The vibrational spectra and structures of dimethyl oxaloacetate and dimethyl oxaloacetate- d_2^*

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Abstract—The complete vibrational spectra of dimethyl oxaloacetate and dimethyl oxaloacetate- d_2 have been recorded and analyzed. The i.r. spectra were recorded at liquid N₂ as well as ambient temperature. Tentative vibrational assignments are proposed based on an enol structure in the crystalline phase. In solution, dimethyl oxaloacetate exists as a tautomeric mixture of keto and enol forms. Evidence for the existence of different enol conformers in CCl₄ and CS₂ solutions is also presented.

INTRODUCTION

Oxaloacetic acid and its derivatives are important biochemical molecules. They have, however, received little attention with regard to their vibrational spectra and detailed structures. In particular, there is a lack of a complete vibrational spectroscopic study of dimethyl oxaloacetate (H3CO2C-CH2-CO-CO2CH3), DMOA, and dimethyl $oxaloacetate-d_2$ (H₃CO₂C-CD₂ -CO-CO₂CH₃), DMOA- d_2 . As a part of a general project of determining the structural and spectral properties of 1,3-dicarbonyl compounds, we have synthesized DMOA and DMOA-d₂ and subjected them to a complete vibrational analysis. As an aid in the vibrational assignment, we have recorded the vibrational spectra of diethyl oxaloacetate and 4methyl oxaloacetate, which also were synthesized, and commercial oxaloacetic acid.

Generally, 1,3-dicarbonyl compounds enolize to a much greater degree than monocarbonyl compounds [1]. The two carbonyls resonance stabilize the carbanion formed by deprotonation at the central carbon atom, the rate limiting step of enolization. 1,3-Ketoesters, \ddagger of which DMOA and DMOA- d_2 are examples, commonly enolize to a lesser extent than 1,3diketones. There is a small resonance interaction in the carboalkoxy group which creates less of a tendency for the carbonyl to resonance stabilize the carbanion. In the enol form, however, DMOA and DMOA- d_2 's ester carbonyls are conjugated with a double bond, which stabilizes the structure. DMOA and DMOA- d_2 are interesting compounds to study, if only to ascertain which effects are more important in determining their more stable structure.

No spectroscopic or structural studies of DMOA or $DMOA-d_2$ are reported in the literature. Infrared

spectra of oxaloacetic acid have been reported [2, 3] but very few of the bands were assigned. It was determined long ago from u.v. [4] and bromination titrimetric [5] techniques that in solution oxaloacetic acid exists in a tautomeric equilibrium between keto and enol species. Later, NMR studies of oxaloacetic acid [6-8], diethyl oxaloacetate [6], and 4-ethyl oxaloacetate [8] suggest this behavior is common to the oxaloacetate series.

EXPERIMENTAL

DMOA was synthesized using a variation of the method reported by WISLICENUS and GROSSMANN [9]. 0.3 mole of dimethyl oxalate (Aldrich) and 0.3 mole of NaH (Aldrich) were placed in a 1000 ml three-neck, round-bottom flask equipped with an overhead rotary stirrer. The dimethyl oxalate was dissolved in 600 ml of anhydrous diethyl ether. Two drops of dry methanol were added to the mixture. A 30%mole excess of methyl acetate (Aldrich) was added, over the course of a few hours, to the stirred, refluxing (under dry N2) mixture. The refluxing was continued for 2 days, and the resulting sodium enolate salt of DMOA was isolated by vacuum filtration. This salt was dissolved in 150 ml of 10% (v/v) H₂SO₄, and the DMOA was extracted with diethyl ether. After evaporation of the extraction solvent, the product was recrystallized twice from diethyl ether, and its melting point, 74°C, matched the literature value.

DMOA- d_2 was synthesized by placing 0.25 g of DMOA in a round-bottom flask and dissolving it in the minimum amount of D_2O required. The solution was stirred under dry N_2 for 1 day. The D_2O was then removed by vacuum evaporation. The DMOA- d_2 was vacuum distilled (0.6 mm Hg) and the product was isolated on the walls of the condenser and in the receiving flask (the boiling point of DMOA- d_2 at this pressure was not measured). The D/H purity of the product was estimated to be 90%. Repetition of the exchange reaction did not result in a better percentage of exchange.

Diethyl oxaloacetate was prepared by dissolving sodium diethyl oxaloacetate (ICN Nutritional Biochemicals) in 10% (v/v) H_2SO_4 and extracting with diethyl ether. The diethyl ether was evaporated, and the oily product was vacuum distilled twice. The fraction boiling at 64°C at 0.3 mm Hg was collected.

4-Methyl oxaloacetate $(H_3CO_2C-CH_2-CO-CO_2H)$ was synthesized using a procedure similar to that reported for 4ethyl oxaloacetate [10]. 0.2 mole of sodium DMOA, obtained by the method previously described, was dissolved in 100 ml

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of distilled water. 0.1 mole of CuCl₂·2H₂O (Matheson, Coleman and Bell) dissolved in 50 ml of distilled water was added to the enolate salt solution. The resulting green precipitate, the DMOA copper complex, was filtered by vacuum filtration and washed with distilled water. 0.067 mole of this green copper complex was placed in 100 ml of methanol, and the methanol was brought to a boil. The copper complex does not completely dissolve. 0.14 mole of KOH (pellets, Fisher Scientific) dissolved in 100 ml of methanol was added to the mixture. The resulting dark green copper complex of 4-methyl oxaloacetate was isolated by vacuum filtration and washed with cold water. After drying, this dark green complex was powdered using a mortar and pestle. The powder was placed in 100 ml of 1.3 M H₂SO₄. After stirring for a short period of time, 90 ml of distilled water was added. The aqueous mixture was extracted with six 125 ml portions of diethyl ether. After the diethyl ether was evaporated, the product was recrystallized twice from CHCl₃. 4-Methyl oxaloacetate melts at 128–130°C.

