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Thermochemistry of organic and heteroorganic species. Part VIII. Ketene and structurally related species☆

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Abstract

Photoionization mass spectrometry was used to obtain the enthalpies of formation of $CH_2{=}C{=}O \leq -20.5$ and $-24.0\ \mathrm{kcal\ mol^{-1}}$ (from 3-phenylcyclobutanone and diketene, respectively), $CH_3C{\equiv}O^+$ ion 147.3 and $152.3\ \mathrm{kcal\ mol^{-1}}$ (from $CH_3COOCH{=}CH_2$ and CH_3CONH_2 molecules, respectively) and $PhCH_2C{\equiv}O^+$ $175.5\ \mathrm{kcal\ mol^{-1}}$ (from $PhCH_2COOMe$ molecules). The enthalpic shift procedure was applied for the estimation of the enthalpies of formation of ketene and related molecules. The following ΔH_f^0 values were found $CH_2{=}C{=}O$: $-(22–25)$, $CH_2{=}S{=}CH_2$ (67), $CH_2{=}S{=}S$ (60), $S{=}S{=}S$ (51), $HC{\equiv}COH$ ($10\ \mathrm{kcal\ mol^{-1}}$). The low value of ΔH_f^0 (ketene) $\approx -23\ \mathrm{kcal\ mol^{-1}}$ as compared with the currently used value $-11.4\ \mathrm{kcal\ mol^{-1}}$ was supported by the literature data, which have been revised in the present work. Using the new value for ketene's enthalpy of formation, those for ten substituted ketenes and $HC{\equiv}CO^{\cdot}$ ($48.5\ \mathrm{kcal\ mol^{-1}}$) free radical were obtained with the help of macroincremental schemes and introduction of correction terms. Computation of the enthalpies of formation of eight A=B=C molecules by MNDO, AM1, PM3 and MINDO/3 methods revealed that in most cases the latter gives the results closest to the experimental values or to those gained from the enthalpic shift procedure. The brief analysis of possible sources of errors in deducing the thermochemical values from appearance energies measurements has been made. Among those the isomerization processes occurring in molecular ions are considered the most important, which could lead to incorrect values of the enthalpies of formation of fragment ions, free radicals and molecules. With many examples it has been demonstrated that the application of the series of isodesmic reactions could be an effective tool for verifying, correcting and finding new values of the enthalpies of formation of neutral and ionized species.

Keywords: Thermochemistry; Ketene; Isodesmic reactions

Ketene $CH_2{=}C{=}O$ is an important species widely used in organic synthesis [2]. The knowledge of its enthalpy of formation and its fragments $C_2HO^{\cdot}$, C_2HO^+, C_2O, CH_2 is important for the description of the processes of combustion of fuels [3] and photolytic reactions [4,5]. Much attention was paid to thermochemistry of ketene and substituted ketenes in theoretical works [6–13]. The importance of the knowledge of the ΔH_f^0 value for ketene and the recent publication of Aubry et al. [14] on the thermochemistry of ketene and methylsubstituted ketenes impelled us to make: (i) a thorough analysis of the known experimental data from which the gas enthalpies of formation $\Delta H_f^0(g)$ for ketene could be obtained; (ii) to

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☆ For part VII see Ref. [1].

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represent our own experimental and computed data on RCH=C=O molecules and related species. (The enthalpy of formation ΔH_f^0(298.15 K) (ideal gas) for all species is substituted in the text by shorter form ΔH_f^0.) Another objective of this paper is to find out how reliable are the values of the enthalpies of formation for neutral and charged species related to the thermochemistry of ketene if those values are gained from appearance energies (AEs) measurements by mass spectrometric methods. The possible sources of errors in this aspect are discussed. Finally, we will show that the thermochemical data should be checked using simple and accessible macroincremental schemes and enthalpic shifts procedures for molecules and isodesmic reactions for radical cations, cations and free radicals.

1. The enthalpy of formation of ketene is from structurally related compounds

The currently used value of ΔH_f^0 (ketene) is -11.4 kcal mol^{-1} [15–19]. Some reference books give the value -14.2 [20,21] or -14.6 kcal mol^{-1} [22]. The enthalpy of formation of ketene $CH_2{=}C{=}O$ could be calculated by the macroincremental additive scheme [23–25] from the known ΔH_f^0 value -23.4 kcal mol^{-1} [15,16] for carbonsuboxide O=C=C=C=O, which is closely related in its structure to ketene:

$$\begin{aligned}\Delta H_f^0(\mathrm{O{=}C{=}C{=}C{=}O}) &= 2[\Delta H_f^0(\mathrm{CH_2{=}C{=}O})] + \Delta H_f^0(\mathrm{CH_2{=}C{=}CH_2}) \\ &\quad - 2[\Delta H_f^0(\mathrm{CH_2{=}CH_2})] \qquad (1)\end{aligned}$$

$$\begin{aligned}\Delta H_f^0(\mathrm{CH_2{=}C{=}O}) &= [\Delta H_f^0(\mathrm{C_3O_2}) - \Delta H_f^0(\mathrm{CH_2{=}C{=}CH_2}) \\ &\quad + 2\Delta H_f^0(\mathrm{C_2H_4})] : 2 \\ &= [-23.4[15] - 45.6[15] + 2(12.5[15])] : 2 \\ &= -22.0\ \mathrm{kcal\ mol^{-1}} \qquad (2)\end{aligned}$$

In C_3O_2, the repulsion between two electron-withdrawing CO-groups is expected (see Ref. [26]), which is however absent in ketene. Hence, ΔH_f^0(ketene) < -22 kcal mol^{-1}. Therefore we do not foresee any chemical reasons for violation of Eqs. (1) and (2). At the same time C_3O_2 is a stable liquid, safely treated, [6] whereas ketene is a highly reactive species. Therefore, one can expect difficulties in finding the experimental value of ΔH_f^0 for ketene rather than for carbonsuboxide.

The CO_2 molecule also could be used for estimation of ketene's enthalpy of formation

$$\begin{aligned}\Delta H_f^0(\mathrm{CH_2{=}C{=}O}) &= [\Delta H_f^0(\mathrm{O{=}C{=}O}) + \Delta H_f^0(\mathrm{CH_2{=}C{=}CH_2})] : 2 + \Delta \\ &= [-94.0[15] + 45.6[15]] : 2 + \Delta \\ &= -24.2\ \mathrm{kcal\ mol^{-1}} + \Delta \qquad (3)\end{aligned}$$

Δ is the correction term revealing the possible additional stabilization of CO_2 caused by the presence of two oxygen atoms at the carbon atom. Such an effect is called sigma-conjugation [27], incremental geminal stabilization [28,29], anomeric effect [30] or combined polarization [31] and is related to the compounds possessing several OR, F, or NR_2 groups at the saturated carbon atom. This effect is a small one (e.g. 1–2 kcal mol^{-1} for F-atoms [26]) when those atoms or groups are bound to the unsaturated carbon atom. If such an effect exists in the CO_2 molecule this should make the ΔH_f^0 value for ketene several kilocalories more positive (-21 to -23 kcal mol^{-1}) (Eq. (3)). However, we take the currently used value -11.4 kcal mol^{-1} for ΔH_f^0 (ketene) (see above) and it will give an improbably high gem-stabilization of ≈ 25 kcal mol^{-1} in CO_2. Thus, from the application of macroincremental estimation schemes it comes out that the currently used value of ΔH_f^0 (ketene) -11.4 is doubtful.

Earlier, Benson noticed [32] that $\Delta\Delta H_f^0$ [$\Delta H_f^0(R_2C{=}O \rightarrow R_2C{=}S)$] or $\Delta\Delta H_f^0(\mathrm{RBr} \rightarrow \mathrm{RSH})$ have more or less constant values. Later [25] the permanency of the $\Delta\Delta H_f^0$ values for $RX \rightarrow R'X$ or $RX \rightarrow RY$ replacement was found for many classes of organic and elementorganic compounds and systematically used for correcting known or deducing new values of the enthalpies of formation for different compounds. Recently, this procedure called the “enthalpic shift” method [25] was used by some other workers [1,33–36]. We used Eqs. (4) and (5) for the estimation of the enthalpy of formation of ketene (ΔH_f^0 and $\Delta\Delta H_f^0$ values in kcal mol^{-1}; deduced values are in square brackets)

$$\begin{tikzcd}
S{=}S{=}O \arrow[r, "-24", "\Delta\Delta H_f^\circ"'] & S{=}C{=}O \\
-10[18] \arrow[d, "+8"] & -34[15] \arrow[d, "{[+8]}"] \\
CH_2{=}S{=}O \arrow[r, "{[-24]}"] & CH_2{=}C{=}O \\
-2[37] & {[-26]}
\end{tikzcd} \tag{4}$$

$$\begin{tikzcd}
O{=}S{=}O \arrow[r, "+69", "\Delta\Delta H_f^\circ"'] & CH_2{=}S{=}O \\
-71[32] \arrow[d, "-23"] & -2 \arrow[d, "{[-23]}"] \\
O{=}C{=}O \arrow[r, "{[+69]}"] & CH_2{=}C{=}O \\
-94 & {[-25]}
\end{tikzcd} \tag{5}$$

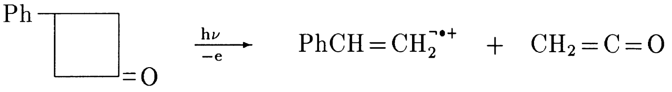
The close values for ΔH_f^0 of ketene obtained from Eqs. (4) and (5) reveal the absence of the noticeable stabilization of CO_2 due to sigma-conjugation (see above) as compared with CH_2CO. The value 39 kcal mol^{-1} [17] for the thioanalog of ketene $CH_2{=}C{=}S$ gained from the ionization energy (IE) of $CH_2{=}C{=}S$ [38] and ΔH_f^0 $CH_2{=}C{=}S^{\cdot+}$ [17] combined with the known value of the enthalpic shift $\Delta\Delta H_f^0$ for =C=O → =C=S replacement 61–62 kcal mol^{-1} [32] (see also Eqs. (20)–(22)) gives $-(21–23)$ kcal mol^{-1} for ΔH_f^0 (ketene). The usage of -11.4 kcal mol^{-1} for the latter gives improbably low $\Delta\Delta H_f^0$ $39 - (-11.4) = 50.4$ kcal mol^{-1} for the =C=O → =C=S shift, observed nowhere. Thus, the application of the enthalpic shift procedure also gives much lower ΔH_f^0 values for ketene than is currently accepted (-11.4 kcal mol^{-1}).

From the schemes similar to Eqs. (4) and (5) we found ΔH_f^0 values of some other molecules related to ketene $CH_2{=}S{=}CH_2$, $CH_2{=}S{=}S$ and $S{=}S{=}S$ (see later).

2. ΔH_f^0 of ketene from some AE measurements

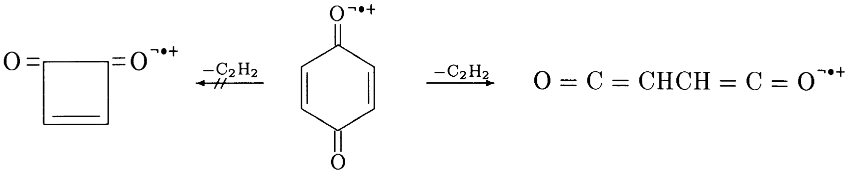
Support for a lower value of $\Delta H_f^0(CH_2{=}C{=}O)$ can be found in photoionization (PI) studies of some molecules giving neutral or ionized ketenes. From fragmentation of 3-phenylcyclobutanone (I) we obtained the value -20.4 kcal mol^{-1} for ΔH_f^0 (ketene) (Scheme 1) (for details see Appendix A).

Since IE 8.83 and AE $(M–CH_2{=}C{=}O)^{\cdot+}$ 8.86 eV are nearly identical if the values of the accuracies are taken into consideration (0.03 eV for IE and 0.05–0.08 eV for AEs) the thermochemical threshold for $[M–CH_2{=}C{=}O]^{\cdot+}$ formation could be even smaller than measured AE, thus shifting ΔH_f^0 (ketene) to lower values than -20.4 kcal mol^{-1}.



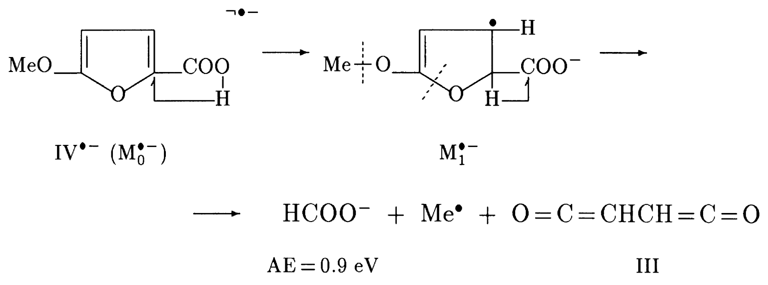
I IE 8.83 eV AE 8.86 eV

Scheme 1.

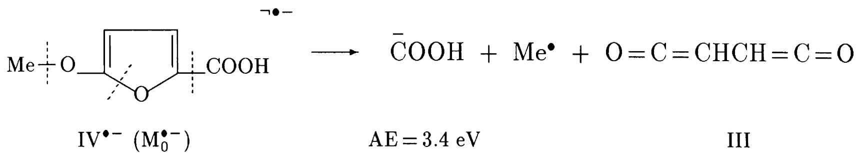


II a•+ II•+ III•+

Scheme 2.



Scheme 3.



Scheme 4.

Similarly, our present analysis of the thermochemistry of $[M-C_2H_2]^{\cdot+}$ ion formation from compound II [38] (Scheme 2) gives ΔH_f^0 (ketene) $-(20-23)$ kcal mol^{-1} (see Appendix A).

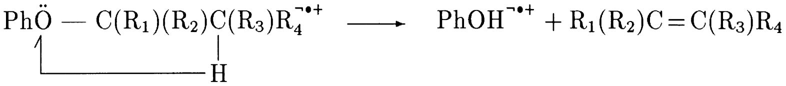
In our earlier investigation [39] we measured AEs CHO_2^- ions from compound IV and showed that fragmentation occurs following Schemes 3 and 4.

The values of ΔH_f^0 bisketene III -40.0 and -37.2 kcal mol^{-1} were obtained from the reactions in Schemes 3 and 4, respectively, which gave ΔH_f^0 ($CH_2{=}C{=}O$) -21.5 and -20.0 kcal mol^{-1}, respectively (for details see Appendix A).

