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Thermochemistry of Acetonyl and Related Radicals

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Density functional and ab initio calculations at CBS-QB3 levels of theory were employed with a series of isodesmic reactions to determine the thermochemistry of the 2-oxopropyl or acetonyl radical ($CH_3COC^\bullet H_2$). In turn, this was used to determine formation enthalpies of 2-oxoethyl or formylmethyl ($C^\bullet H_2CHO$), 2-oxobutyl ($C^\bullet H_2COC_2H_5$), 1-methyl-2-oxopropyl or methylacetonyl ($C^\bullet H(CH_3)COCH_3$), 1-methyl-2-oxobutyl ($C^\bullet H(CH_3)$-COC_2H_5), and 3-oxopentyl ($C^\bullet H_2CH_2COC_2H_5$). Our computed standard enthalpy of formation of −34.9 ± 1.9 kJ mol^{-1} and a resonance stabilization energy of ∼22 kJ mol^{-1} for acetonyl are in good agreement with recent re-determinations, which have indicated a substantial lowering in the long-established value for ΔH_f°(298.15 K). A bond dissociation energy of 401 kJ mol^{-1} is suggested for the C−H bond in acetone with consistent values for the others. The calculations support the enthalpy of formation of acetaldehyde obtained from combustion experiments of −166.1 kJ mol^{-1} rather than the figure of −170.7 kJ mol^{-1} extracted from enthalpies of reduction and, in addition, serve to reduce the uncertainty in ΔH_f° of the 2-oxoethyl radical to +13 ± 2 kJ mol^{-1}.

Introduction

The components of petrol absorb in the vacuum ultraviolet and are therefore transparent to the laser wavelengths normally used to induce fluorescence for the purpose of "gaining insight into the spatial and temporal dynamics of chemical phenomena including the formation of species, their destruction, and transport and to link this information with whether an engine is running efficiently".[1]

Hence small amounts of a compound, a "fuel tracer", are added that both absorbs and fluoresces and matches the physical properties of a representative hydrocarbon; for example, the important constituent of petrol, iso-octane, may be followed by adding trace amounts of the ketone 3-pentanone using planar laser-induced fluorescence as an imaging technique in optically accessible internal combustion engines.[2]

Although the majority of the applications of fuel tracers until now have been to processes inside internal combustion engines, the technique can be applied to any reactive or nonreactive flow.[3−21]

Note that the physical properties are matched but, of course, the chemical properties cannot be matched since chemical bonding determines whether the compound will absorb light of the required wavelength.

However, very little is known of the chemical fate of the currently used fuel tracers such as acetone and 3-pentanone (and others under development) in hot oxidizing atmospheres; consequently, it is not really understood over what range of temperatures and pressures and, crucially, times are these compounds usable. Observed decreases in fluorescence signal strength in 3-pentanone/iso-octane mixtures have been shown to be due to differential evaporation in the stored sample rather than any more recondite explanation.[22]

Acetone and other ketones are also of importance in atmospheric chemistry[23,24] because they are formed not just biogenically but also from the atmospheric oxidation of hydrocarbons[25] through a series of reactions of secondary alkyl radicals with oxygen and reaction of the resultant peroxy radicals with nitric oxide:

$$(CH_3)_2\mathbf{C}^\bullet H + O_2 \rightarrow (CH_3)_2CHO\mathbf{O}^\bullet \xrightarrow{NO} (CH_3)_2CH\mathbf{O}^\bullet \xrightarrow{O_2} (CH_3)_2C{=}O$$

Indeed acetone is the most abundant oxygenated organic[26] in the upper troposphere, impacting on global ozone formation.[27] Hence accurate thermochemical properties, such as enthalpies of formation and bond energies,[28] of radicals related to acetone are necessary in the assembly of credible detailed chemical kinetic models for both atmospheric and combustion chemistry.[29]

In this regard, the long-established[30] standard enthalpy of formation of the acetonyl or 2-oxopropyl radical of −23.0 ± 7.5 kJ mol^{-1} (a similar value of −23.8 kJ mol^{-1} from the same group was considered less reliable because of surface effects)[31] was questioned by Holmes et al.[32] because acetonyl behaved in an anomalous manner when barriers to rotation about the R−C bond in the radicals $R-C^\bullet H_2$ against the homolytic bond dissociation energy $D(H-CH_2R)$ were considered. From mass spectrometric experiments, they derived a value of −50 kJ mol^{-1}.

