$ kJ mol$^{-1}$ respectively. The latter result closely parallels earlier isothermal distillation results and shows a temperature dependence in the enthalpy of enolization.

These earlier photoelectron studies were confined to the low ionization energy region where the keto and enol bands are only partly separated. Retrieval of a complete He I spectrum for each tautomer requires a spectral subtraction procedure such as that employed in the extraction of the rotational isomer photoelectron spectra of the dihalo-substituted ethanes,[19,20] This investigation extends previous studies of the photoelectron spectra of the keto and enol tautomers to include all bands accessible to He I radiation and, furthermore, the coefficients yielded by the numerical spectrum subtraction provide more accurate values for the equilibrium constant at the operating temperatures which can be compared to earlier reported data. The low ionization energy molecular orbitals provide information about electronic interactions within the tautomers and careful *ab initio* calculations have been performed to interpret the molecular orbital splittings in this region. It is found necessary to conduct a detailed examination of the geometry dependence of the keto tautomer eigenvalues to reproduce the experimental splitting of its lowest ionization energies, though the calculations are unable to determine unambiguously the dihedral angle between the carbonyl groups. In the enol case differing electronic relaxation effects must be

[28] Catalan, J., Yanez, M., and Fernandez-Alonso, J. I., *J. Am. Chem. Soc.*, 1978, **100**, 6917, and references cited therein.

[29] Brown, R. S., Tse, A., Nakashima, T., and Haddon, R. C., *J. Am. Chem. Soc.*, 1979, **101**, 3157.

[30] Clark, D. T., and Harrison, A., *J. Electron Spectrosc. Relat. Phenom.*, 1981, **23**, 39.

[31] Egan, W., Gunnarsson, G., Bull, T. E., and Forsen, S., *J. Am. Chem. Soc.*, 1977, **99**, 4568.

[32] Barna, J. C. J., and Robinson, M. J. T., *Tetrahedron Lett.*, 1979, **16**, 1455.

[33] Dewar, M. J. S., and Shanshal, M., *J. Chem. Soc. A*, 1971, 25.

[34] Houk, K. N., Davis, L. P., Newkome, G. R., Duke, R. E., and Nauman, R. V., *J. Am. Chem. Soc.*, 1975, **95**, 8364.

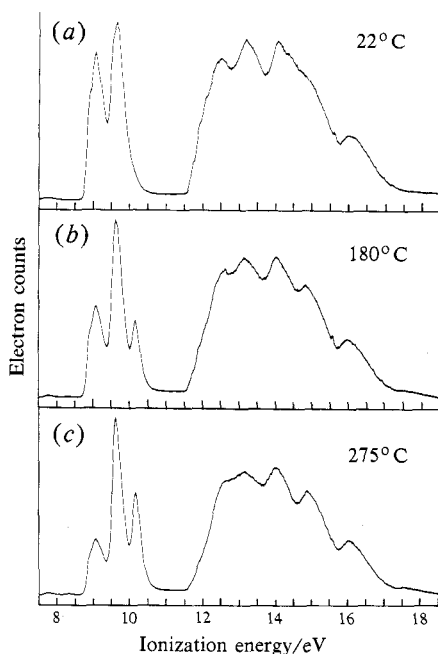N. S. Hush, M. K. Livett, J. B. Peel and G. D. Willett



**Fig. 1.** He I photoelectron spectra of pentane-2,4-dione at
(a) 22°C;
(b) 180°C;
(c) 275°C;
showing varying proportions of the keto and enol tautomers.

invoked to explain the smaller than expected Koopmans[35] difference between the two lowest ionization energies.

## Experimental

A commercial sample of pentane-2,4-dione was introduced into the photoelectron spectrometer through a 20 cm long, $0 \cdot 6$ cm outer diameter, glass tube which can be heated up to 400°C with a bifilar wound (to minimize stray magnetic fields) nichrome wire. This tube is surrounded by a $2 \cdot 6$-cm glass jacket which serves as the vacuum feedthrough. The ambient temperature of this tube in the experiment was measured at several points by using a ceramic jacketed thermocouple and, temperatures over the range 0–275°C were used to examine the temperature dependence of the photoelectron spectrum.

