Introduction

Malonic acid is considered as a prominent member of the most abundant dicarboxylic acids found in the atmosphere. It is directly emitted to the atmosphere by the incomplete combustion of fossil fuel, biomass burning as well as secondary photochemical oxidations of both biogenic and anthropogenic organic precursors. The ubiquitous persistence of malonic acid as a sizable fraction of organic matter in atmospheric aerosols play an important role in cloud formation and maintaining global radiation balance via its hygroscopic features and capability of acting as cloud condensation nuclei. Malonic acid based compounds are also known as potential inhibitors of matrix metalloproteinase in curing various diseases like tumor invasion and joint destruction compare to conventional inhibitors. Due to its extreme importance decomposition of malonic acid has been paid much attention by researchers of both experimental and theoretical domains. The decarboxylation of malonic acid expected to be proceed through a two step mechanism with activation energy in the range of 25–40 kcal mol\(^{-1}\) to produce acetic acid and CO\(_2\). Interestingly previous experimental reports suggest that dehydration of malonic acid do not produce malonic anhydride whereas it undergoes double dehydration leading to the formation of carbon-suboxide and water. Carbon-suboxide is also found in a sizable fraction in the atmosphere. However, the detail mechanism of malonic acid dehydration is still unknown. In a recent study, Perrin et al. shows that malonic anhydride decompose at room temperature to produce atmospherically relevant compounds like ketene and CO\(_2\). Now the question arises is there any possibility for the formation of ketene from decomposition of malonic acid? This motivated us to perform comprehensive study on a sound theoretical basis. Three plausible decomposition pathways of malonic acid are considered during the present investigation.

I. Decarboxylation

\[
\text{CH}_3(\text{COOH})_2 \rightarrow^{\text{TS}_1} \text{CO}_2 + \text{CH}_2(\text{COOH})_2 \rightarrow^{\text{TS}_2} \text{CH}_2(\text{COOH}) + \text{CO}_2
\]

II. Dehydration

\[
\text{CH}_3(\text{COOH})_2 \rightarrow^{\text{TS}_3} \text{H}_2\text{O} + \text{COCHCOOH} \rightarrow^{\text{TS}_4} \text{C}_3\text{O}_2 + 2\text{H}_2\text{O}
\]

III. Decarboxylation–dehydration

\[
\text{CH}_2(\text{COOH})_2 \rightarrow^{\text{TS}_5} \text{CO}_2 + \text{H}_2\text{O} + \text{CH}_2\text{CO}
\]

Theoretical investigation on unimolecular decomposition of malonic acid: a potential sink for ketene†

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identification; and (3) give deep insights into the mechanism of unimolecular decomposition of the malonic acid.

Computational methods

Density functional calculations were performed with the Gaussian 09 suite of program.9 Geometry optimization and harmonic vibrational frequency calculation of the reactants, transition states, intermediates and products were obtained at the meta hybrid MPWB1K8 and M06-2X11 levels of theory using standard 6-31+G(d,p) basis set. In order to study the effect of basis set on geometry, optimization and frequency calculation are also performed at M06-2X level using Pople’s split-valence triple-ζ quality 6-311++G(d,p) basis set with single polarization and double diffuse functions on all atoms. All the stationary points had been identified to correspond to stable minima with real positive values. However, the transition states were characterized by the presence of only one imaginary frequency. To ascertain that the identified transition states connect reactants and products smoothly, intrinsic reaction coordinate (IRC) calculations were also performed at all above mentioned theoretical level. Energetic calculation has been further refined by using couple cluster [CCSD(T)] method at M06-2X/6-311++G(d,p) optimized geometries. As the reaction energy barriers are very much sensitive to the theoretical levels, the higher-order correlation corrected relative energies along with the density functional energies are necessary to obtain theoretically consistent reaction energies. Therefore, a potentially high-level method such as G2(MP2) has been used for single-point energy calculations. The G2(MP2)31 energy is calculated in the following manner:

$$E_{\text{G2(MP2)}} = E_{\text{base}} + \Delta E_{\text{MP2}} + \text{HLC} + \text{ZPE}$$

where, $E_{\text{base}} = E_{\text{QCISD(T)/6-311G(d,p)}}$, $\Delta E_{\text{MP2}} = E_{\text{MP2/6-311+G(3df,2p)}} - E_{\text{MP2/6-311G(d,p)}}$, and HLC (High Level Correction) = $-0.00481n_x - 0.00019n_y$ ($n_x$ and $n_y$ are the number of $\sigma$ and $\beta$ valence electrons with $n_x \geq n_y$) and ZPE = zero-point energy.

