Symmetries of Hydrogen-Bonded Enol Forms of Diketones as Determined by X-ray Photoelectron Spectroscopy

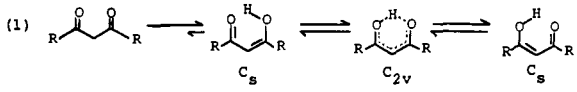
R. S. Brown,* A. Tse, T. Nakashima, and R. C. Haddon†

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada, and Bell Laboratories, Murray Hill, New Jersey 07974. *Received January 4, 1979*

Abstract: The O_{1s} ionization regions of malonaldehyde (**1a**), hexafluoroacetylacetone (**1c**), tropolone (**3a**), 9-hydroxyphenalenone (**4**), and 6-hydroxy-2-formylfulvene (**5**) all show two dominant ionizations arising from oxygens made inequivalent by virtue of an asymmetric H bond. ^1H NMR studies of the transoid enol form of malonaldehyde in deuterated ethanol show that the apparent symmetry of the molecule on the NMR time scale cannot be explained by keto-enol equilibria since this latter process is far too slow. Additional NMR studies of the intramolecularly H bonded cisoid form of malonaldehyde in $CFCl_3$-CD_2Cl_2 solvents indicate that the upper limit for the effective barrier to interconversion of the C_s forms via the C_{2v} form is no greater than 6 kcal/mol. Similar results were obtained with deuterated malonaldehyde.

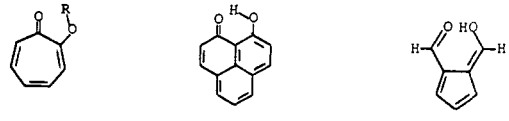
Introduction

The symmetries of the enol forms of dicarbonyls (**1** → **2**) have recently proved to be an active area for experimental and theoretical work. The simplest of these species, malonaldehyde (MA, **1a**), has been intensively investigated using a variety of

(1) 

1 a R = H; b R = CH_3; c R = CF_3 — **2**

experimental[1] and theoretical[2,3] methods, and it is now accepted that the intramolecularly H bonded enol form (**2a**) exists in asymmetric C_s forms which are rapidly interconverted via the symmetric C_{2v} form as in eq 1. The most recent calculations put the C_s-C_{2v} energy difference at 10.6,[2b] 11.6,[2a] and 11.5[2g] kcal/mol and reemphasize that the barrier height is a sensitive function of the O-O separation.[3b] Related but more complicated (and therefore less amenable to detailed calculations) are the enolized diketones **3a-5**, which can also exist in C_{2v} or C_s forms with a five-, six-, and seven-membered H-bonded ring, respectively.



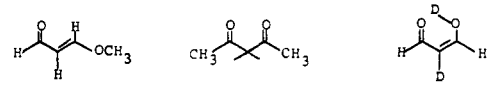
3 a R = H; b R = CH_3 — **4** — **5**

Several lines of experimental evidence such as gas-phase electron diffraction,[4a] near-UV spectroscopy,[4b,c] X-ray crystallography,[4d-f] and solution-phase ^1H[4g] and ^{13}C NMR studies[4h,i] point to C_s structures for tropolone (**3a**) which are rapidly interconverting via the C_{2v} form, but each of the above methods has some experimental, time-scale, or interpretive difficulty which detracts from the conclusions.

From ^1H and ^{13}C NMR studies,[5a] **4** (9-hydroxphenalenone) appears to have C_{2v} symmetry in solution down to 130 K, but could of course be rapidly interconverting between its two C_s forms. An IR investigation[5b] of the solution and solid states of **4** found no absorption due to the O-H stretching vibration. An X-ray crystallographic study[5c] has shown **4** to possess a short O-O distance (<2.5 Å).

A more demanding case would appear to be 6-hydroxy-2-formylfulvene (**5**). ^1H NMR data[6a] has shown the C_{2v} symmetry on the NMR time scale, but the IR spectrum was interpreted[6a] as arising from interconverting C_s forms. On the other hand, gas-phase microwave data for **5** and some deuterated analogues[6b] have been interpreted as arising from either a C_{2v} form or a C_s form in which the proton oscillates between the terminal oxygens faster than 2×10^{12} s^{-1}. Solid-state X-ray and neutron diffraction data[6c] indicate a slightly asymmetric H bond with the two O-H distances at 1.214 and 1.343 Å, but it is not clear that the crystal structure is the same as that of the isolated molecule.

