of this model and the experimental data. We may thus have some confidence in the basic structure of the mechanism, though better quantitative agreement between experiment and simulation would be highly desirable. Such improvement might be obtained by a more accurate treatment of ionic strength effects and/or by inclusion of N_2O_3, N_2O_4, NO_2^-, and NO^+ as independent species in addition to NO, NO_2, and HNO_2. We hesitate, however, to introduce additional species and further adjustable parameters into the model without more experimental information about the reactions involved. Nevertheless, the results obtained even with this simplified model make the Fe(II)–HNO_3 reaction one of the best understood of the known bistable systems.

Whether this system, like several earlier bistable reactions, can be modified so as to produce oscillation in a CSTR is still open to question. Our initial attempts have not met with success. The cross-shaped phase diagram approach[4b] suggests that we search for a feedback reaction which affects the stabilities of the two bistable branches differently. However, the theory also requires that the feedback reaction be much slower than the relaxation to the steady states of the Fe^{2+}–HNO_3 subsystem. Unfortunately, this relaxation is relatively slow compared with that of the bistable oxyhalogen systems which lead to oscillation,[6,7] and we have not yet been able to find a feedback species which acts sufficiently slowly to modify the effective concentration of one of the reactants.

A possible solution to this problem may lie in complexing the iron with various ligands in order to accelerate reactions P1–P3. Also, reaction P4 may have a damping effect on the system by removing NO which is a key species in the autocatalysis.[8] If a ferrous complex (or a different species) can be found which still reacts autocatalytically, but does not bind NO as strongly, the relaxation process may be speeded and the prospects for oscillation enhanced. We note that a number of nitric acid oxidations, including those of arsenite,[19] thiocyanate,[20] and hydroxylamine,[21] have been reported to be autocatalytic. Investigation of these possibilities is under way.

Acknowledgment. This work was supported by Grant No. CHE-7905911 from the National Science Foundation. We thank Patrick De Kepper and Kenneth Kustin for a number of thoughtful suggestions.

Registry No. Fe, 7439-89-6; nitric acid, 7697-37-2.

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X-ray Photoelectron Spectroscopic Study of the Enol–Enethiol Tautomerism of Thioacetylacetone and Related β-Thioxoketones[1]

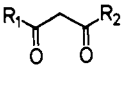
Flemming S. Jørgensen,*[2a] R. S. Brown,[2b] Lars Carlsen,[2c] and Fritz Duus[2d]

Contribution from the Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark, the Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada, the Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark, and the Institute of Life Sciences and Chemistry, Roskilde University, DK-4000 Roskilde, Denmark. *Received October 15, 1981*

Abstract: X-ray photoelectron spectroscopy has been used to record the O_{1s} and S_{2p} ionization spectra of thioacetylacetone, 2-acetylcyclohexanethione, 2-thioacetylcyclohexanone, the *S*-methyl derivative of thioacetylacetone, and propyl 3-mercaptocrotonate in the gas phase. It is shown that both the enol and the enethiol tautomers of the β-thioxoketones can be detected, and the enol/enethiol ratios for thioacetylacetone, 2-acetylcyclohexanethione, and 2-thioacetylcyclohexanone were determined to be 61:39, 30:70, and 80:20, respectively, based on the intensities of the oxygen ionizations. The conclusions derived from the sulfur region support the above, although they are less clear due to sulfur spin–orbit splitting. The enol/enethiol ratios obtained in the gas phase by XPS are compared with data from other methods, showing good agreement between results obtained in the gas phase and in solution. The binding energy (BE) shifts of the O_{1s} and S_{2p} orbitals have been discussed and suggest that geometrical factors affect the strength of the intramolecular hydrogen bond.

Introduction

In recent years much effort has been devoted to study the keto–enol tautomerism in β-diketones **1**.[3] Replacement of one of the oxygen atoms by a sulfur atom leads to β-thioxoketones **2**.[4,5] In contrast to the oxygen analogues the β-thioxoketones exist principally as rapidly interconverting tautomeric forms, the enol **2D** and enethiol **2C** forms, whereas the thioxoketone structure has never been observed.[6–12]



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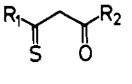

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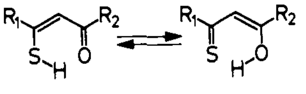

2 C 2 D

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(1) β-Thioxoketones. Part 8. For part 7, see ref 6.