In a single-pulse shock tube study of the decomposition of a series of ketones, Tsang[33] derived an enthalpy of formation of −12.6 kJ mol^{-1} for acetonyl; this implied that it had an effectively zero resonance stabilization energy, in contrast to previous work,[34] which had suggested a resonance energy of ∼25 kJ mol^{-1}.

Bouchoux et al.[35] carried out ion−cyclotron mass spectrometric measurements and determined $\Delta H_f^\circ(298K) = -34.6 \pm 8.4$ kJ mol^{-1}; in addition, they re-evaluated the data of Holmes and co-workers to yield −31.7 ± 6.4 kJ mol^{-1}. Theoretical calculations at the G2(MP2,SV) level, which gave a value of −36.2 kJ mol^{-1}, confirmed their findings.

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Zhu and Bozzelli[36] in the course of determining the thermochemistry of chlorinated aldehydes computed the standard enthalpy of formation at different levels of theory at -35.7 ± 4.8 kJ mol^{-1}.

A comprehensive series of theoretical calculations, at various levels of theory employing the isodesmic procedure,[37] by Espinosa-García et al.[38] led to a value of -32 ± 4 kJ mol^{-1}, which is in reasonable agreement with the mass spectrometric experiments.

Janoschek and Rossi[39] used G3MP2B3 calculations to compute the thermochemical properties of a large number of radicals, including acetonyl, for which they obtained ΔH_f°(298 K) of -33.3 kJ mol^{-1}.

Later computations by Hassouna and co-workers[40] using the atomization energy method are in substantial agreement at -32.9 ± 2.0 kJ mol^{-1}, the average of results from G3MP2B3 and CBS-QB3 levels of theory based on B3LYP DFT optimized geometries with 6-311+G(3df,2p) basis sets.

Farkas and co-workers[41] used laser-induced fluorescence (LIF) detection of acetonyl in a flow tube to measure the rate at which it H-abstracts from HBr, and from it, they estimate $\Delta H_f^\circ(298\text{ K}) =$ either -24.3 ± 7.5 or -28.1 ± 3.1 kJ mol^{-1} depending upon much earlier measurements of the reverse reaction[30] or from their own determination of the photobromination of acetone.[42] However, as the authors themselves acknowledge, their results cannot be used to resolve the question because of the fourfold uncertainty in the rate of the reverse reaction.

Interestingly, almost two decades earlier, photoionization mass spectrometric work by Orlov and co-workers,[43] not cited in any of the previous articles,[35,38−41] had already flagged a lower value of -41 kJ mol^{-1}. They reasoned that since replacement of H by methyl generally stabilizes a C-centered radical, this meant that the then-known enthalpies for the reaction

$$C^{\bullet}H_2CHO + CH_3COCH_3 \rightarrow CH_3CHO + C^{\bullet}H_2COCH_3$$

could not be reconciled and hence cast doubt on the heat of formation of acetonyl.

An equally neglected paper by Leroy et al. published at about the same time on the enthalpies of substituted methyl radicals came up with a low value of -36.9 kJ mol^{-1} in MP4 computations of the above-mentioned isodesmic reaction.[44]

Ponomarev and Takhistov[45] also derived a low value of -38 kJ mol^{-1} from a consideration of infrared spectra, using a correlation between wavenumber shifts and bond dissociation energies first enunciated by McKean.[46]

The reaction of acetonyl with oxygen, nitrogen oxides, and H-atoms has been reported by Imrik et al.[47] using time-resolved fast discharge flow and flash photolysis experiments. They found that acetonyl behaves similarly to alkyl radicals and conclude that the reduced reactivity observed toward O_2 and NO may be due to the resonance stabilization of acetonyl.