In view of the ambiguities concerning the symmetries of these molecules,[5d] we have extended our earlier X-ray photoelectron (XPS) studies of the O_{1s} binding energies of **1a-c**[1d] to incorporate molecules **3-5** and some methylated derivatives (**6, 7**). Since these determinations are made on isolated gas-



6 — **7** — **8**

phase molecules on a time scale of 10^{-16} s, they contribute probably the most definitive experimental evidence for the molecular symmetry. At the same time, in view of the relatively high calculated barrier to interconversion of the two C_s forms of **1a** via the C_{2v} form (which is possibly reduced by proton tunneling[1a,2a]) we have conducted variable-temperature NMR studies on hydrogenated malonaldehyde (H-MA) and its deuterated form (D-MA, **8**), with the aim of retarding the exchange process so that the frozen C_s form might be observed. The following represents our findings concerning these questions.

Experimental Section

XPS spectra were determined on gaseous samples using Mg $K\alpha_{1,2}$ radiation ($h\nu$ = 1253.6 eV) with a MacPherson 36 ESCA spectrometer, and were calibrated using a neon Auger line at 804.56 eV kinetic energy.[7] Experimental data were least squares analyzed[8] assuming Gaussian peaks, and the reported values are the averages of at least three calibrated runs. Routine IR and NMR spectra were determined using a Nicolet FT IR spectrophotometer and Bruker WP-60 FT NMR spectrometer, respectively. Variable-temperature NMR studies of H-MA (**2a**) and D-MA (**8**) were determined on the latter instrument using 5×10^{-3} to 4×10^{-2} M solutions in a solvent of 1:1 $CFCl_3$-CD_2Cl_2. NMR solvents were dried using $CaSO_4$ (which had been flamed dry under vacuum) and then distilled into holding receivers using vacuum-line techniques. H-MA was prepared as published[1d] and sublimed five times into a holding receiver where it could be stored at −78 °C for several weeks without visible signs of decomposition. NMR samples were then made up as required using vacuum-line techniques to ensure the absence of moisture.

† Bell Laboratories.

0002-7863/79/1501-3157$01.00/0

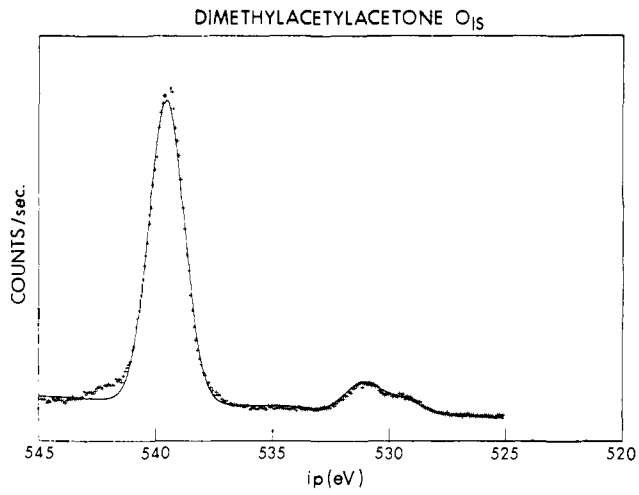


Figure 1. An unrestricted computer fit of the O_{1s} ionization region of dimethylacetylacetone (7).

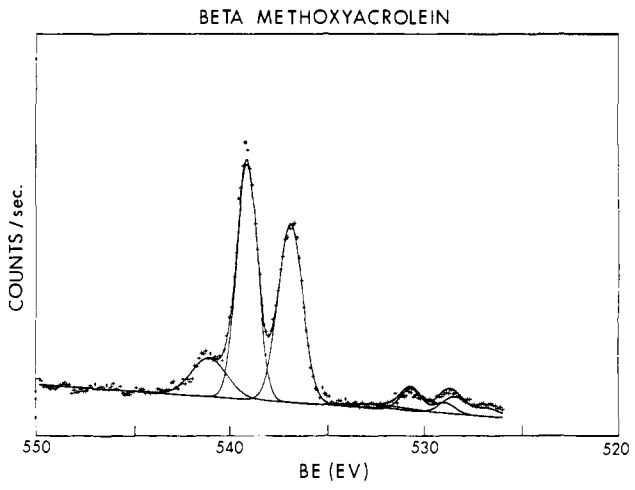


Figure 2. An unrestricted computer deconvolution of the O_{1s} ionization region of β-methoxyacrolein (6).

