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Overtone-Induced Decarboxylation: A Potential Sink for Atmospheric Diacids

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Atmospheric photochemistry induced by solar excitation of vibrational overtone transitions has recently been demonstrated to be of importance in cleaving weak bonds (in HO_2NO_2) and inducing intramolecular rearrangement followed by reaction (in H_2SO_4). Here, we propose another potentially important process: the decarboxylation of organic acids. To demonstrate this possibility, we have calculated the decarboxylation pathways for malonic acid and its monohydrate. The barrier to the gas-phase decarboxylation was calculated to be in the range 26−28 kcal/mol at the B3LYP/6-311++G(3df,3pd) level of theory, in good agreement with previous results. The transition state is a six-membered ring structure which is accessed via concerted O−H and C−C stretches; excitation of $\upsilon_{OH} \geq 3$ of either one of the OH stretching modes is sufficient to supply the energy needed for the decarboxylation. A low-energy isomer of the malonic acid−water complex forms an eight-membered, multiply hydrogen bonded structure, bound by 3−6 kcal/mol, somewhat less stable than the lowest energy, six-membered ring isomer. Decarboxylation of such complexes uses water as a catalyst; the water accepts an acidic proton from one malonic acid group and transfers a proton to the carbonyl of the other acid group. The barrier for this process is 20−22 kcal/mol, suggesting that complexes excited to $\upsilon_{OH} \geq 2$ possess sufficient energy to react. Using estimated absorption cross sections for the OH overtone transitions, we suggest that the overtone-induced decarboxylation of malonic acid and its water complex is competitive with wet deposition of the acid and with gas-phase reaction with OH for removal of the acid.

Introduction

With the increasing sophistication of atmospheric modeling and measurement capabilities, attention is now being directed to increasingly subtle processes which have hitherto been ignored. Examples include heterogeneous chlorine activation, the role of organics particles in cloud formation, and gas-phase ozonation of unsaturated organic compounds. Another such process is the photodissociation of OH-containing compounds via excitation of OH stretching vibrational overtones, the subject of a recent review by Donaldson et al.[1]

Photodissociation following excitation of OH stretching overtones occurs in HONO,[2,3] H_2O_2,[4,5] $HONO_2$,[6] HO_2NO_2,[7] and HO_2NO.[8] In these compounds, vibrational excitation is followed by rapid intramolecular vibrational energy transfer (IVR), depositing sufficient energy into a weak chemical bond to effect its rupture. In HO_2NO_2, inclusion of overtone-initiated dissociation is required to explain the "sudden" component of stratospheric HO_X production at dawn, as well as to give quantitative agreement with in-situ nitrogen oxide measurements.[9−11]

As well as such "direct" dissociation, important for the compounds listed above, overtone-driven molecular rearrangements followed by dissociation are also possible. Here, the initial overtone excitation acts to energize the molecule, which then undergoes a more complex unimolecular reaction. This type of overtone-induced chemistry has also been proposed for molecules of atmospheric importance.[1] It differs from "direct" dissociation in an important way: the photon energy need not be greater than the energy of a bond; it only needs to supply sufficient energy to overcome any barrier to the unimolecular reaction. OH-containing molecules which undergo thermal decomposition at low to moderate temperatures represent candidates for such overtone-driven chemistry. An important atmospheric example of such a process is the dehydration of sulfuric acid: Vaida et al.[12] showed that OH stretching overtone transitions of H_2SO_4 and its hydrate, $H_2SO_4(H_2O)$, are sufficient energetically to cause dehydration, forming sulfur trioxide (SO_3) and water. Measurements of the absolute absorption cross sections for these transitions allowed calculation of the *J* values for this process (assuming a unit quantum yield). The rate of overtone-driven dehydration of sulfuric acid is sufficient to explain stratospheric and mesospheric sulfur dioxide concentrations.[12]

In the following, we report the results of quantum chemical calculations which suggest another potentially important overtone-driven unimolecular process: the decarboxylation of atmospheric dicarboxylic acids. Low molecular weight dicarboxylic acids are common in the atmosphere, having been identified as some of the major water soluble organic species in atmospheric aerosols in both urban and rural areas.[13−16] Malonic acid ($HOOC{-}CH_2{-}COOH$) represents a sizable fraction of the total of such diacid species. The major removal process for atmospheric dicarboxylic acids is thought to be wet deposition, with gas-phase reaction with OH considered to contribute to a lesser degree.[17] These give rise to an average atmospheric lifetime of about 10 days for such compounds.[17]