In this method the geometry and frequency calculations were performed at MPWB1K/6-31+G(d,p) level. The ZPE thus obtained was corrected with a scale factor of 0.9537 to partly eliminate the systematic errors.10 This dual level calculation G2(MP2)/MPWB1K/6-31+G(d,p) is known to produce reliable thermochemical and kinetic data.14-20

Results and discussion

The optimized geometries, structural parameters and harmonic vibrational frequencies for reactant, transition states, intermediates and products of three above mentioned reaction channels at MPWB1K and M06-2X levels are shown in ESI (Fig. S1 and Table S1†). Fig. S1† reveals that optimized geometrical parameters obtained at both levels are in good agreement with each other. Furthermore, the effect of basis set on geometries at M06-2X level is marginal. Transition states (TS) are characterized by the occurrence of only one imaginary frequency at 399i, 2167i, 1796i and 336i cm$^{-1}$ for TS1, TS2, TS3, TS4 and TS5, respectively as recorded in Table S1 of ESI.† In order to access the multi-reference characteristics and verify the reliability of the results of the single reference CCSD(T) wave function, $T_1$ diagnostic21 calculation has been also performed at the CCSD(T) level of theory for all the species. Examining the $T_1$ values we have found that $T_1$ values for all species considerably lower than 0.045. It has been established that a $T_1$ value larger than 0.045 indicates significant multi-reference character.22 Therefore, we can conclude that the transition states reported in this work do not present a multi-reference character and single reference CCSD(T) wave function is expected to yield reliable energetic for all the species. CCSD(T) energies of all species including zero point energy (ZPE) correction estimated at M06-2X/6-311++G(d,p) level along with $T_1$ values are recorded in Table S2 of ESI.† The associated energy barriers corresponding to decomposition channels calculated at different levels is recorded in Table 1. Conformational landscape of malonic acid has been investigated by Han et al.23 and Macacos et al.24 by means of theoretical tools. The predicted most stable conformer of malonic acid is one in which one carboxyl group is perpendicular to the plane through the three carbon atoms and other carboxyl group lies on the plane without existence of any intramolecular hydrogen bonds. The most stable conformer of malonic acid considered during present study is in agreement with previous studies.23,24 A schematic potential energy surface of the three different decomposition channels of malonic acid are plotted and shown in Fig. 1. In the construction of energy diagram, ZPE corrected total energies at CCSD(T)/M06-2X/6-311+G(d,p) level as recorded in Table S2† are utilized and relative energy are calculated by considering the ground state energy of the reactant arbitrarily as zero.

To explore further the electronic mechanism of malonic acid decomposition, we examine the topology of the electron density of all transition states using atoms-in-molecule (AIM) technique.25 AIM calculations are performed at M06-2X/6-311++G(d,p) level to generate the electron densities and subsequently analyzed with AIMALL package.26 The Wiberg bond indices (WI) are calculated at the same level and all results are summarized as a graphical representation in Fig. 2.

The following sections discuss the fate of unimolecular decomposition of malonic acid:

Decarboxylation

Decarboxylation pathway of malonic acid involve a six-membered cyclic transition state, TS1 resemble the McLafferty rearrangement in which the oxygen of the $\beta$-keto group act as a proton acceptor towards the oxygen of the hydroxyl group and simultaneous cleavage of C1–C2 bond to produce the enol of acetic acid (IM1) and CO$_2$. This process is calculated to be endothermic by 15.91 kcal mol$^{-1}$ and proceed with an energy barrier of 32.16 kcal mol$^{-1}$. Our calculated barrier heights amount to be 32.16 kcal mol$^{-1}$ at CCSD(T)/6-311++G(d,p) level of theory whereas the same obtained from the G2(MP2) results amount to be 30.75 kcal mol$^{-1}$. Thus, our calculated energy barrier (32.16 and 30.75 kcal mol$^{-1}$) is in a reasonable...
Table 1  Calculated energy barriers at different level of theories. All values are in kcal mol$^{-1}$

<table>
<thead>
<tr>
<th>Reaction channels</th>
<th>Transition states</th>
<th>G2(MP2)</th>
<th>MPWB1K/6-31+G(d,p)</th>
<th>CCSD(T)/6-311++G(d,p)</th>
<th>Literature value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decarboxylation</td>
<td>TS1</td>
<td>30.75</td>
<td>31.36</td>
<td>32.16</td>
<td>28.5$^a$</td>
</tr>
<tr>
<td></td>
<td>TS2</td>
<td>44.38</td>
<td>44.92</td>
<td>45.03</td>
<td>27.6$^b$</td>
</tr>
<tr>
<td>Dehydration</td>
<td>TS3</td>
<td>65.82</td>
<td>66.10</td>
<td>67.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS4</td>
<td>60.39</td>
<td>63.93</td>
<td>62.47</td>
<td></td>
</tr>
<tr>
<td>Decarboxylation–dehydration</td>
<td>TS5</td>
<td>44.18</td>
<td>45.11</td>
<td>44.75</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ref. 5e.  $^b$ Ref. 5f.