Deuterated MA (8) was prepared with great precaution since the high acidity of this system (pK_a H-MA = 4.46[1c]) leads to extremely rapid OD-OH exchange when the slightest source of exchangeable proton is present. Sodium malonate[9] was dried under vacuum over refluxing xylene for 2 days. All glassware which would come in contact with 8, including the vacuum rack, was conditioned with D_2O and either oven dried or flamed out under vacuum. Two grams (0.021 mol) of sodium malonate[9] was dissolved at 0 °C in a solution comprised of 20 mL of D_2O (99.7%) containing 4 g of P_2O_5 in a serum-stoppered 100-mL Erlenmeyer flask with a magnetic stirring bar. The 8 produced was then extracted via syringe techniques with ten 10-mL aliquots of sodium-dried ether (to remove traces of protium) and the combined ether extracts were transferred via syringe to a second serum-stoppered Erlenmeyer flask which contained 15 g of a roughly 1:1 mixture of $CaSO_4$-Na_2CO_3 which had been flamed dry under vacuum. After standing at −5 °C overnight this mixture was filtered in a glove bag and the residual ether removed at ambient temperature under house vacuum. The pale yellow solid residue was immediately flushed with N_2 and connected to a vacuum rack where the rest of the manipulations were conducted analogously to those used for H-MA. Final transfer was made as necessary to NMR tubes which had been freshly conditioned with D_2O, then flamed out under vacuum. If this latter procedure was omitted, the sample invariably showed residual traces of protium. Utilizing the above procedure, samples of 8 could routinely be prepared which had *no* detectable H-MA by NMR.

Materials **3a**,[10] **3b**,[11] **4**,[12] and **5**[6a,13] were prepared by literature methods. β-Methoxyacrolein (6) was prepared following the procedure of Kalinina et al.:[14] ^1H NMR ($CDCl_3$) δ 3.77 (s, 3 H), 5.58 (d of d, J = 13.0, 8.0 Hz, 1 H), 7.45 (d, J = 13.0 Hz, 1 H), 9.43 (d, J = 8.0 Hz, 1 H). The large vinyl coupling constants suggest that 6 exists completely in solution as the indicated trans enol ether.

Results and Discussion

The O_{1s} binding energies for the dominant peaks in the XPS spectra of **1**–**7** are presented in Table I, and for ease of visualization the computer deconvoluted spectra of compounds **1b** and **3**–**7** are presented in Figures 1–7.[15] Our original premise was that symmetric C_{2v} enol forms of these molecules should show a single O_{1s} ionization arising from the two equivalent oxygens, while the asymmetric C_s forms should give rise to two distinct ionizations (in approximately a 1:1 area ratio assuming equal ionization cross sections) which might lead to considerably broadened, or even separated, peaks. Hence the nonenolizable but symmetric dimethylacetylacetone (7) shows a single narrow (half width = 1.77 eV) peak as indicated in Figure 1. On the other hand, β-methoxyacrolein (6) has two inequivalent oxygens and as Figure 2 shows gives rise to two dominant O_{1s} ionizations[16] in a roughly 1:1 area ratio. Considering the data for the H-bonded forms of **1a**, **1c**, **4**, and **5** it is clear that these molecules can most simply be analyzed as being in a C_s form with the two oxygens made inequivalent by virtue of an asymmetric H bond.

In the event that the molecules exist in an equilibrium distribution of C_s and C_{2v} forms, at least three distinct ionizations should be apparent, the C_s form contributing two and the C_{2v} form a third which should overlap the other two. We have not chosen to analyze any of our spectra in these terms, although such suggestions have been made[2b] concerning the data[1d] for malonaldehyde (**1a**) and hexafluoroacetylacetone (**1c**). These

Table I. O_{1s} Binding Energies for Dicarbonyls[a,b]