Oxaloacetic acid $(HO_2C-CH_2-CO-CO_2H)$ was purchased from the Aldrich Chemical Co. Prior to use it was precipitated twice from hot acetone by the addition of hot benzene.

Films of DMOA were prepared for mid i.r. investigations by dissolving an appropriate amount of the compound in spectroscopic grade acetone (Fisher Scientific) and applying the solution to a CsI window heated with a floodlight. After the solvent evaporated, a film of crystalline DMOA was left on the window. Samples of DMOA- d_2 were prepared as hexachlorobutadiene and Nujol mulis. Both compounds were run as Nujol mulls in the far i.r. 1% (w/v) solutions of DMOA were prepared for mid i.r. investigation by dissolving 0.02 g of the compound in spectroscopic grade solvent (Fisher Scientific) and adjusting the volume to 2 ml in volumetric test tubes. The i.r. spectra of the CCl4 and diethyl ether solutions were recorded in a NaCl amalgamated sealed solution cell with a pathlength of 0.1 mm, whilst the i.r. spectra of the 2propanol, anhydrous ethanol and methanol solutions were recorded in a demountable NaCl cell with a 0.1 mm spacer. Saturated solutions of DMOA were prepared in CCl₄ and CS2, and the i.r. spectra of these solutions were recorded in the sealed cell.

A conventional liquid N_2 cell was used to obtain low temperature spectra in the mid and far i.r. regions.

Infrared spectra from 4000-400 cm⁻¹ were recorded on a Digilab FTS-14C/D Fourier Transform i.r. spectrometer with a coiled hot wire source and a TGS detector. 150 single beam scans were collected at a 0.5 cm⁻¹ resolution. Double precision word size and triangular apodization were used in the calculation of the spectra. The single beam spectra of the samples were ratioed against background and plotted in the percentage transmittance mode. All spectra were baseline corrected using the BASELINE program supplied with the Digilab FTS-14C/D. Typical liquid N₂ temperature mid i.r. spectra of DMOA and DMOA- d_2 are shown in Figs 6 and 7, respectively. Far i.r. spectra from 500-62 cm⁻¹ were recorded on a Perkin-Elmer Model 180 spectrophotometer. A Globar source was employed down to 125 cm⁻¹; a mercury arc lamp was used from 125-62 cm⁻¹. A TGS detector was used in the far i.r. A typical spectral slit width was 2.5 cm⁻¹ at 500 cm⁻¹ using programmable slits and automatic gain control. Raman spectra down to 50 cm⁻¹ were recorded using an Instruments SA Ramanor U-1000 Raman spectrometer. The 514.5 nm green line from a Lexel Model 150 Ar⁺ laser was passed through a premonochromator and into the macro sample compartment where the light (130 mW) was focussed on a capillary tube filled with sample. The scattered radiation was collected, passed through a 1 m double monochromator, and detected with an RCA C31034-02 photomultiplier tube contained in a thermoelectrically cooled housing (Products for Research, Inc.). A data point interval of 1 cm⁻¹ and a collection time of 1 sec per point were employed. Three scans were added. Typical ambient temperature Raman spectra of **DMOA** and **DMOA**- d_2 are shown in Figs 8 and 9, respectively.

RESULTS AND DISCUSSION

Although no previous structural studies have been reported for DMOA or DMOA- d_2 , structural studies have been reported for other molecules of this type. Complete enolization has been reported for 5,5dimethyl-1,3-cyclohexanedione [11], malonaldehyde [12], bromomalonaldehyde [13] and methyl acetopyruvate [14] in the crystal state. In solution, 1,3dicarbonyl compounds exist as an equilibrium mixture of keto and enol forms. It is known that the keto-enol tautomerization is solvent dependent [3, 4, 6, 7, 15]. The proportion of the keto form increases with increasing solvent polarity.

a. Solution studies

The i.r. spectra of DMOA in solvents of differing polarities have been recorded in the 1900-1500 cm⁻¹ region and are shown, in absorbance, in Fig. 1. The solutions were 1% w/v in concentration and the pathlengths were 0.1 mm. The spectra have been solvent compensated using Digilab's automatic subtraction program and are plotted on the same scale throughout. For the CCl₄ solution, we observe six bands with appreciable intensity. These bands are located at 1759, 1743, 1672 (shoulder), 1664, 1641 and 1620 cm⁻¹. A small increase in solvent polarity does not result in a great change in the spectrum. The i.r. spectrum of DMOA in diethyl ether (dielectric constant = 4.34) is not that much different than that in CCl_4 (dielectric constant = 2.24). The lower frequency bands at 1672, 1664, 1641 and 1620 cm⁻¹ progressively decrease in intensity when the i.r. spectra of DMOA are recorded in 2-propanol (dielectric constant = 18.3), absolute ethanol (dielectric constant = 24.3) and methanol (dielectric constant = 32.6). The diminished intensity of these bands as solvent polarity increases is consistent with their assignment to enol vibrational modes. The absorbance increase (relative to the aforementioned enol vibrational modes) near 1740 cm⁻¹ as solvent polarity increases is due to an increasing proportion of keto species and a consequent intensification of the carbonyl stretches of the keto form. The solution spectra indicate that DMOA exists in a keto-enol equilibrium (Fig. 2) in solution, and the position of this equilibrium is solvent dependent. As stated previously, the keto form of 1,3-dicarbonyl compounds increases in concentration as solvent polarity increases.