**Fig. 1** Schematic potential energy diagram for three plausible unimolecular decomposition pathways of malonic acid. Relative energies (ZPE corrected) in kcal mol$^{-1}$ are obtained at CCSD(T)/6-311++G(d,p) level.

agreement with the value of 28.5 and 27.6 kcal mol$^{-1}$ reported by Huang et al.$^5$ and Staikova et al.$^6$ respectively. In the next step the enol form undergo subsequent 1,3-hydrogen shift via TS2 to give the corresponding acetic acid. This process is exothermic by 3.15 kcal mol$^{-1}$ involving energy barrier of 45.03 and 44.38 kcal mol$^{-1}$, respectively at CCSD(T) and G2(MP2) levels. Overall decarboxylation of malonic acid is exothermic by 12.76 kcal mol$^{-1}$. In TS1, bond distances of forming O5–H8 bond and breaking C1–C2, O7–H11 bonds are calculated to be 1.017, 1.017, 1.017, 1.017, 1.017 and 1.017 Å, respectively. Whereas in TS2 the bond distance of the forming C1–H8 and breaking O3–H8 bond are 1.503 and 1.256 Å, respectively. From AIM calculation as shown in Fig. 2 reveals that the migrating H atom carries a net positive charge of 0.673 and 0.492 in TS1 and TS2, respectively. It gives the indication of proton transfer rather than hydride transfer along the transition states of decarboxylation process. Existence of bond critical point (BCP) in both transition states confirms the partial forming and breaking of bonds when the system reaches transition states. The six and four-membered cyclic character of TS1 and TS2 are supported by the presence of ring critical point (RCP). The Wiberg bond indices (WBI) at BCP vary from 0.12 to 0.45 for breaking bonds in TS1 which suggests that O7–H11 bond breaks ahead of C1–C2 bond. This provides further support to the asynchronous character of bond breaking within the concerted TS1. However, in TS2 bond orders between forming C1–H8 (WBI = 0.35) bond and breaking O3–H8 (WBI = 0.32) bond are marginal.

**Dehydration**

First step of malonic acid dehydration is expected to be proceed though a four member cyclic transition state TS3 in which oxygen of the β-keto group accept a proton from –CH$_3$ moiety and instantaneous cleavage of C1–O7 bond to produce the intermediate (IM2) COCHCOOH and H$_2$O. This process is endothermic by 26.20 kcal mol$^{-1}$ with an energy barrier of 67.13 and 65.82 kcal mol$^{-1}$, respectively at CCSD(T) and G2(MP2) levels. Because in the formed intermediate the –COOH fragment remain still intact, reaction may follow via another four-membered concerted transition state (TS4) with the elimination of second H$_2$O molecule to produce carbon suboxide (C$_3$O$_2$).

Calculation shows that this process is also endothermic by 19.6 kcal mol$^{-1}$ and proceeds with an energy barrier of 62.47 and 60.39 kcal mol$^{-1}$, respectively at CCSD(T) and G2(MP2) levels. Overall subsequent dehydration of malonic acid is endothermic by 45.80 kcal mol$^{-1}$. The bond distances of forming O7–H9 and breaking C1–O7 and C2–H9 bonds in TS3 are found to be 1.223, 1.560 and 1.480 Å, respectively. While in TS4, bond distances of forming O6–H8 and breaking (C2–H8 & C3–O6) bonds are calculated to be 1.20, 1.425 and 1.626 Å, respectively. The AIM calculation performed for TS3 and TS4 shows that the migrating H atom bears a positive charge. Its gives authentication about a proton transfer process within the transition states. Existence of BCP and RCP in the transition states also supports the concerted mechanism involving four-membered cyclic transition states. Interestingly AIM map for TS3 shows another six-membered ring like structure together with the usual four-membered ring which is expected due to the weak hydrogen bonding interaction between H11 and O5 (WBI = 0.016) when the system reaches transition state. The Wiberg bond indices (WBI) at BCP vary from 0.33 to 0.66 and 0.34 to 0.57 for breaking bonds in TS3 and TS4, respectively. It gives evidence about the asynchronous character of bond breaking within the concerted transition states (TS3 & TS4).