(2) (a) University of Copenhagen; (b) University of Alberta; (c) Risø National Laboratory; (d) Roskilde University.

(3) S. Forsén and M. Nilsson in "The Chemistry of the Carbonyl Group", Vol. 2, J. Zabicky, Ed., Interscience, London, 1970, Chapter 3.

(4) The β-thioxoketones are named as such for simplicity, regardless of which tautomer is present. The notation of the tautomeric forms is consistent with that in previous parts.

(5) For a recent review see F. Duus (D. N. Jones, Vol. Ed.) in "Comprehensive Organic Chemistry", Vol. 3, D. H. R. Barton and W. D. Ollis, Eds., Pergamon Press, Oxford, 1979, Chapter 11.22.

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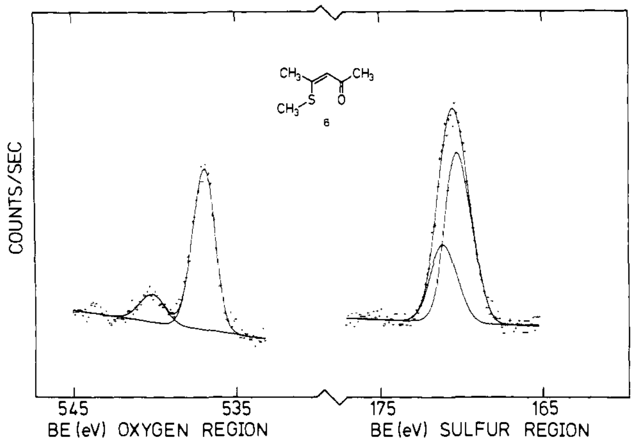
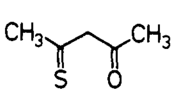


Figure 1. Computer-analyzed O_{1s} and S_{2p} ionization regions of 4-(methylthio)pent-3-en-2-one (**6**). The smaller peak at high binding energy is assigned to shake-up events.

Ultraviolet photoelectron spectroscopy has already proved to be an efficient technique for study conformational-dependent systems (rotamers, tautomers, etc.) in organic chemistry,[13] and X-ray photoelectron spectroscopy (XPS, ESCA)[14] has been applied successfully not only to the determination of symmetry characteristics of β-diketones[15-17] and trithiapentalenes[18-21] but also to the nonsymmetric tautomeric 2-hydroxypyridine ⇄ 2-pyridone equilibrium.[22] The latter study showed that it was possible to identify the species present as well as determine the equilibrium position from both the N_{1s} and O_{1s} ionization regions. Even for the more complicated 2-hydroxypyridine *N*-oxide ⇄ *N*-hydroxy-2-pyridone tautomeric equilibrium it was possible to determine the equilibrium position.[22]

This paper reports an XPS study of thioacetylacetone (**3**), 2-acetylcyclohexanethione (**4**), and 2-thioacetylcyclohexanone (**5**). These compounds were chosen to represent β-thioxoketones with comparable concentrations of both the enethiol and enol forms (**3**),[11] and with predominant concentration of the enethiol (**4**) and enol (**5**) form, respectively.[12] The compounds 4-(methylthio)-pent-3-en-2-one (the *S*-methyl derivative of thioacetylacetone) (**6**) and propyl 3-mercaptocrotonate (**7**) have been included to assist the interpretation of the electron spectra of **3–5**.



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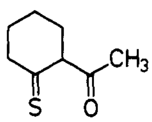

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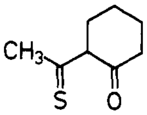

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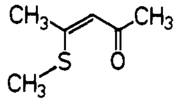

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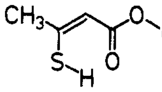

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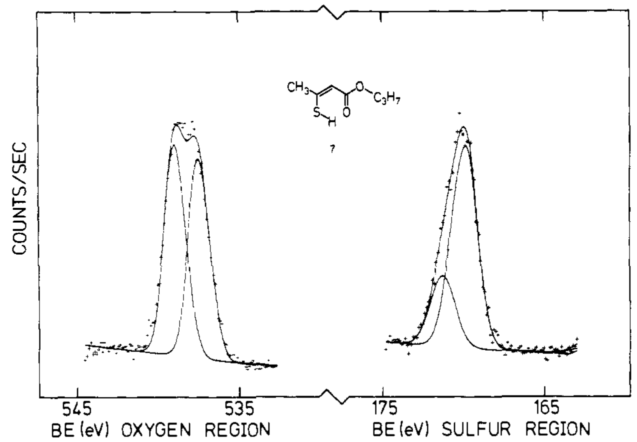

Figure 2. Computer-analyzed O_{1s} and S_{2p} ionization regions of propyl 3-mercaptocrotonate (**7**).