In past years the accurate methods of mass spectrometry (MS) (among those PI MS and MS with monoenergetic electrons) have been applied for determination of the molecules' enthalpies of formation in the gas phase. The possible sources of errors in such determinations are common with those for ions' enthalpies of formation. Some of them were discussed above, the others are considered here in relation to ketene's thermochemistry. The sources of errors discussed here are of general character; therefore, we analyze them in detail.

Before we analyze the MS data of Aubri et al. [14] dealing with thermochemistry of ketene eliminated from $PhOCOCH_3$ molecules, we consider in detail the process of alkene elimination from structurally close alkylphenyl ethers [40–42] (Scheme 5).

The authors claimed [40,41] that in all cases (12 compounds) they obtained ionized phenol according to Scheme 5. The thermochemistry of $PhOH^{\urcorner\cdot+}$ and alkenes is well known and the enthalpies of formation of initial molecules could be safely estimated. However, the AEs for M–alkene$^{\urcorner\cdot+}$ ions were found to be 8–28 kcal mol^{-1} higher than expected. The largest deviation 27.7 kcal mol^{-1} was registered for AE $PhOH^{\urcorner\cdot+}(+C_2H_4)$ from $PhOCH_2CH_2$–H. Only for two molecules, $PhOCMe_3$ and $PhOCMe_2Et$ $AE_{exp} = AE_{calc}$ for $PhOH^{\urcorner\cdot+}$ + alkene. For all other molecules the observed deviations were explained [40,41] by the occurrence of excess energy necessary for the production of the transition state. However it looks very strange that the elimination of C_2H_4 from $PhOCH_2CH_3^{\urcorner\cdot+}$-ions requires additional 28(!) kcal mol^{-1} whereas the elimination of alkenes from molecules comprising bulky substituents whose methyl groups interact with ortho-hydrogens of the Ph-group takes place without excess energy. We also mention that the Woodward–Hofmann rule is not valid for ionized molecules [43,44]. This eliminates the possibility of using this rule for the explanation of high E_{cr} ($= E_{activation}$) values. It is notable that for the process $PhOCOCH_3^{\urcorner\cdot+} \rightarrow PhOH^{\urcorner\cdot+} + CH_2{=}C{=}O$ the authors of Ref. [14] do not suggest the occurrence of excess energy for the process (as they did for $PhOCH_2CH_3$ molecules) although the



$$\text{Ph}\ddot{\text{O}}-\text{C}(\text{R}_1)(\text{R}_2)\text{C}(\text{R}_3)\text{R}_4^{\urcorner\bullet+} \longrightarrow \text{PhOH}^{\urcorner\bullet+} + \text{R}_1(\text{R}_2)\text{C}=\text{C}(\text{R}_3)\text{R}_4$$

Scheme 5.

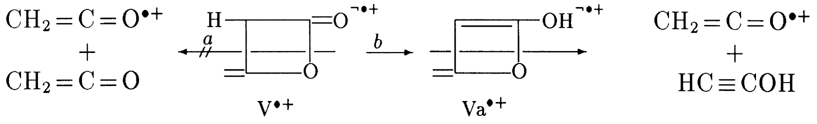
transition states for the fragmentation of both molecules $PhOCH_2CH_3$ and $PhOCOCH_3$ are similar.

We suggest the interpretation of the events taking place with PhOR molecules under EI which differs from that given in Refs. [14,40,41]. As shown in detail in Refs. [43,44] all rearrangement processes in a particular ion have to be analyzed only in conjunction with the energetically lowest process of simple bond cleavage in this ion. In $PhOCH_2CH_3$ such a simple bond cleavage is CH_3-loss which requires ~2.5 eV (~58 kcal mol^{-1}) whereas in $PhOCMe_3$ Me-loss requires only 0.8 eV (~18 kcal mol^{-1}) (see Appendix A). Therefore, the $PhOC_2H_5^{\urcorner\cdot+}$ molecular ion—in the large energy gap ($E_{cr} = 2.5$ eV) can rearrange (through H-shifts, ring opening, skeletal rearrangements) to the molecular ion(s) of other structure(s) possessing higher enthalpy of formation. These new isomers when eliminating C_2H_4 would give $C_6H_6O^{\cdot+}$ fragments with the structures differing from the expected ionized phenol. These $C_6H_6O^{\cdot+}$ isomers will be produced at higher AEs. For the $PhOCMe_3$ molecule E_{cr} for Me-loss is only 0.8 eV and the initial $M^{\cdot+}$ cannot give isomers with high enthalpies of formation without decomposing. Consequently, the ionized phenol is obtained at the expected threshold. Similar interpretation could be applied to fragmentation of $PhOCOCH_3$ and $PhOCOCHMe_2$ molecules. Although simple bond cleavage with lowest energy, i.e. formation of $CH_3C{\equiv}O^+$ or $Me_2CHC{\equiv}O^+$ ions, respectively, gives close AE values 9.94 and 9.88 eV, respectively, in $PhOCOCHMe_2^{\urcorner\cdot+}$ molecular ion there appears a possibility of obtaining the isomerized molecular ion $Ph\overset{+}{O}(H)CO\dot{C}Me_2$. This isomerized molecular ion is much more stable than its analog $Ph\overset{+}{O}(H)CO\dot{C}H_2$ (from $PhOCOCH_3^{\urcorner\cdot+}$). The former decomposes to give $PhOH^{\urcorner\cdot+} + Me_2C{=}C{=}O$ whereas $PhOCOCH_3^{\urcorner\cdot+}$ instead of producing $Ph\overset{+}{O}(H)CO\dot{C}H_2$ species gives an isomer, formed through the H-shift process to the benzene ring. This isomer after fragmentation could give $C_6H_6O^{\cdot+}$ ion differing from $PhOH^{\urcorner\cdot+}$.

Our interpretation of the events with $PhOR^{\cdot+}$ isomerization and fragmentation is not a new one. Recently, we analyzed similar cases in detail in special Account [43].

The authors examining PhOR molecules showed that collisional activation (CA) spectra of fragment ions $C_6H_6O^{\cdot+}$ from all 17 compounds [14,40,41] were identical with the CA spectrum of ionized phenol. This result together with AE ($C_6H_6O^{\cdot+}$) measurements was interpreted in the sense that $C_6H_6O^{\cdot+}$ ions from all compounds studied, possessed the structures of ionized phenol at the threshold of their formation. Here we express our opinion about the validity of application of CA spectra to the thermochemistry of ionized and neutral fragments including ketene.

The identity of the CA spectra does not necessarily confirm the structure of ionized phenol for $C_6H_6O^{\cdot+}$ species from PhOR molecules since other $C_6H_6O^{\cdot+}$ isomers (which are abundant) could have similar CA spectra. To give one example, the CA spectra of $CH_3C{\equiv}O^+$ and $CH_2{=}\overset{+}{C}OH$ isomers are similar [45]. However, what is even more important, is that a structurally pure species may, upon CA, isomerize rapidly and then fragment [46]. Such isomerizations are well documented: $HC{\equiv}O^+$ to $H\overset{+}{O}{=}C:$ ions [47], diverse $C_2H_3S^+$ isomers to $CH_3C{\equiv}S^+$ ions [48], the skeleton of many R-fragments changes in pyridinium ions [49,50] $C_5H_4\overset{+}{N}{-}R \rightarrow C_5H_4N: + R_1^+$. Other examples can be found in Ref. [46]. Despite the high barrier for $HC{\equiv}COH^{\urcorner\cdot+} \rightarrow CH_2{=}C{=}O^{\cdot+}$ isomerization 79 kcal mol^{-1} CA spectrum of ketene contains the intense peak of the rearrangement ion with *m*/*z* 29 ($HO\ddot{C}^+/HC{\equiv}O^+$) whereas the CA spectrum of ethynol $HC{\equiv}COH^{\cdot+}$ gives the signal of the peak of the $CH_2^{\cdot+}$ rearrangement ion [51]. In general, this is not surprising. In spite of the differences in the excitation methods used to obtain the EI and CA spectra of molecules, there are marked similarities between the two phenomena [46]. It is hardly possible to find out the compounds lacking in their EI mass spectra, the



Scheme 6.

peaks of rearrangement ions [25,43,44] and the wide occurrence of rearrangement processes under CA is expected as well. Therefore, the initially formed $C_6H_6O^{\cdot+}$ ions from phenylalkylethers PhOR [40,41] or phenylesters PhOCOR' [14] may possess one structure (or the mixture of structures) whereas in course of the CA process they rearrange to the $PhOH^{\cdot+}$ isomer as the most stable among the $C_6H_6O^{\cdot+}$ species. In general, many problems exist in the interpretation of the CA spectra [52] so the latter should be applied for the interpretation of the thermochemical data with great caution.

3. ΔH_f^0 (ketene) from computation

The range of the computed values of the enthalpies of formation for ketene is extremely large (for details see Appendix A) (kcal mol^{-1}):19 [6], −4.3 [6], −9.7 [7], −10.2 [6], −10.8 [9], −11.1 [9], −12.1 [8], −12.4 [10], −12.6 [9], −17.2 [6], −24.0 (from computed ΔH_f^0 $CH_2=C=O^{\cdot+}$ [9] and IE [38] $CH_2=C=O$. What is most disturbing is that in the same publication, [6] using the same computational method MP2/6-31G* + ZPVE//MP2/6-31G** but different model reactions, the authors obtained 19, −4.3 and −10.2 (or −17.2) kcal mol^{-1} for ΔH_f^0 (ketene). In another publication [13] it was computed that bisketene III is by 3.2 kcal mol^{-1} less stable than its cyclic isomer IIa. This leads (for details see Appendix A) to 1.6 kcal mol^{-1} for ΔH_f^0 ($CH_2=C=O$). Our computation using MNDO, AM1, PM3 and MINDO/3 methods gives ΔH_f^0 ($CH_2=C=O$) values −6.83, −5.71, −9.27 and −20.74 kcal mol^{-1}, respectively, the latest being close to the value deduced in this work.

The accuracy of computation increases or, better to say, the deviation from experiment decreases when the *relative* values for isomers enthalpies of formation are computed. The computed values of $\Delta\Delta H_f^0$ for $CH_2=C=O \rightarrow HC\equiv COH$ are 35.13 [53] or 36.3 [54]. The enthalpy of formation for the $HC\equiv COH$ isomer can be safely estimated using the enthalpic shifts procedure (see above). The systematic application of this procedure to $CH_2=CHX \rightarrow PhX$ systems allowed Luo et al. [35] not only to demonstrate the reliability of such a procedure but to deduce many unknown data. Similarly, we take six couples of compounds $RCH=CH_2/RC\equiv CH$ with well-established values of the enthalpies of formation (see Appendix A) and arrive at 40.6 ± 2 kcal mol^{-1} for $RCH=CH_2 \rightarrow RC\equiv CH$ replacement. Then, taking the known value −30.6 ± 1.1 kcal mol^{-1} [55] for ΔH_f^0 ($CH_2=CHOH$) we obtain $\Delta H_f^0 = (HC\equiv COH) = -30.6 + 40.6 = 10.0$ kcal mol^{-1}. Using theoretical values for $\Delta\Delta H_f^0(CH_2=C=O \rightarrow HC\equiv COH)$35.1 [53] and 36.3 [54] we get the values −25.7 and −26.9 kcal mol^{-1}, respectively, for $\Delta H_f^0(CH_2=C=O)$.

In the attempt to find out the enthalpy of formation of ketene by PI MS we selected diketene V expecting the formation of ionized and neutral ketene (Scheme 6, route a). We obtained IE 9.53 eV and AE ($C_2H_2O^{\cdot+}$) 10.98 eV (253.21 kcal mol^{-1}). Taking ΔH_f^0 V − 45.46 kcal mol^{-1} [15,16] and IE ($CH_2=C=O$) 9.614 eV [38] (221.71 kcal mol^{-1}), we expected to get ΔH_f^0 (ketene) from Eqs. (6)–(8)

$$\begin{aligned} &AE(CH_2=C=O)^{\cdot+} \\ &\quad = \Delta H_f^0(CH_2=C=O)^{\cdot+} + \Delta H_f^0(CH_2=C=O) \\ &\qquad - \Delta H_f^0(V) \end{aligned} \tag{6}$$

$$\begin{aligned} &\Delta H_f^0(CH_2=C=O) \\ &\quad = AE(CH_2=C=O)^{\cdot+} - \Delta H_f^0(CH_2=C=O)^{\cdot+} \\ &\qquad + \Delta H_f^0(V) \end{aligned} \tag{7}$$

since

$$\begin{aligned} &\Delta H_f^0(CH_2=C=O)^{\cdot+} \\ &\quad = \Delta H_f^0(CH_2=C=O) + IE(CH_2=C=O) \end{aligned}$$

we finally have:

$$\begin{aligned}\Delta H_{\mathrm{f}}^{0}(\mathrm{CH_2{=}C{=}O}) &= [\mathrm{AE}(\mathrm{CH_2{=}C{=}O})^{\cdot +} - \mathrm{IE}(\mathrm{CH_2{=}C{=}O}) \\ &\quad + \Delta H_{\mathrm{f}}^{0}(\mathrm{V})] : 2 \\ &= 253.24 - 221.71 - 45.46 \\ &= -6.98 \approx -7.0\ \mathrm{kcal\ mol^{-1}} \end{aligned} \tag{8}$$

The latter value appeared to be doubtful since most of the experimental and theoretical data give much lower values $-(11–26)$ kcal mol^{-1} (see above). We suggested, instead—in agreement with our recent publication [43] on regularities of rearrangement processes in ions—that molecular ion V$^{\cdot+}$ rearranges to Va$^{\cdot+}$ in the energy gap E_{cr} = AE-IE for route “a”. Since ionized enol Va$^{\cdot+}$ has smaller $\Delta H_{\mathrm{f}}^{0}$ value than its tautomer V$^{\cdot+}$ (see Ref. [56]) the isomerization through route “b” followed by expected fragmentation of newly born molecular ion Va$^{\cdot+}$ is quite accessible. IEest (HC≡COH) is 9.75 eV from $\Delta H_{\mathrm{f}}^{0}$ (HC≡COH) 10 kcal mol^{-1} (see above) and 235 kcal mol^{-1} [57] for HC≡COH$^{\urcorner\cdot+}$, i.e. IE(HC≡COH) is higher IE(CH$_2$=C=O)9.614 eV [38] and this coincides with route b: according to the Stevenson–Audier rule the charge resides on the fragment with lower IE (see Ref. [43]). From Eqs. (9)–(12) following from Scheme 6 (route “b”) we have $\Delta H_{\mathrm{f}}^{0}$(CH$_2$=C=O) − 24 kcal mol^{-1}.