A lowering of the carbonyl stretching frequency in the enol form of 1,3-dicarbonyl compounds has been reported [16] and is indicative of a chelate structure in which the carbonyl is both conjugated and hydrogen bonded. This interaction lowers the carbonyl stretching frequency to a much greater extent than conjugative effects alone. The effect, known as conjugate chelation, has been described by others [16, 17, 18], and is depicted in Fig. 3.



Fig. 1. The i.r. spectra of 1% (w/v) solutions of dimethyl oxaloacetate in (1) CCl₄, (2) diethyl ether, (3) 2propanol, (4) anhydrous ethanol and (5) methanol. The spectra are recorded in the carbonyl and C=C stretching region.



Fig. 2. The keto-enol tautomerization of dimethyl oxaloacetate in solution.



Fig. 3. Depiction of the resonance exhibited by enols of 1,3-dicarbonyl compounds.

For enolic DMOA, one i.r. absorption band would be expected for the hydrogen bonded, conjugated carbonyl stretch, and one i.r. absorption band would be expected for the C=C stretch. We observe four bands in the 1700–1600 cm^{-1} region (CCl₄ solution), however. This behavior can be explained in terms of a conformational equilibrium between enol forms as shown in Fig. 4. This type of conformational equilibrium has been previously reported for conjugated molecules, e.g. acrylic acid [19, 20]. These are the most likely structures DMOA would assume based on theoretical grounds. Our conclusion concerning the exact structures of the conformers in solution is admittedly somewhat speculative and proof requires further work. The bands at 1672 (shoulder) and 1664 cm⁻¹ (CCl₄ solution) are assigned to the conjugate chelated carbonyl stretches of the two conformers. This assignment agrees well with the 1667 cm⁻¹ value observed for the conjugate chelate carbonyl stretch of enolic ethyl acetoacetate, a simpler 1,3-ketoester [21]. The 1641 and 1620 cm^{-1} bands (CCl₄ solution) are assigned to C=C stretches of the enol conformers. Two other pieces of evidence point to the presence of a conformational equilibrium. First, i.r. absorption bands of solid DMOA at 1103, 857 and 680 cm^{-1} (Table 1) are also split when observed in solution. Secondly, two C=C stretching modes are observed at 1642 and 1623 cm⁻¹ in the Raman spectrum of a saturated solution of DMOA in CCl₄ (Fig. 5). The conjugate chelated carbonyl stretching bands are not observed in the Raman spectrum. It is not known why these bands are not observed in the Raman spectrum, but this behavior is common to enolic oxaloacetate and other enolic 1,3-dicarbonyl compounds [22]. The assignment of bands from 1800-1700 cm⁻¹ in the solution spectra is complicated due to band overlap, the presence of different enol conformers and the keto-enol tautomerization. The 1759 and 1743 cm⁻¹ bands (CCl₄ solution) are most likely non-hydrogen bonded carbonyl stretches of the two aforementioned enol conformers. We believe the enol species predominates in non-polar solvents, and due to this fact, a keto carbonyl stretch would not be expected to be as intense as these bands. The situation becomes more complex when polar solvents are used. The 1759 cm⁻¹ band reduces in intensity (as do the lower frequency bands) when more polar solvents are used. The 1743 cm^{-1} band appears to intensify. The evidence suggests this intensification is due to an increasing proportion of keto species and a consequent absorbance increase of keto carbonyl stretches. Keto DMOA would be expected to have three carbonyl stretches. Three bands are not observed, however. The keto carbonyl stretches are observed as two unresolved bands (in methanol solution) near 1740 cm^{-1} . It is not surprising these bands are not resolved; interactions between DMOA molecules and solvent molecules no doubt broaden these bands.

b. Crystal structure considerations

As stated previously, some 1,3-dicarbonyl compounds have been shown to exist exclusively in an enol structure in the solid phase [11-14]. The data indicate DMOA and DMOA- d_2 are also enols in the solid phase. This conclusion is based on several points. A broad band centered around 3120 cm^{-1} is present in the i.r. spectrum of DMOA (Fig. 6). This band shifts to 2338 cm⁻¹ in the i.r. spectrum of the heavy compound (Fig. 7). These bands are assigned to the OH and OD stretches, respectively, of the enol form. A strong band is also observed at $1665 \,\mathrm{cm}^{-1}$ in the i.r. spectrum of DMOA (1658 cm⁻¹ in the i.r. spectrum of DMOA- d_2). As was discussed previously, this band is due to the conjugate chelated carbonyl stretch and is characteristic of enols of 1,3-dicarbonyl compounds. The strongest bands in the Raman spectra of DMOA (Fig. 8) and DMOA- d_2 (Fig. 9) are located at 1634 and 1610 cm⁻¹, respectively. These bands are undoubtedly due to C=C stretches. C=C stretching modes give rise to very strong Raman bands [17] and these bands are also within the frequency range expected.