The spectra shown in Fig. 1 are the result of time-averaging for 1 h over 1024 points at a maximum count rate of $3500 \mathrm{~s}^{-1}$ for each spectrum. Calibration by using mixtures of methyl iodide, acetylene, buta-1,3-diene and nitrogen was used to determine the ionization energy scale. At room temperature the photoelectron spectrum is mainly due to the enol tautomer. With increasing temperature the band at $9 \cdot 1$ eV diminishes and that at $10 \cdot 2$ eV grows relative to the central band at $9 \cdot 6$ eV. Earlier photoelectron studies have established that this central band arises from a superposition of enol and keto contributions while the bands at lower and higher ionization energy are due to the enol and keto tautomers respectively.[2,22] Variable temperature photoelectron spectra thus illustrate the shift in the pentane-2,4-dione tautomerization equilibrium towards the keto form with increasing temperature. Further evidence of this enhancement of keto concentration is provided by the filling in of the 13 and 14 eV spectral regions together with development of additional photoelectron bands at 15 and $17 \cdot 5$ eV.

After normalization of the total spectral intensities (with kinetic energy scaling) of the 'hot' and 'cold' spectra, the application of the spectrum-stripping procedure[19,20] to the spectra shown in Fig. 1a and Fig. 1c enables the extraction of photoelectron spectra emanating from the individual pentane-2,4-dione tautomers. Visual assessment of the necessary spectral subtraction was rendered quite straightforward by the well defined bands of each species in the low ionization

---

[35] Koopmans, T., *Physica (Utrecht)*, 1934, **1**, 104.

**Fig. 2.** He I photoelectron spectra of (a) enol (b) keto forms of pentane-2,4-dione obtained by spectrum-stripping.
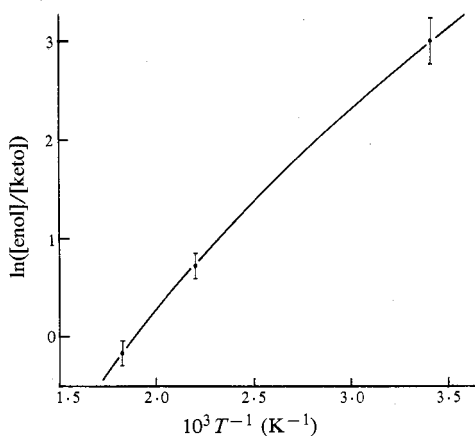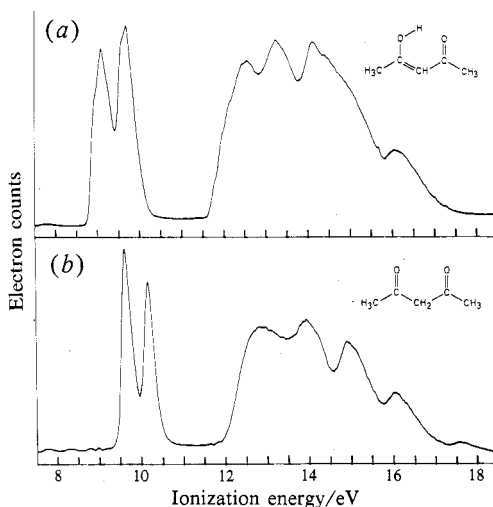


**Fig. 3.** Plot of $\ln K$ against $T^{-1}$ for the enol–keto equilibrium of pentane-2,4-dione, obtained from the spectrum-stripping data.

energy region. The resulting stripped spectra representing the enol and keto tautomers of pentane-2,4-dione are displayed in Fig. 2. Smoothing by convolution with a four-point halfwidth Gaussian function has been used to offset the noise inherent in a difference spectrum. The associated stripping coefficients allow the evaluation of the relative concentrations of the two species with the enol proportions at 22°C, 180°C and 275°C as 95%, 68% and 44% respectively. Similar results were obtained by the more rudimentary intensity analysis outlined by Mines and Thompson.[2]