$$\begin{aligned}\mathrm{AE}(\mathrm{CH_2{=}C{=}O})^{\cdot +} &= \Delta H_{\mathrm{f}}^{0}(\mathrm{CH_2{=}C{=}O})^{\cdot +} + \Delta H_{\mathrm{f}}^{0}(\mathrm{HC{\equiv}COH}) \\ &\quad - \Delta H_{\mathrm{f}}^{0}(\mathrm{V}) \end{aligned} \tag{9}$$

$$\Delta H_{\mathrm{f}}^{0}(\mathrm{CH_2{=}C{=}O})^{\cdot +} = \Delta H_{\mathrm{f}}^{0}(\mathrm{CH_2{=}C{=}O}) + \mathrm{IE}(\mathrm{CH_2{=}C{=}O}) \tag{10}$$

$$\begin{aligned}\mathrm{AE}(\mathrm{CH_2{=}C{=}O})^{\cdot +} &= \Delta H_{\mathrm{f}}^{0}(\mathrm{CH_2{=}C{=}O}) + \mathrm{IE}(\mathrm{CH_2{=}C{=}O}) \\ &\quad + \Delta H_{\mathrm{f}}^{0}(\mathrm{HC{\equiv}COH}) - \Delta H_{\mathrm{f}}^{0}(\mathrm{V}) \end{aligned} \tag{11}$$

$$\begin{aligned}\Delta H_{\mathrm{f}}^{0}(\mathrm{CH_2{=}C{=}O}) &= \mathrm{AE}(\mathrm{CH_2{=}C{=}O})^{\cdot +} - \mathrm{IE}(\mathrm{CH_2{=}C{=}O}) \\ &\quad - \Delta H_{\mathrm{f}}^{0}(\mathrm{HC{\equiv}COH}) + \Delta H_{\mathrm{f}}^{0}(\mathrm{V})] \\ &= 253.21 - 221.71 - 10.0 - 45.46 \\ &= -23.96\ \mathrm{kcal\ mol^{-1}} \end{aligned} \tag{12}$$

There are two theoretical values for $\Delta\Delta H_{\mathrm{f}}^{0}[(\mathrm{CH_2{=}C{=}O})^{\cdot +} \rightarrow (\mathrm{HC{\equiv}COH})^{\cdot +}]$ 36.0 [51] and 45.2 kcal mol^{-1} [58]. Taking $\Delta H_{\mathrm{f}}^{0}$(HC≡COH)$^{\cdot+}$ 235 kcal mol^{-1} [57] (gained from AE measurements) we have $\Delta H_{\mathrm{f}}^{0}$(CH$_2$=C=O)$^{\cdot+}$ 199 and 189.8 kcal mol^{-1}, respectively. Subtracting from these values IE(CH$_2$=C=O) 221.7 kcal mol^{-1} (9.614 eV [38]) we obtain −22.7 and −32 kcal mol^{-1} for the enthalpy of formation for the CH$_2$=C=O molecule.

Ketene’s enthalpy of formation could be deduced from the related free radicals thermochemistry. The measured value of the reaction enthalpy ΔH_{r} 35.3 ± 2.5 kcal mol^{-1} [59] Eq. (13) could be used for estimation of the ketene’s enthalpy of formation

$$\mathrm{CH_2{=}C{=}O + F^{\cdot} \rightarrow FCH_2\dot{C}{=}O} \tag{13}$$

Taking $\Delta H_{\mathrm{f}}^{0}$ values 19 [17,18] (F$^{\cdot}$) and −43 kcal mol^{-1} (FCH$_2\dot{\mathrm{C}}$=O—see Appendix A) we arrive at the value ≈ −26.5 kcal mol^{-1} for $\Delta H_{\mathrm{f}}^{0}$(CH$_2$=C=O).

4. Ketene’s enthalpy of formation from its proton affinity and $\Delta H_{\mathrm{f}}^{0}$ CH$_3$C≡O^{+} ion

One of the possible ways to define the ketene’s enthalpy of formation is to use ketene’s proton affinity (PA) (see later) from the process CH$_2$=C=O + H^{+} → CH$_3$C≡O^{+} + PA for which the value of $\Delta H_{\mathrm{f}}^{0}$(CH$_3$C≡O^{+}) should be unambiguously determined. The currently used value for $\Delta H_{\mathrm{f}}^{0}$(CH$_3$C≡O^{+}) is 156 kcal mol^{-1} [17,60]. The higher value 156.67 ± 0.19 kcal mol^{-1} is given in Ref. [61]. In Reference Edition [62] the value 150.5 is recommended. We collected in Table 1 some data on the enthalpies of formation for C$_2$H$_3$O^{+} ions (CH$_3$C≡O^{+} and other isomers) gained from their AEs measured by accurate methods of PI, PI-photoelectron coincidence spectroscopy (PIPECO) or electron

Table 1
The enthalpies of formation of $C_2H_3O^+$ ions from AE measurements (in kcal mol^{-1})

N	Precursor molecule	Neutral partner (ΔH_f^0)	ΔH_f^0 $C_2H_3O^+$	Structure of $C_2H_3O^+$ ion	Reference
1.	$CH_3CO{-}OCH{=}CH_2$	$\dot{O}CH{=}CH_2 \leftrightarrow \dot{C}H_2CHO$ (3.7) [63,64]	147.04	$CH_3C{\equiv}O^+$	[a]
2.	$CH_3CO{-}CH_3$	$CH_3^{\cdot}$ (34.8) [25,64]	148.48	$CH_3C{\equiv}O^+$	[65]
			151.48	$CH_3C{\equiv}O^+$	[66]
			152.63	$CH_3C{\equiv}O^+$	[67]
3.	$CH_3CO{-}CH_2CH_2OH$	$\dot{C}H_2CH_2OH$ (−7.4) [64,68]	149.6	$CH_3C{\equiv}O^+$	[69]
4.	$CH_3CO{-}OC_2H_5$	$\dot{O}C_2H_5$(−4.1) [63]	151.6	$CH_3C{\equiv}O^+$	[70]
5.	$CH_3CO{-}COOCH_3$	$\dot{C}OOCH_3$ (−40.4) [63]	152.74	$CH_3C{\equiv}O^+$	[69]
6.	$CH_3CO{-}OH$	$\dot{O}H$ (9.4) [63]	153.28	$CH_3C{\equiv}O^+$ [b]	[67]
7.	$CH_3CO{-}NH_2$	$\dot{N}H_2$ (45.1) [63,64]	152.3	$CH_3C{\equiv}O^+$	[a]
8.	$CH_3CO{-}C_2H_5$	$C_2H_5^{\cdot}$ (26.5) [64]	153.98	$CH_3C{\equiv}O^+$ [b]	[66]
			154.44	$CH_3C{\equiv}O^+$ [b]	[71]
9.	$CH_3CO{-}COOH$	$\dot{C}OOH$ (−47.3) [25,64]	155.67	$CH_3C{\equiv}O^+$ [b]	[69]
		$[CO_2 + H^{\cdot}]$ (42.0) [18]	150.17	$CH_3C{\equiv}O^+$	
10.	$CH_3CO{-}COCH_3$	$CH_3\dot{C}{=}O$ (−5.8) [63]	155.46	$CH_3C{\equiv}O^+$ [b]	[61]
		$\dot{C}H_2CHO$ (0.2) [72]	149.46	$CH_3C{\equiv}O^+$	
		$\dot{C}H_2CHO$ (3.7) [73]	145.96	$CH_3C{\equiv}O^+$	
11.	$CH_3CO{-}H$	$H^{\cdot}$(52.1) [18]	154.77	$CH_3C{\equiv}O^+$ [b]	[67]
			155.69	$CH_3C{\equiv}O^+$ [b]	[38]
			157.53	$CH_3C{\equiv}O^+$ [b]	[38]
12.	$CH_3CO{-}C{\equiv}CH$	$HC{\equiv}C^{\cdot}$ (138.7) [9]	152.1	$CH_3C{\equiv}O^+$	[38]
		(122) [64]	169	$CH_3C{\equiv}O^+$ [b]	
13.	$CH_2{=}CHO{-}H$	$H^{\cdot}$	178.55	$CH_2{=}\overset{+}{C}-OH$	[74]
14.	$CH_2{=}CHO{-}CH_3$	$CH_3^{\cdot}$	183	$CH_2{=}\overset{+}{C}OH$ [b]	[75,76]
15.	Propyleneoxide	$CH_3^{\cdot}$	185.66	$CH_2{=}\overset{+}{C}OH$ [b]	[65]
16.	Ethyleneoxide	$H^{\cdot}$	202.29	$\overset{+}{C}H_2CHO$	[38]
17.	1,4-dioxane	$\dot{O}C_2H_5$	204.4	$\overset{+}{C}H_2CHO$	[77]
		$[CH_2{=}O + Me^{\cdot}]$ (−8.8)	191.5	$HC{\equiv}C\overset{+}{O}H_2$	

[a] This work.

[b] For these ions the contribution of the ions with higher values of enthalpies of formation is suggested (see text).

Table 2
The enthalpies of formation of $C_2H_5C{\equiv}O^+$ ions from AE measurements

Precursor molecule	Neutral partner	ΔH_f^0 ($C_2H_5C{\equiv}O^+$) in kcal mol^{-1}	Reference
$C_2H_5CO{-}CH_3$	CH_3	144	[60]
		142.45	[66]
		136.45	[78]
Cyclo-propanol	H	142	[86]
$C_2H_5CO{-}OCH_3$	$\dot{C}H_3$	138.25	[78]
	$\dot{C}H_2OH$	141.17	[78]
Cyclopentanol	C_2H_5	≤ 139.67	[78]
$C_2H_5C({=}O){-}H$	H	138.53	[38]
		138.30	[78]
$C_2H_5CO{-}C_2H_5$	C_2H_5	138.09	[78]
$C_2H_5CO{-}OH$	OH	135.88	[78]

impact (EI) with monoenergetic electrons. We recalculated and reinterpreted all the data using the experimental AE values (for details see Appendix A). The introduction by Traeger et al. [61,71,78,79] about the thermal energy correction term 3–7 kcal mol^{-1} to the AE$_{exp}$ values which increases the enthalpies of formation of fragment ions was questioned by Holmes [80]. We also question, whether or not, ab initio MO calculations of those correction terms for complex organic ions can give precise values. The obvious source of errors in such calculations is the usage of frequencies of parent molecules, for example, RCHO instead of RC≡O$^+$ ions, which are unknown. Therefore, we used the experimental AE values of the authors (Tables 1 and 2).

Several conclusions can be made from analysis of the data represented in Table 1. For popular molecules like acetaldehyde CH_3CHO and acetone CH_3COCH_3 there are several values of AEs for the $CH_3C{\equiv}O^+$ ion and hence several values for $\Delta H_f^0(CH_3C{\equiv}O^+)$ 148.5–152.6 from acetone and 154.8–155.7 kcal mol^{-1} from CH_3CHO. The variety of the values from acetone can be explained by differences in sensitivities of the instruments and methods. It is reasonable to select the lowest value since the $CH_3C{\equiv}O^+$ ion is the most stable among $C_2H_3O^+$ isomers and one cannot explain the lower value by contribution of the isomers with lower enthalpies of formation. The higher values $>$153–155 kcal mol^{-1} manifest the contribution of the ions with higher ΔH_f^0 values to the ion efficiency curve. For example, it was shown that for fragmentation of the CH_3CO–OH molecule, the $CH_2{=}C^+$–OH isomer contributes to the formation of $CH_3C{\equiv}O^+$ ions [45] thus increasing the ΔH_f^0 value for the latter by shifting the threshold of its formation. The minor contribution of the isomer with higher enthalpy of formation was noticed for acetone [81].

The partial or complete isomerization of the molecular ions before fragmentation is a well-known fact. The detailed analysis of the problem of increasing of experimental AE values and, hence, the enthalpies of formation of fragment ions is given elsewhere [43]. The detailed analysis of experimental and theoretical data made in Ref. [75] leads to the following values of the enthalpies of formation for $C_2H_3O^+$ isomers: 149.5 ($CH_3C{\equiv}\overset{+}{O}$), 178.5 ($CH_2{=}\overset{+}{C}OH$), 204 kcal mol^{-1} ($\overset{+}{C}H_2CHO$). In addition $\Delta H_f^0(HC{\equiv}C\overset{+}{O}H_2)$ 193 kcal mol^{-1} was estimated [25]. Other high energy isomers $CH_3\overset{+}{O}{=}C:$ and cyclic oxiranyl ions were considered in Ref. [45].

Table 1 illustrates the contribution of the isomers with higher ΔH_f^0 values than acetyl ion to the formation of the latter. The correct interpretation of the thermochemical data could be further complicated by the possible variation in stoicheometry of the fragmentation processes which could change the fragment ions ΔH_f^0 values and their structures (items 9 and 17). This can happen, when $C_2H_3O^+$ ions are formed in either one-step or two-step processes. An additional difficulty in gaining the correct thermochemical data for fragment ions can arise from possible isomerization of the part of the molecular ion, which gives free radical. Thus, the production of $CH_3\dot{C}HOH$ instead of $C_2H_5O^{\cdot}$ (or mixture of both) (items 4 and 17) or instead of $\dot{C}H_2CH_2OH$ (item 3) will increase the resulting value of the enthalpy of formation for the $C_2H_3O^+$ ion. Similarly, partial or complete isomerization of the free radical part in 2,3-butanedione (item 10) will decrease the ΔH_f^0 value of the $CH_3C{\equiv}O^+$ ion. One of the possible ways for molecular ions $CH_3COR^{\rceil\cdot+}$ isomerization is its enolization. The lower value of the ΔH_f^0 $CH_2{=}C(OH)R^{\rceil\cdot+}$ as compared with its tautomer $CH_3COR^{\rceil\cdot+}$ [56] is the driving force for such isomerization. The newly born molecular ion can produce, after further isomerization, any of the $C_2H_3O^+$ isomers or their mixtures [43].

