Scientific paper

Acetylacetone: Metal Complexes and Keto-Enol Tautomerism – Which Tautomer is more/less stable?

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Abstract

Tautomerism is a fundamental concept that studies the transfer of a proton between two constitutional isomers, i.e. keto and enol tautomers, where the enol tautomers are usually less stable than the corresponding carbonyl compound. However, this is not the case with acetylacetone. This article discusses two rapidly inter-converting tautomeric forms of acetylacetone, the archetypal (and now textbook) example of tautomerism in organic chemistry from a thermochemical perspective.

Keywords: Thermochemistry; tautomerism; keto-enol; acetylacetone

1. Introduction

Much of the interest in acetylacetone (pentane-2,4-dione) and derived metal acetylacetonates relates to the study of the acetylacetonate anion and metal ions, is contemporaneous with, the beginnings of coordination chemistry.[1] Such species derived from acetylacetone metals spanning the periodic table have been called salts, derivatives and complexes (e.g., see the early chronologically arranged refs. for Be[2], Th[3] and U[4]. The corresponding study with the lightest metal Li was reported many decades later).[5]

Since these neutral metal complexes can be easily extracted by organic solvents, they have found widespread use in analytical chemistry. Their properties can be significantly modified by substitution at both the central CH and the terminal $-CH_3$ units. Remarkably, the entire $-CH_3$ fragment can be substituted with a variety of other groups, significantly altering properties such as stability, solubility, volatility, color and melting point. This adaptability led to in-depth studies of metal acetylacetonates during the Manhattan Project, particularly with regard to their potential role in the separation and purification of uranium.[6] By 1982, neutral complexes with over 60 metals had been documented.[7] The versatility and usefulness of these complexes was further enhanced by the introduction of competing complexing agents into the system.[8] Various organic solvents, selected on the basis of the ionic or ionization potentials of the central metal ions, were found to effectively extract these complexes.[9] Figure 1 shows some of the possible binding arrangements for the acetylacetone ligand with a metal ion.

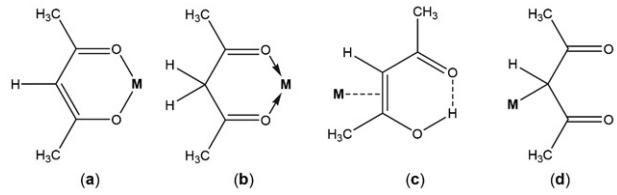

Figure 1: Some possible binding arrangements of the acetylacetone ligand with the metal ion.

The use of metal acetylacetonate complexes goes beyond analytical chemistry. Metal acetylacetonate complexes are used as catalysts in chemical transformations such as oligomerization, polymerization, hydrogenation, isomerization of alkynes, coupling of organic halides and trans-esterification. They are also used as latent accelerators that

increase selectivity and the formation of catalytically active sites. Examples include curing agents for epoxy resins, as supported reagent systems and precursors for the production of metal nanoparticles. In spectroscopic studies, they are used as nuclear magnetic resonance shift reagents.[10]

As noted in numerous early papers, acetylacetone, being the simplest β-diketone, exhibits tautomerism, that long-known example of isomerism associated with atom or group migration and necessarily accompanied by bond shuffling. Indeed, one may say that the concept of tautomerism evolved along with the understanding of these species and of related ethyl acetoacetate and malonate esters wherein one or both CH_3 groups respectively in acetylacetone were replaced by $C(O)OC_2H_5$. Acetylacetone is the archetypical (and now organic chemistry textbook) example of tautomerism, not uncommonly accompanied with discussion of these esters. Nonetheless, in the name of brevity, we will avoid further mention here of both acetoacetate and malonate esters and their derivatives and only cite chronologically a few early papers all taken from the late 19th and early 20th centuries.[11–25]

The enol form of a ketone is normally less stable than the corresponding carbonyl form, and yet we know that the enol tautomer of acetylacetone is the more stable. The keto → enol equilibrium constant in the gas phase and nonpolar solvents, was measured by ^{1}H NMR spectroscopy.[26]

Let us simplify our discussion by considering only to gas phase species and therefore isolated molecules so that we can bypass the numerous complications from intermolecular interactions. These interesting, but here ignored, phenomena include different solvent effects on the stability of the two tautomers and thereby affect their relative stability, concentrations, equilibria. Even pure acetylacetone has many of these complications because both tautomers are polar, and the enol has the possibility of intra and intermolecular hydrogen bonds. To simplify further, let us consider only enthalpies, but not entropies nor free energies. After all, such concepts such as resonance structures, intramolecular hydrogen-bonding and push-pull olefins are generally portrayed as enthalpic in origin, magnitude, and thereby consequences. We will also avoid here substituted derivatives and consider only the two $C_5H_8O_2$ species, most simply written as the acyclic β-diketone $CH_3C(O)CH_2C(O)CH_3$ and its tautomer, the "resonance assisted hydrogen-bonded" cyclic enol $CH_3C(O)CH{=}C(OH)CH_3$ respectively.[27] There are experimentally determined enthalpies of formation of the separate keto and enol tautomeric forms of acetylacetone[28], whereby with keto we implicitly mean 2,4-pentanedione and by the corresponding enol (*Z*)-4-hydroxy-3-penten-2-one respectively (Figure 2).