Very recently the reaction of acetonyl with molecular oxygen has been reported by Hassouna et al.[40] as a function of temperature, 291−520 K, and pressure, 0.042−10 bar. Their theoretical calculations result in a recommended enthalpy of formation for the adduct, $CH_3COCH_2OO^{\bullet}$, of -142.1 ± 4 kJ mol^{-1} based on G3MP2B3 and CBS-Q values of -139.4 and -144.7 kJ mol^{-1}.

Computational Methods

All electronic structure calculations have been performed with the Gaussian-03 suite of programs.[48] Geometry optimizations and vibrational frequency calculations were carried out using density functional theory (DFT) at the B3LYP/6-31+G(d,p) level,[49,50] which includes polarization functions over all atoms and diffuse functions on non-hydrogen atoms.

TABLE 1: Assumed ΔH_f°(298.15K) in kJ mol^{-1}

species	ΔH_f°	ref	species	ΔH_f°	ref
CH_3CHO	−166.1	79	$C^{\bullet}H_2CHO$	14.7	60
$CH_2{=}CH_2$	52.5	80	$CH_2{=}CH$	299.6	29
CH_2O	−108.8	81	$HC^{\bullet}{=}O$	43.5	80
CH_3CH_3	−83.8	82	$CH_3C^{\bullet}H_2$	120.5	83
CH_3COCH_3	−217.9	59,79	$CH_3C^{\bullet}O$	−10.3	84
CH_3OCH_3	−184.1	85	$CH_3OC^{\bullet}H_2$	−0.42	86
$CH_3CH{=}CH_2$	20.4	87	$C^{\bullet}H_2CH{=}CH_2$	166.1	88
$CH_3COC_2H_5$	−238.7	56,66	$C_2H_5COC_2H_5$	−257.9	70
CH_3COOCH_3	−413.8	89	$C^{\bullet}H_2COOCH_3$	−219.2	43
$CH_3COOC_2H_5$	−444.8	89	$C^{\bullet}H_2COOC_2H_5$	−249.8	this work

Energies were further refined using the procedures of the complete basis method developed by Petersson and co-workers, CBS-QB3,[51,52] a series of calculations that generally gives gas-phase energies with an average error of approximately ±4 kJ mol^{-1} as compared with experimentally measured values for the G3 data set.[53]

CBS-QB3 is a multilevel model chemistry that combines the results of several electronic structure calculations and empirical terms to predict molecular energies with high accuracy and relatively low computational cost.[54] The required electronic structure calculations are outlined as follows: (i) B3LYP/6-311G(2d,d,p) geometry optimization and frequencies; (ii) MP2/6-311G(3df,2df,2p) energy and CBS extrapolation; (iii) MP4-(SDQ)/6-31G(d(f),p) energy; (iv) CCSD(T)/6-31G† energy.

We used a number of isodesmic and isogyric reactions, which although a less elegant procedure than the atomization method can result in higher accuracies due to cancelation of errors, and it does not require quite such heroic levels of theory[55] to compute the reaction enthalpies.

The standard enthalpies of formation at 298.15 K of the reference species used in these working reactions are summarized in Table 1.

Results and Discussion

2-Oxopropyl Radical (Acetonyl). Bouchoux et al.[35] measured the proton affinity of acetonyl in an ion−cyclotron resonance mass spectrometer and hence determined the enthalpy of formation as -34.6 kJ mol^{-1}. In theoretical calculations conducted at the G2(MP2,SVP) level, they obtained -36.2 kJ mol^{-1} based on the atomization reaction:

$$CH_3COC^{\bullet}H_2 \rightarrow 3C(^3P) + 5H(^2S) + O(^3P)$$

They also re-examined the work of Holmes et al.[32] and, using a more complete treatment of the relationship between proton affinity, appearance energies, and enthalpy, derived a value of -31.7 ± 6.4 kJ mol^{-1} from the latter's initial value of -50 kJ mol^{-1}.