compd	peak[e]	rel area	binding energy, eV	fwhm[c]
malonaldehyde[d]	1	0.16 ± 0.05	542.52	1.60
(**1a**)	2	0.96 ± 0.05	539.71	1.49
	3	1.0 ± 0.04	538.14	1.62
acetylacetone[d]	1	0.1 ± 0.01	541.68	1.86
(**1b**)	2	1.43 ± 0.08	538.83	1.95
	3	1.0 ± 0.11	537.33	1.65
hexafluoro-	1	0.37 ± 0.03	543.06	2.24
acetylacetone[d]	2	1.47 ± 0.17	540.48	1.75
(**1c**)	3	1.66 ± 0.16	539.03	1.91
3,3-dimethyl-	1	1.0	538.08	1.77
acetylacetone (**7**)				
3-methoxyacrolein[d]	1	0.31 ± 0.03	541.74	2.27
(**6**)	2	1.0 ± 0.04	539.79	1.26
	3	0.91 ± 0.02	537.53	1.52
tropolone (**3a**)	1	1.0	539.27	1.72
	2	0.71 ± 0.05	536.95	1.46
2-methoxytropone	1	1.0	539.60	1.82
(**3b**)	2	0.71 ± 0.03	537.08	1.63
6-hydroxy-2-	1	0.14 ± 0.02	543.45	2.16
formylfulvene[d]	2	0.15 ± 0.02	541.39	1.61
(**5**)	3	1.0	539.07	1.69
	4	1.1 ± 0.12	537.74	1.68
9-hydroxyphenal-	1	1.	539.23[f]	2.88
enone (**4**)	2	0.99 ± 0.03	536.64	2.88

[a] Referenced to a Ne Auger line at 804.56 eV kinetic energy.[7] [b] Binding energy values reported are the average of at least three runs and have a precision of ±0.03 eV. [c] Full width at half maximum height. [d] Low-intensity peaks (assigned as peaks 1 for **1a**, **1b**, **1c**, and **6** and peaks 1 and 2 for **5**) are believed to arise from shakeup phenomena (see text). [e] Each compound investigated shows the presence of one or more low-intensity peaks to the high binding energy side of the main ionization lines. The table includes this peak only if its intensity is greater than 10% of the main lines, but it is clearly present in every case (cf. Figures 1–7). [f] Average of two calibrated runs; precision ±0.06 eV.

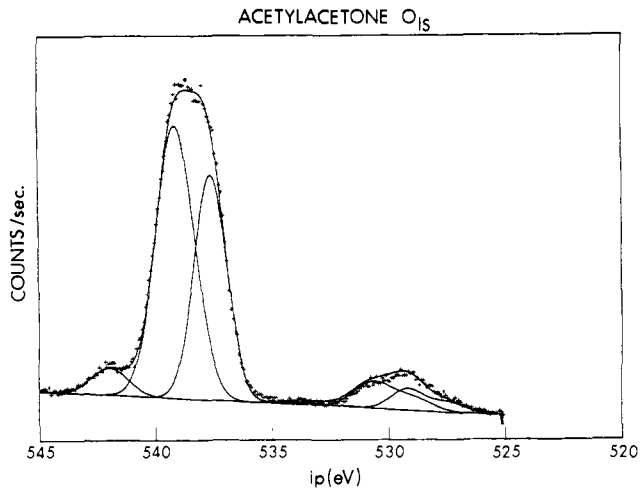


Figure 3. An unrestricted computer deconvolution of the O_{1s} ionization region of acetylacetone (**1b**).

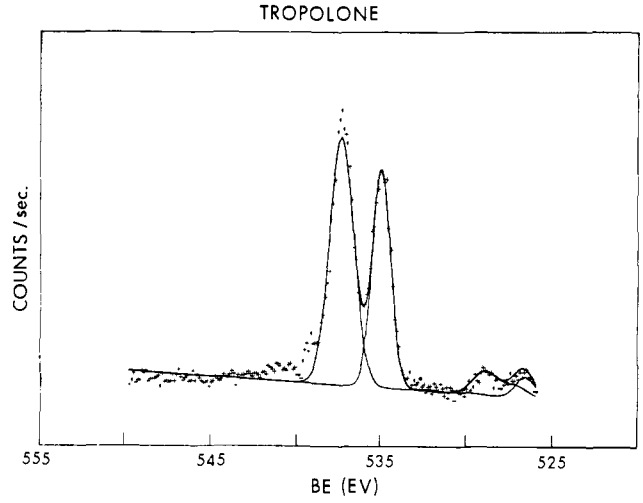


Figure 4. An unrestricted computer deconvolution of the O_{1s} ionization region of tropolone (**3a**). There appear to be small but real deviations from baseline to the high binding energy side of the deconvoluted peaks that we tentatively assign to shake-up events (see text).