To verify the value of ΔH_f^0 $CH_3C{\equiv}O^+$ ion we measured AE($C_2H_3O^+$) 9.80 eV from CH_3COO-$CH{=}CH_2$ molecules (IE 9.43 eV, $\Delta H_f^0(M) -$ 75.26 kcal mol^{-1} [15,16]] and taking ΔH_f^0 3.7 kcal mol^{-1} [63,64] for the $CH_2{=}CHO^{\cdot} \leftrightarrow \dot{C}H_2CHO$ radical we obtain $\Delta H_f^0(CH_3C{\equiv}O^+)$ 147.04 kcal mol^{-1}. If the lower values 3.0 [25] or 0.2 kcal mol^{-1} [72] for the $\dot{O}CH{=}CH_2$ free radical are applied, then ΔH_f^0 $CH_3C{\equiv}O^+$ will shift to 147.7 or 150.5 kcal mol^{-1}, respectively.

We also measured by PI MS IE 8.87 eV, AE $(M$–$OMe)^+$ 10.87 eV and AE$(M - MeOH)^{\cdot+} \le 10.97 \pm$ 0.1 eV from $PhCH_2COOMe$ molecules. The ion current for the M–MeOH$^{\rceil\cdot+}$ ion was very weak so we could not get reliable values for the $PhCH{=}C{=}O^{\rceil\cdot+}$ enthalpy of formation. From AE M–OMe$^{\rceil+}$, ΔH_f^0 ($PhCH_2COOMe$) -71.13 (estimated by the additive scheme [25,82]) and ΔH_f^0 ($\dot{\mathrm{O}}\mathrm{Me}$) 4.2 kcal mol^{-1} [63] we obtained ΔH_f^0 ($\mathrm{PhCH_2C{\equiv}O^+}$) 175.33 kcal mol^{-1}. When we involve this value in the isodesmic reaction (Eq. (14)), which reflects the relative stabilities of $\mathrm{CH_3C{\equiv}O^+}$ and $\mathrm{PhCH_2C{\equiv}O^+}$ ions we find out that $\mathrm{PhCH_2C{\equiv}O^+}$ ion is by ≈2.6 kcal mol^{-1} more stable than the $\mathrm{CH_3C{\equiv}O^+}$ ion if the value 149.5 kcal mol^{-1} [25] for the latter is used. At higher values for ΔH_f^0 $\mathrm{CH_3C{\equiv}O^+}$ ion Q values in Eq. (14) become 9–10 kcal mol^{-1} (ΔH_f^0 and Q in kcal mol^{-1})

$$\underset{\substack{149.5[25]\\156[60,17]\\156.67[61]}}{\mathrm{CH_3C{\equiv}O^+}} + \underset{-11.31\mathrm{est}}{\mathrm{PhCH_2CHO}} \longrightarrow \underset{-39.73[15]}{\mathrm{CH_3CHO}} + \underset{175.33}{\mathrm{PhCH_2C{\equiv}O^+}} + \underset{\substack{+2.6\\+9.1\\+9.8}}{Q} \tag{14}$$

Since the H → Ph replacement in the $\mathrm{RCH_2C{\equiv}O^+}$ ion takes place in a non-conjugated and relatively remote β-position to positive charge, one expects a small stabilization of the cationic center caused only by polarizability of the Ph-group. If we compare, for example, the values of proton affinities PAs of some bases B: we shall realize that the ΔPAs values at H → Ph replacement in the β-position to the protonation site, which reflect the relative stabilities of the $\mathrm{BH^+}$ ions are rather small: ΔPA($\mathrm{H{-}CH_2\ddot{N}H_2} \rightarrow \mathrm{Ph - CH_2\ddot{N}H_2}$) 2.7 kcal mol^{-1} (from PAs 214.1 and 216.8 kcal mol^{-1}, respectively [83]) or 3.0 kcal mol^{-1} for $\mathrm{H - CH_2\ddot{N}Me_2} \rightarrow \mathrm{Ph - CH_2\ddot{N}Me_2}$ replacement (PAs 225.1 and 228.1 kcal mol^{-1}, respectively [83]). Hence, the experimental value of ΔH_f^0 ($\mathrm{PhCH_2C{\equiv}O^+}$) supports the low (149.5 kcal mol^{-1}) value for ΔH_f^0 $\mathrm{CH_3C{\equiv}O^+}$ (Eq. (14)).

Taking the ΔH_f^0 value 149.5 kcal mol^{-1} [25] for the $\mathrm{CH_3C{\equiv}O^+}$ ion and the known PA values for ketene $\mathrm{CH_2{=}C{=}O}$ 192.9 ± 2 [84], 195.3 ± 0.7 [85] or 198.0 kcal mol^{-1} [17,83] we obtain ΔH_f^0 ($\mathrm{CH_2{=}C{=}O}$) −23.3, −20.9 or −18.2 kcal mol^{-1}, respectively, from the known equation [83]

$$\begin{aligned}\Delta H_f^0(\mathrm{CH_2{=}C{=}O}) &= \Delta H_f^0(\mathrm{CH_3C{\equiv}O^+})\\ &\quad - \Delta H_f^0(\mathrm{H^+})\ (365.7\ [82]\ \mathrm{kcal\ mol^{-1}})\\ &\quad + \mathrm{PA}(\mathrm{CH_2{=}C{=}O})\end{aligned}$$

We again see that the thorough inspection of the thermochemistry of the $\mathrm{CH_3C{\equiv}O^+}$ ion leads to a lower value of ΔH_f^0 for the $\mathrm{CH_2{=}C{=}O}$ molecule than is currently accepted.

Now we make a brief analysis of the values of the enthalpies of formation for the $\mathrm{RC{\equiv}O^+}$ ions (R = alkyl). The known data for the $\mathrm{C_2H_5C{\equiv}O^+}$ ions are given in Table 2. We recalculated all the data using experimental AE values (for details see Appendix A).

The Q values in isodesmic reactions (Eqs. (15)–(17)) reflect the tendencies in the stabilization of the $\mathrm{RC{\equiv}O^+}$ ions at $\mathrm{CH_3} \rightarrow \mathrm{C_2H_5}$, $\mathrm{C_2H_5} \rightarrow n$-Pr and $\mathrm{C_2H_5} \rightarrow \mathrm{(CH_3)_2CH}$ replacement (the derived values are given in square brackets).

$$\underset{(\mathrm{kcal\ mol^{-1}})}{\Delta H_f^0}\quad \underset{\substack{156[60,17]\\149.5[25]\\ [149]}}{\mathrm{CH_3C{\equiv}O^+}} + \underset{-44.36[15]}{\mathrm{C_2H_5CHO}} \longrightarrow \underset{\substack{138.5\text{–}142\\138.5[78]\\ [140.5]}}{\mathrm{C_2H_5C{\equiv}O^+}} + \underset{-39.73[15]}{\mathrm{CH_3CHO}} + \underset{\substack{12.9\text{–}9.4\\6.4\\3.9}}{Q} \tag{15}$$

$$\underset{\substack{138.5[78]\\ \\ [140.5]}}{\mathrm{C_2H_5C{\equiv}O^+}} \longrightarrow \underset{\substack{134.5[66]\\125.94[87]\\134.5[66]\\125.9[87]}}{n - \mathrm{C_3H_7C{\equiv}O^+}} + \underset{\substack{-0.6\\+8.0\\+1.4\\+9.9}}{Q} \tag{16}$$

$$\underset{\substack{138.5\\140.5}}{\mathrm{C_2H_5C{\equiv}O^+}} \longrightarrow \underset{\substack{131.7[66]\\131.7\\ [131]}}{\mathrm{(CH_3)_2CHC{\equiv}O^+}} + \underset{\substack{-0.42\\+1.58\\ [2.3]}}{Q} \tag{17}$$

The low value of ΔH_f^0 (n-$\mathrm{C_3H_7C{\equiv}O^+}$) obtained from PEPICO studies [87] of PrCOOH molecules could be explained, possibly, by the contribution of the low energy ion pair formation $\mathrm{PrC{\equiv}O^+ + HO^-}$. Finally, we suggest the following values of the enthalpies of formation for acyl ions as a compromise to the different literature values (Eq. (18)) (ΔH_f^0 and Q values in kcal mol^{-1}).

The tendencies in stabilization of acyl ions at H → Me replacement in the β-position to the cationic center Eq. (18) are supported by the tendencies in the IE change (ΔIE values) in $\mathrm{C_6H_5R}$, $\mathrm{CH_2{=}CHR}$ and $\mathrm{HC{\equiv}CR}$ compounds (R = Me, Et, n-Pr, $\mathrm{Me_2CH}$) [38,62]. We take notice that $-\Delta\mathrm{IE} = -[\mathrm{IE(C_6H_5Me)} - \mathrm{IE(C_6H_5Et)}] = Q$ for the corresponding isodesmic reaction with radical ions $\mathrm{C_6H_5Me^{\urcorner\cdot+}} \rightarrow \mathrm{C_6H_5Et^{\urcorner\cdot+}}$. Since the IE of any free radical, i.e. $\mathrm{R\dot{C}{=}O}$ gives the main numerical contribution to the total value of $\Delta H_f^0[\mathrm{R - C^+{=}O}] = \Delta H_f^0(\mathrm{R - \dot{C}{=}O}) + \mathrm{IE}[\mathrm{R - \dot{C}{=}O}]$ the comparison of the tendencies in the $\Delta\Delta H_f^0$

$$\begin{tikzcd} \underset{149}{CH_3C\equiv O^+} \arrow[r, "+3.9"] & \underset{140.5}{CH_3CH_2C\equiv O^+} \arrow[r, "+1.4"] \arrow[d, "+2.3"] & \underset{134.5[66]}{CH_3CH_2CH_2C\equiv O^+} \\ & \underset{131}{(CH_3)_2CHC\equiv O^+} & \end{tikzcd} \tag{18}$$

shift at $CH_3 \rightarrow C_2H_5 \rightarrow n\text{-}C_3H_7$ (or iso-C_3H_7) replacement at the ionization center in the free radical and in the neutral molecule is justified. Those shifts in Δ IE are small 0.1–0.2 eV (2–4 kcal mol^{-1}) [38,62] since the substitution takes place at the β-position to the ionization center. Hence, the value 156 kcal mol^{-1} for the $CH_3C{\equiv}O^+$ ion is doubtful since it gives very high *Q* values (9–3 kcal mol^{-1}) for β-(H → CH_3) substitution in the $CH_3C{\equiv}O^+ \rightarrow C_2H_5C{\equiv}O^+$ isodesmic reaction. It is possible that the ΔH_f^0 ($CH_3C{\equiv}O^+$) value should be decreased to 148–147 kcal mol^{-1}. Consequently, the ΔH_f^0 values of other $RC{\equiv}O^+$ ions in Eq. (18) will be shifted down as well.

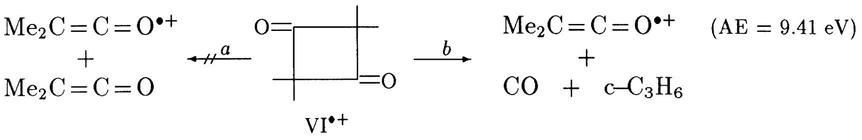
5. Thermochemistry of substituted ketenes and its heteroanalogs

The data for ΔH_f^0 (MeCH=C=O) is a matter of controversy. Its enthalpy of formation could be derived from PA(MeCH=C=O) and ΔH_f^0 ($EtC{\equiv}O^+$) 140.5 kcal mol^{-1} (see above). Although two publications give close values of PA MeCH=C=O 201.96 [84] and 201.24 [85] leading to ΔH_f^0 (MeCH=C=O) −23.24 and −23.96 kcal mol^{-1}, respectively, the PA values for other compounds measured in these works are doubtful thus making the PA data on MeCH=C=O questionable. Thus, the measured PA($Me_2C{=}CH_2$) 197.9 kcal mol^{-1} is given in Ref. [84] whereas the recently obtained values are 192.83 [88] and 191.68 kcal mol^{-1} [89]. The PA value, 205.5 kcal mol^{-1} for $HN{=}CH_2$ [85], combined with ΔH_f^0 ($C^+H_2NH_2$) 178 kcal mol^{-1} [17] gives the improbably low value of 18 kcal mol^{-1} for the $HN{=}CH_2$ molecule whereas other workers gained from experiments, values of 22–26 (see Ref. [90]) or even 32 kcal mol^{-1} [17]. The ΔH_f^0 − (23–24) kcal mol^{-1} for MeCH=C=O does not coincide with the value −23 kcal mol^{-1} for $CH_2{=}C{=}O$, obtained in this work. If Benson's additive scheme is applied [82] then we get ΔH_f^0 (MeCH=C=O) ≈ −30.5 kcal mol^{-1} based on ΔH_f^0 ($CH_2{=}C{=}O$) −23 kcal mol^{-1}.

Now we consider the thermochemistry of the $Me_2C{=}C{=}O$ molecule. We reinterpreted the data of Aubry et al. [14] (see Appendix A) and gained ΔH_f^0 ($Me_2C{=}C{=}O$) −37.3 kcal mol^{-1} from AE $PhOH^{\cdot+}$ being produced in the process $PhOCOCHMe_2^{\cdot+} \rightarrow PhOH^{\cdot+} + Me_2C{=}C{=}O$. Similarly, from AE $Me_2C{=}C{=}O^{\cdot+}$ (in the process $PhOCOCHMe_2 \rightarrow Me_2C{=}C{=}O^{\cdot+} + PhOH$) and IE ($Me_2C{=}C{=}O$) 8.38 [17] or 8.45 eV [91] we obtained ΔH_f^0 ($Me_2C{=}C{=}O$) −34.10 or −35.71 kcal mol^{-1}, respectively. We also suggest the different stoicheometry of the $Me_2C{=}C{=}O^{\cdot+}$ ion formation at its threshold from 2,2,4,4-tetramethylcyclobutanedione-1,3 (VI) which coincides with CO elimination from the molecular ion $VI^{\cdot+}$ [14] (Scheme 7).

Taking AE($Me_2C{=}C{=}O^{\cdot+}$) 9.41 eV [92] from compound VI and IEs 8.38 [17] or 8.45 eV [91] for $Me_2C{=}C{=}O$ we have ΔH_f^0 ($Me_2C{=}C{=}O$) −36.31 or −37.92, respectively. Finally, we take ΔH_f^0 ($Me_2C{=}C{=}O$) −37 kcal mol^{-1}.

Now we consider in detail the effect of Me-substitution in ketene. There are two sets of data on $\Delta\Delta H_f^0$



Scheme 7.