Zhu and Bozzelli[36] used the work reactions

$$CH_3COC^{\bullet}H_2 + CH_4 \rightarrow CH_3COCH_3 + C^{\bullet}H_3$$

$$CH_3COC^{\bullet}H_2 + CH_3CH_3 \rightarrow CH_3COCH_3 + CH_3C^{\bullet}H_2$$

to compute the reaction enthalpy from density functional B3LYP calculations with the basis sets 6-31G(d,p) and 6-311+G(3df,-2p), the quadratic configuration interaction method QCISD(T)/6-31G(d,p), and finally the complete basis set method with quadratic configuration interaction CBS-Q in each case employing a B3LYP/6-31G(d,p) optimized geometry. From the known enthalpies of the other species present, the standard enthalpy of formation of acetonyl was reported as −35.7 ± 4.8 kJ $\mathrm{mol^{-1}}$ taken from the average of the CBS-Q and the B3LYP/6-311+G-(3df,2p) results.

Espinosa-García et al.[38] used a number of working reactions at different levels of theory to calculate the enthalpy of formation of the acetonyl radical. They estimated a value of −32 ± 4 kJ $\mathrm{mol^{-1}}$ based on single-reference methods, MP4SDTQ/6-311++G-(2d,2p), G3, B3LYP/6-31++G(2df,2pd), and CCSD(T)/cc-pVTZ. They also concluded that single-reference methods give accurate results comparable with the MR-MP2 multireference calculations for the vinyloxy or formylmethyl radical, $\mathrm{C^{\bullet}H_2CHO}$, but that MR-MP2 calculations were computationally just too expensive for acetonyl.

Hence they used five working reactions, three of which, reactions 1−3, gave a large degree of scatter in ΔH_f° ranging in the worst case for reaction 1 from +9.6 to −41.8 kJ $\mathrm{mol^{-1}}$, probably because the reactant side has electron delocalization, whereas the product side has no such interaction:

$$\mathrm{CH_3COC^{\bullet}H_2 + H_2 \rightarrow CH_3COCH_3 + H^{\bullet}} \tag{1}$$

$$\mathrm{CH_3COC^{\bullet}H_2 + H_2 \rightarrow CH_3CHO + C^{\bullet}H_3} \tag{2}$$

$$\mathrm{CH_3COC^{\bullet}H_2 + CH_4 \rightarrow CH_3COCH_3 + C^{\bullet}H_3} \tag{3}$$

Reactions 4 and 5 are isodesmic[37] (conservation of the number of bonds of a given formal type),

$$\mathrm{CH_3COC^{\bullet}H_2 + CH_3CHO \rightarrow CH_3COCH_3 + C^{\bullet}H_2CHO} \tag{4}$$

$$\mathrm{CH_3COC^{\bullet}H_2 + CH_2{=}CH_2 \rightarrow CH_3COCH_3 + CH_2{=}C^{\bullet}H} \tag{5}$$

and are therefore expected to produce much more consistent results. This is indeed the case with reaction 4 yielding values between −29.4 and −34.6 and for reaction 5 between −27.3 and −30.2 kJ $\mathrm{mol^{-1}}$. Zhu and Bozzelli had previously found that reaction 3 did not give consistent results across the levels of theory that they employed.

In this study, we have selected nine isodesmic reactions, two of which, reactions 4 and 5, are identical to those used by Espinosa-García et al.[38] The results that we obtain are in substantial agreement for both reaction 4, −33.4 against −32.4,[38] and for reaction 5 where −31.1 is to be compared with −30.6[38] kJ $\mathrm{mol^{-1}}$. The differences can be ascribed to the differences in the standard heats of formation used by the two groups, which amount to 1.2 kJ $\mathrm{mol^{-1}}$.