Within the limits of the sensitivity of the experimental techniques used, there is no evidence for the presence of the keto structure in the solid phase. One would expect three bands due to carbonyl stretches in the normal ester and ketone ranges if keto DMOA or DMOA- d_2 were present. There is only one strong band observed in this range, however. This is true for both the i.r. and Raman spectra. This band is due to the nonhydrogen bonded carbonyl stretch of the enol form. The band is in the frequency range expected for esters [17, 18].

Enols of 1,3-dicarbonyl compounds have been reported to crystallize as hydrogen bonded polymers



Fig. 4. The most likely structures of the two enol conformers of dimethyl oxaloacetate.

	Infrar	ed	Raman		
77 K	298 K†	298 K ‡	298 K	Assignment	
3452 vw	3450 vw			$2 \times 1732 = 3464$	
3358 vw	3353 vw			1634 + 1732 = 3366	
~3120 br	~3120 br			vOH (en)	
3113 w	3111 m	3121 w	3113 m	vCH (en)	
3050 vw			3048 w	vCH ₃ , asym.	
3036 vw		3031 w	3036 m	vCH ₃ , asym.	
3011 m	3008 m	3004 w	3010 m	vCH ₃ , asym.	
2963 m	2960 m	2955 m	2965 s	vCH ₃ , sym.	
2876 vw	2873 vw	2870 vw	2874 vw	$2 \times 1443 = 2886$	
2010 14	2860 vw	20/010	2861 w	1398 + 1466 = 2864	
2797 vw				1165 + 1634 = 2799	
2733 vw	2729 v w			1273 + 1460 = 2733	
2633 vw				1194 + 1443 = 2637	
2612 w				947 + 1665 = 2612	
2602 w	2603 vw			870 + 1732 = 2602	
2577 vw				947 + 1634 = 2581	
2271 vw				870 + 1407 = 2277	
2262 vw				857 + 1407 = 2264	
2195 w				1030 + 1165 = 2195	
2131 w				680 + 1451 = 2131	
2112 w				947 + 1165 = 2112	
1998 vw				537 + 1460 = 1997	
1988 w				537 + 1451 = 1988	
1929 w				297 + 1634 = 1931	
1904 vm				$2 \times 947 = 1894$	
1870				$777 \pm 1103 = 1880$	
1830 ch				431 + 1407 = 1838	
1803 m	1800 ch			$857 \pm 947 = 1804$	
1605 11	1000 811		1794 1/11	$343 \pm 1445 = 1788$	
1774 ch	1780		1777	$417 \pm 1366 = 1778$	
1774 S A	1/00 VW	17508 .	1111 W	*C-O	
1743-1		1/3985	1753	510 + 1325 - 1744	
1742 SN	1722 -	1742 -	1722 -	319 + 1223 = 1744	
17328	1/328	17435	17325	VC=0	
1709 w	1098 W		1700 W	$2 \times 32 = 1/14$	
			1089 W	293 + 1398 = 1091	
		16/2§sn		vC=O	
1665 s	1600 5	1004 s		VC=O (en)	
1648 W	1642 m		1034 W	/94 + 857 = 1031	
1638 s (1633 sh	1641 s	1634 vs	vC=C (en)	
10342)		16208 s		$\nu C = C (en)$	
1606 sh				752 + 857 = 1609	
1524 w				297 + 1225 = 1522	
1507 m				537 + 976 = 1513	
1484 w				537 + 947 = 1484	
1473 m				680 + 794 = 1474	
1460 €	1459 ch		1466 m	δCH ₂ asym	
1451 6	1451 s	1440 c	1457 m	δCH ₂ , asym	
14430	14436	1438 6	1445 m	δCH, sym	
1407.0	1405 m	1307 m	1308	AOH (en)	
14075	1405 m	1397 01	1370 ₩	$537 \pm 857 = 1304$	
1390 Ш				537 + 857 = 1594	
1360 8	1355 m	1352 m	1342 w	vC-O (en)	
1332 80 3				527 + 704 - 1321	
1329 W	1212			337 + 794 = 1331	
1315 VW	1313 VW			540 + 970 = 1310	
1310w				519 + 794 = 1313	
1297 w		1050	10/0	519 + 111 = 1290	
1273 s	1265 s	1259 vs	1260 s	vC-OCH ₃ , vC-C (en	
1225 s	1218 s	122 2 v s		vC-OCH ₃	
1203 m	1201 vw		1204 w	CH ₃ rock	
1194 m	1190 w	1185 m	1 194 m	CH ₃ rock	
1175 m 👌	1171 w		1162.w	CH ₃ rock	
1165 w ∫			11V2 H		
1136 vw				340 + 794 = 1134	
		1106§m		δCH (en)	
1103 s	1103 s	1102 m	110i m	δCH (en)	
1030 s	1026 s	1027 m	1021 vw	CH ₃ rock	

Table 1. The observed vibrational spectra of dimethyl oxaloacetate (in cm⁻¹) and their tentative assignments^{*}