The temperature dependence of the enolization equilibrium constant $K$, [enol]/[keto], as shown in Fig. 3, can be used to determine the enthalpy of enolization, $\Delta H_{enol}$. The data are too limited to confirm the temperature-dependence of $\Delta H$ observed by Mines and Thompson but the average $\Delta H_{enol}$ over the 22–275°C range is determined to be $-17 \pm 2$ kJ mol$^{-1}$, which is in closer agreement with the measurements of Mines and Thompson[2] than those of Schweig *et al.*[22]

## Calculations and Discussion

There is a twofold purpose in performing calculations on the electronic structures of the keto and enol pentane-2,4-dione tautomers. First it is aimed to simulate the experimentally observed patterns of ionization energies and thus assign as fully as

possible their photoelectron spectra. It is also of interest to reproduce the band separations in the low ionization energy region and so gain some understanding of the electronic interactions operating in the two species. With these aims in mind the GAUSSIAN80 molecular orbital program[36] was employed, using its geometry optimization facility together with two basis sets.

### The Enol Tautomer

The enol tautomer was examined with the STO-3G[37] basis set and the 4-31G[38] split valence basis set. Eigenvalues of the uppermost molecular orbitals and the total molecular energy at $C_s$ and $C_{2v}$ geometries are given in Table 1. The starting geometries were derived from the STO-3G optimized results obtained by Bouma *et al.* for $\beta$-hydroxyacrolein[39] followed by acetone. Both STO-3G and 4-31G basis set calculations confirm the $C_s$ structure as the preferred configuration. The O···O distances for the $C_s$ and $C_{2v}$ structures are 2·57 and 2·29 Å respectively, in agreement with the conclusion of Isaacson and Morokuma[40] that an optimized O···O separation in excess of 2·3 Å is necessary for the $C_s$ structure of $\beta$-hydroxyacrolein to be preferred over the $C_{2v}$ form.
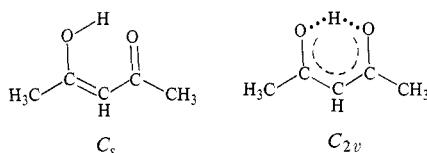


Table 1. Comparison of the calculated ionization energies (eV) and total molecular energies (hartree) for $C_s$ and $C_{2v}$ geometries of enol pentane-2,4-dione

| Energy compared | $C_s$ | | $C_{2v}$ | |
| --- | --- | --- | --- | --- |
| | STO-3G ($-\epsilon$) | 4-31G ($-0\cdot9\epsilon$) | STO-3G ($-\epsilon$) | 4-31G ($-0\cdot9\epsilon$) |
| $I_1$ ($\pi_{CC}$) | 7·12 | 8·71 | 6·51 | 8·53 |
| $I_2$ ($n_O{}^-$) | 8·67 | 10·33 | 8·04 | 10·19 |
| $I_1 - I_2$ | 1·55 | 1·62 | 1·53 | 1·66 |
| $E$ (hartree) | $-339\cdot318$ | $-343\cdot206$ | $-339\cdot311$ | $-343\cdot193$ |

According to the calculated molecular electronic structure electrons contributing to the first photoelectron band of the enol tautomer emanate from a $\pi$ molecular orbital which is strongly CC bonding with some OO antibonding character. The $\pi_{CC}$ orbital is followed by an antibonding combination of the in-plane oxygen 2p orbitals, $n_O{}^-$, which is dominated by the carbonyl oxygen contribution. Its ionization energy is virtually unchanged from the corresponding value of 9·61 eV observed for

[36] Binkley, J. S., Whiteside, R. A., Krishnan, R., Seeger, R., DeFrees, D. J., Schlegel, H. B., Topiol, S., Kahn, L. R., and Pople, J. A., Program No. 446, Quantum Chemistry Program Exchange, Carnegie–Mellon University, Pittsburg, PA.

[37] Hehre, W. J., Stewart, R. F., and Pople, J. A., *Chem. Phys.*, 1969, **51**, 2657.

[38] Ditchfield, R., Hehre, W. J., and Pople, J. A., *J. Chem. Phys.*, 1971, **54**, 724.

[39] Bouma, W. J., Vincent, M. A., and Radom, L., *Int. J. Quantum Chem.*, 1978, **14**, 767.