The keto carboxylic acids, such as malonic acid, decarboxylate thermally, with activation energies in the range of 25−40 kcal/mol.[18] This range of activation energy suggests that

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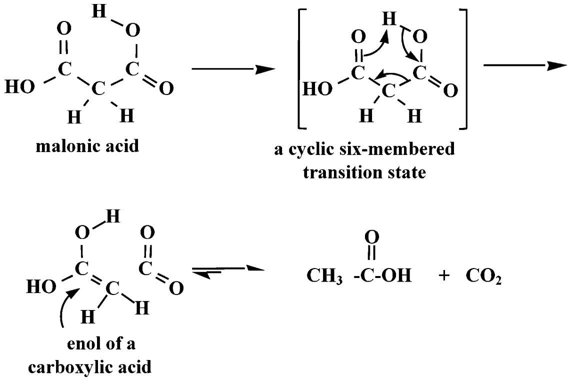

Figure 1. Reaction mechanism for the decarboxylation of malonic acid.

relatively low levels of vibrational excitation in the OH stretch mode might induce decarboxylation. There have been several experimental[19−25] and theoretical[18,26−29] investigations of organic acid decarboxylation. Current thinking is that decarboxylation takes place via proton transfer through six-membered ring-transition structures (see Figure 1). Chemical intuition suggests that achieving this transition state should involve motion of an acidic hydrogen. If this type of motion facilitates achieving a transition state, one would anticipate that excitation of vibrational overtones of the O−H stretch could induce decarboxylation. In this paper, we demonstrate the likelihood of this process for malonic acid and its monohydrate by calculating the relevant stationary points on the ground-state potential energy surfaces, using quantum mechanical methods. Our results for the monomer are in excellent agreement with those given in ref 18.

We believe this to be the first report of the structure and chemistry of a malonic acid−water complex. In a forthcoming paper, we will present an experimental and theoretical study of water interactions with several dicarboxylic acids.[30] Intermolecular interactions in hydrated clusters can sometimes alter the reaction pathways of chemical reactions, changing their activation energies.[31] An important example of such of behavior is the hydrolysis of SO_3,[32] the reverse reaction to the dehydration process described above. There is an energetic barrier to the gas-phase hydration of SO_3 of ∼25 kcal/mol; when a second water molecule is involved in the process, the formation of a six-membered ring-transition state is possible, allowing a barrierless double-proton-transfer reaction. This implies as well that a sulfuric acid−water complex can undergo dehydration at lower energies than the uncomplexed acid, as pointed out by Vaida et al.[12] Such an involvement by water is certainly conceivable for malonic acid decarboxylation as well.

Computational Details

All calculations were carried out using the GAUSSIAN 98 suite of programs and basis sets.[33] The geometries of all species considered were optimized using the 6-31G(d,p) basis set and both MP2 and density functional theory using the B3LYP functional,[34] to verify the nature of the stationary points. Since no differences of significance were observed, only the lower cost DFT structures are reported here. The optimized geometries of bound species were determined to be true minima by the absence of imaginary frequencies in the calculated vibrational spectrum; those of transition states were identified by their single imaginary frequency. Transition-state structures were located using the Synchronous Transit-Guided Quasi-Newton method,[35] as implemented by the GAUSSIAN 98 package. In this approach, an initial guess for the transition-state structure is automatically generated by the program, given optimized reagent and product geometries as input. A full geometry optimization is then performed on this guess, resulting in an optimized transition-state geometry. In the present calculation, the input geometries for the transition-state foe decarboxylation of uncomplexed malonic acid were the fully optimized malonic acid ground state and the enol ($CH_2C(OH)_2$) and CO_2; the malonic acid hydrate and the enol hydrate and CO_2 were used for the malonic acid hydrate calculation. All the stationary points of relevance were then recalculated at the B3LYP/6-311++G(3df,3dp) level of theory. Harmonic vibrational frequencies were calculated at the B3LYP/6-31G(d,p) level and used without correction; we take these to represent an upper limit to the true values. Basis set superposition errors (BSSE) were calculated for the stationary points of the hydrated complex using the counterpoise method at the full B3LYP/6-311++G(3df,3dp) level. As we have reported for similar complexes,[31,36] the BSSE calculated in this manner contributes insignificantly to the relative energies reported here.