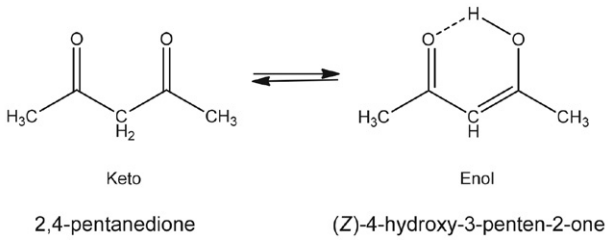

Figure 2: Keto–enol tautomeric equilibrium of the archetypical acyclic β-diketone and hydrogen bonded cyclic enol, and correspond to structures "d" and "a" in Figure 1 wherein M = H.

In the current study we admit we have no intent at providing a comprehensive discussion – a quick SciFinder^n search[29] gives ca. 48,000 references to "acetylacetone" but it is generally unclear which tautomer is meant in these references and it seems most likely that the references refer to the unseparated mixture of tautomers. We relatedly note that a concomitant literature search[10] shows there are ca. 1000 citations to the pioneering paper on resonance assisted hydrogen bonding[8] including some that offer dissent and/or extended scope toother tautomeric pairs of compounds, e.g. refs.[30–32]

For most pairs of tautomers, the individual enthalpies of vaporization, and of formation in both the gas and condensed phase of each of the species, have not been determined as separate quantities. One of the very few examples of this dual enthalpy of formation knowledge is the premier and archetypal β-diketone, 2,4-pentanedione[9] (this reference[9] cites 15 other references) (Table 1). We recognize the equilibrium keto/enol mixture as acetylacetone. We note that we may plausibly discuss the other enols such as 1,3-pentadien-2,4-diol, as both (*Z*)- and (*E*)-$CH_2{=}C(OH)CH{=}C(OH)CH_3$, and 1,4-pentadien-2,4-diol, $CH_2{=}C(OH)CH_2C(OH){=}CH_2$ and 2,3-pentadien-2,4-diol, $CH_3C(OH){=}C{=}C(OH)CH_3$ and for completeness, (*E*)-4-hydroxy-3-penten-2-one. However, since the thermochemical data are absent for these last species, we will not further discuss them in our current study (some photochemical and/or spectroscopic studies on a few of these tautomeric species were also reported).[33–37]

Table 1: Enthalpies of formation of 2,4-pentanedione and (*Z*)-4-hydroxypent-3-en-2-one in gas and liquid phase.[28]

	ΔH_f° (kJ mol^{-1})	
	gas	liquid
2,4-pentanedione	–(358.9 ± 2.5)	–(410.1 ± 1.2)
(*Z*)-4-hydroxypent-3-en-2-one	–(378.2 ± 1.2)	–(429.0 ± 1.0)

In the current study we also avoid discussion of the energetics of the complexes and chelates of acetylacetone and its derivatives, i.e., β-diketonates in general, even though these species M[RC(O)C(R')C(O)R] and the related, simpler enolates M[RR'CC(R)O] have been discussed in a thermochemical context for nearly all metals M.[38,39] However, a careful reading of the chemical literature shows

that there are disappointingly few examples where there are comparisons of structurally related β-diketonate and simpler enolate species.

To put the keto-enol tautomerism of acetylacetone in context, let us now consider acyclic enols with a brief comparison of the benzo-annelated related phenols. Enols, both as reaction intermediates and as isolated species, have long been investigated. An entire Patai volume ("The Chemistry of Functional Groups") was devoted to enols suggesting correctly that their study is an important activity of organic chemists.[40]

Ethenol (vinyl alcohol) and the three isomeric propenols ((*E*)-1-, (*Z*)-1-, and 2-,) are considered as archetypical enols. Conversely, mentioning but briefly the parent phenol, its multiring analogs, and their substituted derivatives are seemingly more often recognized as examples of phenols than as enols. Admittedly, phenols as a functional group belatedly appeared in the Patai volumes[41], accompanied by the acknowledgement that this volume discussed the first aromatic functional group[42] in the series. This enolic description of phenols is especially poignant when we recognize these enols are more stable and more thoroughly studied than their ketone tautomers, the corresponding carbonyl compounds, e.g., the isomeric 2,4- and 2,5-cyclohexadienones. This is easily documented by the observation that SciFinder^{n} [29] gives us ca. 650,000 references for phenol but only scarcely more than 300, *in toto*, of the isomeric cyclohexadienones.

Indeed, we hesitantly acknowledge that the carbonyl tautomers of some arenols have been studied separately from their hydroxylic counterparts, e.g., 9(10*H*)-anthrone and 9-anthracenol, for which the former is more stable[43–45], and phloroglucinol (1,3,5-trihydroxybenzene) and its substituted derivatives[46] and some highly strained phenols (e.g., suitably small [n]-metacyclophanes, the 2,6-polymethylene-4-nitrophenols)[47]). Nonetheless, let us hereby ignore phenols and other hydroxyarenes.

2. Is the β-diketone Tautomer Less Stable Than the Enol or is the Enol Tautomer More Stable Than the Diketone?

We now return to the acyclic species of direct interest here, acetylacetone, and thereby return to the complex, indeed plausibly enigmatic, questions explicitly asked in the title of this paper. It is quite unequivocal that the answer to the first question is the β-diketone tautomer of 'acetylacetone' less stable than the corresponding enol? is an emphatic "Yes!" in marked contradistinction to most ketones which are significantly more stable than their enol counterparts. Does this not mean our second question: Is the enol tautomer of 'acetylacetone' more stable than the corresponding diketone is also answered "Yes"? After all, is our second question not the same as the first, i.e., do we not have an identity, a redundancy and repetition, a tautology about tautomers? After all, if A > B, then doesn't it automatically follow that B < A?