Table 3
The thermochemistry of substituted alkenes at H → Me, (ΔH_f^0 in kcal mol^{-1})

	ΔH_f^0	$\Delta\Delta H_f^0$
$CH_2{=}CH_2$	12.55 [16]	
$CH_2{=}CHBr$	18.93 [16]	
$CH_2{=}CHCHO$	−16.84 [25]	
$CH_2{=}CHCOOH$	−79.04 [94]	
$MeCH{=}CH_2$	4.78 [16]	−7.77
Z–MeCH=CHBr	9.75 [16]	−9.18
E–MeCH=CHBr	10.49 [16]	−8.70
Z–MeCH=CHCHO	−26.22 [94]	−9.38
E–MeCH=CHCOOH	−88.07 [94]	−9.03

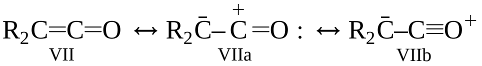
values in

$$CH_2{=}C{=}O \xrightarrow{\Delta\Delta H_f^0(1)} MeCH{=}C{=}O \xrightarrow{\Delta\Delta H_f^0(2)} Me_2C{=}C{=}O$$

molecules. Aubry et al. [14] and Deming et al. [93] advocate the high values for $\Delta\Delta H_f^0$ (1) −9.8 [14] or −13.6 [93] and $\Delta\Delta H_f^0$ (2) −10.0 [14] or $-12\ \mathrm{kcal\ mol^{-1}}$ [93], respectively. Scott et al. [10] computed −3.85 and $-5.75\ \mathrm{kcal\ mol^{-1}}$, respectively, for $\Delta\Delta H_f^0$ (1) and $\Delta\Delta H_f^0$ (2). Our analysis of thermochemistry of methylated ketenes and related compounds gives the following results. We found a few but quite clear examples that H → Me substitution in alkenes possessing strong electron-withdrawing substituents provokes larger stabilization than in alkenes lacking such substituents (Table 3).

Electron withdrawing groups (Br, CHO, COOH) induce the positive charge at the terminal C_d atom. Therefore Me group response is higher than at the C_d atom in molecules lacking such groups, i.e. $MeCH{=}CH_2$. Since=C=O in ketene is a strong electron-withdrawing group the authors of Refs. [14,93] suggest an even stronger response of the Me group in ketenes than in alkenes.

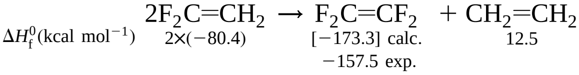
However, the structure of ketene and its substituted analogs differs drastically from that of alkenes [95]:



$$\underset{\text{VII}}{R_2C{=}C{=}O} \leftrightarrow \underset{\text{VIIa}}{R_2\bar{C}{-}\overset{+}{C}{=}O:} \leftrightarrow \underset{\text{VIIb}}{R_2\bar{C}{-}C{\equiv}O^+}$$

The contribution of resonance forms VIIa ↔ VIIb to ketene's molecule VII was supported by IR frequencies shifts in $(4{-}XC_6H_4)_2C{=}C{=}O$ molecules, where X = MeO, H or CN and by some other data [95]. The electron-withdrawing CN group stabilizes the negative charge in the VIIa ↔ VIIb form whereas the electron-releasing MeO-group destabilizes such a charge. Methyl is an electron-releasing group, therefore, in alkanes lacking the atoms with high electronegativities (ENs), the $\Delta\Delta H_f^0(H \rightarrow Me)$ shift is only $-5\ \mathrm{kcal\ mol^{-1}}$. [15,16,82] as compared, with $\Delta\Delta H_f^0 - 7.77$ [15,16] or $-10.35\ \mathrm{kcal\ mol^{-1}}$ [15,16] at $CH_2{=}CH_2 \rightarrow MeCH{=}CH_2$ and $HC{\equiv}CH \rightarrow MeC{\equiv}CH$ replacement, respectively, owing to the higher ENs of atoms in **sp**$_2$ and **sp** hybridization states. We think that computation [10] correctly reveals these tendencies at least qualitatively giving low $-(4\text{–}6)\ \mathrm{kcal\ mol^{-1}}$ for $\Delta\Delta H_f^0$ values at H → Me substitution in ketene. It is obvious that Me would destabilize the negative charge in ketene. For example, compare electron affinities (EAs) [17] 1.83(OH) and 1.58(OMe) or 2.31(SH) and 1.87 eV (SMe). Taking −23 and $-37\ \mathrm{kcal\ mol^{-1}}$ for $\Delta\Delta H_f^0$ values for $CH_2{=}C{=}O$ and $Me_2C{=}C{=}O$ molecules, respectively (see above) and following the tendencies in $CH_2{=}CH_2 \xrightarrow{(1)} MeCH{=}CH_2 \xrightarrow{(2)} Me_2C{=}CH_2$[$\Delta\Delta H_f^0(1)$ and $\Delta\Delta H_f^0(2)$ are −7.77 [15,16] and $-8.78\ \mathrm{kcal\ mol^{-1}}$ [15,16], respectively] we get ΔH_f^0 ($MeCH{=}C{=}O$) $-29.5\ \mathrm{kcal\ mol^{-1}}$ with −6.5 and $-7.5\ \mathrm{kcal\ mol^{-1}}$ for $\Delta\Delta H_f^0(1)$ and $\Delta\Delta H_f^0(2)$, respectively, for $CH_2{=}C{=}O \xrightarrow{(1)} MeCH{=}C{=}O \xrightarrow{(2)} Me_2C{=}C{=}O$ substitution.

Taking the new value for ΔH_f^0 ($CH_2{=}C{=}O$) $-23\ \mathrm{kcal\ mol^{-1}}$ we estimated the enthalpies of formation for some substituted ketenes (for details see Appendix A). We used both macro- and microincremental (Benson's) schemes introducing minor correction terms for repulsion of electron-withdrawing halogen and the CO-group. These correction terms were estimated using the isodesmic reactions like Eq. (19) (ΔH_f^0 values—from Refs. [15,16]).



$$\underset{\Delta H_f^0(\mathrm{kcal\ mol^{-1}})}{} \quad \underset{2\times(-80.4)}{2F_2C{=}CH_2} \rightarrow \underset{\substack{[-173.3]\ \text{calc.} \\ -157.5\ \text{exp.}}}{F_2C{=}CF_2} + \underset{12.5}{CH_2{=}CH_2} \tag{19}$$

Eq. (19) displays the destabilization of $-157.5 - (-173.5) = 16\ \mathrm{kcal\ mol^{-1}}$ owing to the repulsion between two CF_2-groups. The electron-withdrawing properties of CO- and CF_2-groups are similar: compare ENs (covalent potentials) 2.83 and 2.84 for the OCH- and F_2CH-groups, respectively [96]. Hence, taking the CF_2-group as a model for the CO-group we used the known values of the enthalpies of formation for $X(Y)C{=}CH_2$ and $X(Y)C{=}CF_2$ ethylenes for calculation of the enthalpies of formation for target X(Y)C=C=O molecules.

When we compare the ΔH_{acid} values (deprotonation enthalpies) for $PhCH_3$ (381), Ph_2CH_2 (361.5), CH_2F_2 (390), CH_3Cl (396), CH_2Cl_2 (374),CH_3Br (393) and CH_3I (386.5 kcal mol^{-1}) (all data—from Ref. [17]) we see that most of the compounds are very weak acids and the participation of the resonance form VIIa is hardly expected.

For $Ph_2C{=}C{=}O$ and $Cl_2C{=}C{=}O$ we introduced the small $-(1–1.5)$ correction terms reflecting the possible contribution of the VIIa ↔ VIIb form. Finally, we obtained the following new values of the enthalpies of formation ΔH_f^0 (in kcal mol^{-1}): PhCH=C=O (−0.2), $Ph_2C{=}C{=}O$ (21.5), FCH=C=O (−60.0), $F_2C{=}C{=}O$ (−100.5), ClCH=C=O (−22.5), $Cl_2C{=}C{=}O$ (−25), BrCH=C=O (−11), ICH=C=O (2). The values for phenylated ketenes differ from earlier calculated values 6 [93] or 17.3 kcal mol^{-1} [11] for PhCH=C=O and 29 kcal mol^{-1} [93] for $Ph_2C{=}C{=}O$ molecules. Our values for FCH=C=O and $F_2C{=}C{=}O$ values differ drastically from recently computed values [7] −35.2 and −69.4 kcal mol^{-1}, respectively. If we take the authors' values for ketene −12.4 (or −9.7) we get $\Delta\Delta H_f^0$ shifts −22.8 (or −25.5) and −34.2 kcal mol^{-1} for $CH_2{=}C{=}O \rightarrow FCH{=}C{=}O \rightarrow F_2C{=}C{=}O$ substitution. Taking $\Delta H_f^0(CH_2{=}C{=}O)$ − 23 kcal mol^{-1} we have only −12 kcal mol^{-1} for H → F replacement: compare $\Delta\Delta H_f^0$ −45 and −47 kcal mol^{-1} for $CH_2{=}CH_2 \rightarrow FCH{=}CH_2 \rightarrow F_2C{=}CH_2$ substitution, respectively (from Refs. [15,16]). We do not see any chemical reasons for such high destabilization of fluorinated ketenes as compared with fluorinated ethylenes. For example, repulsion in tetrafluoroethylene C_2F_4 destabilizes the molecule as compared with $F_2C{=}CH_2$ only by 16 kcal mol^{-1} (Eq. (19)).

For unknown reasons the computation of the enthalpies of formation for fluorinated molecules very often gives unreliable results. In addition to the examples considered above we represent such a simple molecule as FC≡CH. The computation of its enthalpy of formation gives the values 24.7, (25.3) [97] or 25.3 kcal mol^{-1} [98] whereas the enthalpic shift procedure from either $FCH{=}CH_2$ or HC≡COH molecules using $\Delta\Delta H_f^0(RCH{=}CH_2 \rightarrow RC{\equiv}CH) \sim 40$ [15,16] or $\Delta\Delta H_f^0(ROH \rightarrow RF) \sim -4$ kcal mol^{-1} [36] leads to the values 6.5 or 6 kcal mol^{-1}, respectively. The reference book [99] gives ΔH_f^0 (FC≡CH) 10.0 kcal mol^{-1}.

From the value −23 kcal mol^{-1} for ΔH_f^0 (ketene) the unknown values of the enthalpies of formation for some structurally related compounds could be derived (Eqs. (20)–(22)) with the help of the enthalpic shift procedure (see Eqs. (4) and (5)) (ΔH_f^0 and $\Delta\Delta H_f^0$—in kcal mol^{-1}) the derived

$$\begin{tikzcd}
\begin{matrix}CH_2=C=CH_2\\ 45.5[15]\end{matrix} \arrow[d, "\Delta\Delta H_f^o"', "{[+21]}"] & \begin{matrix}CH_2=C=O\\ -23\end{matrix} \arrow[l, "+68.5"'] \arrow[d, "+21"] \arrow[dr, "+62"] & \\
\begin{matrix}CH_2=S=CH_2\\ {[66.5]}\end{matrix} & \begin{matrix}CH_2=S=O\\ -2[37]\end{matrix} \arrow[l, "{[+68.5]}"'] & \begin{matrix}CH_2=C=S\\ 39[17]\end{matrix}
\end{tikzcd} \tag{20}$$

$$\begin{tikzcd}
\begin{matrix}O=S=O\\ -71[31]\end{matrix} \arrow[r, "+69"] & \begin{matrix}CH_2=S=O\\ -2\end{matrix} \arrow[r, "{[+69]}"] \arrow[d, "{[+62]}"] & \begin{matrix}CH_2=S=CH_2\\ {[67]}\end{matrix} \\
 & \begin{matrix}CH_2=S=S\\ {[60]}\end{matrix} &
\end{tikzcd} \tag{21}$$

values are in square brackets):

$$\begin{tikzcd}
\begin{array}{c}S=C=S\\28[32]\end{array} & \begin{array}{c}O=S=O\\-71[32]\end{array} \arrow[d, "+61"] & \begin{array}{c}S=C=S\\28\end{array} \arrow[d, "{[+23]}"] \\
\begin{array}{c}O=C=S\\-34[15]\end{array} \arrow[u, "+62"] \arrow[r, "+24"] & \begin{array}{c}O=S=S\\-10[82]\end{array} \arrow[r, "{[+61]}"] & \begin{array}{c}S=S=S\\ {[51]}\end{array}
\end{tikzcd} \qquad (22)$$

It is noteworthy that the =S=O → =S=S substitution gives nearly identical enthalpic shift $\Delta\Delta H_f^0$ with that for =C=O → =C=S substitution of 61–62 kcal mol^{-1}. =C= → =S= substitution gives 21–23 kcal mol^{-1} enthalpic shift. The latter could be more certain if the lower value −24 kcal mol^{-1} is taken for ΔH_f^0 (CH$_2$=C=O). It is noteworthy that the linear molecule S=S=S is less stable than its cyclic isomer S$_3$ (ΔH_f^0 34 ± 2 kcal mol^{-1} [17]). In Table 4 we represent our computed data on ΔH_f^0 values for ketene and its heteroanalogs. We see that A=B=C molecules are yet difficult for computation. Among the computational methods being tried, MINDO/3 appeared to be the most reliable. It is demonstrated that the enthalpic shift procedure could be an alternative to computation.