Results and Discussion

We consider the decarboxylation of malonic acid and its monohydrated complex:

$$HOOC-CH_2-COOH \rightarrow TS1 \rightarrow H_2C{=}C(OH)_2 + CO_2 \qquad (1)$$

$$\mathrm{HOOC-CH_2-COOH} + H_2O \rightarrow HOOC-CH_2-COOH\cdot(H_2O) \rightarrow TS2 \rightarrow H_2C{=}C(OH)_2\,(H_2O) + \mathrm{CO_2} \qquad (2)$$

where the energies of all species in italics are of interest. The decarboxylation mechanism of malonic acid has been given previously[18] and is illustrated in Figure 1. The calculated structures for the stationary points determined here are displayed in Figure 2. Table 1 presents electronic energies calculated at the B3LYP/6-311++G(3df,3dp) level and zero-point energies calculated at the lower level of theory. The calculated energetics for the decarboxylation of malonic acid and its hydrate are given in Table 2, with and without the zero-point correction. Table 3 presents the harmonic vibrational frequencies calculated for the stable structures shown in Figure 2. Figure 3 displays the reaction energetics of the two systems, together with estimates for the first three overtone levels of the OH stretch in malonic acid.

Overtone-Induced Decarboxylation of Malonic Acid. The calculated lowest energy structure for malonic acid is illustrated in Figure 2a. It is the same as that identified in Huang et al.[18] There is an internal hydrogen bond between the acidic proton of one carboxylate group (labeled H_a) and the carbonyl oxygen of the other. As illustrated in Figure 1, the lowest energy pathway for the decarboxylation of malonic acid[18] involves the concerted transfer of this hydrogen atom together with the lengthening of the C−C bond, shown with a double-headed arrow in Figure 2b. The energetics of the lowest energy pathway for malonic acid decarboxylation are illustrated by the upper line in Figure 3. Malonic acid is connected through transition-state TS1 to an enol + CO_2; this enol may further rearrange through a second transition state, TS1a, to acetic acid. The energetics of this process were calculated here under the assumption that the nascent CO_2 molecule had departed. A concerted decarboxylation−rearrangement (enol→ keto) is conceivable, though seems unlikely (see Figure 1).

The energy of the reaction forming acetic acid and CO_2, calculated before zero-point correction, is practically identical

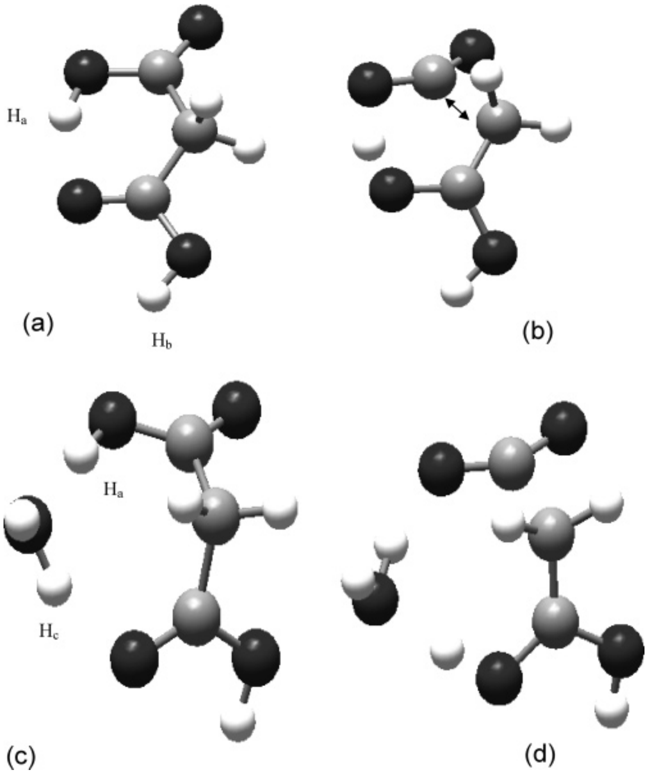

Figure 2. Structures of the stationary points calculated on the decarboxylation potential energy surfaces for malonic acid and its monohydrate. (a) and (b) represent the lowest energy malonic acid structure and the transition state for decarboxylation, respectively. (c) and (d) show, respectively, the low-lying malonic acid−water complex of interest here and the transition state for its decarboxylation.