In fact, the word acetylacetone and the two questions just asked suggest different reference species, i.e., normal and suitably archetypical, compounds for comparison. Can we do any better than saying acetylacetone is anomalous, somehow special because carbonyl compounds are normally more stable than the corresponding enol but for this species, the two-carbonyl species is the less stable tautomer? Can we do any better than saying acetylacetone is anomalous, somehow special because enols are normally less stable than the corresponding carbonyl compound and here the enol is the more stable tautomer? In this paper, our objective is to not only analyze acetylacetone's unique characteristics but also to compare enols with other enols and carbonyl compounds with other carbonyl compounds.

Our chosen set of two species, 2,4-pentanedione, $CH_3C(O)CH_2C(O)CH_3$, and (*Z*)-4-hydroxy-pent-3-en-2-one, $CH_3C(O)CH{=}C(OH)CH_3$, share another key structural, and likewise conceptual similarity other than that they constitute a pair of tautomers. They are both acetyl derivatives. Both species, individually, may be recognized as $CH_3C(O)X$ species regardless of their individual choice of X. Let us recall a simple definition of the resonance energy of acetyl derivatives that was earlier applied to amides and esters in reaction (1), i.e., generically X = $–NR_2$ and –OR with diverse affixed R groups respectively.[48]

$$CH_3C(O)CH_3 + CH_3X \rightarrow CH_3C(O)X + C_2H_6 \quad (1)$$

This approach was subsequently generalized for amides using the "Methyl capping experimental" (MCE) and "Carbonyl substitution nitrogen atom replacement reasoning (COSNAR)" respectively.[49,50]

In that these approaches result in no loss of conceptual understanding for the current paper we will use the earliest definition. In the current study, reaction (1) will be implicitly applied to gas phase species. As precedented by a collection of earlier studies with a wide choice of X[48,51–54], the exothermicity of reaction (1) is now equated to the resonance energy of $CH_3C(O)X$.)

Let us start our discussion with that of the archetypical β-diketone, 2,4-pentanedione, $CH_3C(O)CH_2C(O)CH_3$, wherein X is thus identified as $–CH_2C(O)CH_3$, and accordingly, CH_3X is recognized as 2-butanone. For the tautomer (*Z*)-4-hydroxypent-3-en-2-one, $CH_3C(O)CH{=}C(OH)CH_3$, X is therefore $–CH{=}C(OH)CH_3$, and CH_3X is recognized as (*Z*)-2-buten-2-ol. Our relevant reactions are thus identified as reactions (2) and (3) respectively.

$$CH_3C(O)CH_3 + CH_3CH_2C(O)CH_3 \rightarrow CH_3C(O)CH_2C(O)CH_3 + C_2H_6 \quad (2)$$

$$CH_3C(O)CH_3 + CH_3CH=C(OH)CH_3 \rightarrow CH_3C(O)CH=C(OH)CH_3 + C_2H_6 \quad (3)$$

We now acknowledge that with one fewer carbon, 1,3-butanedione and its enol are simpler than the just mentioned 2,4-pentanedione and its enol. However, the study of the energetics of these 4-carbon species is limited to computational theory. We also note that the 2,4 pentanedione is well-established from both theory and experiment to be nonplanar, presumably to thereby minimize electrostatic and lone pair/lone pair repulsion of the two negative oxygens.[55]

We now turn to the energetics of these reactions (2) and (3) separately. Let us accept the enthalpy of formation of 2,4-pentanedione[28] acknowledging at this time also that the classic thermochemical archive by Pedley[56] will be the implicit reference for any otherwise uncited species. As written, reaction (2) is endothermic by (13 ± 3) kJ mol^{-1}. We may calibrate our thinking about the energetics of reaction (2) by considering an analogous reaction involving 2-pentanone, an altogether normal species wherein X = CH_2CH_3 as found in reaction (4)

$$CH_3C(O)CH_3 + CH_3CH_2CH_2CH_3 \rightarrow CH_3C(O)CH_2CH_2CH_3 + C_2H_6 \quad (4)$$

As written reaction (4) is endothermic by (0 ± 1) kJ mol^{-1}, sensibly indistinguishable from strict thermoneutrality. We may thus conclude that 2,4-pentanedione is destabilized by 13 kJ mol^{-1} relative to normal ketones.

We may ascribe the destabilization of 2,4-pentanedione to include the Coulomb/electrostatic repulsion of the positive carbons that compose the two carbonyl groups. If so, its isomeric α-diketone, 2,3-pentanedione, should be even more unstable than its 2,4-isomer because the two positively charged carbons are closer in the former species. Accordingly, consider reaction (5) and the enthalpy for this 2,3-dione where its enthalpy of formation is taken from Kercher et al.[57]

$$CH_3C(O)CH_3 + CH_3C(O)CH_2CH_3 \rightarrow CH_3C(O)C(O)CH_2CH_3 + C_2H_6 \quad (5)$$

This reaction is endothermic by (28 ± 3) kJ mol^{-1} documenting 2,3-pentanedione is even more destabilized than its 2,4-isomer, with an additional destabilization of (15 ± 3) kJ mol^{-1}. Our (28 ± 3) kJ mol^{-1} value is essentially indistinguishable with the 25 kJ mol^{-1} [58] for the destabilization of α-diketones (also see paper by Liebman[54]) and in particular, 2,3-butanedione. This near equality gives us increased confidence in the current analysis and hereby conclude that 2,4-pentanedione, explicitly as the diketone tautomer, is destabilized.