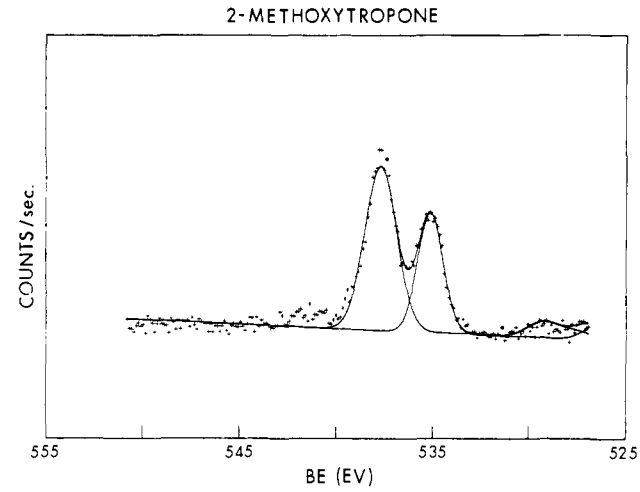


Figure 5. An unrestricted computer deconvolution of the O_{1s} ionization region of 2-methoxytropone (**3b**) assuming only two main peaks. There appear to be small but real deviations from base line to the high binding energy side of the main bands that we tentatively assign to shakeup events (see text).

suggestions[2b] were made based on the observation of a third higher binding energy peak of low intensity in each of the enol forms of **1a–c.** We feel that several lines of evidence belie this interpretation. Firstly, even nonenolizable dimethylacetylacetone shows such a low-intensity peak (Figure 1), although we have not included it in the analysis. Secondly, this low-intensity peak is *always* to the high binding energy side of those from the C_s forms. One expects that a C_{2v} form should have equivalent oxygens which are intermediate between those of the C_s form, and therefore such ionizations would show intermediate binding energies, not higher binding energies. Thirdly, if we remove the possibility of any symmetric form by creating an ether from the alcohol (for example, β-methoxyacrolein (**6**) from malonaldehyde (**1a**)) then no peaks from a C_{2v} form can be present. Nevertheless, ether **6**, as illustrated in Figure 2, shows this low-intensity high binding energy peak. From these data it would seem most likely that the small peak arises from a shakeup phenomenon[17] in which an electron in a high-lying occupied MO is promoted to a low-lying virtual orbital accompanying core ionization.

Acetylacetone (**1b**) shows two dominant O_{1s} ionizations in approximately a 3:2 ratio as shown in Figure 3. It seems certain from other data[18] that **1b** is not completely enolized in solution or gas phase and therefore the observed spectrum must result from ionization from both keto and enol forms, the latter probably being asymmetric in view of our data for the other enols.

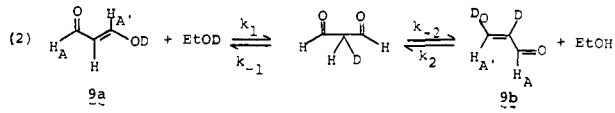
Tropolone (**3a**) represents an interesting case in that it demonstrates that an unequal peak area may not necessarily be due to ionization from two or more species. The similarity of the spectra of **3a** (Figure 4) and its methylated derivative **3b** (Figure 5), which *both* show inequivalent areas for the two O_{1s} ionizations (1.0:0.7), would seem to indicate a C_s enol form for **3a,** and that a preferential shakeup process occurs from ionization of the lower binding energy oxygen which detracts from its intensity.[19-21]

Compound **4** (9-hydroxyphenalenone) is rather nonvolatile and it was necessary to heat the sample to obtain any spectrum at all. Heating the inlet system to 50 °C[22] allowed us to obtain the XPS spectrum shown in Figure 6, which admittedly has poor statistics. Nevertheless the breadth of the O_{1s} ionization as well as the satisfactory deconvolution into two peaks of equal intensity leads us to believe that **4** exists in an asymmetric intramolecularly H bonded form.

Figure 7 shows the O_{1s} ionization region of 6-hydroxy-2-formylfulvene (**5**), which cleanly deconvolutes into two major equal area bands as well as (at least) two others to higher binding energy. The former bands come from the ionization of inequivalent oxygens, and the latter probably from shakeup processes[17-20] which we cannot assign at this time.

It seems clear then from these observations that every enolized diketone investigated is predominantly (if not exclusively) in a C_s form.

^{1}H NMR Studies on H-MA and D-MA. It is well known that MA exists as a trans enol in water and hydroxylic solvents[1f,g,23] but as an intramolecularly H bonded cis enol in less polar chlorinated hydrocarbons.[1f] Nevertheless the trans enol form in the former solvents appears to be symmetric and our first question concerned the mechanism by which the terminal hydrogens (H_A and H_A' in structure **9a**) become equivalent.