TABLE 1: Energies of Stationary Points (Calculated at the B3LYP/6-311++G(3df,3dp) Level) and Zero-Point Energies (Calculated at the B3LYP/6-31G(d,p) Level)

species	energy (hartree)	zero-point correction (hartree)
malonic acid	−417.8212	0.07797
TS1	−417.7772	0.07481
enol	−229.1386	0.06087
CO_2	−188.6553	0.009452
TS1a	−229.0643	0.05641
CH_3COOH	−229.1814	0.06196
H_2O	−76.4645	0.02137
MA−H_2O	−494.2948	0.10368
TS2	−494.2586	0.10033
enol−H_2O	−305.6104	0.08680
TS2a	−305.5769	0.08148

TABLE 2: Reaction Energies

reaction	Δ*E* (kcal/mol)	Δ*E*(zpc) (kcal/mol)
$MA \rightarrow CH_3COOH + CO_2$	−9.7	−13.8
$MA + H_2O \rightarrow MA(H_2O)$	−5.7	−3.0
$MA \rightarrow TS1$	+27.6	+25.6
$MA(H_2O) \rightarrow TS2$	+22.7	+20.6
$enol \rightarrow TS1a$	+46.6	+43.8
$enol(H_2O) \rightarrow TS2a$	+21.0	+17.6

with the experimental enthalpy[37] of $\Delta H = -9.6$ kcal/mol. The energy required to achieve the transition state for decarboxylation is predicted to be ∼28 kcal/mol before and ∼25 kcal/mol after zero-point correction. These values are within the range of the literature values[24,25] for the activation energy of the reaction and compare well with that given by Huang et al.[18] at the MP4SDTQ(FC)/6-311++G** level: 28.5 kcal/mol after zero-point correction. The transition-state structure is a six-membered ring, also in accordance with previous reports.[18,26−29]

TABLE 3: Harmonic Vibrational Frequencies of the Stable Species in Figure 2

species:	malonic acid	malonic acid−water	type of motion
	3739 cm^{-1}	3744 cm^{-1}	acidic OH str.
	3487	3320	acidic OH str.
		3881	water OH str.
		3590	water OH str.
	3146	3183	CH str.
	3059	3107	CH str.
	1881	1872	C=O str.
	1797	1793	C=O str.
		1661	water bend
	1464	1489	
	1442	1428	
	1417	1393	
	1296	1299	
	1267	1285	
	1212	1228	
	1176	1134	
	969	968	
		967	
	931	930	
	880	897	
	790	783	
	711	722	
	692	697	
	624	641	
	590	587	
		536	
	474	468	
	404	399	
	385	381	
	256	280	
		229	
		215	
		156	
		114	
	90	83	
	42	49	

The OH stretching frequencies are estimated using the OH harmonic frequencies calculated at the B3LYP/6-31G(d,p) level and anharmonicity corrections calculated by Kjaergaard[38] for similar hydrogen-bonded compounds. The OH_a stretching vibration is the mode involved in the proton transfer. Using its calculated harmonic frequency of 3487 cm^{-1} and assuming an OH-stretching anharmonicity, $\omega_e\chi_e$, of 85 cm^{-1}, we obtain a value of ω_e of 3657 cm^{-1}. The anharmonic vibrational transitions are then estimated to be 10.0 kcal/mol for $v_{OH} = 1$; 6804 cm^{-1} (19.5 kcal/mol) for $v_{OH} = 2$; 9951 cm^{-1} (28.4 kcal/mol) for $v_{OH} = 3$, and 12928 cm^{-1} (37.0 kcal/mol) for $v_{OH} = 4$. These calculated values may be compared with the corresponding ones derived from infrared spectra of malonic acid in an argon matrix.[39] The fundamental was recorded at 3250 cm^{-1} (9.3 kcal/mol) and the first overtone at 6365 cm^{-1} (18.2 kcal/mol); we may extrapolate to $v_{OH} = 3$ (9345 cm^{-1}; 26.7 kcal/mol) and $v_{OH} = 4$ (12190 cm^{-1}; 34.8 kcal/mol). Thus, it appears that excitation of the OH stretch to $v = 3$ or 4 will provide sufficient energy to overcome the barrier to decarboxylation. Even if the barrier lies at the high end of the calculated range, decarboxylation of malonic acid could still occur by excitation of $v_{OHa} = 3$, aided by thermal rotational energy, as is observed in HNO_3[6] and HO_2NO_2,[7] or by excitation to $v_{OHa} = 4$.