Consider now the other tautomer, (*Z*)-4-hydroxy-3-penten-2-one and recall reaction (3) where we accept the enthalpy of formation of *(E)*-2-buten-2-ol.[59] So doing, we deduce stabilization of *(Z)*-4-hydroxypent-3-en-2-one to be ca. (31 ± 10) kJ mol^{-1} relative to normal enols that lack the affixed keto group. For comparison, consider the related olefinic reaction (6), wherein the enolic OH is replaced by the isoelectronic, isosteric, non-hydrogen bonding CH_3.

$$CH_3C(O)CH_3 + CH_3CH=C(CH_3)CH_3 \rightarrow CH_3C(O)CH=C(CH_3)CH_3 + C_2H_6 \quad (6)$$

Using the average of the reported enthalpies of formation of 4-methylpent-3-en-2-one (historically also called "mesityl oxide")[60,61], –(181 ± 3) kJ mol^{-1}, we deduce a stabilization of but (6 ± 4) kJ mol^{-1}.

Consider now reaction (7) wherein one of the oxygens in 2,4-pentanedione is relatedly replaced by the isoelectronic and isosteric CH_2. In other words, consider the unconjugated 4-methyl-4-penten-2-one (alternatively but only rarely named "isomesityl oxide".

$$CH_3C(O)CH_3 + CH_3CH_2C(=CH_2)CH_3 \rightarrow CH_3C(O)CH_2C(=CH_2)CH_3 + C_2H_6 \quad (7)$$

Base-catalyzed equilibration reactions show the conjugated 4-methyl-3-penten-2-one to be 13 kJ mol^{-1} more stable than its unconjugated isomer, 4-methyl-4-penten-2-one.[62] In that 2-methyl-2-butene is ca. 16 kJ mol^{-1} more stable than 3-methyl-1-butene. From archival enthalpies of formation of acetone, 2-methyl-1-butene and ethane (see reaction (8)), it is thus deduced to be nearly thermoneutral. Comparing the results from reactions (2) and (8) (i.e., =O vs. =CH_2), we conclude the keto form of acetylacetone is destabilized by ca. 28–16 = 12 kJ mol^{-1} while comparison of reactions (3) and (6) (i.e., –OH vs. –CH_3) shows the enol form of acetylacetone is stabilized by ca. 25 kJ mol^{-1}.

$$CH_3C(O)CH_3 + CH_3CH_2C(=CH_2)CH_3 \rightarrow CH_3C(O)CH_2C(=CH_2)CH_3 + C_2H_6 \quad (8)$$

The enthalpy of formation of mesityl oxide is –(181 ± 3) kJ mol^{-1}.[60,61] Consider the related olefinic reaction (9), wherein the enolic OH is replaced by the isoelectronic, isosteric, non-hydrogen bonding CH_3.

$$CH_3C(O)CH_3 + CH_3CH=C(CH_3)CH_3 \rightarrow CH_3C(O)CH=C(CH_3)CH_3 + C_2H_6 \quad (9)$$

Using the above cited average of the reported enthalpies of formation of 4-methyl-3-penten-2-one (mesityl oxide), –(181 ± 3) kJ mol^{-1} [60,61] we deduce a stabilization of but (6 ± 4) kJ mol^{-1}.

This species is plausibly more stabilized than methyl vinyl ketone because the positive charge as found in the ionic resonance structure $CH_3C(O^-)=CHC^+<$ is stabilized by the attached methyl groups. From reaction (10)

$$CH_3C(O)CH_3 + CH_3CH=CH_2 \rightarrow CH_3C(O)CH=CH_2 + C_2H_6 \quad (10)$$

using the recently determined enthalpy of formation of methyl vinyl ketone –(111 ± 6) kJ mol^{-1} [63], we deduce a stabilization of –(2 ± 6) kJ mol^{-1}, indistinguishable from a small degree of stabilization (and for that matter, of destabilization) in the absence of the two affixed methyl groups. (For a review of the energetics of larger derivatives of methyl vinyl ketone, i.e., general enones, see Liebman and Pollack[64] and for later primary studies of related cyclic species.[65,66]

We now return to enols directly by mentioning two enols related to mesityl oxide and isomesityl oxide, 4-methyl-1,3-pentadien-2-ol and (both *(E)*- and (*Z*))-4-methyl-2,4-pentadien-2-ol.[67–69] While we are provided with rates and activation values, the only relevant thermochemical information we can deduce therein is that the *(Z)*-4-methyl-2,4-pentadien-2-ol is less stable than isomesityl oxide.

We now return to acetylacetone and turn to an alternative thermochemical analysis of this species. Consider reaction (11)

$$CH_3C(O)CH_2CH_3 + CH_3CH_2C(O)CH_3 \rightarrow CH_3C(O)CH_2C(O)CH_3 + C_3H_8 \quad (11)$$

This reaction is endothermic by (13 ± 3) kJ mol^{-1}: that is, 2,4-pentanedione is destabilized by some 13 kJ mol^{-1}. Encouragingly, this value is very nearly the same degree of destabilization as found using the earlier reaction (2). Paralleling multiple names for some other β-diketones such as dipivaloylmethane (i.e., 2,2,4,4-tetramethyl-1,3-pentanedione and dibenzoylmethane (i.e., 1,3-diphenyl-1,3-propanedione), let us rename, however temporarily, 2.4-pentanedione as diacetylmethane. As such, we additionally recognize reaction (11) for the keto tautomer of acetylacetone as an example of the more general reaction (12) for diacetyl derivatives wherein Z = CH_2, NH and O. Having discussed the Z = CH_2 case, let us now consider Z = NH (wherein the required thermochemical data for *N*-methyl acetamide[70], diacetimide (diacetylamine)[71] and dimethylamine[72] the methyl acetate, acetic anhydride and dimethyl ether data are from ref.[56] for Z = O respectively (reaction (12)).