[40] Isaacson, A. D., and Morokuma, K., *J. Am. Chem. Soc.*, 1975, **97**, 4453.

$H_2C{=}CHCOCH_3$.[41] The $\pi_{CC}/n_O{}^-$ separation of 0·55 eV can be compared with the calculated results given in Table 1. Calculations at the STO-3G and 4-31G levels on $C_s$ and $C_{2v}$ molecular geometries grossly overestimate the ionization energy spacing predicted by equating the ionization energies to the negative of the molecular orbital eigenvalues.[35] It is proposed that neglect of electronic relaxation effects is responsible for this poor correlation.[42]

Application of the Koopmans approximation to photoelectron assignment reduces photoionization to a one-electron process and ignores the accompanying effects of electronic relaxation.[35] This simplification has little effect when molecular orbitals yielding widely variant relaxation energies are well separated in energy, but its limitations become obvious when molecular orbitals confined to a small energy interval are considered. Relaxation effects are most significant for ionic states possessing highly localized valence holes.[42] In such cases photoionization of an essentially non-bonding electron considerably alters the electronic environment in the vicinity of the residual atom, prompting redistribution of the remaining electrons. The effect is diffused when the ionized molecular orbital is delocalized over the molecular framework.



Fig. 4. Koopmans and ΔSCF ionization energies for the 5a″ and 15a′ molecular orbitals of enol pentane-2,4-dione.
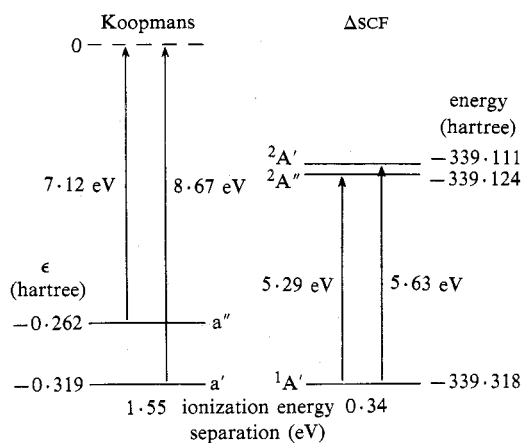
Since the $\pi_{CC}$ and $n_O{}^-$ orbitals of enol pentane-2,4-dione differ considerably in their extent of electron delocalization it is necessary to take account of the expected variation in electronic relaxation energy when assigning their ionization energies. This can be achieved by equating each ionization energy with the difference between the self-consistent-field total energies of the neutral molecule and cation (ΔSCF). The experimentally observed separation of the $\pi_{CC}$ and $n_O{}^-$ ionization energies is closely approximated by the ΔSCF results of STO-3G calculations. A comparison of the Koopmans and ΔSCF approaches is illustrated by Fig. 4. While retaining the Koopmans ordering of ionization energies the ΔSCF calculation improves agreement with their observed spacing and thus indicates the influence of electronic relaxation effects on localized molecular orbitals.

The assignment of the enol spectrum provided by a Koopmans ordering of ionization energies is given by the comparison of experimental band maxima and

[41] Tam, W.-C., Yee, D., and Brion, C. E., *J. Electron Spectrosc. Relat. Phenom.*, 1974, **4**, 77.
[42] Rabalais, J. W., 'Principles of Ultraviolet Photoelectron Spectroscopy' p. 110 (Wiley-Interscience: New York 1976).

**Table 2.** Comparison of experimental and calculated ionization energies (in eV) and molecular orbital assignments ($C_s$) of the enol form of pentane-2,4-dione