The OH_a stretch is effectively coupled with the C−C lengthening mode for the CO_2 departure, indicated by the double arrow in the TS1 in Figure 2b. The C−C distance in TS1 is 2 Å, longer by 0.5 Å than it is in malonic acid. It thus seems very reasonable to expect that overtone excitation could act to promote the decarboxylation process.

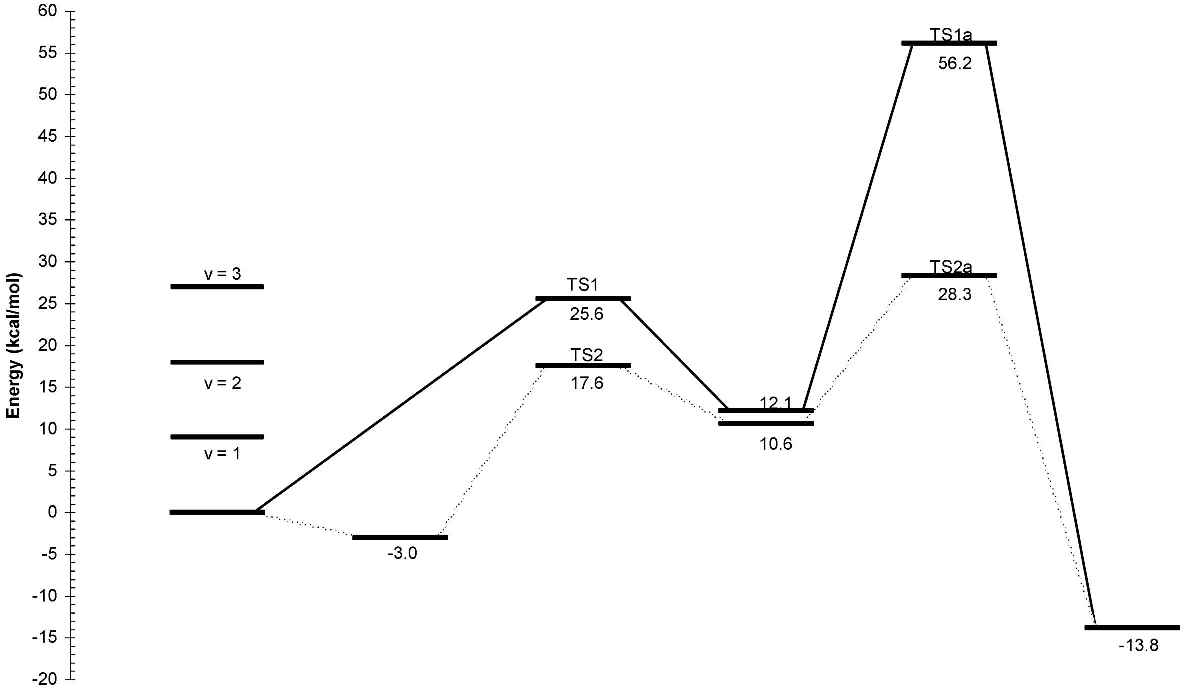

Figure 3. Calculated energetics of the decarboxylation pathways of malonic acid and its monohydrate. The estimated energies of the first three vibrational levels of the OH stretch are shown as well. See text for details.