	Infrared Raman		Raman	
77 K	298 K †	298 K‡	298 K	Assignment
1010 w, br				yOH (en)
976 m	974 m	985 w	972 s	vCO-CH ₁
947 m	945 m	945 w	944 s	VCO-CH ₃ , VC-C
928 w				412 + 519 = 931
901 vw	902 vw		902 vw	127 + 777 = 904
870 s	867 s	866 m	868 m	δCO_2
857 s	851 m	856 sh	847 m	δCO_2
		833§ w		δCO_2
79 4 s	790 sh	793 sh	799 vw	yCH (en)
783 sh (783 sh (
777 s 🗍	777s ∫	783 s	77 9 s	γCO2
770 sh				256 + 519 = 775
752 s	7 46 s	730 m	7 4 3 vw	γCO ₂
		691§vw		$\delta C = \overline{C} - O$ (en)
680 s	680 s	680 w	681 vw	$\delta C = C - O$ (en)
608 w				90 + 519 = 609
579 vw			582 vw	239 + 340 = 579
537 s	534 m		534 w	δССО
519 s	517 m		515 w	δCCO
431 vw			443 vw	δ skeleton
412 vw	411 w		409 w	δCOC
373 m			370 w	δርΟር
340 m			343 vw	δ skeleton
			319 vw	72 + 248 = 320
297 vw			293 m	y skeleton
256 m			248 w	TCO2
239 w			235 w	τCO2
214 vw				90 + 127 = 217
194 w				vH-bond (en)
158 w				y skeleton
136 w			139 s	TOCH ₃
127 m			134 s	τOCH₃
1 11 vw				τCH ₃
90 m			95 s	τCH ₃
			83	Lattice
			72	Lattice

Table 1. (Contd.)

*Abbreviations: v, very; s, strong; m, medium; w, weak; br, broad; sh, shoulder. en indicates that the vibration is associated with the enol portion of the molecule. Symbols: v, bond stretch; δ , in-plane bend; γ , out-of-plane bend; τ , torsion.

†Crystalline solid.

\$Vibrational band of second enol conformer.



Fig. 5. A Raman spectrum of a saturated solution of dimethyl oxaloacetate in CCl4 (in the carbonyl and C=C stretching region).



Fig. 6. A typical mid i.r. spectrum of dimethyl oxaloacetate at liquid N₂ temperature.



Fig. 7. A typical mid i.r. spectrum of dimethyl oxaloacetate- d_2 at liquid N₂ temperature. (The broad band near 3200 cm⁻¹ is due to a small amount of ice which has crystallized on the window.)

[11, 13] and as internally hydrogen bonded monomers [14]. Hydrogen bonded dimers in solution have been reported as well [16]. The evidence suggests DMOA assumes an internally hydrogen bonded enolic structure in the solid phase. In dilute solution, we do not observe a free OH stretch due to a non-hydrogen bonded hydroxyl group. This indicates DMOA is internally hydrogen bonded in dilute solution. The solution and solid phase spectra are very similar, and therefore it is concluded the structures are the same in both cases. The most probable structure of DMOA is the *cis-trans* structure shown in Fig. 4. When double bonds are *trans* to one another, as in this structure, resonance stabilization is theoretically maximized. If DMOA was a dimer, noncoincidence of i.r. and Raman bands would be expected as is observed with carboxylic acid dimers [23]. Pseudo C_{2h} or C_i selection rules would be followed in the dimer case, and this would lead to the noncoincidence. Noncoincidence is not observed when comparing Raman and i.r. data, and it is therefore concluded that DMOA is not a dimer in the solid phase.

c. Vibrational assignment

Complete vibrational assignments of large molecules such as DMOA and DMOA- d_2 , which have no significant symmetry, are difficult due to the complexity of the spectra. Nevertheless, most of the bands may be assigned with reasonable certainty by using well known group frequencies [17, 18] and by com-



Fig. 8. A typical ambient temperature Raman spectrum of dimethyl oxaloacetate.



Fig. 9. A typical ambient temperature Raman spectrum of dimethyl oxaloacetate- d_2 .

parison with the vibrational spectra of diethyl oxaloacetate, 4-methyl oxaloacetate and oxaloacetic acid. The latter two molecules have also undergone complete vibrational assignments in connection with structural considerations [24]. In addition, vibrational assignments of enolic acetyl acetone derivatives [25, 26] are helpful in assigning modes associated with the enol portion of DMOA and DMOA- d_2 . The observed spectral bands of DMOA and DMOA- d_2 , and their tentative assignments are presented in Table 1 and Table 2, respectively. Unless otherwise

noted, the frequencies used in the following discussion were taken from the low temperature i.r. spectra.

The assignment of the olefinic CH stretch of DMOA and the CD stretch of DMOA- d_2 is straightforward. The 3113 cm⁻¹ band in the i.r. spectrum of DMOA is shifted to 2318 cm⁻¹ in the heavy compound. A corresponding shift is also observed in the Raman spectra of the materials. The frequency of the CH stretch is higher than normally observed for olefins [17, 18] but deuterium substitution allows an unequivocal assignment.

Table 2. (Contd.)

Table 2.	The	observed		vibratio	nal	spec	tra	of
dimethyl	oxaloa	icetate-d2	(in	cm ⁻¹)	and	their	tenta	ative
		999	ionn	nents*				

Infrared

77 K 3450 w 3347 w 3050 vw

3013 m 2994 vw 2963 m

2938 vw 2915 vw 2866 w 2785 vw 2772 vw 2736 vw 2612 vw 2469 vw

2369 w

2338 w

2318 m

2265 vw 2246 vw 2207 vw 2139 vw 2109 vw 2090 vw 2016 vw 1970 vw 1956 vw 1929 m 1888 vw 1804 vw 1734s

1678 sh 1658 s

1641 w

1632 si

1622 s(

1582m 1560 w 1527 w

1458 m

1448 m

1442 s

1371 m

1344 m

1323 sh

1309 s

1276 sh

1244 s

1226 sh

1211 m

1205 m]