| Experimental[A] ionization energy | Assignment[B] MO | 4-31G ($-0.9\epsilon$) | Experimental[A] ionization energy | Assignment[B] MO | 4-31G ($-0.9\epsilon$) |
|---|---|---|---|---|---|
| 9·08 | 5a″ ($\pi_{CC}$) | 8·71 | | ⌈ 12a′ ($\sigma_{CH_3}$) | 13·70 |
| 9·63 | 15a′ ($n_O{}^-$) | 10·33 | | ∣ 11a′ ($\sigma_{CO}$) | 14·55 |
| 12·5 | 4a″ ($\pi_{CO}$) | 12·24 | 14·1 | ∣ 2a″ ($\pi_{CH_2CO^-}$) | 14·59 |
| | | | | ∣ 10a′ ($\sigma_{CO}$) | 14·99 |
| | ⌈ 3a″ ($\pi_{CH_2O}$) | 13·03 | | ⌊ 1a″ ($\pi_{CH_2CO^+}$) | 15·26 |
| 13·2 | ∣ 14a′ ($\sigma_{CH_3}$) | 13·22 | | | |
| | ⌊ 13a′ ($n_O{}^+$) | 13·31 | 16·0 | ⌈ 9a′ ($\sigma_{CO^-}$) | 16·56 |
| | | | | ⌊ 8a′ ($\sigma_{CO^+}$) | 16·97 |

[A] Accuracies vary between ±0·01 eV and ±0·1 eV. Above 12·5 eV only band maxima are provided

[B] Orbital numbering within the valence shell for the $C_s$ point group.

4-31G eigenvalues in Table 2. While electronic relaxation effects are instrumental in the splitting of the two ionization energies, they are less likely to prejudice the assignment of the remainder of the spectrum for which the molecular orbitals are largely delocalized. This expectation is reflected in the agreement between the calculated eigenvalue grouping and the band structure of the photoelectron spectrum. After kinetic energy scaling the band intensities were normalized to the total of 13 valence p plus hydrogen 1s derived molecular orbitals expected to have ionization energy less than 17 eV. Band minima were used to segment the spectrum. The resulting distribution, 1·8 : 2·3 : 5·2 : 1·6, for the spectral region above 12 eV, is in reasonable agreement with the 1 : 3 : 5 : 2 grouping provided by a Koopmans ordering of ionization energies.

Assignment of the bonding $\pi_{CO}$ orbital to the third photoelectron band is confirmed by the vibrational structure apparent on its low ionization energy edge. This region is not complicated by an underlying keto contribution. The progression has a mean spacing of $1375 \pm 30$ cm$^{-1}$, which may be compared with the molecular C=O stretching frequency of 1620 cm$^{-1}$ obtained by infrared spectroscopy.[2] It exhibits the expected reduction from the neutral molecule frequency which accompanies photoionization from a strongly bonding orbital and the third band is thus assigned to the $\pi_{CO}$ molecular orbital.

Insight into the electronic interactions operating in enol pentane-2,4-dione can be gained by a comparison of its ionization energies with those of related molecules. Conjugation with the out-of-plane 2p orbital of the hydroxy oxygen, $n_O{}^\perp$ can be regarded as destabilizing the $\pi_{CC}$ and $\pi_{CO}$ molecular orbitals of the acroloyl moiety[43] by 1·9 and 1·5 eV respectively, which reflects their relative proximity to the oxygen atom. The 4-31G calculation on the $C_s$ enol structure supports this view, providing $\pi_{CC}$ and $\pi_{CO}$ molecular orbitals with hydroxy oxygen contributions of 19% and 13% respectively. Both electron donation by the CH$_3$ moiety and minimal through-space interaction between the in-plane non-bonding oxygen 2p orbitals, $n_O{}^-$, in the enol are instrumental in destabilizing the related orbital of the acroloyl moiety by 0·5 eV. While a corresponding stabilization of the $n_O{}^-$ ionization energy from the 10·64 eV

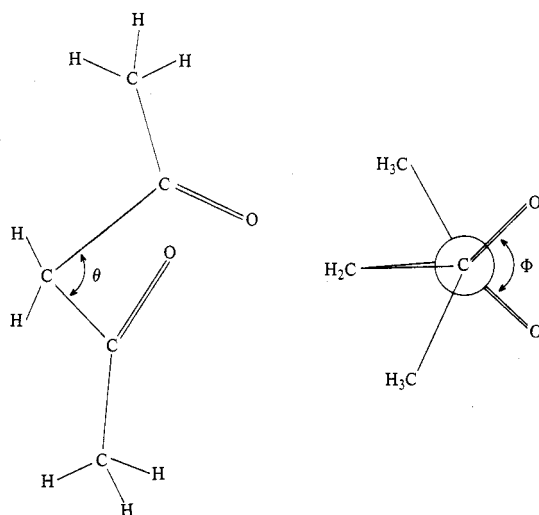[43] Van Dam, H., and Oskam, A., *J. Electron Spectrosc. Relat. Phenom.*, 1978, **13**, 273.