The other seven isodesmic reactions, reactions 6−12, represent different attempts at balancing the amount of electron delocalization on both sides:

$$\mathrm{CH_3COC^{\bullet}H_2 + H_2C{=}O \rightarrow CH_3COCH_3 + HC^{\bullet}{=}O} \tag{6}$$

$$\mathrm{CH_3COC^{\bullet}H_2 + CH_3CH_3 \rightarrow CH_3COCH_3 + CH_3C^{\bullet}H_2} \tag{7}$$

$$\mathrm{CH_3COC^{\bullet}H_2 + CH_3CHO \rightarrow CH_3COCH_3 + CH_3C^{\bullet}O} \tag{8}$$

$$\mathrm{CH_3COC^{\bullet}H_2 + CH_3OCH_3 \rightarrow CH_3COCH_3 + CH_3OC^{\bullet}H_2} \tag{9}$$

$$\mathrm{CH_3COC^{\bullet}H_2 + CH_3CH{=}CH_2 \rightarrow CH_3COCH_3 + C^{\bullet}H_2CH{=}CH_2} \tag{10}$$

$$\mathrm{CH_3COC^{\bullet}H_2 + CH_3COOCH_3 \rightarrow CH_3COCH_3 + C^{\bullet}H_2COOCH_3} \tag{11}$$

$$\mathrm{CH_3COC^{\bullet}H_2 + CH_3COOC_2H_5 \rightarrow CH_3COCH_3 + C^{\bullet}H_2COOC_2H_5} \tag{12}$$

Although these are all isodesmic reactions, reactions 5, 6, and 8 are not homodesmic (conservation of bond type *and* order).

Results for all nine of the working reactions are shown in Table 2; all of our enthalpy of formation values are very consistent, averaging at −34.9 ± 1.9 kJ $\mathrm{mol^{-1}}$. There is no correlation between the reaction enthalpy and the enthalpy of formation computed. It is quite clear that reaction 5 produces a result out of line with the rest; in retrospect, it was probably not a good choice to have made because the reference species, ethene/vinyl, are just too different from acetone/acetonyl.

It might be argued that the enthalpy computed from reaction 4 is somewhat higher in value than the others, Table 2, and this might suggest that the enthalpy of formation of acetaldehyde is incorrect. We have used a value of −166.1 ± 0.5 kJ $\mathrm{mol^{-1}}$, obtained from normally reliable oxygen bomb calorimetry experiments[56] and recommended in an authoritative review,[57] but some sources, such as the NIST Web Book,[58] prefer −170.7 ± 1.5 kJ $\mathrm{mol^{-1}}$, which was derived by Wiberg et al.[59] from measurements of the enthalpy of reduction of acetaldehyde and its product, ethanol, by lithium triethyl borohydride in triglyme solution. Wiberg and co-workers validated their procedure by comparing their results with those from bomb calorimetry, but in seven out of the eight aldehyde, ketone, and ester compounds that they consider, their values are more negative by as much as 7 kJ $\mathrm{mol^{-1}}$. Adjusting our value for acetaldehyde to −170.7 kJ $\mathrm{mol^{-1}}$ would change ΔH_f°(298 K) for acetonyl to −28.7 from eq 4, which is now in considerable disagreement with the rest; hence our calculations do not support the Wiberg value.

An alternative explanation for the discrepancy between reaction 4 and the rest could be ascribed to the value used by us for the 2-oxoethyl radical (ethanal-2-yl) of +14.7 kJ $\mathrm{mol^{-1}}$; this was partially computed[60] from the reverse of reaction 4, which is of course a circular procedure. Unfortunately, the only other literature values,[57,61] 10.5 ± 9.2, due to Berkowitz et al.[29] and Rossi and Golden[62] who determined the enthalpy of formation of the formylmethyl radical as 12.0 ± 8.4 kJ $\mathrm{mol^{-1}}$ in a study of the pyrolysis of vinyl ethers in a low-pressure reactor, have rather large error limits. Based on the final acetonyl value, not excluding the result from reaction, the enthalpy of formation of 2-oxoethyl is computed to be +12.6 kJ $\mathrm{mol^{-1}}$; consequently, we believe that this can now be confidently set at 13 ± 2 kJ $\mathrm{mol^{-1}}$.