9a **9b**

Equation 2 outlines one possible mechanism in which the enol form (**9a**) ketonizes and then reenolizes toward the other oxygen. To test this possibility, the rate of exchange of the methine H for D (which can only occur through some keto

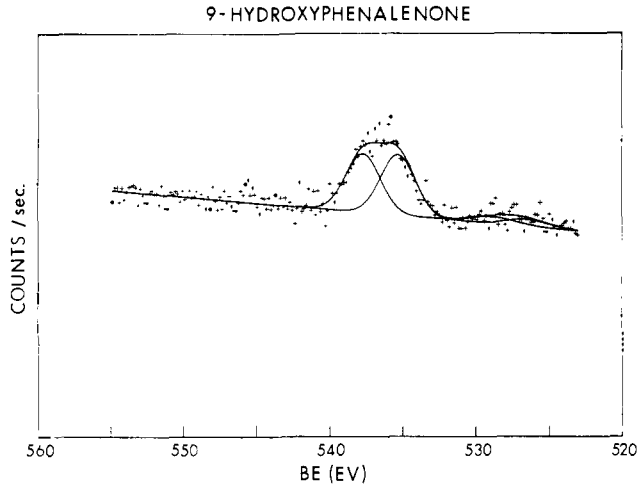


Figure 6. A computer deconvolution of the O_{1s} ionization region of 9-hydroxyphenalenone (**4**). Owing to the poor statistics we were forced to restrict the deconvolution of the broad experimental peak into two peaks of equal area.

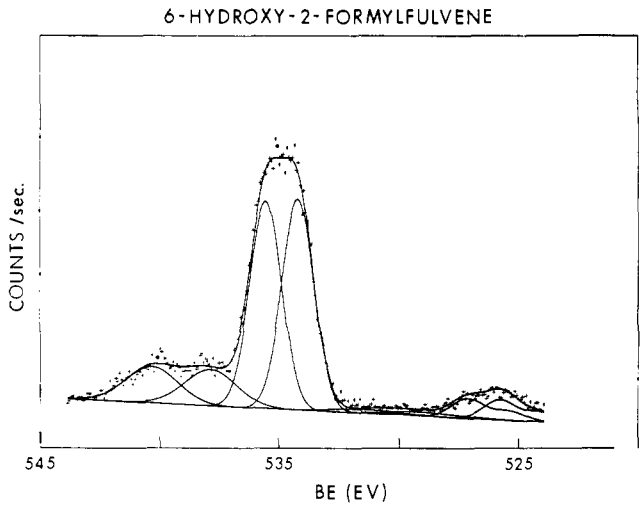


Figure 7. An unrestricted computer deconvolution of the O_{1s} ionization region of 6-hydroxy-2-formylfulvene (**5**). The high binding energy peaks are presumably due to shakeup phenomena accompanying ionization of the oxygens.

form) was followed under pseudo-first-order conditions in ethanol-d_6 at 303 K in an NMR tube.[24] The rate of disappearance of **9a** (which is experimentally equal to the rate of appearance of **9b**) gives a convenient measure of the ketonization-reenolization process according to the equation

$$\frac{-d[\mathbf{9a}]}{dt} = \frac{d[\mathbf{9b}]}{dt} = \frac{k_1 k_{-2}[\mathbf{9a}][\mathrm{EtOD}]}{k_{-1} + k_{-2}} = k_{obsd}[\mathbf{9a}] \quad (3)$$

derived from steady-state kinetics and assuming that reversal from **9b** to **9a** is negligible (i.e., k_2[HOEt] is small) and yields a k_{obsd} of 1.7×10^{-3} s^{-1}. Although the absolute values of k_{-1} and k_{-2} are not known, they are related by a primary isotope effect which if maximal should set k_{-2} to be roughly $7k_{-1}$,[25] so that eq 3 reduces to the expression[26]

$$\frac{-d[\mathbf{9a}]}{dt} = \frac{d[\mathbf{9b}]}{dt} = \frac{k_1[\mathbf{9a}][\mathrm{EtOD}]}{1.14} = k_{obsd}[\mathbf{9a}] \quad (4)$$

Therefore, under these conditions, k_{obsd} gives a good measure of the rate constant for ketonization, which is found to be rather slow at 303 K.