Fig. 5. The molecular geometry of the keto form of pentane-2,4-dione, showing central angle $\theta$ and dihedral angle $\Phi$.

Table 3. Ionization energy separations (in eV) between the $n_O{}^-$ and $n_O{}^+$ molecular orbitals of the keto form of pentane-2,4-dione as a function of carbonyl dihedral angle, $\Phi$, calculated by using the STO-3G basis set

| $\Phi$ | 0° | 30° | 60° | 90° | 120° | 150° | 180° |
|---|---|---|---|---|---|---|---|
| $\theta^A$ | 116·3° | 114·3° | 111·3° | 110·3° | 110·6° | 110·0° | 111·6° |
| $I_1$ ($n_O{}^-$) | 8·08 | 8·21 | 8·51 | 8·61 | 8·59 | 8·56 | 8·56 |
| $I_2$ ($n_O{}^+$) | 9·27 | 9·24 | 9·10 | 9·03 | 9·02 | 9·03 | 9·07 |
| $I_1 - I_2$ | 1·19 | 1·03 | 0·59 | 0·42 | 0·43 | 0·47 | 0·51 |
| $E + 339·0^B$ | −0·3307 | −0·3331 | −0·3358 | −0·3363 | −0·3366 | −0·3376 | −0·3386 |

$^A$ Optimization central CCC angle.    $^B$ $E$ in hartree.

observed in ethanol[44] undoubtedly occurs its magnitude is indefinite due to the uncertain assignment of bands in the 13–14 eV region of the photoelectron spectrum.

*The Keto Tautomer*

Calculations of the molecular electronic structure of keto pentane-2,4-dione must take into account the uncertainty of its geometry. To this end conformations of the keto tautomer with the dihedral angle between the carbonyl units, $\Phi$, varying from 0° (*cis*) to 180° (*trans*) conformations have been considered. Fig. 5 illustrates the molecular geometry parameters.

The STO-3G optimized $CH_3C$ moiety of $CH_3CHO$ obtained by Bouma *et al.*,[39] was included in an STO-3G optimization of the C=O bond length and CCC bond angle of $CH_3COCH_3$. These results were then employed in a two-angle optimization of the $CH_3COCH_2COCH_3$ molecule. For several fixed values of $\Phi$ in the range 0°–180° its central CCC bond angle, $\theta$, was optimized. The results are provided in Table 3. Also included are the total molecular energy and two uppermost eigenvalues obtained for each configuration providing criteria for evaluation of the geometrical results. The

[44] Kimura, K., Katsumata, S., Achiba, Y., Yamazaki, T., and Iwata, S., 'Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules' (Japan Scientific Societies Press: Tokyo 1981).

calculations predict an energy minimum at the *trans* arrangement where $\Phi$ equals 180°.

An interval of 0·53 eV separates the two lowest ionization energies in the photoelectron spectrum of the keto form of pentane-2,4-dione. The non-bonding orbital of acetone, with its ionization energy of 9·7 eV, would be expected to contribute to this region of the spectrum. The STO-3G results confirm this expectation and yield an $n_O^- < n_O^+$ ordering for the antisymmetric and symmetric combinations of the carbonyl in-plane 2p orbitals. This result is consistent with investigations of other $\beta$-dicarbonyls.[45]

The *cis* conformation, for which the through-space interaction is maximized, yields a calculated splitting of 1·19 eV between the two eigenvalues. With an increase in the angle separating the carbonyl groups the theoretical splitting approaches the experimental measurement. All configurations which deviate by more than 60° from the planar molecular skeleton give results in reasonable agreement with experiment. The calculated separation increases slightly towards a $\Phi$ value of 180° due to alterations in the through-bond interactions. Molecular conformations resulting from rotation of only one $CH_3C{=}O$ entity are calculated to have greater energy than those produced by symmetric rotation. Single point 4-31G calculations at the STO-3G optimum geometries yield results which follow the trends observed in the STO-3G calculations.