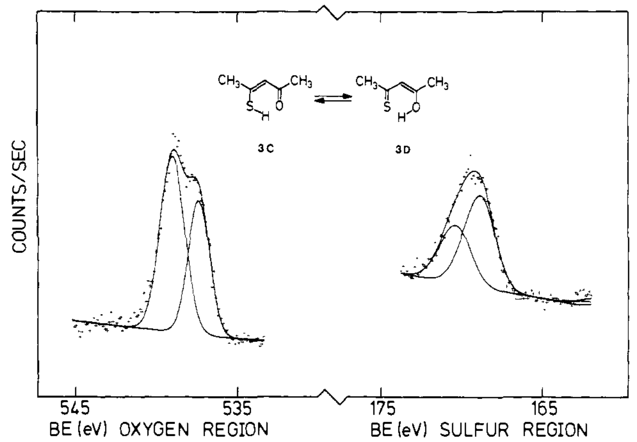

Figure 3. Computer-analyzed O_{1s} and S_{2p} ionization regions of thioacetylacetone (**3**).

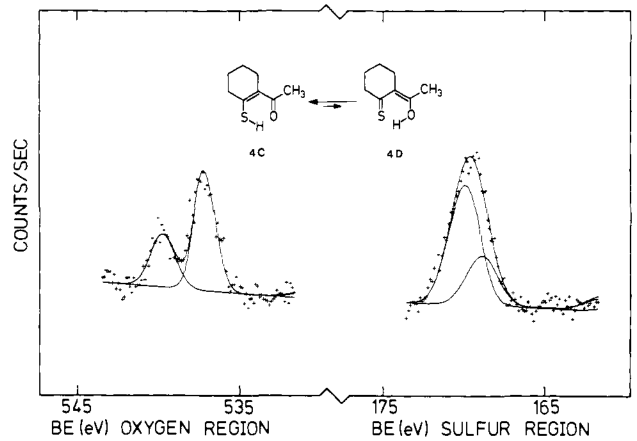

Figure 4. Computer-analyzed O_{1s} and S_{2p} ionization regions of 2-acetylcyclohexanethione (**4**).

Experimental Section

The syntheses of the compounds **3–7** have been reported previously.[11,12,23] X-ray photoelectron spectra were obtained with a MacPherson 36 ESCA spectrometer using Mg $K\alpha_{1,2}$ radiation ($h\nu$ = 1253.6 eV). The gaseous samples were introduced together with Ne gas using the neon

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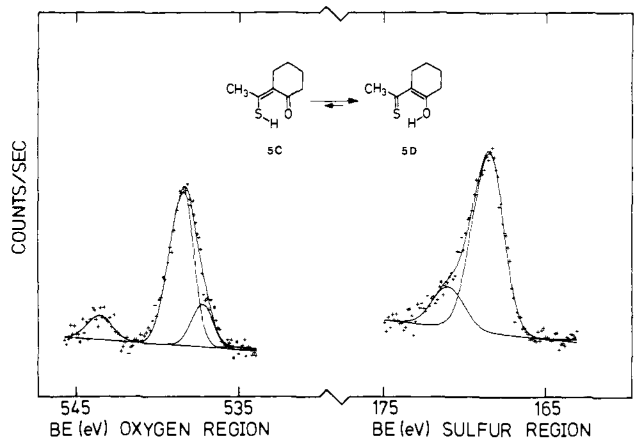

Figure 5. Computer-analyzed O_{1s} and S_{2p} ionization regions of 2-thioacetylcyclohexanone (**5**). The small peak at high binding energy is O_2 (see Table I, footnote *e*).