After complete exchange had occurred (as evidenced by total absence of the methine hydrogen in the NMR spectrum of **9b**), this same sample was subjected to variable-temperature NMR study. At ambient temperature H_A and $H_{A'}$ in **9b** appear as a ^{2}H-coupled singlet centered at δ 8.52. Cooling causes this signal to broaden and at temperatures lower than 145 K it separates into two broad singlets centered at δ 9.38 and 7.67 corresponding to the formyl (H_A) and hydroxyvinyl ($H_{A'}$) protons, respectively.[27] From these data and a coalescence temperature of 145 K, the rate constant for equivalencing H_A and $H_{A'}$ at the coalescence temperature is $k_{eq} = 2.26 \times 10^2$ s^{-1}.[28] Comparison of k_{eq} with k_{obsd} shows the latter process to be far too slow to account for the apparent equivalence of H_A and $H_{A'}$ as measured by NMR. We therefore feel that the mechanism for this must involve simple intermolecular proton transfers in this medium.[29]

Intramolecular Forms. For dilute solutions of H-MA in a 1:1 mixture of $CFCl_3$-CD_2Cl_2 at ambient temperatures, the ^{1}H NMR spectrum shows a triplet centered at δ 5.68, J = 3.5 Hz, 1 H, a doublet centered at δ 8.37, J = 3.5 Hz, 2 H, and no indication of a low-field intramolecularly H bonded OH. Temperatures lower than 200 K produced the ^{1}H NMR spectrum illustrated in Figure 8, which clearly shows the intramolecularly H bonded OH at δ 16.40, J = 6.1 Hz, coupled equivalently to the terminal hydrogens, which themselves

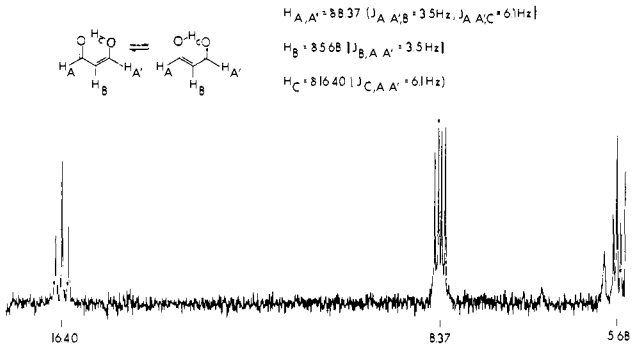


Figure 8. The ^{1}H NMR spectrum of malonaldehyde (**1a**, **2a**) at 153 K in a solvent of 1:1 $CFCl_3$-CD_2Cl_2. The small peak at ~δ 6 is attributable to a spinning sideband from adventitious $HCDCl_2$.

appear as a doublet of doublets centered at δ 8.37, J = 3.5, J' = 6.1 Hz. From these data there is no doubt about the cisoid conformation of the molecule, and, because the OH is coupled equivalently to the terminal hydrogens, the molecule must have C_{2v} symmetry on the NMR time scale down to 133 K, where the solution freezes. No broadening of the terminal hydrogens' signal other than that attributable to viscosity effects was observed at low temperatures. If we assume that the formyl and hydroxyvinyl hydrogens in the cisoid form (**2a**) should have roughly similar chemical shifts to those of the transoid form (**9a**) ($\Delta\nu(H_A-H_{A'})$ = 102 Hz at 60 MHz) then the upper limit for the barrier to interconversion of the two C_s forms via the C_{2v} form should be 6.1 kcal/mol.

A possibility exists that replacing OH for OD might well slow down the D transfer between the oxygens because of a primary isotope effect and reduced efficiency of deuterium tunneling.[2a] Deuterated MA (**8**) was subjected to similar variable-temperature NMR studies in the same solvent mixture. Figure 9 illustrates the ^{1}H NMR spectrum which shows only a singlet centered at δ 8.37 (for the terminal hydrogens) down to 130 K, at which point the mixture freezes. No evidence of site exchange broadening could be detected so that even the intramolecular exchange of the O-D is rapid under these conditions, and if some primary isotope effect is operative in the intramolecular exchange process we are unable to observe it. Again utilizing the same assumptions as for the H-MA, we can say that the actual barrier to interconversion of the C_s forms via the C_{2v} form is no greater than about 6 kcal/mol.