The surprisingly good result obtained by Leroy and co-workers[44] for acetonyl of −36.9 kJ $\mathrm{mol^{-1}}$ using reaction 4 with STDQ 6-31+G**2df//MP2/6-31G** calculations is probably somewhat fortuitous because they also computed a ΔH_f° of −6.3 kJ $\mathrm{mol^{-1}}$ for $\mathrm{C^{\bullet}H_2CHO}$.

Janoschek and Rossi[39] used G3MP2B3 calculations from the appropriate atomization reaction to compute the thermochemical properties of a large number of radicals, including acetonyl, for which they obtained ΔH_f°(298 K) of −33.3 kJ $\mathrm{mol^{-1}}$ as did

TABLE 2: CBS-QB3 Standard Enthalpies of Reaction and Formation at 298.15 K (kJ mol^{-1}) for Acetonyl

reaction	ΔH_r°	ΔH_f°
4	−3.8	−33.4
5	60.3	−31.1
6	−29.9	−35.8
7	23.0	−36.7
8	−27.0	−35.1
9	3.3	−37.7
10	−37.6	−34.7
11	11.3	−35.1
12	11.3	−34.3
mean		**−34.9 ± 1.9**

TABLE 3: Acetonyl Enthalpy in Date Order

source	ΔH_f°(298 K), kJ mol^{-1}
experiment[30]	−23.0 ± 7.5
experiment[33]	−12.6
experiment[32]	−50.0 ± 6.0
experiment[43]	−41.0
MP4[44]	−36.9
experiment[35]	−34.6 ± 8.4
G2MP2,SVP[35]	−36.2
experiment[32,35]	−31.7 ± 6.4
correlation[69]	−23.3
B3LYP and CBS-Q[36]	−35.7 ± 4.8
G3 and MP4SDTQ[38]	−32.0 ± 4
G3MP2B3[39]	−33.3 ± 7.5
correlation[45]	−38.0
G3MP2B3 and CBS-QB3[40]	−32.9 ± 2.0
experiment[41,42]	−28.1 ± 3.1
experiment[41,30]	−24.3 ± 5.8
this work	−34.9 ± 1.9

Hassouna and co-workers.[40] These last have also used CBS-QB3 theory and obtained −32.6 kJ mol^{-1}.

A detailed comparison of all experimental and calculated values in date order is shown in Table 3; there is a clear consensus in favor of the "lower" value, with particularly excellent agreement between what is possibly the best experimental value of Bouchoux et al. and our computed value.

Unfortunately, a recent re-evaluation of Benson's group additivity method[63] for estimating the thermochemistry of C/H/O radicals used $\Delta H_f^\circ(CH_3COC^\bullet H_2$, 298 K) = −50.21 ± 6.28 kJ mol^{-1} to "calibrate" its procedure.[64]

Our computed geometrical parameters for acetonyl are in excellent agreement with those from (5,4)-CASSSCF/6-31G-(d,p) computations by Williams and co-workers[65] with a maximum deviation of 0.01 Å in bond lengths and 0.3° in bond angles.

Isogeitonic Reactions. Homodesmic reactions do not necessarily maintain constancy in neighboring interactions; it should be possible to postulate a reaction that does this, an *isogeitonic* reaction, for example,

$$CH_3COC^\bullet H_2 + CH_3COC_2H_5 \rightarrow CH_3COCH_3 + C^\bullet H_2COC_2H_5 \quad (13)$$

where the five different interactions, C−C═O, C$^\bullet$−C═O, C−C−C, C$^\bullet$−C−C, and C−C═O, in the reactants are mirrored in the products.