Table I. O_{1S} Binding Energies for β-Thioxoketones

compd	peak	BE(O_{1S})[a]	fwhm[b]	rel area[c]
4-(methylthio)pent-3-en-2-one (6)	1[d]	536.89 ± 0.04	1.56	
propyl 3-	1	539.07 ± 0.07	1.54	1.0
mercaptocrotonate (7)	2	537.56 ± 0.06	1.57	0.94 ± 0.08
thioacetylacetone (3)	1	539.11 ± 0.08	1.80[f]	1.58 ± 0.17
	2	537.47 ± 0.10	1.56[f]	1.0
2-acetylcyclohexane-	1	539.5 ± 0.4	1.80[f]	0.42 ± 0.16
thione (4)	2	537.2 ± 0.2	1.56[f]	1.0
2-thioacetylcyclo-	1[e]	538.5 ± 0.5	1.80[f]	3.93 ± 1.95
hexanone (5)	2[e]	537.1 ± 0.3	1.56[f]	1.0

[a] The precision is estimated from the least-squares fit. Values in electron volts. [b] Full width at half-maximum height. Values in electron volts. [c] Errors are from the least-squares fit. [d] The smaller peak at 539.98 eV is believed to arise from shake-up phenomena (see text). [e] The smaller peak at higher binding energy is O_2 (543.1 eV)[14] due to a leak in the inlet system. [f] Fixed value (see text).

Auger line at 804.56-eV kinetic energy[24] as calibrant. Experimental data were least-squares analyzed[25] by assuming Gaussian peaks, and each reported binding energy is the average of at least three separate runs.

Results

The X-ray photoelectron spectra of the β-thioxoketones **3-5**, the *S*-methyl derivative **6**, as well as the β-thioxo ester **7** are depicted in Figures 1-5. The O_{1s} and S_{2p} binding energies are presented in Tables I and II, respectively.

Due to the short time scale (10^{-16} s) of the XPS measurement, a tautomeric mixture such as **2C** ⇄ **2D** will show ionizations from both the enol and the enethiol forms.[16] Therefore, the tautomeric systems **3-5** should display two distinct O_{1s} ionizations arising from the two nonequivalent oxygen atoms. A carbonyl oxygen atom is normally easier to ionize than a hydroxyl oxygen atom and appears therefore at lower binding energy.[26] The ratio between the peak areas reflects the equilibrium position of the tautomeric enol–enethiol system, if equal ionization cross sections are assumed.[27] A similar reasoning can be applied to the thiocarbonyl/thiol pair.

The *S*-methyl derivative **6**[28] exibits a single narrow (half-width = 1.56 eV) ionization in the O_{1s} region from the carbonyl oxygen as indicated in Figure 1. The smaller peak at higher binding energy (539.98 eV) is assigned to a shake-up phenomenon.[29,30] On the other hand, the β-thioxo ester **7**[31] has two nonequivalent oxygen atoms and gives rise to two O_{1s} ionizations of equal intensity (Figure 2). The ionization at lower binding energy is assigned to the carbonyl oxygen (cf. Figure 6). The difference in binding energy (1.51 eV) is similar to differences observed for carboxylic esters.[26]

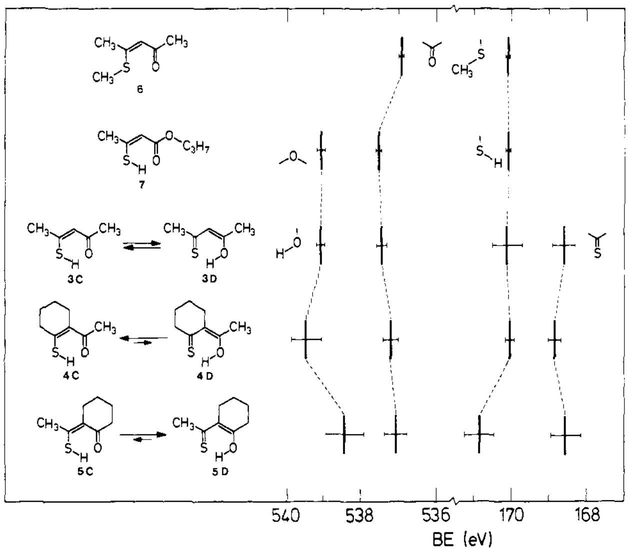

Figure 6. Correlation between the O_{1s} and S_{2p} binding energies of **3-7**. The vertical bars illustrate the precision.