6. Thermochemistry of ketene's fragments

From the known values of the deprotonation enthalpies ΔH_{acid} for PhCH_3 and HC≡CCH_3 380.7 [17] and 381.8 kcal mol^{-1}, respectively (the latter value was calculated from ΔH_{acid} 380.5 kcal mol^{-1} [17] for allene CH$_2$=C=CH_2 and EA 0.893 eV for CH$_2$=C=$\dot{C}$H ↔ $\dot{C}$H$_2$C≡CH free radical-from Ref. [17]) we suggest the similar ΔH_{acid} values for PhOH and HC≡COH molecules. Taking the ΔH_{acid} for PhOH 349.2, 350.4 kcal mol^{-1} [17] we estimated ΔH_{acid}(HC≡COH) ~ 350 kcal mol^{-1}. The electron-withdrawing properties of HC≡C− as compared with the Ph-group are higher (compare ENs [96] 3.00 and 2.74, respectively, σ_p, [100] 0.23 and −0.01 or F(field) [100]—constants 0.22 and 0.12, respectively). However, for negative ions the exclusively high importance of the polarizability effect [101,102] (which is larger for Ph than for the HC≡C-group) makes ΔH_{acid} values for PhXH and HC≡CXH nearly identical. Taking ΔH_{acid}(HC≡COH) 350 kcal mol^{-1} we have ΔH_f^0 (HC≡CO$^-$) = ΔH_{acid}(HC≡COH) − ΔH_f^0(H$^+$) − ΔH_f^0 (HC≡COH) = 350 − 365.7+ 10.0 = −5.7 kcal mol^{-1} and combining the latter value with EA, (HC≡C$\dot{O}$) 2.350 eV [17] (54.2 kcal mol^{-1})

Table 4
Computed values of the enthalpies of formation ΔH_f^0 (gas) of ketene and its heteroanalogs (in kcal mol^{-1})

Molecule	Method				Experimental
	MNDO	AM1	PM3	MINDO/3	
H$_2$C=C=CH$_2$	43.87	46.05	46.98	41.89	45.5 [15,16]
H$_2$C=C=O	−6.83	−5.71	−9.27	−20.74	−23[a]
O=C=O	−75.08	−79.85	−85.08	−95.73	−94.1 [82]
O=S=O	4.43[b]	−47.03	−50.79	−70.72	−70.9 [82]
	(106.8°)[b]	(107.9°)	(106.08°)	(130.6°)	
O=S=O (linear, 180°)	120.26	28.22	31.20	−57.81	−70.9
O=S=O (with fixed angle)	58.85	3.05	0.99	−57.81	−70.9
	(154.4°)	(158.6°)	(156.9°)	(180°C)	
S=C=O (linear)	−22.91	−28.98	−23.77	−50.61	−34 [82]
S=S=O	44.71	9.94	14.55	−0.01	−10 [82]
H$_2$C=S=O	29.56	−8.92	−2.42	+14.03	−1.9 [37]
H$_2$C=S=CH$_2$	61.81	37.47	52.10	82.04	60[a]
S=S=S	73.69	32.16	44.01	73.1	51[a]
	(114.5°)	(180°)	(180°)	(180°)	
S=S=S (fixed, 180°)	110.98	32.16	44.01	73.1	

[a] This work.

[b] The central angle ∠A=B=C is given.

we get $\Delta H_f^0(\mathrm{HC{\equiv}C\dot{O}} \leftrightarrow \mathrm{H\dot{C}{=}C{=}O}) = -5.7 + 54.2 = 48.5\ \mathrm{kcal\ mol^{-1}}$. The literature values for $\Delta H_f^0(\mathrm{HC{\equiv}CO^{\cdot}} \leftrightarrow \mathrm{\dot{C}H{=}C{=}O})$ are 28.8 ± 2.0 [103] or $42.2 \pm 0.7\ \mathrm{kcal\ mol^{-1}}$ [104]. To make the choice for the $\Delta H_f^0(\mathrm{HC{\equiv}C\dot{O}})$ value among the quoted ones we use the isodesmic reactions (Eqs. (20)–(22)). We would like to stress that the submillimeter-wave spectra, [105] of species obtained by two reactions $\mathrm{HC{\equiv}CH + O \rightarrow HC{\equiv}CO^{\cdot}}$ and $\mathrm{H_2C{=}C{=}O + F^{\cdot} \rightarrow H\dot{C}{=}C{=}O}$ are identical supporting the structure of the $\mathrm{C_2HO^{\cdot}}$ free radical as $\mathrm{\dot{C}H{=}C{=}O \leftrightarrow HC{\equiv}CO^{\cdot}}$.

In our recent publication [64] the general principles and rules of quantification of structure–stability relationships for free radicals using series of isodesmic reactions were represented. Using many examples it was demonstrated that the thermodynamically less stable free radical extracts a larger stabilizing effect from the same substituent (say, Me, Ph, HC≡C) than the more stable one. For example (from Ref. [64] (Eq. (23)) (ΔH_f^0 values of free radicals in $\mathrm{kcal\ mol^{-1}}$ are given under the formulae, Q values—at the arrows):

$$\begin{tikzcd}
\underset{34.8}{\mathrm{CH_3^{\bullet}}} \arrow[r, "+6.0"] \arrow[d, "Q"', "-14.6"] & \underset{26.5}{\mathrm{MeCH_2^{\bullet}}} \arrow[r, "+12.0"] \arrow[d, "-5.8"] & \underset{46.5}{\mathrm{PhCH_2^{\bullet}}} \arrow[d, "-1.9"] \\
\underset{9.4}{\mathrm{HO^{\bullet}}} \arrow[r, "+14.9"] & \underset{4.2}{\mathrm{MeO^{\bullet}}} \arrow[r, "+15.8"] & \underset{13.4}{\mathrm{PhO^{\bullet}}}
\end{tikzcd} \quad (23)$$

The isodesmic reactions are given in the short form. For example, $\mathrm{CH_3^{\cdot} \rightarrow HO^{\cdot}}$ ($Q = -14.6\ \mathrm{kcal\ mol^{-1}}$) is the short form of the isodesmic reaction $\mathrm{CH_3^{\cdot} + H_2O \rightarrow CH_4 + \dot{O}H} + Q$, and hence, $Q = \Delta H_f^0(\mathrm{\dot{C}H_3}) + \Delta H_f^0(\mathrm{H_2O}) - \Delta H_f^0(\mathrm{CH_4}) - \Delta H_f^0(\mathrm{\dot{O}H}) = 34.8 - 57.8 - (-17.8) - 9.4 = -14.6\ \mathrm{kcal\ mol^{-1}}$. We use the short form of the isodesmic reaction, omitting the molecules whose structures are obvious. The positive sign ($Q > 0$) reveals stabilization, i.e. $\mathrm{Me\dot{C}H_2}$ is by $6\ \mathrm{kcal\ mol^{-1}}$ more stable than the $\mathrm{CH_3^{\cdot}}$ free radical whereas the negative sign manifests destabilization, i.e. $\mathrm{HO^{\cdot}}$ is by $14.6\ \mathrm{kcal\ mol^{-1}}$ less stable thermodynamically than the $\mathrm{CH_3^{\cdot}}$ free radical in the framework of isodesmic reactions.

O-centered free radicals $\mathrm{RO^{\cdot}}$ (R = H, Me, Ph) (Eq. (23)) are less stable than C-centered free radicals $\mathrm{RCH_2^{\cdot}}$ owing to the larger electronegativity of the oxygen as compared with carbon. Therefore, O-centered radicals extract larger stabilization from the same substituent, here Me or Ph, than the more stable C-centered radicals (compare the Q values 6.0 and 14.9 or 12.0 and 15.8 $\mathrm{kcal\ mol^{-1}}$). The detailed discussion of Eq. (23) was necessary before we introduce to the reader the estimation procedure of $\Delta H_f^0(\mathrm{HC{\equiv}CO^{\cdot}} \leftrightarrow \mathrm{H\dot{C}{=}C{=}O})$ free radicals, which is given in Eqs. (24) and (25) (ΔH_f^0 values of free radicals in $\mathrm{kcal\ mol^{-1}}$ are given below the formulae and Q values—at the arrows; the derived values are in square brackets)

$$\begin{tikzcd}
\underset{13.4[64]}{\mathrm{PhO^{\bullet}}} \arrow[r, "+4.0?", "Q'"'] \arrow[d, "+1.94"] & \underset{42.4[17]}{\mathrm{HC{\equiv}CO^{\bullet}}} \arrow[d, "Q''"', "-4.62"] \\
\underset{46.5[64]}{\mathrm{PhCH_2^{\bullet}}} \arrow[r, "-2.5", "Q'''"'] & \underset{81.4[17,\ 64]}{\mathrm{HC{\equiv}CCH_2^{\bullet}}}
\end{tikzcd} \quad (24)$$

$$\begin{tikzcd}
\mathrm{PhO^{\bullet}} \arrow[r, "{[-2]}"] \arrow[d, "+1.94"] & \underset{[48.5]}{\mathrm{HC{\equiv}C{-}O^{\bullet}}} \arrow[d, "{[+1.5]}"] \\
\mathrm{Ph\dot{C}H_2} \arrow[r, "-2.5"] & \mathrm{HC{\equiv}C\dot{C}H_2}
\end{tikzcd} \quad (25)$$

The negative Q''' value $-2.5\ \mathrm{kcal\ mol^{-1}}$ for the $\mathrm{PhCH_2^{\cdot} \rightarrow HC{\equiv}CCH_2^{\cdot}}$ isodesmic reaction reveals the well-known fact that the HC≡C-group is an electron-withdrawing group as compared with Ph. For example, σ_p-constants are $+0.23$ and -0.01 for HC≡C-and Ph-groups, respectively, and R-(resonance) constants are 0.01 and -0.13, respectively [100].Therefore one expects that $Q' < 0$ (Eq. (24)) as well for the $\mathrm{PhO^{\cdot} \rightarrow HC{\equiv}CO^{\cdot}}$ isodesmic reaction. The negative Q'' value of $-4.6\ \mathrm{kcal\ mol^{-1}}$ for $\mathrm{HC{\equiv}CO^{\cdot} \rightarrow HC{\equiv}CCH_2^{\cdot}}$ is doubtful because is skeptical whether the O-centered free radical is more (by $4.6\ \mathrm{kcal\ mol^{-1}}$) stable than the C-centered free radical (compare with Eq. (23)). The value $48.5\ \mathrm{kcal\ mol^{-1}}$ for $\Delta H_f^0(\mathrm{HC{\equiv}C\dot{O}})$ is further supported by a series of isodesmic reactions (Eq. (26))

(ΔH_f^0 and Q in kcal mol^{-1}) (the data from Ref. 64)

$$\begin{tikzcd}
\underset{39.1}{CH_2=CHCH_2^\bullet} \arrow[r, "-0.1"] \arrow[d, "-2.7"] & \underset{3.7}{CH_2=CHO^\bullet} \arrow[d, "-4.1"] \\
\underset{81.4}{HC\equiv CCH_2^\bullet} \arrow[r, "-1.5"] & \underset{48.5}{HC\equiv CO^\bullet}
\end{tikzcd} \tag{26}$$

It is obvious that the $\Delta H_f^0(HC\equiv CO^\cdot)$ value 28.8 kcal mol^{-1} [103] is doubtful since it gives an improbably high positive Q value of +17.6 for the $Ph^\cdot \rightarrow HC\equiv CO^\cdot$ isodesmic reaction.

From $\Delta H_f^0(HC\equiv CO^- \leftrightarrow H\bar{C}=C=O) - 5.4$ (see above) and the new ΔH_f^0 value −23 kcal mol^{-1} for $CH_2=C=O$ molecules we get $\Delta H_{acid}(H - CH=C=O) = \Delta H_f^0(HC\equiv CO^-) + \Delta H_f^0(H^+) - \Delta H_f^0(CH_2=C=O) = -5.7 + 365.7 - (-23) = 383$ kcal mol^{-1} (compare with the earlier found value 365 kcal mol^{-1} [17]). The resonance stabilization of the anions of the type $HC\equiv CO^- \leftrightarrow H\bar{C}=C=O$ was experimentally demonstrated in our previous work [106]. The problem, still remains with the enthalpy of formation value for carbene: CH_2. The range of known values is 60–100 kcal mol^{-1} [107,108]. Although the value of energy gap between singlet ^1A and triplet $^3B_1$ carbenes CH_2 is determined by spectroscopy methods with high accuracy [109] 9.023 ± 0.014 kcal mol^{-1}, the value of the enthalpy of formation of either carbene is still under question. Whatever is the accurate determination of the bond dissociation energy in ketene $CH_2=C=O \rightarrow: CH_2 + CO$ ($D_0 = 86.1$ kcal mol^{-1} [4]) $\Delta H_f^0(:CH_2)$ still depends on the value of the enthalpy of formation for the former. Taking the value $\Delta H_f^0(CH_2=C=O) -$ 23 kcal mol^{-1} suggested in the present work and using the data from [109,110] we obtain $\Delta H_f^0(298\ K) : CH_2(^1A_1)$ and $:CH_2(^3B_1)$ 90.5 and 81.5 kcal mol^{-1}, respectively (the data for OK were recalculated for 298 K using Refs. [109,110]).

Earlier it was found [43] that both free radicals and even electron ions reveal similar tendencies in their stabilities at $R_1 \rightarrow R_2$ replacement at the free radical and cationic centers $R_1A^\cdot \rightarrow R_2A^\cdot$ and $R_1A^+ \rightarrow R_2A^+$, respectively, although the absolute Q values in both systems are obviously different. For example, the destabilization of $HC\equiv CO^\cdot$ as compared with $HC\equiv C\dot{C}H_2$ free radical (Eq. (25)) is supported by the negative Q value −15 kcal mol^{-1} for the $HC\equiv CCH_2^+ \rightarrow HC\equiv CO^+$ isodesmic reaction if ΔH_f^0 values 281 and 262 kcal mol^{-1}, respectively, are taken for these ions [60].

7. Conclusion

From our own experimental data and thorough analysis of literature sources, most of which have not been earlier considered in relation to ketene's thermochemistry, the new value $\Delta H_f^0(CH_2=C=O) \sim -23$ kcal mol^{-1} is obtained as compared with the currently used −11.4 kcal mol^{-1} [15–18]. This lower value was gained from the thermochemical properties of about 20 different species (molecules, free radicals, ions). Unfortunately, the process of getting the correct value for the enthalpy of formation for the $CH_2=C=O$ molecule by computation appeared to be a difficult task—the computed values range from +19 to −32 kcal mol^{-1} (from about ten literature sources analyzed). Our computation for ΔH_f^0 (ketene) ranges from −6.8 to −20.7 kcal mol^{-1}.

It is demonstrated that the enthalpic shift procedure and macroincremental scheme for molecules, and the usage of isodesmic reactions for cations, radical cations and free radicals (elaborated in our recent publications and in the works of some other workers—see text) could be treated as the general methodology of verifying and correcting the known and finding the new values of the enthalpies of formation for both charged and neutral species. An additional advantage of application of isodesmic reactions is that the well-known properties of the molecules or substituents like σ-constants, ionization energies, proton affinities, ENs and polarizabilities, IR frequencies and some other characteristics could be used for estimation of the enthalpies of these reactions and consequently for estimation of the enthalpies of formation of different species.

The brief analysis of possible sources of errors in getting the correct thermochemical data from AE measurements is made. Among those sources the most important (and mostly often ignored) is the concealed isomerization processes taking place in molecular ions and leading to the reaction products (either charged or neutral) with the structures differing from the fragments of initial molecule [43,111]. The rearrangement of molecular ion is a very serious artifact in EI, PI and CA processes. In the past 30 years we have measured about 350 AE values from more than 200 compounds by PI MS [112,113] but could extract reliable thermochemical data from no more than 50–60 values. The reason is that the experimentally found enthalpies of formation of the fragment ions were inconsistent with the expected structures of either ions or free radicals. Such inconsistency was established for each fragment with the help of isodesmic reactions.