The other OH stretch in malonic acid is associated with the OH_b bond, which does not participate in internal hydrogen bonding. Its calculated harmonic frequency is 3739 cm^{-1}; assuming an OH-stretching anharmonicity[38] of 82 cm^{-1}, the energies for the first, second, and third overtones are estimated to be 21, 31, and 40 kcal/mol, respectively. The argon matrix infrared spectra[39] show a band at 3550−3540 cm^{-1} for the fundamental and 6920 cm^{-1} for the first overtone, again somewhat lower than our estimates for the OH_b stretch. From a strictly energetic viewpoint, overtone excitation of this mode to $v_{OHb} \geq 3$ could also give rise to decarboxylation. However, since it is not strongly coupled to the reaction path, we would expect dissociation to be less efficient via this excitation route. A recent report by Nizkorodov et al.[40] suggests that peroxyalkyl nitrate (PAN) also does not undergo efficient dissociation (to $NO_2 + CH_3C(O)O_2$) following excitation of CH overtone transitions near the energetic threshold. Clearly for unimolecular processes to occur at energies near threshold, the energy must somehow be channeled into the reaction coordinate prior to its dissipation into the microcanonical "bath" of nonreactive modes. Thus, it seems reasonable to expect a more efficient unimolecular transformation when the excitation energy is deposited initially into a mode which is strongly coupled to the reaction coordinate.

Decarboxylation of Malonic Acid Monohydrate. A full discussion of the hydrates of malonic acid will be presented elsewhere.[30] Here, we restrict our attention to the lowest energy decarboxylation pathways of the monohydrate isomer whose optimized minimum-energy structure is displayed in Figure 2c.

As shown there, the addition of one water molecule to malonic acid can create an eight-membered, hydrogen-bonded ring structure by having the acidic proton, H_a, of one of the carboxylic groups hydrogen-bonded to the water oxygen and one of the water hydrogens, H_c, bonded to the carbonyl oxygen of the *second* carboxylic group of the acid. The central carbon of the malonic acid backbone is out-of-plane in this eight-membered ring structure. This structure is bound by 5.7 kcal/mol (3.0 kcal/mol after zero-point correction), somewhat less than the binding energy calculated at the same level of water to nitric and formic acids,[36,41] which form six-membered ring structures. A six-membered ring structure is possible in this case as well, with the water molecule bridging the acidic hydrogen and carbonyl moieties of the same carboxylic acid group. This structure is energetically more favorable than the one pictured in Figure 2c, with a binding energy close to that found for the nitric acid−water complex.[30]

Pathway 2 for decarboxylation involves a double-proton exchange: the H_a of the acid and H_c of water are simultaneously transferred to their neighboring (hydrogen-bonded) oxygens. The water molecule in the malonic acid·(H_2O) complex acts as a bridge between the carboxylic acid group which *donates* a proton and the carbonyl oxygen of the other, which *accepts* it. The water molecule thus acts as a catalyst in this double-proton transfer; the activation energy for decarboxylation of the complex is lowered by about 5 kcal/mol, to 22.7 kcal/mol before, and 20.6 kcal/mol after zero-point correction. With respect to the unclustered malonic acid + water system, the decarboxylation barrier is lowered by about 10 kcal/mol overall.

Similar to TS1, the transition state for reaction 2 is "late", formed when the hydrogen transfers are almost completed. Endoergic hydrogen-transfer reactions with late barriers (i.e., in which the transition state resembles the products) are often aided by vibrational excitation,[42] with rate coefficients increasing by many orders of magnitude.[43] Although this propensity has been most explored for simple reactions, it seems reasonable to assume that vibrational energy might be quite effective at promoting reaction in the present case as well.

The energetics of malonic acid monohydrate decarboxylation are sketched in Figure 3. The same general reaction pathway governs the process in the complex: decarboxylation initially forms an enol species (which we assume binds to the water catalyst), which may subsequently undergo rearrangement to acetic acid. Interestingly, the lowering of the energetic barrier for the enol-keto transformation is quite significant upon complexation with water: from ∼44 kcal/mol to ∼18 kcal/mol in the monohydrate. The details of this process will be the subject of a future publication.

The OH stretches in the complex are consistent with its hydrogen-bonded structure. The fundamental frequency of the hydrogen-bonded acid OH lies about 400 cm^{-1} to the red of the "free" acid OH stretch, about 150 cm^{-1} more red shifted than it appears in the uncomplexed molecule. The "free" acid group shows no shifting from its uncomplexed value. In the water molecule as well, one OH stretch is significantly red shifted, by about 300 cm^{-1}, and the "free" OH is not affected by complexation. The overtone energies in the complex were estimated in the same way as for the uncomplexed malonic acid, using the anharmonicity corrections calculated by Kjaergaard.[39] For the malonic acid moiety of the complex, the values for the hydrogen-bonded OH are 18.7 kcal/mol for $v_{OH} = 2$, 27.0 kcal/mol for $v_{OH} = 3$, and 35.0 kcal/mol for $v_{OH} = 4$. Overtone excitation to $v_{OH} \geq 2$ in the complex should therefore be energetically sufficient to induce decarboxylation.