$$CH_3C(O)ZCH_3 + CH_3ZC(O)CH_3 \rightarrow CH_3C(O)ZC(O)CH_3 + (CH_3)_2Z \quad (12)$$

Relatedly, reaction (12) with Z = NH is endothermic by (50 ± 10) kJ mol^{-1}. For Z = O, reaction (9) is endothermic by (70 ± 4) kJ mol^{-1}. The endothermicity of 13 kJ mol^{-1} for Z = CH_2, the destabilization of 2,4-pentanedione, appears entirely plausible. From the above analysis we conclude 2,4-pentanedione is destabilized compared to normal ketones. As was asked very early in this paper, we now find that it is unequivocal that the answer to the first question asked in the title: Is the β-diketone tautomer less stable than the enol? is an emphatic "Yes! "because the diketone is destabilized. Likewise, the enol *(Z)*-4-hydroxy-3-penten-2-one with its gas phase enthalpy of formation of –(378 ± 1) kJ mol^{-1} is stabilized compared to normal enols.

It is unequivocal that the answer to the second question asked in the title of this paper is the enol tautomer more stable than the diketone? is also an emphatic "Yes!" because the enol is stabilized. We conclude that acetylacetone being (predominantly) an enol is due to both stabilization and destabilization of related molecular features. (We are now reminded of the conflicting and complementary roles of stabilizing and destabilizing influences in the ion chemistry interconverting ethynol and its O-deprotonated species.[73])

In principle we can replace both oxygens in the diverse tautomers of acetylacetone by carbon. That is, we may ask about the relative stabilities of the isomeric dienes $CH_3C(=CH_2)–CH_2–C(=CH_2)CH_3$ and $CH_3C(=CH_2)–CH=C(CH_3)CH_3$. In principle, one may make this comparison by the analysis of direct enthalpy of combustion measurements of both species. Alternatively, this comparison may be made using results of

a. their basicity/proton affinity (solution or gas phase) measurements since the resultant protonated species, a stabilized tertiary carbonium ion, is the same for both isomers, $CH_3C(=CH_2)–CH_2–C^+(CH_3)_2$,
b. their acidity measurements because the same resonance stabilized anion, $CH_3C(=CH_2)–CH^–C(=CH_2)CH_3$ is formed from both isomers
c. by complete hydrogenation measurements since the resultant saturated product is the same alkane, $(CH_3)_2CHCH_2CH(CH_3)_2$.

However, we know of no relevant studies for these comparisons and so we are thwarted in our thermochemical comparison of the dienes of interest.

Dare we compare the related doubly demethylated derivatives, the isomeric 1,4- and 1,3-pentadienes for which the former is less stable by ca. 30 kJ mol^{-1}? This value is not altogether different from the enthalpy of formation difference of the diketone and keto-enol tautomers of acetylacetone. In this all-carbon case, we are missing both the Coulomb/electrostatic repulsion between the two trigonal carbons and the two oxygens, that destabilizes the diketone tautomer, and the resonance assisted hydrogen bond that stabilizes the enolic tautomer. Most assuredly, having two trigonal carbons next to each other is not necessarily destabilizing – indeed, adjacent C=C bonds are generally stabilizing as is well known for conjugated dienes.

And yet we recall the two reactions (13) and (14)

$$2RCHO \rightarrow RC(O)C(O)R + H_2 \quad (13)$$

$$2RCHCH_2 \rightarrow RC(=CH_2)C(=CH_2)R + H_2 \quad (14)$$

are both roughly thermoneutral. Does this not seemingly provide comparable stabilization, or is it destabilization, for conjugated dienes and α-diketones?[74] Are conjugated dienes stabilizing and α-diketones species destabilizing? For example, consider R = CH_3,[56] both reactions are endothermic by (5 ± 2) kJ mol^{-1}. However, based on our experience with acetyl groups, let us rewrite reaction (13) explicitly for R = CH_3 as (15) and then as (16), the last reaction being a reaction of acetaldehyde here identified as acetyl hydride.

$$2CH_3CHO \rightarrow CH_3C(O)C(O)CH_3 + H_2 \quad (15)$$

$$2CH_3C(O)H \rightarrow CH_3C(O)C(O)CH_3 + H_2 \quad (16)$$

Of the many acetyl derivatives that fill the current paper, one we have not spoken of is this hydride, –H being an atypical and thermochemically varying substituent.[75] We additionally note there are a different number of C–H bonds and of C–C bonds on the left and right-hand sides of reactions (15). Rather than writing reaction (16), let us consider the corresponding (17) involving their methylated derivatives

$$2CH_3C(O)CH_3 \rightarrow CH_3C(O)C(O)CH_3 + (CH_3)_2 \quad (17)$$

Accordingly, reaction (14) becomes (18)

$$2CH_3C(=CH_2)CH_3 \rightarrow CH_3C(=CH_2)C(=CH_2)CH_3 + (CH_3)_2 \quad (18)$$

These two reactions are endothermic by (21 ± 2) and exothermic by (5 ± 2) kJ mol^{-1} respectively. The first value is comparable to the 25 kJ mol^{-1} elsewhere noted in this paper for the destabilization of α-diketones of which 2,3-butanedione is an archetypical example.