Therefore, it was not surprising that the structure of the $[M - CH_2{=}C{=}O]^{\cdot +}$ ion from the $PhOCOCH_3$ molecule did not possess the expected structure of $PhOH^{\cdot +}$ as suggested by the authors [14] or that fragmentation of many CH_3COR molecules did not lead to the structurally pure $CH_3C{\equiv}O^+$ ion but rather to the mixture of $C_2H_3O^+$ isomers (see text). Systematic application of the enthalpic shift procedure and macroincremental schemes for molecules and the series of isodesmic reactions for ions and free radicals combined with our own and literature experimental data allowed us to get many new or corrected values of the enthalpies of formation for about 20 species, among those (ΔH_f^0 in kcal mol^{-1}): MeCH=C=O (−29.5), $Me_2C{=}C{=}O$ (−37), PhCH=C=O (0), $Ph_2C{=}C{=}O$ (21.5), FCH=C=O (−60), $F_2C{=}C{=}O$ (−100.5), ClCH=C=O (−22.5), $Cl_2C{=}C{=}O$ (−25), BrCH=C=O (−11), ICH=C=O (2), $(O{=}C{=}CH)_2$ (−43), $CH_2{=}S{=}CH_2$ (67), $CH_2{=}S{=}S$ (60), S=S=S (51), HC≡COH (10), $HC{\equiv}CO^{\cdot}$ (−48.5), $FCH_2\dot{C}{=}O$ (−43), $CH_3C{\equiv}O^+$ (149), $PhCH_2C{\equiv}O^+$ (175.5). The new values 383 and 350 for kcal mol^{-1} ΔH_{acid}(*H*–CH=C=O) and HC≡CO–H molecules, respectively, were derived.

8. Experiment

The purchased compounds methyl ester of phenylacetic acid $PhCH_2COOCH_3$, vinylacetate $CH_3COOCH{=}CH_2$, acetamide CH_3CONH_2, and synthesized compounds 3-phenylcyclobutanone (I) and diketene (V) (details of synthesis are given in Ref. [33]) were distilled before AE measurements. The purity of the compounds was controlled by GC and then by MS (EI and PI) methods. Mass spectra did not contain any noticeable peaks of impurities. The compounds $CH_3COOCH{=}CH_2$ and CH_3CONH_2 were specially controlled by GC in the possible presence of acetic acid which could give in its MS spectra the common acetyl ion $CH_3C{\equiv}O^+$. Similarly, no traces of $PhCH_2COOH$, as a possible source of the $PhCH_2C{\equiv}O^+$ ion were observed in GC. EI mass spectra were run on the Russian mass spectrometer MH-1303. The PI mass spectra and AEs measurements were performed on a modified PI mass spectrometer MS-1302 (Russia). Earlier experiments (see, for examples Refs. [33,36,43,44,75,94,106,112,113,119, 121]) on about 200 compounds indicated that the accuracy of AE values is better than ±0.08 eV.

The recently appeared communication [121] presents the following ΔH_f^0 values (in kcal mol^{-1}): $CH_3CH{=}C{=}O$ (−16.25), $(CH_3)_2C{=}C{=}O$ (−22.0), $CH_3CH_2C{\equiv}O^+$ (147.7), $(CH_3)_2CHC{\equiv}O^+$ (139.3), and PAs values: $CH_2{=}C{=}O$ (196.0), $CH_3CH{=}C{=}O$ (201.2) and $(CH_3)_2C{=}C{=}O$ (204.3). These justify once more the necessity of analysis of experimental and theoretical thermochemical values, related to ketene which was performed in this publication.

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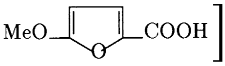
Appendix A

The enthalpies of formation of the molecules examined or used in isodesmic reactions are taken from Refs. [15,16]. In addition, other literature sources were used (ΔH_f^0 in kcal mol^{-1}): $CH_2{=}CHC{\equiv}CH$ (69.2 [114]), PhC≡CH (78.4[114]), C_2H_5F (−62.9[36]), FCH_2CHO (−78.7[36]), $CH_2{=}CHOH$ (−30.6[55]) dimethylenecyclobutene (80.2[115]). For ΔH_f^0 ($ClCH{=}CH_2$) we took a theoretical value 5.2 [8] rather than an experimental one of 8.9 kcal mol^{-1} [15,16] since it was shown [1,26] that the latter value is incorrect. Benson’s microincremental scheme using group contributions [25,82] was applied for estimation of enthalpies of formation of the following molecules: $CH_3COC{\equiv}CH$ (9.8), CH_3COCH_2-CH_2OH (92.7), $PhCH_2COOCH_3$ (−71.1). For more complex compounds their enthalpies of formation were estimated using either the macroincremental scheme or the latter combined with the microincremental scheme (Eqs. (A1)–(A10)) (group contributions were taken from Refs. [25,82]).

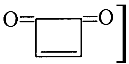
The enthalpies of formation for BrCH=CH$_2$, ICH=CH$_2$ and cyclo-C$_3$H$_5$CH=CH$_2$ were estimated using the observation, [25,35] that ΔH_f^0 (XCH=CH$_2$) = ΔH_f^0(XPh) − 7.2 kcal mol^{-1}. Taking 25.2 [15,16], 39.4 [15,16] and 36.0 kcal mol^{-1} [117] for PhBr, PhI and cyclo-C$_3$H$_5$Ph molecules, respectively, we obtain ΔH_f^0 values 18.0, 32.2 and 28.8 kcal mol^{-1} for XCH=CH$_2$ molecules, where X = Br, I and cyclo-C$_3$H$_5$, respectively. The ΔH_f^0 value for ClCH=CH$_2$ molecules (5.2 kcal mol^{-1}) calculated using ΔH_f^0 (ClC$_6$H$_5$) 12.4 kcal mol^{-1} [15,16] supports the theoretical value [8] (see above). The experimental ΔH_f^0 value 31.2 kcal mol^{-1} [116] for cyclo-C$_3$H$_5$CH=CH$_2$ is not in consensus with ΔH_f^0 (cyclo-C$_3$H$_5$Ph) 36.0 kcal mol^{-1} [117] and was replaced by the estimated value 29 kcal mol^{-1}. ΔH_f^0 (exp.) cyclo-C$_3$H$_5$C≡CH 69.8 kcal mol^{-1} [116], used here coincides with a suggested here value for ΔH_f^0 for cyclo-C$_3$H$_5$CH=CH$_2$.

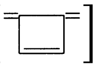
We calculated the values of the enthalpies of formation for fluorinated and chlorinated ketenes X(Y)C=C=O using the known values for ΔH_f^0 X(Y)=CF$_2$ molecules, [15,16]. The application of the additive scheme for the estimation of ΔH_f^0 (FCH=C=O) (Eq. (A6)) gives the deviation from the experimental value 9.1 kcal mol^{-1} similar estimation scheme for ClCH=C=O gives a deviation of 7.7 kcal mol^{-1}. They reflect the repulsion between halogen and the CO-group. We extrapolated those values for BrCH=C=O and ICH=C=O ~ 6.5 and 5 kcal mol^{-1}, respectively, and using the estimation scheme similar to Eq. (A6) and the correction terms we obtained ΔH_f^0 −11 and 2 kcal mol^{-1} for BrCH=C=O and ICH=C=O molecules.

$$
\begin{aligned}
&\Delta H_f^0(\mathrm{CH_3\dot{C}OCOOCH_3})\\
&\quad = \Delta[\Delta H_f^0(\mathrm{CH_3COCOCH_3})\\
&\qquad + \Delta H_f^0(\mathrm{CH_3OCOCOOCH_3})] :2\\
&\quad = (-78.18 - 169.43) : 2 = -123.8\ \mathrm{kcal\ mol^{-1}} \qquad \text{(A1)}
\end{aligned}
$$

ΔH_f^0[](III)

$$
\begin{aligned}
&= \Delta H_f^0[\,p\text{-}\mathrm{MeOC_6H_4COOH}] - \Delta H_f^0(\mathrm{C_6H_6})\\
&\quad + \Delta H_f^0(\text{ furane})\\
&= -108.01 - 19.74 - 8.34 = -136.09\ \mathrm{kcal\ mol^{-1}} \qquad \text{(A2)}
\end{aligned}
$$

ΔH_f^0[]

= ΔH_f^0[]

$$
\begin{aligned}
&\quad - 2[\mathrm{C_d(H)_2}] - 2[\mathrm{C_d(C_d)_2}]\\
&\quad - 2[\mathrm{C_d(H)(C_d)}] + 2[\mathrm{CO(C_d)(CO)}]\\
&\quad + 2[\mathrm{C_d(H)(CO)}]\\
&= 80.2 - 2(6.26) - 2(4.6) - 2(6.78)\\
&\quad + 2(-27.0) + 2(6.0) = 2.9 \sim 3\ \mathrm{kcal\ mol^{-1}} \qquad \text{(A3)}
\end{aligned}
$$

$$
\begin{aligned}
&\Delta H_f^0[\mathrm{PhO-COCHMe_2}]\\
&= \Delta H_f^0[\mathrm{PhOCOMe}] + \Delta H_f^0[\mathrm{MeOCOCHMe_2}]\\
&\quad - \Delta H_f^0[\mathrm{MeOCOMe}]\\
&= -66.85 - 115.13 - (-98.45)\\
&= -83.43\ \mathrm{kcal\ mol^{-1}} \qquad \text{(A4)}
\end{aligned}
$$

$$
\begin{aligned}
&\Delta H_f^0[\mathrm{PhOCHMe_2}]\\
&= \Delta H_f^0[\mathrm{Me_2CH\text{–}OCHMe_2}] - 2[\mathrm{C(H)_3-}]\\
&\quad - [\mathrm{C(H)(C)_2(O)}] - [\mathrm{O(C)_2}] + [\mathrm{O(C)(C_B)}]\\
&\quad + \mathrm{C_B(O)} + 5[\mathrm{C_B(H)}]\\
&= -76.29 - (-20.16) - (-7.2) - (-23.2)\\
&\quad - 23.0 - 1.5 + 16.5\\
&= -33.73\ \mathrm{kcal\ mol^{-1}} \qquad \text{(A5)}
\end{aligned}
$$

$$\begin{aligned}
&\Delta H_f^0[\mathrm{FCH{=}CF_2}]\\
&\quad = \Delta H_f^0[\mathrm{FCH{=}CH_2}] + \Delta H_f^0[\mathrm{CH_2{=}CF_2}]\\
&\qquad - \Delta H_f^0[\mathrm{CH_2{=}CH_2}]\\
&\quad = 33.46 - 80.40 - 12.55 = -126.41\\
&\Delta H_f^0[\mathrm{FCH{=}CF_2}]_{\mathrm{exp}} = -117.35\ \mathrm{kcal\ mol^{-1}};\\
&\Delta\Delta H_f^0 = -117.35 - (-126.41) = +9.06\ \mathrm{kcal\ mol^{-1}}
\end{aligned} \tag{A6}$$

$$\begin{aligned}
&\Delta H_f^0[\mathrm{FCH{=}C{=}O}]\\
&\quad = \Delta H_f^0[\mathrm{FCH{=}CF_2}] + \Delta H_f^0[\mathrm{CH_2{=}C{=}O}]\\
&\qquad - \Delta H_f^0[\mathrm{CH_2{=}CF_2}]\\
&\quad = -117.35 - 23.0 - (-80.40)\\
&\quad = -60.0\ \mathrm{kcal\ mol^{-1}}
\end{aligned} \tag{A7}$$

$$\begin{aligned}
&\Delta H_f^0[\mathrm{ClCH{=}C{=}O}]\\
&\quad = \Delta H_f^0[\mathrm{ClCH{=}CF_2}] + \Delta H_f^0[\mathrm{CH_2{=}C{=}O}]\\
&\qquad - \Delta H_f^0[\mathrm{CH_2{=}CF_2}] = -79.7 - 23.0 - (-80.4)\\
&\quad = -22.3\ \mathrm{kcal\ mol^{-1}}
\end{aligned} \tag{A8}$$

$$\begin{aligned}
&\Delta H_f^0[\mathrm{Ph_2C{=}C{=}O}]{=}\Delta H_f^0[\mathrm{Ph_2C{=}CH_2}]\\
&\quad + \Delta H_f^0[\mathrm{CH_2{=}C{=}O}] - \Delta H_f^0[\mathrm{CH_2{=}CH_2}] + \Delta\\
&\quad = 58.70 - 23.0 - 12.55 - 1.5(\text{see text})\\
&\quad = \sim 21.5\ \mathrm{kcal\ mol^{-1}}
\end{aligned} \tag{A9}$$

$$\begin{aligned}
&\Delta H_f^0[\mathrm{O{=}C{=}CHCH{=}C{=}O}](\mathrm{III})\\
&\quad = 2\Delta H_f^0(\mathrm{CH_2{=}C{=}O}) - 2\Delta H_f^0[\mathrm{C_d(H)_2}]\\
&\qquad + 2[\mathrm{C_d(H)(C_d)}] + \Delta\\
&\quad = 2\Delta H_f^0[\mathrm{CH_2{=}C{=}O}] - 2(6.26) + 2(6.78) + \Delta\\
&\quad = 2\Delta H_f^0(\mathrm{CH_2{=}C{=}O}) - 2(6.26) + 2(6.78)\\
&\qquad + 2(\text{see text})\\
&\quad = 2\Delta H_f^0(\mathrm{CH_2{=}C{=}O}) + 3\ \mathrm{kcal\ mol^{-1}}
\end{aligned} \tag{A10}$$

Eq. (A5) needs comments. To take into account the steric interaction in $\mathrm{PhOCHMe_2}$, $\mathrm{PhOCMe_3}$ and similar compounds the estimation scheme was suggested [25] based on equalizing the steric demands of certain groups. For example, it was shown [118] that Ph- and $\mathrm{Me_2CH}$-groups possess similar "sizes". Taking as the model, compounds $\mathrm{Me_2CHOCHMe_2}$ and $\mathrm{Me_2CHOCMe_3}$ (ΔH_f^0: -76.29 [15,16] and -85.47 kcal mol^{-1} [15,16], respectively) for $\mathrm{PhOCHMe_2}$ and $\mathrm{PhOCMe_3}$ molecules, respectively, the enthalpies of formation for the latter were estimated -33.73 (Eq. (A5)) and -42.91 kcal mol^{-1}, respectively. Since in bisketene (III) the polar interaction between the electron-withdrawing CO-groups (destabilizing the molecule) is expected we introduce a small correction term ~2 kcal mol^{-1} like for other electron-withdrawing groups [25] (Eq. (A10)). Using estimation schemes similar to Eqs. (A1)–(A10) the following ΔH_f^0 values were obtained (see also text) (in kcal mol^{-1}): $\mathrm{PhCH_2CHO}$ (-11.3), cyclopropanol (-28.3), 3-phenylcyclobutanone (6.1). $\Delta H_f^0(\mathrm{PhCH{=}CH_2})^{\cdot+}$ (Scheme 1) was calculated using the following data: $\Delta H_f^0(\mathrm{PhCH{=}CH_2})^{\cdot+} = \Delta H_f^0(\mathrm{PhCH{=}CH_2}) + \mathrm{IE}(\mathrm{PhCH{=}CH_2}) = 35.35[15] + 195.33[38]$ (8.47 eV) $= 230.68$ kcal mol^{-1}. From AE 11.2 ± 0.05 eV (258.3 kcal mol^{-1}) [38] for $[\mathrm{M{-}C_2H_2}]^{\cdot+}$ ion from compound II (ΔH_f^0 -29.37 kcal mol^{-1} [15,16]) we gain ΔH_f^0 $[\mathrm{M{-}C_2H_2}]^{\cdot+}$ 174.7 kcal mol^{-1}. ΔH_f^0 $\mathrm{IIa}^{\cdot+}$ (Scheme 2) $= \Delta H_f^0(\mathrm{II}) + \mathrm{IE(II)} = 3.0$ (see Eq. (A3)) $+225.8$ kcal mol^{-1}(9.79 [38] eV) $= 228.8$ which is much higher than the experimental value 174.7 kcal mol^{-1} (from AE).