1201 m (

1186 m

1174 w 🕻

1165 vw

1119 w

1055 s

1034 s

993 s

978 m

931 w

916 s

880 w

870 w 1

854 vw

1153 w

1060 s

1034 m

994 s

977 m

930 vw

914 s

878 w

869 w 1 1162 w

1034 vw

986 m

972 s

929 w

914 m

867 w

CH₃ rock

 δOD (en)

CH₃ rock

vCO-CH₃

vC-C vCO-CH₃

 δCO_2

362 + 756 = 1118

409 + 524 = 933

133 + 725 = 858

assignments*			Infrared		
xd	Raman		77 K	2	
298 K	298 K	Assignment	846 m)	8	
		2	840 m)	ð. 91	
		$2 \times 1/34 = 3408$ 1622 + 1734 = 3256	705 m (7	
	1047 m	1022 + 1734 = 3330	777 s	7	
	3047Ш 3036 m	WCH, asym	769 w	'	
3010 m	3010 m	vCH, asym.	764 w		
3010 III	J010	1371 + 1622 = 2993	756 w		
2961 m	2965 s	vCH ₂ , svm.	725 m	72	
2/01 III	27000	1205 + 1734 = 2939	669 w 1	66	
		$2 \times 1458 = 2916$	658 m 🕯	65	
	2862 m	$2 \times 1442 = 2884$	624 m	61	
		1055 + 1734 = 2789	610 m	60	
		1034 + 1734 = 2768	582 s	574	
		$2 \times 1371 = 2742$	524 m	52	
		880 + 1734 = 2614	501 m	49	
2444 w		1226 + 1244 = 2470	446 vw		
2373 w		916 + 1458 = 2374	409 w	41	
2332 w		vOD (en)	384 sh		
2318 m	2317 m	vCD (en)	362 w		
		805 + 1458 = 2263	322 m		
		803 + 1443 = 2247	295 sn		
		1034 + 1174 = 2208	251 S (242 sh (
		910 + 1220 = 2142	243 sn j		
		$2 \times 1033 = 2110$ 846 \ 1244 - 2000	230 w		
		$367 \pm 1658 = 2090$	153 w		
		$916 \pm 1055 = 1971$	155 ₩		
		$2 \times 978 = 1956$	133 w		
		$756 \pm 1174 = 1930$	123 w		
		582 + 1309 = 1891	103 vw		
		362 + 1442 = 1804	90 m		
	1777 m	867 + 914 = 1781			
1734 s	1732 s	vC=O			
	1682 m	236 + 1442 = 1678			
1659 s	1655 m	vC=O	*Abbre	viatio	
1640 w		725 + 916 = 1641	broad; sh	, sho	
1630 s (1610 10	»C-C (en)	bend; y, o	ut-of	
1618 s (1010 13				
1584 m		409 + 1174 = 1583			
		582 + 9/8 = 1560			
1450	1468	658 + 870 = 1528	The as:	signt	
1458 m	1465 \$	OCH ₃ , asym.	clear. The	e bro	
1430 m	14578	SCH sum	to the er	iol (
1272	1269.00	$\nu C = \Omega$ (ep)	broader	and	
1J/2Ш	1300 W	$501 \pm 846 = 1347$	normal h	uno urde	
		409 + 916 = 1325	normal n	iyara	
1310s		vC-OCH	and lowe	r irea	
		362 + 916 = 1278	strong hy	/dro	
	1246 w	vC-OCH ₃	situation	is 1	
	1227 s	vC-C (en)	DMOA-4	dz. 7	
1210 m		236 + 978 = 1214	region fr	- - 	
1204 m		CH. rock	are obser		
1204Ш		UII3 IOWA		ຸກວັບ	
1182 m	1188 m	CH ₃ rock	assign th	C 23	

Infrared		Raman			
77 K	298 K	298 K	Assignment		
846 m (845 w (848 w (
840 m∫	839 m∫	836s j	0002		
805 m (804 m (804 s	δCD		
795 m (785 sh (
777 s	775 s	772 w	γCO ₂		
769 w			362 + 409 = 771		
764 w			243 + 524 = 767		
756 w		751 s	γCO ₂		
725 m	723 w		γOD (en)		
669 w (668 w	660 w	$\delta C = C - O$ (en)		
658 m j	659 m∫				
624 m	619 w	613 w	123 + 501 = 624		
610 m	605 w	600 vw	90 + 524 = 614		
582 s	574 s	562 w	γCD (en)		
524 m	523 w	519 w	scco		
501 m	497 m	496 w	δCCO		
446 vw		443 vw	δ skeleton		
409 w	411 w	406 w	δCOC		
384 sh			90 + 295 = 385		
362 w			SCOC		
322 m			δ skeleton		
295 sh		293 m	yskeleton		
251 s {		741 eb	* CO.		
243 sh 🤇		241 511	1002		
236 w		232 w	τCO2		
211 w			90 + 123 = 213		
153 w			y skeleton,		
			vD-bond?		
133 w		129 s	τOCH3		
123 w			τOCH3		
103 vw			τСН3		
90 m.		94 s	τCH3		
		81 s	Lattice		
		70 s	Lattice		

*Abbrev	viations: v,	very; s, str	ong; w, v	weak; m,	medium; b,
broad; sh,	shoulder.	Symbols:	v, bond	stretch;	δ , in-plane
bend; y, ou	it-of-plane	bend; 7, t	orsion.		

ment of the enol OH stretch of DMOA is had band centered near 3120 cm^{-1} is due OH stretch. This band is considerably 100-300 cm⁻¹ lower in frequency than ogen bonded alcohols. The broadening quency of this band is an indication of the gen bond formed in this molecule. The more complex for the OD stretch of There are three bands observed in the 2450 to 2335 cm⁻¹. None of these bands in the Raman spectrum. We prefer to 38 cm^{-1} band as the OD stretch. This assignment is based on the close proximity of the OH stretch to the CH stretch in the light compound. The 2338 cm⁻¹ band is the closest band to the CD stretch in the i.r. spectrum of DMOA- d_2 . It is also stronger than the other two bands, which are assigned as combination bands.