We close this discussion of destabilization of diones with a brief mention of the γ-dicarbonyl species, 4-oxopentanal, $CH_3COCH_2CH_2CHO$. We realize this species is yet another isomer of acetylacetone. As was the case for most of the diverse isomers of acetylacetone, there is no experimentally determined enthalpy of formation of this compound. Let us therefore turn our attention to its 1-methylated derivative, 2,5-hexanedione, $CH_3C(O)CH_2CH_2C(O)CH_3$ for which its destabilization is expected to be nearly equal to that of 4-oxopentanal. There is no measured enthalpy of formation value for this latter compound either. However, reaction kinetics studies on 2,5-hexanedione[76,77] suggest this species lacks destabilization in contrast to 2,3-butanedione and 2,4-pentanedione.

3. Conclusions

Summarizing, to both questions given earlier in the text "Is the β-diketone tautomer less stable than the enol or is the enol tautomer more stable than the diketone?" we answer with an emphatic "Yes!".

Epilogue: To Boris

Born in his mind, borne in the laboratory
Original thinking becoming chemical reality
Research done with joy, friendship and respect
Insights and findings arising from diligence and intellect
Sharing with, encouraging, colleagues, students, family

Zois award, and many papers are seen on his cv
Each of us now with so many memories of Boris
Mourning now, we walk by his now emptied office
Viewing and talking, amidst crying let us rejoice
All of us remembering Boris, his work, his voice

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Conflicts of interest

There are no conflicts to declare.

4. References

1. A. Werner, A. Vilmos, *Z. Anorg. Chem.* **1899**, *21*, 145–158. **DOI:**10.1002/zaac.18990210116
2. A. Combes, *Compt. Rendu*, **1894**, *119*, 1221–1123.
3. G. Urbain, *Bull. Soc. Chim. Fr.* **1896**, *18*, 347–349. **DOI:**10.1021/ja02090a004
4. W. Biltz, J. A. Clinch, *Z. Anorg. Chem.,* **1904**, *40*, 218–224. **DOI:**10.1002/zaac.19040400114
5. R. Mecke, E. Funck, Zeit. *Elektrochem. Angew. Physik. Chem.*, **1956**, *60*, 1124–1130. **DOI:**10.1002/bbpc.19560600934
6. E. Arslan, R. A. Lalancette, I. Bernal, *Struct. Chem.* **2017**, *28*, 201–212. **DOI:**10.1007/s11224-016-0864-0
7. J. Stary, O. J. Liljenzin, *Pure Appl. Chem.* **1982**, *54*, 2557–2592. **DOI:**10.1351/pac198254122557
8. A. Krishen, H. Freiser, *Anal. Chem.* **1957**, *29*, 288–290. **DOI:**10.1021/ac60122a033
9. T. Shigematsu, M. Tabushi, *Bull. Inst. Chem. Res., Kyoto Univ.* **1961**, *39*, 35–42.
10. R. K. Sodhi, S. Paul, *Catal. Surv. Asia* **2018**, *22*, 31–62. **DOI:**10.1007/s10563-017-9239-9
11. W. H, Perkin, *J. Chem. Soc., Trans.* **1892**, *61*, 800–864. **DOI:**10.1039/CT8926100800
12. J. B. Weems, *Amer. Chem. J.* **1894**, *16*, 569–588. **DOI:**10.1007/BF01844780
13. R. S. Curtiss, *Amer. Chem. J.* **1895**, *17*, 435–443.