Working reactions of this type would probably be even better at canceling out systematic errors but are normally impractical, if, as in this case, only the enthalpy of formation of methyl ethyl ketone, −238.7 ± 0.8 kJ mol^{-1}, is known;[56,66] that of its radical, $C^\bullet H_2COC_2H_5$, has not been determined; however, with a firm value for acetonyl now in place the latter can be calculated to be = (−238.7) + (−34.9) − (−217.9) − (−0.2) = −55.5 from the CBS-QB3 enthalpy of −0.2 kJ mol^{-1} for reaction 13. The near zero value for ΔH_r° of course supports the whole concept of group additivity.[67]

TABLE 4: Bond Energies and Formation Enthalpies (kJ mol^{-1})

H−R	this work	literature	$\Delta H_f^\circ(R^\bullet)$
$H-CH_2CHO$	397	395[29]	+13.0
$H-CH_2COCH_3$	401	401,[35] 422,[74] 385,[44] 393,[71] 385,[32] 411[30]	−34.9
$H-CH_2COCH_2CH_3$	401		−55.5
$H-CH(CH_3)COCH_3$	378	393,[69] 386[68]	−77.9
$H-CH_2CH_2COCH_3$	427		−29.9
$H-CH(CH_3)COCH_2CH_3$	380	368,[71] 397[69]	−95.1
$H-CH_2CH_2COCH_2CH_3$	426		−49.3

The procedure can be extended to include the following species derived from methyl ethyl ketone (not isogeitonic reactions):

$$CH_3C^\bullet HCOCH_3 + CH_3COCH_3 \rightarrow CH_3CH_2COCH_3 + CH_3COC^\bullet H_2 \Rightarrow \Delta H_f^\circ(298\ K)\ CH_3C^\bullet HCOCH_3 = -238.7 + (-34.9) - (-217.9) - (+22.2) = -77.9\ kJ\ mol^{-1} \quad (14)$$

which is to be compared with −70.3 ± 7.1 from Solly et al.[68] and −66.0 kJ mol^{-1} from Tumanov et al.[69] For the radical arising from the abstraction of a primary H atom, we have

$$C^\bullet H_2CH_2COCH_3 + CH_3COCH_3 \rightarrow CH_3CH_2COCH_3 + CH_3COCH_2 \Rightarrow \Delta H_f^\circ(298\ K)\ C^\bullet H_2CH_2COCH_3 = -238.7 + (-34.9) - (-217.9) - (-25.8) = -29.9\ kJ\ mol^{-1} \quad (15)$$

For radicals derived from 3-pentanone, based on ΔH_f° = −257.9 kJ mol^{-1} for $(C_2H_5)_2C{=}O$ from combustion measurements,[70] we have

$$CH_3C^\bullet HCOC_2H_5 + CH_3COCH_3 \rightarrow CH_3CH_2COC_2H_5 + CH_3COC^\bullet H_2 \Rightarrow \Delta H_f^\circ(298\ K)\ CH_3C^\bullet HCOC_2H_5 = -257.9 + (-34.9) - (-217.9) - (+20.2) = -95.1\ kJ\ mol^{-1} \quad (16)$$

which compares to previous estimates of −108 ± 21 from Bordwell and Harrelson[71] and to −79.7 kJ mol^{-1} from Tumanov et al.[69]

Finally, the primary C−H bond energy in 3-pentanone can be computed from reaction 17:

$$C^\bullet H_2CH_2COC_2H_5 + CH_3COCH_3 \rightarrow CH_3CH_2COC_2H_5 + CH_3COC^\bullet H_2 \Rightarrow \Delta H_f^\circ(298\ K)\ C^\bullet H_2CH_2COC_2H_5 = -257.9 + (-34.9) - (-217.9) - (25.6) = -49.3\ kJ\ mol^{-1} \quad (17)$$

Bond and Resonance Energies. Bond dissociation energies can be computed from the formation enthalpies of the radicals from

$$D(R-H) = \Delta H_f^\circ(R^\bullet) + \Delta H_f^\circ(H^\bullet) - \Delta H_f^\circ(RH)$$

using $\Delta H_f^\circ(H^\bullet)$ = 218.0 kJ mol^{-1} with the results shown in Table 4. There is now a consistency about the values, which was lacking heretofore.