Atmospheric Implications. To estimate the atmospheric *J* value for overtone-induced decarboxylation, the integrated absorption cross sections for O−H stretching overtones in acetic acid were used, since data for malonic acid are not available. For the $v_{OH} = 3$ transition, which is predicted to lie in the 1005−1070-nm range, a value of 3.21×10^{-20} cm^2 $molecule^{-1}$ cm^{-1} was used,[44] and for $v_{OH} = 2$, possibly relevant for reaction of the complexes, a value of 4.98×10^{-19} cm^2 $molecule^{-1}$ cm^{-1} was taken from Lange et al.[45] With these values, the solar flux taken from tabulated data,[17,46] and assuming unit decarboxylation quantum yield, the rate constant for overtone-induced dissociation of malonic acid was calculated to be 1.15×10^{-6} s^{-1} for excitation to $v_{OH} = 3$, corresponding to an atmospheric lifetime of about 10 days. This order of lifetime suggests that decarboxylation can be competitive with wet deposition, which has a lifetime of about 9 days,[17] or reaction with OH, which is the secondary mechanism for removal of organic acids from the atmosphere. The lifetime of HCOOH against reaction with OH is 26 days at [OH] of 1×10^6 radicals cm^{-3};[47] the malonic acid lifetime is probably similar.

It is of some interest to speculate on the fate of the enol fragment of the dissociation. In solution, the thermal process yields acetic acid; our results indicate that the enol→keto rearrangement barrier drops significantly because of the presence of even a single water molecule. In the gas-phase, nonhydrated species, our results suggest that the enol will be formed and will persist for some time (unless a concerted decarboxylation rearrangement does take place). Its most likely fate then would be reaction with OH (which would probably be very facile) or dissolution into aqueous particulate material, which would then promote acetic acid formation.

We estimate a *J* value for decarboxylation of the hydrated malonic acid species following excitation of $v_{OH} = 2$ to be about 1×10^{-5} s^{-1}, yielding a lifetime of about 1 day. The atmospheric abundance of malonic acid−water complexes is difficult to access. Still, the temperature-dependent thermodynamic equilibrium constant, K(T), can be estimated using standard statistical mechanical methods from the vibrational and rotational partition functions of the complex and its constituents[48] and the altitude profile of temperature and water vapor concentration.[49] In the present case, the partition functions are obtained from our quantum chemical calculation, giving an estimate for K(T) at tropopause temperatures of 7.1×10^{-4} atm^{-1} for the monohydrate. At temperatures corresponding to 2−3 km above the ground level, the equilibrium constant diminishes by about 1 order of magnitude. The small value of the equilibrium constant suggests that only a tiny fraction of atmospheric malonic acid will be present as the 1:1 hydrate complex. However, malonic acid in the condensed phase shows a reasonable propensity to take up water, both in the pure form and in mixtures with ammonium sulfate.[50,51] It thus seems possible that malonic acid associated with atmospheric aerosols or adsorbed on ice crystal surfaces might show an enhancement in the decarboxylation *J* value over that of the monomer.

Conclusions

Malonic acid undergoes thermal decarboxylation at low temperatures. We have shown that the lowest energy decarboxylation pathway is energetically and dynamically accessible to malonic acid excited to low-lying ($v_{OH} \geq 3$) OH vibrational overtone levels. Using estimated absorption cross sections for the overtone transitions, we calculate a *J* value for the overtone-driven decarboxylation of 10^{-6} s^{-1}, which implies that decarboxylation can compete favorably with rainout and OH reaction for removal of malonic acid from the atmosphere. We have also calculated the decarboxylation pathway for an isomer of the 1:1 complex of malonic acid with water. The energetic barrier to decarboxylation is lowered significantly, such that overtone transitions $v_{OH} \geq 2$ will be sufficient energetically to induce reaction. Water acts as a catalyst in this process, donating one hydrogen to the malonic acid, and accepting another. Although the atmospheric abundance of this isomer is probably not great, catalysis by water molecules could take place in condensed-phase malonic acid, potentially becoming an important atmospheric sink for this, and similar, diacids.

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