**Decarboxylation–dehydration**

This process facilitate through a concerted six-membered transition state (TS5) in which oxygen of the β-keto group accept a proton from –COOH group and in situ cleavage of C2–C3 and C1–O7 bonds to generate CO$_2$, H$_2$O and ketene. This process is
endothermic by 19.10 kcal mol\(^{-1}\) and proceeds with an energy barrier of 44.75 and 44.18 kcal mol\(^{-1}\), respectively at CCSD(T) and G2(MP2) levels. The bond distances of forming O7–H8 and breaking O6–H8, C2–C3 and C1–O7 bonds are estimated to be 1.007, 1.573, 1.868 and 1.951 Å, respectively. Moreover TS5 involve a cyclic six-membered transition state with concertedness of breaking and forming bond as characterized by RCP and BCP, respectively (cf. Fig. 2). The variation of WBI from 0.10 to 0.52 at BCP for breaking bonds in TS5 reveals that O6–H8 bond breaks ahead of C1–O7 and C2–C3 bond. This validates asynchronous character of bond breaking within the concerted transition state. The significant positive charge (0.670) on migrating H atom in TS5 gives the evidence of proton transfer during the course of reaction.

Fig. 2  AIM molecular graphs of transition states involved in the unimolecular decomposition of malonic acid. Small red spheres, small green spheres and black lines represent bond critical points (BCPs), ring critical points (RCPs), and bond path (BP), respectively. The values in the parentheses at BCPs indicate the Wiberg bond indices (WBI).
According to the experimental enthalpy of formation ($\Delta H_f$) of acetic acid, $^{27}$ CO$_2$, $^8$ C$_2$O$_2$, $^{27}$ H$_2$O, $^7$ ketene ($-433.0 \pm 3.0$, $-393.50$, $-93.64$, $-241.83$ and $-47.5$ kJ mol$^{-1}$) and estimated $\Delta H_f^\circ$ of malonic acid $^{28}$ ($-783$ kJ mol$^{-1}$), the unimolecular decomposition of malonic acid via decoxylation pathway is about 10.40 kJ mol$^{-1}$ exothermic whereas dehydration and decarboxylation–dehydration pathways are endothermic by 49.16 and 23.93 kJ mol$^{-1}$, respectively. These results are in a reasonable agreement with our calculated values of $-12.76$, 45.80 and 19.10 kJ mol$^{-1}$, respectively for decomposition pathways at the CCSD(T)//M06-2X/6-311++G(d,p) level.

The rate constants are calculated using Canonical Transition State Theory (CTST) $^{29}$ given by the following expression:

\[
dk = \frac{k_b T}{h} \frac{Q_{TS}}{Q_k} \exp \left(-\frac{\Delta E}{RT}\right) \tag{1}\n\]

where, $Q_{TS}$ and $Q_k$ are the total partition function (per unit volume) for the transition states and reactants, respectively. $\Delta E$ is the barrier height including zero-point energy correction, $k_b$ is the Boltzmann constant and $h$ is the Planck's constant. $R$ represents the universal gas constant. The partition functions for the respective transition states and reactants at 298 K are obtained from the vibrational frequency calculations made at MPWB1K/6-31+G(d,p) level. The calculated rate constants at different level of theories for decomposition pathways are recorded in Table 2. It can be seen that the calculated A-factor for decomposition pathways at G2(MP2)//MPWB1K and CCSD(T)//M06-2X levels are of same order. The calculated A-factors for decomposition channels are found to be in the range of 1.12–8.78 $\times$ 10$^{-12}$ s$^{-1}$ which are in a reasonable agreement with values calculated by Clark $et$ $al$. $^{28}$ for decarboxylation and dehydration pathways for saturated and unsaturated carboxylic acids. We could not find any experimental or theoretical data available in the literature to make a comparison with the calculated values obtained during the present investigation. We expect that the present study may provide useful information for future laboratory investigations.

### Conclusions

Three plausible unimolecular decomposition pathways of malonic acid have been considered in detailed by using meta-hybrid density functional and couple cluster methods. In this study we explored the mechanism of dehydration process as well as proposed a novel in situ decarboxylation–dehydration decomposition channel for the first time. Electronic structure calculations suggest that decomposition pathways (1–2) are multistep process while pathway (3) is found to prefer a one step route and all results are consistent with a concerted but asynchronous mechanism. The formation of ketene via decarboxylation–dehydration pathway involving a lower barrier height (44.75 kJ mol$^{-1}$) in compare to dehydration pathway (67.13 kJ mol$^{-1}$) leading to the formation of carbon suboxide. Thus our results strongly proposed that formation of ketene may take place in the atmosphere via unimolecular decomposition of malonic acid. The thermal rate constants and pre-exponential factor for the above decomposition pathways are also evaluated using canonical transition state theory at 298 K. We hope our present study may provide useful guideline for future experimental investigation.

### References


9 M. J. Frisch, et al., Gaussian 09, Revision B.01, Gaussian, Inc, Wallingford, CT, 2010.