The spectra in the methyl stretching region are atypical of organic compounds in general. Four bands are observed in this region for both DMOA and DMOA- d_2 . Based on the intensity of the bands in the Raman spectra, and their position, we have assigned the 2963 cm⁻¹ bands of DMOA and DMOA- d_2 to symmetric methyl CH stretching modes. The data suggest the two symmetric methyl CH stretching modes of each molecule are accidentally degenerate. No other bands are observed in the expected frequency range for symmetric methyl CH stretches of esters. The remaining three bands are therefore assigned as asymmetric methyl CH stretches. Asymmetric methyl CH stretching modes of isolated methyl groups are often accidentally degenerate due to the pseudo C_{3v} symmetry of the methyl group. In the case of DMOA and DMOA- d_2 this degeneracy has been split for one of the methyl groups. This gives rise to the observation of three bands instead of two. Although the overtone of a methyl deformation can give a band in Fermi resonance with CH stretches of methyl groups, such an assignment does not fit in this case. The strength of the Raman bands observed argues for their assignment as fundamentals. The overtones of the methyl deformations are observed at lower frequencies. Another anomaly is the much greater intensity of two of the asymmetric methyl stretches in the Raman spectra than in the i.r. spectra. The 3036 cm⁻¹ Raman band of $DMOA-d_2$ is not observed in the i.r. Generally, asymmetric methyl stretches are stronger in i.r. spectra than in Raman spectra. The bands in the 2920-2860 cm⁻¹ range are assigned as overtones of methyl bending modes. The intensification of the Raman bands is presumably due to a Fermi resonance interaction with the methyl stretching fundamentals.

The assignment of the fundamental modes in the carbonyl and C=C stretching region is aided by the previously discussed solution studies, the Raman spectra, and the documented vibrational assignments of enols of 1,3-dicarbonyl compounds [25, 26]. The 1732 and 1734 cm⁻¹ bands of DMOA and DMOA- d_2 , respectively, are assigned as the non-hydrogen bonded ester carbonyl stretches. The frequencies of these bands are in the expected range [17, 18]. As stated before, the 1665 cm⁻¹ band of DMOA and the 1658 cm⁻¹ band of DMOA- d_2 are assigned to the hydrogen bonded, conjugated carbonyl stretch. The assignment of these bands is based on the absorbance decrease of the 1664 cm⁻¹ band of DMOA in polar solvents (due to its origination from an enol vibrational mode) and the conjugate chelated carbonyl stretching frequencies reported in the literature [16-19, 25, 26]. The frequencies of DMOA and DMOA- d_2 's conjugate chelate carbonyl stretches are 50 cm⁻¹ lower than observed for conjugated esters [17, 18]. This decrease in frequency points out the significant resonance and hydrogen bonding effects occurring in these molecules. The assignment of the C=C stretches were made based on the intensity of these bands in the Raman spectra as was discussed previously. The remainder of the bands in this region were assigned to overtone or combination bands whose intensification is probably due to a Fermi resonance interaction with the carbonyl stretches.

The methyl CH bending modes were assigned with the aid of the group frequencies available [17, 18]. Three bands are observed in the i.r. and Raman spectra; two are assigned to asymmetric motions and one to a symmetric motion.

Deuterium substitution helps provide a clear assignment of the in-plane bend of the enol hydroxyl group. The 1407 cm⁻¹ band of DMOA is shifted to 1055 cm^{-1} in the i.r. spectrum of the heavy compound. The assignment of the enol C-O stretches is based on the observation of Raman bands in the region above 1350 cm^{-1} . From the ionic resonance structure illustrated in Fig. 3, it is clear that the enol C-O bond has partial double bond character and its frequency would be expected to be higher than that observed at 1334 cm^{-1} in 4-methyl oxaloacetate, 1311 cm^{-1} in liquid diethyl oxaloacetate.

The assignment of the ester C-OCH₃ stretches is unambiguous. Ester C-OCH₃ stretches are known to be quite strong in the i.r., and this is observed in the case of DMOA and DMOA- d_2 . These vibrational modes give rise to the strongest bands in the i.r. spectrum of DMOA. The ester C-OCH₃ stretches of DMOA are assigned to the 1273 and 1225 cm⁻¹ bands; the ester C-OCH₃ stretches of DMOA- d_2 are assigned to the 1309 and 1244 cm⁻¹ bands. C-OCH₃ stretches are generally weak in the Raman. In the Raman spectrum of DMOA, a strong band is observed at 1260 cm⁻¹ that is coincident with a strong i.r. band (ambient temperature i.r. spectrum). A Raman band coincident with the other ester C-OCH₃ stretch is not observed. This apparent ambiguity is clarified upon examination of the spectra of DMOA- d_2 . In the Raman spectrum of DMOA- d_2 , a strong band is observed at 1227 cm^{-1} which is coincident with a weaker, unresolved i.r. band at 1226 cm^{-1} . The evidence suggests that the 1227 cm⁻¹ Raman band (and the 1226 cm⁻¹ i.r. band) of DMOA- d_2 is due to the C-C stretch of the enol protion of the molecule. This vibration is accidentally degenerate with a C-OCH₃ stretch in the vibrational spectra of DMOA, which explains the strength of the 1260 cm⁻¹ Raman band. C-C stretches are normally associated with strong Raman bands. The C-C stretch is coupled with another vibration, possibly the olefinic CH in-plane bend. When uncoupled in the heavy compound, the band shifts to a lower frequency.