In thioacetylacetone (**3**) the tautomeric enol–enethiol equilibrium is shifted in favor of the enol form.[6,9,11,32] Accordingly, the electron spectrum of **3** (Figure 3) exibits two overlapping peaks in the O_{1s} region, the one at higher binding energy (hydroxyl oxygen) being dominant. Unfortunately, it was impossible to obtain a proper least-squares fit of the experimental data without any constraints.[33] A previous study of β-diketones[16] has shown that peaks corresponding to carbonyl and hydroxyl oxygens exhibit half-widths varying from 1.49 to 1.91 eV and from 1.60 to 1.95 eV, respectively. For **6** and **7** half-widths, of 1.56 and 1.57 eV, respectively, were found for the carbonyl oxygens. Hence, half-widths of 1.56 and 1.80 eV for the carbonyl (enethiol form) and hydroxyl (enol form) oxygen peaks, respectively, were adopted. With these constraints we obtained the deconvolution shown in Figure 3 for thioacetylacetone (**3**), with a 1.58:1 (enol/enethiol) area ratio.[34]

The electron spectra of 2-acetylcyclohexanethione (**4**) and 2-thioacetylcyclohexanone (**5**) (Figures 4 and 5, respectively) were least-squares analyzed analogously yielding hydroxyl/carbonyl area ratios of 0.42:1 and 3.93:1 for **4** and **5**, respectively.[34]

The S_{2p} ionization regions of the electron spectra of the *S*-methyl derivative **6** (Figure 1) and the β-thioxo ester **7** (Figure 2) both show a single broad peak with a half-width of about 2.3 eV. The

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(24) T. D. Thomas and R. W. Shaw, Jr., *J. Electron Spectrosc. Relat. Phenom.*, **5**, 1081 (1974).

(25) R. S. Brown and D. A. Allison, *J. Am. Chem. Soc.*, **99**, 3568 (1977).

(26) S. R. Smith and T. D. Thomas, *J. Am. Chem. Soc.*, **100**, 5459 (1978).

(27) In the previous XPS study of β-diketones (cf. ref 16) the intensities of ionizations arising from the hydroxyl and carbonyl oxygen atoms are similar, except for acetylacetone and tropolone where presence of the diketo form and shake-up events, respectively, are responsible for deviations from the 1:1 ratio.

(28) In this paper we have consequently shown **6** in the cis, *s*-cis form to illustrate the analogy with the compounds **3-5** and **7**.

(29) T. A. Carlson, "Photoelectron and Auger Spectroscopy", Plenum Press, New York, 1975.

(30) Shake-up events have definitively been observed only for **6**, but we believe this may be caused by low probability of shake-up in the other compounds. The shake-up peaks for these compounds may therefore merge into the background and explain the increasing slope to the high binding energy side in the spectra (cf. Figures 1-5). The effects of shake-up phenomena in tautomeric systems have already been discussed by one of us (see ref 16 and references therein).

(31) The β-thioxo ester **7** has been shown by ^{1}H NMR spectroscopy to consist 95% of the cis isomer, i.e., the intramolecular hydrogen-bonded form (see ref 23).

(32) Electronic absorption spectroscopy of **3** in the gas phase (308 K) suggests the enol–enethiol ratio to be ca. 2:1 (L. Carlsen and F. Duus, unpublished results); see also ref 11.

(33) This seems to be a general problem by fitting closely spaced peaks (see, e.g., ref 26).

(34) The enol/enethiol ratios obtained by least-squares fit with different (1.56/1.80 eV) and equal (1.56 eV) half-widths for both oxygen peaks are 61:39 and 55:45, respectively, with a poorer agreement between the experimental and calculated curves in the latter case.

Table II. S_{2p} Binding Energies for β-Thioxoketones

compd	BE(S_{2p})[a]	fwhm[b]	peak	BE(S_{2p})[a]	fwhm[b]	rel area[c]
4-(methylthio)pent-3-en-2-one (6)	170.11 ± 0.02	2.26	1	170.81 ± 0.01	1.92	1.0
			2	169.79 ± 0.05	1.92	2.05 ± 0.15
propyl 3-mercaptocrotonate (7)	170.10 ± 0.04	2.32	1	171.10 ± 0.05	1.89	1.0
			2	169.82 ± 0.01	1.94	3.18 ± 0.15
thioacetylacetone (3)	169.2 ± 0.2	2.92	1	170.1 ± 0.4	2.28[e]	1.0
			2	168.6 ± 0.3	2.28[e]	1.64 ± 0.50
2-acetylcyclohexanethione (4)	169.8 ± 0.1	2.63	1	170.05 ± 0.08	2.28[e]	1.0
			2	168.9 ± 0.1	2.28[e]	0.42[d]
2-thioacetylcyclohexanone (5)	168.8 ± 0.4	2.78	1	170.9 ± 0.4	2.28[e]	1.0
			2	168.6 ± 0.4	2.28[e]	4.65 ± 0.61