The strong C−H bond in acetone, $H-CH_2C(CH_3){=}O$, of 401 kJ mol^{-1} contrasts with the equivalent but much weaker bond in isobutene $H-CH_2C(CH_3){=}CH_2$, which, although not well defined, ranges[72,73,74,75] from 358 to 373 kJ mol^{-1}; of course, this is as a result of the more efficient delocalization in the 2-methylallyl radical. Computing the reaction enthalpy of

$$C^{\bullet}H_2(CH_3)C{=}CH_2 + (CH_3)_2C{=}O \rightarrow (CH_3)_2C{=}CH_2 + C^{\bullet}H_2(CH_3)C{=}O \quad (18)$$

as 31.2 kJ mol^{-1} at the CBS-QB3 level, allied with the heat of formation of isobutene[76] of -17.9 kJ mol^{-1}, gives rise to ΔH_f° of $+133.9$ kJ mol^{-1} for the 2-methylallyl radical and consequently D(C$-$H) of 370 kJ mol^{-1}. This value straddles what are possibly the most reliable results obtained in shock tube experiments by Roth et al.[73] of 363 and that by Tsang[74] of 373 kJ mol^{-1}. A similar bond dissociation energy for 2-methylallyl is obtained if acetone and acetonyl are replaced by propene and allyl in reaction 18.

The resonance stabilization energy,[77] or RSE, of a typical allylic species such as 2-methylallyl[34] is 53 kJ mol^{-1}; the enthalpy change of $+31.2$ kJ mol^{-1} for reaction 18 is an indication that the acetonyl radical has a *lower, but not zero,* resonance energy of $\sim$22 kJ mol^{-1}. This is in good agreement with the findings of Bouchoux et al.[35] who deduced an RSE of 21 kJ mol^{-1} from the isodesmic endothermic reaction

$$C^{\bullet}H_2COCH_3 + CH_3CH_2CH_3 \rightarrow CH_3COCH_3 + C^{\bullet}H_2CH_2CH_3$$

In comparison with isobutane, whose primary C$-$H BDE ranges[61] from 415 to 425 kJ mol^{-1}, the resonance energy of acetonyl is calculated, from RSE $= D(\text{C}-\text{H}) - D(\text{acetonyl}-\text{H})$, to lie somewhere between 14 and 24 kJ mol^{-1}. Note that at CBS-QB3 level of theory the C=O bond elongates by $+0.024$ Å and the C$-$C bond contracts by -0.079 Å in going from acetone to acetonyl, whereas for isobutene to methylallyl the changes are $+0.051$ and -0.107 Å, respectively.

BMK Functional. Boese and Martin[78] have recently developed a DFT exchange$-$correlation functional for thermochemical kinetics, which they claim offers a single functional (BMK) capable of describing all aspects of the potential surface$-$energetics, kinetics, structures; if true, this would represent a significant development simplifying the acronymic nightmare faced by end-users of computational chemistry software. We have tested this by repeating some of the computations listed above; for example, the enthalpy of formation of acetonyl computed from reactions 4$-$12 is -31.4 ± 2.2 kJ mol^{-1}, a slightly disappointing result because by contrast the popular B3LYP functional gives -35.7 ± 2.7 kJ mol^{-1}.

Conclusions

Theoretical calculations using a number of working reactions converge on a value of -34.9 kJ mol^{-1} for the enthalpy of formation of acetonyl and consequently a resonance stabilization energy of 22 kJ mol^{-1} and a C$-$H bond energy of 401 kJ mol^{-1}. Adoption of this value then leads to enthalpies of formation and C$-$H bond energies for a number of related radicals.

The calculations further suggest that the enthalpy of formation for acetaldehyde derived from combustion calorimetry is to be preferred over that obtained from reduction calorimetry and that the enthalpy of formation of 2-oxoethyl can be narrowed down to $+13 \pm 2$ kJ mol^{-1}.

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Supporting Information Available: Optimized structures and Cartesian coordinates of acetonyl and related species. This material is available free of charge via the Internet at http://pubs.acs.org.

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