DOI:10.1007/BF01841889
14. R. Schiff, *Ber. Deutsch. Chem. Gesell.* **1898**, *31*, 205–209. **DOI:**10.1002/cber.18980310141
15. K. Schaum, *Ber. Deutsch. Chem. Gesell.* **1898**, *31*, 1964–196. **DOI:**10.1002/cber.189803102126
16. G. Leser, *Compt. Rendu* **1899**, *128*, 371–373. **DOI:**10.3406/ccmaa.1899.10537
17. P. Rabe, *Ber. Deutsch. Chem. Gesell.* **1899**, *32*, 86. **DOI:**10.1002/cber.18990320117
18. H. Goldschmidt, L. Oslan, *Ber. Deutsch. Chem. Gesell.* **1899**, 32, 3390–3399. **DOI:**10.1002/cber.189903203112
19. F. Gach, F., *Monat. Chem.* **1900**, *21*, 98–117. **DOI:**10.1007/BF01526814
20. H. Stobbe, *J. Liebigs Annal. Chem.* **1903**, *352*, 132–146. **DOI:**10.1002/jlac.19073520108
21. L. Knorr, *Ber. Deutsch. Chem. Gesell.* **1904**, *37*, 3488–3489. **DOI:**10.1002/cber.190403703171
22. J. W. Brühl, H. Schröder, *Ber. Deutsch. Chem. Gesell.* **1905,** *38*, 1868–1873. **DOI:**10.1002/cber.190503802110
23. K. H. Meyer, *Ber. Deutsch. Chem. Gesell.* **1912**, *44*, 2729–3272. **DOI:**10.1002/cber.191104403106
24. F. O. Wilson, *Ber. Deutsch. Chem. Gesell.* **1914**, *47*, 832–837. **DOI:**10.1002/cber.191404701132
25. J. Scheiber, P. Herold, *J. Liebigs Annal. Chem.* **1914**, 405, 295–346. **DOI:**10.1002/jlac.19144050303
26. C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, Wiley VCH, Weinheim, Germany, **2003**. **DOI:**10.1002/3527601791
27. G. Gilli, F. Bellucci, V. Ferretti, V. Bertolasi, *J. Am. Chem. Soc.* **1989**, *111*, 1023–1028. **DOI:**10.1021/ja00185a035
28. M. Temprado, M. V. Roux, P. Umnahanant, H. Zhao, J. S. Chickos, *J. Phys. Chem. B* **2005**, *109*, 12590–12595. **DOI:**10.1021/jp0515131
29. SciFinder^n (assessed: May 31, 2024)
30. I. Alkorta, O. Mó, J. Elguero, M. Yañez, J. E. Del Bene, *Mol. Phys.* **2004**, *102*, 2563–2574. **DOI:**10.1080/00268970412331292885
31. R. M. Claramunt, C. Lopez, S. Lott, M. D. Santa Maria, I. Alkorta, J. Elguero, *Helv. Chim. Acta* **2005**, 88, 1931–1942. **DOI:**10.1002/hlca.200590148
32. P. Sanz, O. Mó, M. Yañez, J. Elguero, *J. Phys. Chem. A* 2007, **111**, 3585–3591. **DOI:**10.1021/jp067514q
33. N. Nagashima, S. Kudoh, M. Takayanagi, M, Nakata, *J. Phys. Chem. A* **2001**, *105*, 10832–10838. **DOI:**10.1021/jp012557m
34. S. Coussan, C. Manca, Y. Ferro, P. Roubin, *Chem. Phys. Lett.* **2003**, *370*, 118–125. **DOI:**10.1016/S0009-2614(03)00037-X
35. P. K. Verma, F. Koch, A. Steinbacher, P. Nuernberger, T. Brixner, *J. Am. Chem. Soc.* **2014**, 136, 14981–14989. **DOI:**10.1021/ja508059p
36. A. Gutierrez-Quintanilla, M. Chevalier, C. Crepin, *Phys. Chem. Chem. Phys.* **2016**, *18*, 20713–20725. **DOI:**10.1039/C6CP02796B
37. I. G. Karvounis, P. Siafarika, A. G. Kalampounias, *J. Mol. Struct.* **2023**, *1286*, 135592. **DOI:**10.1016/j.molstruc.2023.135592
38. D. N. Zeiger, J. F. Liebman, M. Ponikvar-Svet, Aspects of the Energetics of Metal β-Diketonates and Their Derivatives, in: J. Zabicky (Ed.), Patai's Chemistry of Functional Groups: The Chemistry of Metal Enolates, Vol. 2, Wiley, Chichester, United Kingdom, **2016**, 1–24. **DOI:**10.1002/9780470682531.pat0912
39. J. F. Liebman, S. W. Slayden, Thermochemical Considerations of Metal Enolates, in: J. Zabicky (Ed.) The Chemistry of Metal Enolates, Wiley, Chichester, United Kingdom, **2009**, 185–221. **DOI:**10.1002/9780470682531.pat0420
40. Z. Rappoport (ed.) The Chemistry of Enols, John Wiley and Sons, New York, United States, **1990**.
41. Z. Rappoport (ed.) The Chemistry of Functional Groups. The Chemistry of Phenols, Wiley, Chichester, United Kingdom, **2003**. **DOI:**10.1002/0470857277
42. Foreword text in: Z. Rappoport (ed.) The Chemistry of Functional Groups. The Chemistry of Phenols, Wiley, Chichester, United Kingdom, **2003**, IX.
43. L. E. Watik, R. Sabbah, *Bull. Soc. Chim. Fr.* **1991**, *128*, 344–349.
44. B. Freiermuth, B. Hellrung, S. Peterli, M. F. Schultz, D. Wintgens, J. Wirz, *Helv. Chim. Acta* **2001**, *84*, 3796–3809. **DOI:**10.1002/1522-2675(20011219)84:12<3796::AID-HLCA3796>3.0.CO;2-T
45. R. Notario, M. V. Roux, J. F. Liebman, *Mol. Phys.* **2004**, *102*, 623–625. **DOI:**10.1080/00268970410001671549
46. M. Ruaysap, S. R. Kennedy, C. M. Mayhan, S. P. Kelley, H. Kumari, C. A. Deakyne, J. L. Atwood, *Chem. Commun.* **2020**, *56*, 12985–12988. **DOI:**10.1039/D0CC03639K
47. V. Prelog, K. Wiesner, W. Ingold, O. Haflinger, *Helv. Chim. Acta* **1948**, *31*, 1325–1341. **DOI:**10.1002/hlca.19480310518
48. J. F. Liebman, A. Greenberg, *Biophys. Chem.* **1974**, *1*, 222–226. **DOI:**10.1002/hlca.19480310518
49. A. Greenberg, D. T. Moore, T. D. DeBois, *J. Am. Chem. Soc.* **1996**, *118*, 8658–8668. **DOI:**10.1021/ja960294h
50. A. Greenberg, in A. Greenberg, C. M. Breenan, J. F. Liebman (Eds.) The Amide Linkage. Structural Significance in: Chemistry and Materials Science, John Wiley & Sons, Inc., New York, United States, **2003**.
51. J. Morgan, A. Greenberg, J. F. Liebman, *Struct. Chem.* **2012**, *23*, 197–199. **DOI:**10.1007/s11224-011-9851-7
52. J. F. Liebman, A. Greenberg, *Struct. Chem.* **2019**, *30*, 1631–1634. **DOI:**10.1007/s11224-019-01404-y
53. M. Ponikvar-Svet, J. F. Liebman, *Struct. Chem.* **2003**, *34*, 51–54. **DOI:**10.1007/s11224-022-02023-w
54. J. F. Liebman, *Struct. Chem.* **2023**, *34*, 729–732. **DOI:**10.1007/s11224-023-02155-7
55. N. V. Belova, H. Oberhammer, N. H. Trang, G. V. Girichev, *J. Org. Chem.* **2014**, *79*, 5412–5419. **DOI:**10.1021/jo402814c
56. J. B. Pedley, Thermochemical Data and Structures of Organic Compounds. TRC data series, vol 1. TRC, College Station, United States, **1994**.
57. J. P. Kercher, E. A. Fogleman, H. Koizumi, B. Sztáray, T. Baer, *J. Phys. Chem. A* **2005**, *109*, 939–946. **DOI:**10.1021/jp0458497
58. A. A. Zavitsas, D. W. Rogers, N. Matsunaga, *Aust. J. Chem.* **2011**, *64*, 390–393. **DOI:**10.1071/CH10394