[a] The precision is estimated from the least-squares fit. Values in electron volts. [b] Full width at half-maximum height. Values in electron volts. [c] Errors are from the least-squares fit. [d] It was not possible to obtain convergence of the least-squares fit in the case of 4, for which reason the relative area was assumed to be identical with the previously determined one from the O_{1s} region. [e] Fixed value (see text).

broadness of these peaks clearly indicates the presence of more than a single ionization, as expected due to the spin–orbit splitting of the sulfur 2p level into the $2p_{1/2}$ and $2p_{3/2}$ subshells.[14,29] A two-peak resolution of the broad S_{2p} peak in **6** leads to a peak separation of 1.02 eV and an area ratio of 1:2.1 between the high-energy ($2p_{1/2}$) and low-energy ($2p_{3/2}$) peaks. The corresponding values for **7** are 1.28 eV and 1:3.2, respectively.[35]

In the case of compounds **3**–**5** deconvolution of the sulfur region will be extremely complicated due to the presence of two tautomeric forms, each contributing with an unsymmetrical spin-orbit doublet. Since a four-peak resolution of the broad sulfur peaks depicted in Figures 3–5 has no meaning,[36] we tentatively chose to approximate the unsymmetrical $2p_{1/2},2p_{3/2}$ doublet with a symmetrical Gaussian peak. Least-squares analyses of the sulfur regions of **3**–**5** into two Gaussian peaks with fixed half-widths (fwhm = 2.28 eV, similar to the ones observed for **6** and **7**) gave for **3** and **5** relative areas with large uncertainties (cf. Table II).

Discussion

The appearance of two distinct peaks with a separation of 1.4–2.3 eV in the O_{1s} ionization region of the compounds **3**-**5** clearly reveals the presence of nonequivalent oxygen atoms. The separation is similar to the difference observed between the two oxygen atoms in carboxylic acids[26] and confirms that the β-thioxoketone system consists of two structurally different species, i.e., enol and enethiol tautomers.[37] Interpretations in terms of two-species systems such as rotameric enols[38] or rotameric enethiols[39] are inconsistent with the XPS data.

The position of the tautomeric enol–enethiol equilibrium for the β-thioxoketones **3**–**5** corresponds to the relative area ratios for the deconvoluted ionization bands. For thioacetylacetone (**3**), the agreement between the enol/enethiol ratio derived from the O_{1s} region (61:39) and S_{2p} region (62:38) is satisfactory and further confirms the absence of thioxoketone (**2A**, $R_1 = R_2 = CH_3$) at least to the limits of XPS detection (~10%). By UV spectroscopy the enethiol content has been determined to be 27–50% depending upon the solvent,[11,40] and in the gas phase, the enol/enethiol ratio is about 2:1,[32] in agreement with the XPS results.

For the cyclic systems, 2-acetylcyclohexanethione (**4**) and 2-thioacetylcyclohexanone (**5**) the enol/enethiol ratios are 30:70 and 80:20, respectively, based on the ratios of the O_{1s} ionization bands. Here the S_{2p} region yields no direct result for **4** due to the uncertainties in deconvolution of the S_{2p} region discussed above. For **5** the enol/enethiol ratio is 82:18. Although this result is tentative, it supports the O_{1s} result. Both compounds have been studied by UV spectroscopy in various solvents and the enethiol content has been determined to be 77–90% for **4** and 7–29% for **5**.[12] The agreement between the gas-phase XPS and solution UV spectroscopic results is gratifying and indicates that the position of the tautomeric equilibrium is not markedly different in the two phases.