The photoelectron spectrum cannot then be used to determine unambiguously the angle between the carbonyl groups of the keto form of pentane-2,4-dione, but indicates that a value in excess of 60° is likely. An independent electron diffraction study obtained a dihedral angle of 48°.[7]

**Table 4.** Comparison of experimental and calculated ionization energies (in eV) and molecular orbital assignments ($C_2$) of the keto form of pentane-2,4-dione

| Experimental[A] ionization energy | Assignment[B] MO | 4-31G[C] $(-0{\cdot}9\epsilon)$ | Experimental[A] ionization energy | Assignment[B] MO | 4-31G[C] $(-0{\cdot}9\epsilon)$ |
|---|---|---|---|---|---|
| 9·63 | 10b ($n_O^-$) | 9·99 | | ⌈7a | 14·70 |
| 10·16 | 10a ($n_O^+$) | 10·40 | 14·9 | 6b | 14·80 |
| | | | | ⌊6a | 14·89 |
| 12·9 | ⌈ 9b ($\pi_{CO}^+$) | 11·62 | | | |
| | ⌊ 9a ($\pi_{CO}^-$) | 12·28 | | ⌈5b | 15·99 |
| | | | 16·0 | 4b | 16·30 |
| | | | | ⌊5a | 16·43 |
| | ⌈8b | 13·43 | | | |
| 13·9 | 8a | 13·69 | 17·6 | 4a | 17·75 |
| | ⌊7b | 13·97 | | | |

A Accuracies vary between ±0·01 and ±0·1 eV. Above 12 eV only band maxima are provided.
B Orbital numbering within the valence shell for the $C_2$ point group.
C Calculated results for $\Phi$ equals 90°.

The mean ionization energy of the $n_O^+$ and $n_O^-$ molecular orbitals of the keto form is 9·9 eV. This result is in excellent agreement with the mean of 10·0 eV of the ionization energies of carbonyl non-bonding molecular orbitals of acetaldehyde (10·26 eV)[44] and acetone (9·70 eV).[44] These molecules could be considered as fragments combining to form the keto tautomer.

[45] Dougherty, D., Brint, P., and McGlynn, S. P., *J. Am. Chem. Soc.*, 1978, **100**, 5597.

While there is some dependence of molecular orbital ordering on the dihedral angle between carbonyl groups the overall pattern of the higher ionization energies varies little with changes in $\Phi$. A comparison of the 4-31G results for a 90° configuration with the experimental measurements is given in Table 4. The distribution of eigenvalues into five distinct groups is reflected in the shape of the photoelectron spectrum above 12 eV. There is some discrepancy between the intensity results $2 \cdot 8 : 3 \cdot 4 : 2 \cdot 9 : 1 \cdot 9 : 0 \cdot 4$ obtained from an analysis of the kinetic energy scaled spectrum and the $2 : 3 : 3 : 3 : 1$ distribution predicted by the calculations. This disagreement is partly due to the approximation inherent in dividing the spectrum according to inter-band minima.

Assignment of the symmetric and antisymmetric combinations of localized $\pi_{CO}$ contributions to the band centred at $12 \cdot 9$ eV is verified by its agreement with the mean of $12 \cdot 9$ eV obtained for the $\pi_{CO}$ molecular orbitals of acetone and acetaldehyde. The similarity of their ionization energies is consistent with the minimal through-space interaction expected for $\pi$ electrons separated by over 2 Å. Any splitting is due to antibonding through-bond interaction with the bridging $CH_2$ orbitals, a destabilization available only to the symmetric combination.

## Conclusion

This investigation of the enol–keto tautomerism of pentane-2,4-dione illustrates the application of variable temperature photoelectron spectroscopy and spectrum stripping to exploit the energy differences between conformers in extracting their individual complete He I photoelectron spectra. An average enthalpy of enolization of $-17$ kJ $mol^{-1}$ was obtained over the temperature range studied. Photoionization of the outermost molecular orbitals of the enol tautomer must be explained in terms of electronic relaxation effects while a consideration of the geometry of the keto tautomer is necessary to an interpretation of its photoelectron spectrum.

## Acknowledgments