59. F. Tureček, L. Brabec, J. Korvola, *J. Am. Chem. Soc.* **1988**, *110*, 7984–7990. **DOI:**10.1021/ja00232a006
60. J. P. Guthrie, *Can. J. Chem.* **1978**, *56*, 962–973. **DOI:**10.1139/v78-162
61. W. V. Steele, R. D. Chirico, A. B. Cowell, S. E. Knipmeyer, A. Nguyen, *J. Chem. Eng. Data* **1997**, *42*, 1052–1066. **DOI:**10.1021/je970099y
62. G. Hesse, R. Hatz, U. Dutt, *Chem. Ber.* **1967**, *100*, 923–929. **DOI:**10.1002/cber.19671000329
63. P. Weidner, A. W. Ray, A. Bodi, J. Sztáray, *J. Phys. Chem. A* **2021**, *125*, 848–856. **DOI:**10.1021/acs.jpca.0c10665
64. J. F. Liebman, R. M. Pollack, Thermochemistry of Enones and Related Species, in: S. Patai, J. Zabicky (Eds.) The Chemistry of the Enone Functional Group, Wiley, Chichester, United Kingdom, **1989**, 107–128. **DOI:**10.1002/9780470772218.ch4
65. D. W. Rogers, Y. Zhao, M. Trætteberg, M. Hulce, J. F. Liebman, *J. Chem. Thermodyn.* **1998**, *30*, 1393–1400. **DOI:**10.1006/jcht.1998.0407
66. A. L. R. Silva, C. Moura, M. D. M. C. Ribeiro da Silva, *J. Chem. Thermodynam.* **2019**, *132*, 390–396. **DOI:**10.1016/j.jct.2019.01.012
67. C. S. K. Wan, A. C. Weedon, *J. Chem. Soc. Chem. Commun.* **1981**, 1235–1236. **DOI:**10.1039/C39810001235
68. R. M. Duhaime, A. C. Weedon, *J. Am. Chem. Soc.* **1985**, *107*, 6723–6724. **DOI:**10.1021/ja00309a058
69. R. M. Duhaime, A. C. Weedon, *Canad. J. Chem*. **1987**, *64*, 1867–1872. **DOI:**10.1139/v87-313
70. M. V. Roux, P. Jiménez, J. Z. Dávalos, O. Castaño, M. T. Molina, R. Notario, M. Herreros, J. L. M. Abboud, *J. Am. Chem. Soc.* **1996**, *118*, 12735–12737. **DOI:**10.1021/ja962792w
71. J. O. Hill, I. Wadsö, *Acta Chem. Scand.* **1968**, *22*, 1590–1594. **DOI:**10.3891/acta.chem.scand.22-1590
72. O. V. Dorofeeva, M. A. Filimonova, I. I. Marochkin, *J. Chem. Eng. Data* **2019**, *64*, 5630–5647. **DOI:**10.1021/acs.jced.9b00680
73. B. J. Smith, L. Radom, A. J. Kresge, *J. Am. Chem. Soc.* **1989**, *111*, 8297–9899. **DOI:**10.1021/ja00203a051
74. J. F. Liebman, *Struct. Chem.* **1992**, *3*, 449–450. **DOI:**10.1007/BF00672018
75. Y. R. Luo, S. W. Benson, *J. Am. Chem. Soc*., **1989**, *111*, 2480–2482. **DOI:**10.1021/ja00189a018
76. F. Zabel, S. W. Benson, D. M. Golden, *Intl. J. Chem. Kinet.* **1978**, *10*, 295–306. **DOI:**10.1002/kin.550100306
77. J. P. Guthrie, J. Guo, *J. Am. Chem. Soc.* **1996**, *118*, 11472–11487. **DOI:**10.1021/ja954247l

Povzetek

Tavtomerizem je temeljni koncept, ki raziskuje prehajanje protona med dvema konstitucionalnima izomeroma, to je keto in enolnim tavtomerom. Enolni tavtomeri so navadno manj stabilni kot ustrezne karbonilne spojine, vendar pa to ne velja za acetilaceton. Ta članek s termokemijskega vidika obravnava hitro prehajanje keto oblike acetilacetona v enolno obliko, ki predstavlja arhetipski (in učbeniški) primer tavtomerizma v organski kemiji.