Comparison of the binding energies of **3**–**7** as shown in Figure 6 reveals some interesting features. Normally, methylation at sulfur destabilizes the S_{2p} orbital causing its ionization to appear at lower energies than in the S–H analogues (CH_3SCH_3, BE = 169.02 eV; CH_3SH, BE = 169.51 eV).[14,41] In intramolecularly hydrogen-bonded systems, however, it is generally observed that the valence and core ionizations are facilitated relative to the non-hydrogen-bonded isomers.[25] This situation apparently occurs in passing from **6** to **7** as well insofar as the expected decrease in ionization energy for the S_{2p} orbital in **6** is exactly offset by the destabilization introduced by hydrogen-bond formation in **7**. Comparison of the carbonyl oxygen ionizations in **6** and **7** is somewhat more tenuous since the former is a ketone while the latter is an ester. Such changes generally lead to a small increase in binding energy for the carbonyl oxygen in the ester (CH_3COCH_3, BE = 537.73 eV vs. $CH_3CO_2CH_3$, BE = 537.96 eV).[41] The somewhat greater shift in carbonyl oxygen binding energy of 0.58 eV for **7** relative to **6** probably results from the structural change as well as from a hydrogen-bond-induced stabilization analogous to those observed for core ionizations from systems where nitrogen or oxygen is the electron-donating partner in intramolecular hydrogen-bonded systems.[25]

Considerable O_{1s} binding energy shifts are evident in the spectra of thioacetylacetone (**3**) and the cyclic β-thioxoketones (**4** and **5**) relative to the non-hydrogen-bonded compound **6**. Comparison of the values for **4** and **5** seems to indicate that the influence of the hydrogen bond on the binding energies is smallest in the tautomeric structures having the double bond exo to the six-membered ring (i.e., **5C** and **4D**). Hence, the S_{2p} ionization energy of **4C** is significantly smaller than that of **5C**, suggesting greater charge density on sulfur in the former. On the other hand, the converse is true for the O_{1s} bands; the O_{1s} ionization energy of **4D** is much greater than that of **5D**. This probably relates to larger charge densities on the hydrogen-bond proton doner where the double bond is within the six-membered ring (which may be a result of a stronger hydrogen bond), although there appears to be a much smaller effect on the electron-donor atoms.[42]

The intramolecularly hydrogen-bonded forms of thioacetylacetone (**3C** and **3D**) are planar[43,44] and the same is likely to be

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(35) The $2p_{1/2}$, $2p_{3/2}$ splitting of sulfur is 1.20 eV; cf. J. A. Bearden, *Rev. Mod. Phys.*, **39**, 78 (1967). We thank one of the referees for drawing our attention to this reference.

(36) The trithiapentalene case is an illustrative example of the pitfalls associated with deconvolution of broad peaks. Three independent deconvolutions of the sulfur 2p region (solid phase) led to three different results.[18-20] A later XPS study[21] in the gas phase showed the S_{2p} region to consist of a broad and a narrow doublet.

(37) The presence of the thioxoketone form **2A** is umambiguously ruled out by gas-phase IR studies (F. Duus, L. Carlsen, and F. M. Nicolaisen, to be submitted for publication).

(38) G. Klose, R. Lochmann, E. Ludwig, and E. Uhlemann, *J. Mol. Struct.*, **72**, 281 (1981).

(39) J. Gebicki and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 486 (1981); *J. Am. Chem. Soc.*, **103**, 4521 (1981).

(40) J. Fabian, *Tetrahedron*, **29**, 2449 (1973).

(41) B. E. Mills, R. L. Martin, and D. A. Shirley, *J. Am. Chem. Soc.*, **98**, 2380 (1976).

(42) The electron donor is normally less sensitive than the proton donor for observing hydrogen bonding; see ref 25.

(43) L. F. Power, K. E. Turner, and F. H. Moore, *Tetrahedron Lett.*, 875 (1974): *J. Chem. Soc., Perkin Trans. 2.*, 249 (1976).

(44) R. Richter, J. Sieler, J. Kaiser, and E. Uhlemann, *Acta Crystallogr. Sect. B.*, **32**, 3290 (1976).

the case for the two cyclic forms with the carbon–carbon double bond endo (**4C** and **5D**), in which the cyclohexene ring probably assumes a half-chair conformation with the C6–C1–C2–C3 moiety planar.[45] On the other hand, the cyclic forms with exo orientation of the double bond (**4D** and **5C**) prefers a chair conformation of the six-membered rings with a considerable torsional angle about the C1–C2 bond.[46] Increasing this torsional angle from zero weakens the hydrogen bond and may cause the observed shifts in the binding energies.

Conclusions

1. The XPS technique shows that for β-thioxoketones both the O_{1s} and S_{2p} regions exhibit ionizations from the enol (**2D**) as well as the enethiol (**2C**) form, thereby confirming that β-thioxoketones exist as rapidly interconverting enol and enethiol tautomers.