For estimation of IE bisketene III (Scheme 2) we use the principles and estimation schemes described in detail in Ref. [43]. We have to estimate ΔIE for the H → CH=C=O replacement in H–CH=C=O, whose IE value is 9.614 eV [38]. The O=C=CH-group could be qualified as a group with dual, electron-releasing or electron-withdrawing, properties in its influence on IEs of molecules like X = $\mathrm{CH_2Cl}$, COR, C≡CH, CN [43] groups. Such groups increase IEs of the molecules H–R (i.e. destabilize their radical cations) possessing low IEs and decrease IEs of H–R molecules (H–R → X–R), i.e. stabilize their radical cations if these molecules possess the relatively high IE values. For example, H → CHO replacement in H–CHO (IE 10.88 [38] eV) decreases IE (CHO–CHO) to 10.52 eV [38], whereas IE slightly rises when coming from PhH (9.24 [38]) to PhCHO (9.4–9.6 eV [38]). Compare also IEs H–CMe_2CHO (9.705 [38]) and CHO–CMe_2CHO (9.80 eV [38]).

The comparison of neutral groups ENs [96]=CH_2 (2.68), CH=CH_2 (2.70), CHO (2.83), CH=C=O (3.12), =O (3.73) reveals the slightly higher electron-withdrawing properties of –CH=C=O as compared with the CHO-group. Taking in consideration the IEs data mentioned and IE (CH_2=C=O) 9.60 eV we expect that H → CH=C=O replacement in ketene will give IE (O=C=CH–CH=C=O) 9.5–9.7 eV. Close values could be derived from published data [12] on IEs of Me_3SiCH=C=O (threshold at ~8.6 eV) and O=C=C($SiMe_3$)– (Me_3Si)C=C=O (threshold at ~8.0 eV). H–CH=C=O → Me_3Si–CH=C=O replacement gives $\Delta IE \sim 1.0$ eV, then substitution of two H-atoms in bisketene O=C=CHCH=C=O (III) by two strong electron-releasing Me_3Si-groups should give $\Delta IE > 1.0$ eV. Hence, IE(III) > (8.0 + 1.0), i.e. >9.0 eV and the value 9.4–9.7 eV looks quite reasonable. If we take ΔH_f^0 (CH_2=C=O) −11.4 [17] and ΔH_f^0 $(\text{bisketene})^{\cdot+}$ ($\text{III}^{\cdot+}$) 174.7 kcal mol^{-1} (see above) and using the following equation

$$\begin{aligned}\Delta H_f^0(\text{O=C=CHCH=C=O})^{\cdot+} &= \Delta H_f^0(\text{O=C=CHCH=C=O})(\text{III}) \\ &\quad + \text{IE}(\text{O=C=CHCH=C=O})(\text{III}) \qquad \text{(A11)}\end{aligned}$$

we obtain $\text{IE(III)} = \Delta H_f^0(\text{III})^{\cdot+} - \Delta H_f^0(\text{III}) = \Delta H_f^0(\text{III})^{\cdot+} - 2\Delta H_f^0(CH_2{=}C{=}O) - 3(\text{Eq. (A10)}) = 174.7 - 2(-11.4) - 3 = 194.5$ kcal mol^{-1} or 8.43 eV. The latter value is obviously too low for IE (III) (see above). Taking ΔH_f^0 (CH_2=C=O) −23 kcal mol^{-1} we have IE (III) 217.7 kcal mol^{-1} or 9.44 eV.

For Schemes 3 and 4 we made the following calculations: $\Delta H_f^0(HCOO^-) = \Delta H_f^0(HCOO^{\cdot}) - EA(HCOO^{\cdot}) = -35.5[25] - 74.5[17] = -110.0$ kcal mol^{-1} and $\Delta H_f^0(\cdot COOH) = \Delta H_f^0(\cdot COOH) - EA(\dot{C}OOH) = -47.3[64] - 7.2 = -54.4$ kcal mol^{-1}. We took $EA(\cdot COOH) \cong EA(\cdot CHO) = 0.313$ eV(7.22 kcal mol^{-1} [17]). Taking AEs 0.9 eV (20.8 kcal mol^{-1}) and 3.4 eV (78.4 kcal mol^{-1}) for $HCOO^-$ and $\bar{C}OOH$ ions, respectively (Schemes 3 and 4) and ΔH_f^0 ($Me^{\cdot}$) 34.8 kcal mol^{-1} [64] we obtained ΔH_f^0 (O=C=CHCH=C=O) −40.1 and −37.3 kcal mol^{-1}, respectively. From these values, using Eq. (A10) we derived ΔH_f^0 (CH_2=C=O) −21.5 and −20.0 kcal mol^{-1}, respectively.

For the estimation of ΔH_f^0 FCH_2 $\dot{C}$=O free radicals (to use in Eq. (13)) we take the series of isodesmic reactions (Eq. (A12)) (ΔH_f^0 and Q values—in kcal mol^{-1})

$$\begin{tikzcd}[row sep=small] CH_3CH_2^{\bullet} \arrow[r, "+12.3", "Q_1"'] & CH_3\dot{C}=O \\ 26.5[64] \arrow[d, "-2.7"] & -5.4[63] \\ FCH_2CH_2^{\bullet} \arrow[r, "{[\sim 13.5]}", "Q_2"'] & FCH_2\dot{C}=O \\ -13.5[64] & {[-43]} \end{tikzcd} \qquad \text{(A12)}$$

Since $FCH_2\dot{C}H_2$ is 2.7 kcal mol^{-1} less stable than the $CH_3CH_2^{\cdot}$ free radical, the former will extract a slightly larger stabilization at FCH_2–$CH_2^{\cdot}$ → FCH_2–$\dot{C}$=O replacement, i.e. $Q_2 > Q_1$ (see Eqs. (23)–(25)). Taking an arbitrary value $Q_2 \sim 13.5$ kcal mol^{-1} we get $\Delta H_f^0[FCH_2\dot{C}{=}O] - 43$ kcal mol^{-1}.

We revised the interpretation of data on thermochemistry of fragmentation of the $CH_3COCH_2CH_2OH$ molecule [69]. Taking ΔH_f^0 ($CH_3C{\equiv}O^+$) 156 kcal mol^{-1}, the authors obtained $\Delta H_f^0(\dot{C}H_2CH_2OH)$ −13.8 kcal mol^{-1} from AE ($CH_3C{\equiv}O^+$) 10.20 eV. The suggested value −13.8 for the $\dot{C}H_2CH_2OH$ radical is close to $\Delta H_f^0(CH_3\dot{C}HOH) - 15.2$ kcal mol^{-1} [63] whereas the former should be less stable than the latter one: (i) the secondary free radicals are more stable than the isomeric primary ones; (ii) the HO-group in the α-position stabilizes the free radical center whereas in the β-position it destabilizes such center. For example, (Eq. (A13)) the HOCH=$CH^{\cdot}$ free radical in the framework of the isodesmic reaction is 2.6 kcal mol^{-1} less stable than the unsubstituted vinyl radical

$$\begin{aligned}&\underset{(\text{kcal mol}^{-1})}{\Delta H_f^0} \quad \underset{70.5[64]}{CH_2{=}CH^{\cdot}} + \underset{-30.6[55]}{HOCH{=}CH_2} \\ &\rightarrow \underset{12.55[15]}{CH_2{=}CH_2} + \underset{30.0[119]}{HOCH{=}CH^{\cdot}} + \underset{-2.65}{Q} \qquad \text{(A13)}\end{aligned}$$

Earlier [25], ΔH_f^0 ($\dot{C}H_2CH_2OH$) − 7.0 kcal mol^{-1} was estimated using Eq. (A13). This value was later supported by computation, [68] which gave $\Delta\Delta H_f^0$ + 7.8 kcal mol^{-1} for $\Delta\Delta H_f^0(CH_3\dot{C}HOH \rightarrow$

ĊH$_2$CH$_2$OH). Taking ΔH_f^0 (CH$_3$ĊHOH) -15.2 kcal mol^{-1} [63] we obtain ΔH_f^0 (ĊH$_2$CH$_2$OH) $-$ 7.4 kcal mol^{-1} (Eq. (A14))

$$\begin{array}{llll} \Delta H_f^0 & CH_3\dot{C}H_2 & + CH_3CH_2OH & \\ (\text{kcal mol}^{-1}) & 26.5[64] & -56.24[15] & \end{array}$$

$$\begin{array}{llll} \rightarrow CH_3CH_3 & + \dot{C}H_2CH_2OH & + \; Q & \\ -20.02[15] & -13.8[69] & +4.1 & \\ & -7.4[68] & -2.1 & \\ & -7.0[25] & -2.5 & \end{array} \qquad (A14)$$

Taking -7.4 kcal mol^{-1} for the ΔH_f^0 ĊH$_2$CH$_2$OH free radical as a partner for the CH$_3$C≡O$^+$ ion from the CH$_3$COCH$_2$CH$_2$OH molecule we obtain (CH$_3$C≡O$^+$) 149.6 kcal mol^{-1} (Table 1).

We calculated ΔH_f^0 (CH$_2$=C=O) values from the computed ΔE values for the following reactions (from Ref. [13])

$$CH_2{=}C{=}O + H^+ \rightarrow CH_3C{\equiv}O^+ + \Delta E$$

$$= -199.2 \text{ kcal mol}^{-1} \qquad (A15)$$

$$CH_2{=}C{=}O + HO^- \rightarrow CH_3COO^- + \Delta E$$

$$= -106.3 \text{ kcal mol}^{-1} \qquad (A16)$$

$$CH_2{=}C{=}O + H_2O \rightarrow CH_3COOH + \Delta E$$

$$= -41.4 \text{ kcal mol}^{-1} \qquad (A17)$$

Taking ΔH_f^0 (H$^+$) 365.7 [83], CH$_3$COOH (-103.44), OH$^-$ (-33.2), CH$_3$COO$^-$ (-120.5), H$_2$O (-57.8) [17] and CH$_3$C≡O$^+$ (156 [17] or 149 (this work)) kcal mol^{-1} we obtain ΔH_f^0 (CH$_2$=C=O) -10.2 or -17.2 from Eq. (A15), $+19$ (Eq. (A16)) and -4.3 kcal mol^{-1} (Eq. (A15)).

The ΔH_f^0 Ph$\overset{+}{O}$=CMe$_2$ ion was estimated using the series of isodesmic reactions (Eq. (A18)) (ΔH_f^0 and Q values—in kcal mol^{-1})

$$\begin{tikzcd}
\underset{157[17]}{CH_3\overset{+}{O}=CH_2} \arrow[r, "+2.3", "Q'"'] \arrow[d, "+26.8"] & \underset{182.5[120]}{Ph\overset{+}{O}=CH_2 \leftrightarrow Ph\ddot{O}CH_2^+} \\
\underset{114[17]}{CH_3\overset{+}{O}=CMe_2} \arrow[r, "{[O]}", "Q''"'] & \underset{[141.5]}{Ph\overset{+}{O}=CMe_2}
\end{tikzcd} \qquad (A18)$$

The small Q$'$ value could be explained by the absence of direct conjugation of the Ph group with a C-cationic center. Here the Ph-substituent displays only the polarizability effect. Since the CH$_3\overset{+}{O}$=CMe$_2$ ion is much (by ~27 kcal mol^{-1}) more stable than the CH$_3\overset{+}{O}$=CH$_2$ ion then Q$''$ < Q$'$. We take an arbitrary value Q$''$ ~ O. Earlier it was found that in very stable cations, Ph could behave even as a weak electron-withdrawing group. For example, $Q = -0.7$ kcal mol^{-1} for the CH$_3\overset{+}{N}$H=CH$_2$ → Ph$\overset{+}{N}$H=CH$_2$ isodesmic reaction [120]. From the isodesmic reaction CH$_3\overset{+}{O}$=CMe$_2$ → Ph$\overset{+}{O}$=CMe$_2$ (Eq. (A18)) we obtain ΔH_f^0[Ph$\overset{+}{O}$=CMe$_2$] 141.5 and AE[Ph$\overset{+}{O}$=CMe$_2$] 218.2 kcal mol^{-1} (9.46 eV) from the PhOCMe$_3$ molecule. Taking IE(PhOCMe$_3$) 8.66 eV [38] we obtain $E_{cr} = 9.46 - 8.66 = 0.80$ eV for Me elimination. E_{cr} for Me-elimination from the PhOCH$_2$–CH$_3$ molecule is 10.66 [AE(M–Me)$^+$] [120] -8.20 [IE(PhOEt)] [38] = 2.46 eV.

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