The assignment of the methyl rocking modes, as well as most of the other ester vibrations, has been aided by the absence of these bands in the spectra of oxaloacetic acid. The frequencies of the bands due to vibrations of the ester portion of the molecule remain fairly constant upon deuterium substitution, also aiding the assignment. Four methyl rocking modes are expected for DMOA and DMOA- d_2 . In the case of DMOA, these bands are observed at 1203 and 1194 cm⁻¹, a crystal split doublet at 1175 and 1165 cm⁻¹ and at 1030 cm⁻¹. The i.r. spectrum is more complex for DMOA- d_2 in

that many bands are observed in this region. It is believed that this is due to crystal splitting as was observed for DMOA and our assignment bears this out.

The assignment of the in-plane olefinic CH bend, observed at 1103 cm⁻¹ in DMOA, has been made by noting the frequency shift to 805 cm^{-1} in the i.r. spectrum of DMOA- d_2 . This mode has also been assigned as a crystal split doublet in the i.r. spectrum of DMOA- d_2 . The frequency of this vibration occurs in a small range for all of the oxaloacetate molecules we have studied and agrees well with previous assignments of enols of the acetylacetone series of molecules [25, 26].

The assignment of the ester CO-CH₃ stretches is based on the intensity of these bands in the Raman spectra. These vibrations are sometimes denoted as symmetric C-O-C stretches and, due to their symmetric nature, strong Raman bands are generally observed. The second C-C stretch has been assigned as being accidentally degenerate with the 947 cm⁻¹ band, in the case of DMOA. The foundation for this conclusion is a splitting of the degeneracy in the vibrational spectra of DMOA-d2. Bands are observed at 993, 978 and 916 cm^{-1} , which are also present in the Raman spectrum. The 993 cm⁻¹ band is assigned to the C-C stretch whereas the other two bands are assigned to the ester CO--CH₃ stretches.

The OH wag is assigned to the weak, broad 1010 cm⁻¹ band of DMOA. This band shifts to 725 cm⁻¹ in the i.r. spectrum of DMOA- d_2 . Neither of these bands are observed in the Raman spectra, as is the case with many modes involving hydrogen bonded groups.

The assignment of the remaining ester vibrational modes has been made based on the absence of these bands in the vibrational spectra of oxaloacetic acid, and their constancy of frequency between the spectra of DMOA and DMOA- d_2 , as was mentioned before. The ester bands, which occur as doublets (because there are two ester groups) fairly close in frequency in the spectra of DMOA and DMOA- d_2 , occur as singlets in the spectra of 4-methyl oxaloacetate. The assignment of the ester modes to the correct frequencies has been aided by comparison with the vibrational spectra of methyl acetate [27], methyl acrylate [28], monomethyl fumarate [29] and dimethyl fumarate [30].

The olefinic CH wag is assigned to the 794 cm⁻¹ band of DMOA whilst the CD wag of DMOA- d_2 absorbs at 582 cm⁻¹. As was found for the other enolic CH vibrations, the enolic CH wag occurs in a narrow frequency range for all of the oxaloacetate molecules studied.

The 680 cm⁻¹ band of DMOA is present in the spectra of all of the oxaloacetate molecules we have investigated. Therefore, this band must be associated with the enol portion of the molecule. The band has been assigned to a C = C - O in-plane bend. The C=C-O in-plane bend of representative enol ethers absorbs in the range from 670 to 600 cm^{-1} [31]. This

assignment therefore agrees well with the observations of these authors. The remainder of the skeletal bending modes have been assigned to Raman and i.r. bands which have appreciable intensity, with an attempt to make them consistent between the oxaloacetate molecules.

The stretch of the enol hydrogen bond has been assigned to the 194 cm⁻¹ band of DMOA. This band is not observed in the i.r. spectrum of DMOA- d_2 , although no new band is observed which corresponds to the deuterium bond stretch. The enolic deuterium bond stretch i.r. absorption band is either too weak to be observed or is accidentally degenerate with the $153 \,\mathrm{cm}^{-1}$ band.

CONCLUSION

Dimethyl oxaloacetate and dimethyl oxaloacetate d_2 are interesting compounds from a spectroscopic and structural standpoint. They crystallize in an internally hydrogen bonded enol structure. This conjugate chelate structure affects the frequencies of some vibrational modes to a significant degree. Most notable is the frequency of the conjugated, hydrogen bonded carbonyl stretch which is 50 cm^{-1} lower than observed for conjugated esters [17, 18]. The structure of these compounds has not been determined in the greatest detail, but they probably assume a cis-trans configuration (with respect to the carbonyls and C=C bond) in the solid phase. In non-polar solvents, evidence was obtained for the existence of a conformational equilibrium of enol forms. Keto-enol tautomerization also occurs in solution. The keto form is favored in polar solvents.

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