2. The position of the tautomeric enol–enethiol equilibrium has been determined by XPS based on the relative areas of the peaks in the O_{1s} ionization regions. The S_{2p} region seems to be less suitable for quantitative determinations due to the presence of sulfur spin–orbit splitting but confirms nevertheless the conclusions derived from the O_{1s} region. This represents a limitation of the XPS technique for determining positions of tautomeric equilibria in systems having heteroatoms giving rise to spin–orbit splitting. However, fortunately for these systems, the presence of oxygen yields satisfactory results.

3. The nonexistence of the thioxoketone form **2A** has been further confirmed for thioacetylacetone (**3**).

4. The binding energies of the compounds studied (Figure 6) suggest that geometrical constraints in the cyclic β-thioxoketones **4** and **5** may be reflected in the strength of the intramolecular hydrogen bond.

The above conclusions confirm that X-ray photoelectron spectroscopy is suitable for qualitative as well as quantitative studies of tautomeric equilibria in the gas phase, here exemplified by the enol–enethiol equilibrium in the β-thioxoketones.

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Registry No. 3, 14660-20-9; 4, 76698-82-3; **5**, 15578-82-2; **6**, 78429-69-3; **7**, 40553-10-4.

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(45) J. Dale, "Stereokjemi og Konformasjonsanalyse", Scandinavian University Books, Oslo, 1975.

(46) The torsional angle between the exocyclic double bonds in 1,2-dimethylencyclohexane amounts to about 60°; see P. Asmus and M. Klessinger, *Tetrahedron*, **30**, 2477 (1974).

Phase-Transition Behavior of Saturated, Symmetric Chain Phospholipid Bilayer Dispersions Determined by Raman Spectroscopy: Correlation between Spectral and Thermodynamic Parameters

Ching-hsien Huang,*[1] Jeffrey R. Lapides, and Ira W. Levin*

Contribution from the Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes, and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland 20205.
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Abstract: The phase-transition characteristics for the members of an homologous series of saturated, symmetrical phosphatidylcholine bilayer dispersions were investigated by Raman spectroscopy for the even carbon chain length systems extending from C(10) to C(22). Peak-height intensity ratios involving vibrational transitions in the 3000-cm^{-1} acyl chain methylene carbon–hydrogen (C–H) stretching mode region were used to construct temperature profiles reflecting phospholipid order/disorder processes. Although temperature profiles derived from the C–H stretching mode spectral parameters emphasize the gel to liquid crystalline phase transition at T_m, while generally deemphasizing the pretransition bilayer reorganizations in comparison to profiles based upon C–C stretching mode ratios, two-phase transitions are clearly discerned for diC(12)PC. The lower transition exhibits a sensitivity to the thermal history of the sample in contrast to an invariance in the behavior of the higher temperature order/disorder process at 3.3 °C, which we attribute to the primary gel to liquid crystalline phase transition. For diC(10)PC the temperature profile displays a phase transition at −8.5 °C which is associated with the order/disorder process for the system reorganizing from an immobile lamellar phase to possibly a dynamic micellar phase. The temperature profile derived from the Raman spectral parameters for 1-C(16)lysoPC, a system known to form micelles at room temperature, exhibits a sharp phase transition at 5.2 °C, which is also attributed to a transition between the lamellar and micellar phases. For the systems undergoing bilayer gel to liquid crystalline phase transitions, the parameter ΔI_R, which represents changes in the Raman intensity ratio across T_m, is correlated with ΔS, the entropy change determined at T_m for these phospholipids by calorimetric measurements.

Raman spectroscopy has been widely employed in recent years in investigating the lipid conformation and dynamics in both model and biological membranes.[2] The advantage of this technique over many other physical methods lies in the sensitivity of the vibrational spectra of lipid assemblies to bilayer reorganizations and to the changes in population of various bond conformations (gauche/trans ratios). Aqueous dispersions of synthetic phospholipids in bilayers undergo a highly cooperative endothermic phase transition from the gel to the liquid crystalline state when they are heated above a characteristic phase-transition temperature, T_m.[3] Thermodynamically, this phase transition is characterized by a marked increase in entropy; conformationally, it is described by an abrupt increase in intramolecular acyl chain disorder accompanied by a simultaneous decrease in chain–chain

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(1) On sabbatical leave from the Department of Biochemistry, University of Virginia School of Medicine, Charlottesville, Virginia 22908.

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