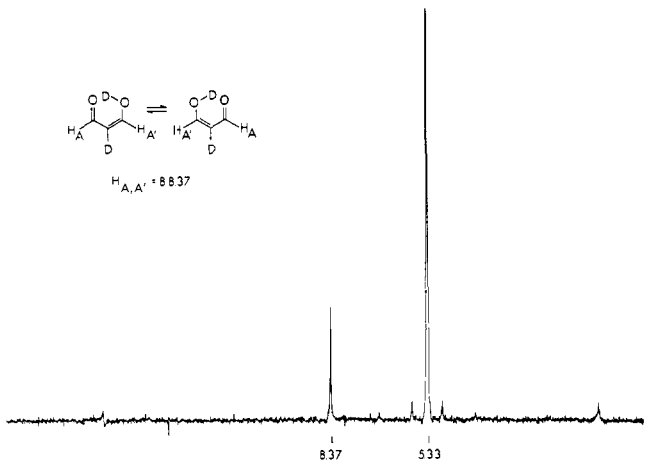


Figure 9. The ^1H NMR spectrum of deuterated malonaldehyde (**8**) at 150 K in a solvent of 1:1 $CFCl_3$-CD_2Cl_2. The large resonance at δ 5.33 is attributable to $HCDCl_2$.

Conclusions

1. Gas-phase XPS techniques show that the O_{1s} ionization regions of the enol forms of malonaldehyde (**1a**), hexafluoroacetylacetone (**1c**), and related compounds such as tropolone (**3a**), 9-hydroxyphenalenone (**4**), and 6-hydroxy-2-formylfulvene (**5**) have two dominant ionizations arising from a C_s structure for each material. Previously unexplained peaks[1d] at higher binding energy than the main O_{1s} ionizations of **1a** which had been assigned by others[2b] as arising from the C_{2v} form have been shown (vide supra) to be due to shakeup phenomena and not to other enol or keto forms. The observation of a C_s form for **5** is particularly significant in view of the apparently near-linear H bond and close proximity of the oxygens which favor an extremely rapid O:---H-O $\leftrightharpoons$ O-H---:O transfer (said to occur faster than 10^{12} s^{-1} [6b]). The time scale of the XPS measurement (10^{-16} s), however, is sufficient to differentiate between the terminal oxygens.

2. Variable-temperature ^1H NMR as well as deuterium exchange studies on H-MA (**1a**) in deuterated ethanol show that the transoid conformation of the molecule cannot be rapidly undergoing ketonization followed by reenolization to make the transoid forms appear symmetric. Other intermolecular proton transfer reactions must account for this apparent symmetry.

3. Recent calculations[2a,b,g] on the enol forms of H-MA (**2a**) place the C_{2v} form about 10.5–11.5 kcal/mol higher in energy than the C_s form. The barrier to interconversion between the two C_s forms via the C_{2v} form is postulated to be reduced by proton tunneling.[1a,2a] The present ^1H NMR studies on malonaldehyde place an *upper* limit of about 6 kcal/mol for the *effective* barrier to interconversion of the two C_s forms via the C_{2v} form.

For deuterated malonaldehyde (**8**) O:---D-O exchange is expected to be slower than O:---H-O exchange in H-MA because of a possible deuterium isotope effect and reduced efficiency of deuteron tunneling. Nevertheless, no differentiation of the terminal hydrogens in **8** could be detected at temperatures down to 130 K, signifying a C_{2v}-C_s barrier for **8** of no higher than 6 kcal/mol.

Acknowledgment. The Canadian authors gratefully acknowledge the financial assistance of the University of Alberta and the National Research Council of Canada. R.C.H. thanks M. L. Kaplan, F. H. Stillinger, and W. Wudl for helpful discussions.

References and Notes

(1) (a) W. F. Rowe, Jr., R. W. Duerst, and E. B. Wilson, *J. Am. Chem. Soc.*, **98**, 4021 (1976); (b) C. Nishijima and H. Nakayama, *Chem. Lett.*, 5 (1975); (c) C. J. Sellskar and R. E. Hoffmann, *J. Am. Chem. Soc.*, **99**, 7072 (1977); (d) R. S. Brown, *ibid.*, **99**, 5497 (1977); (e) M. M. Osman, *Helv. Chim. Acta*, **55**, 239 (1972); (f) W. O. George and V. G. Mansell, *J. Chem. Soc. B*, 132 (1968); (g) A. A. Bothner-By and R. K. Harris, *J. Org. Chem.*, **30**, 255 (1965); (h) R. S. Noi, B. A. Ershov, and A. I. Kol'tsov, *J. Org. Chem. USSR (Engl. Transl.)*, **11**, 1788 (1975); (i) L. J. Altman, D. Laungani, G. Gunnarsson, H. Wennerstrom, and S. Forsen, *J. Am. Chem. Soc.*, **100**, 8264 (1978).

(2) (a) E. M. Fluder and J. R. de la Vega, *J. Am. Chem. Soc.*, **100**, 5265 (1978); (b) J. Catalán, M. Yánez, and J. I. Fernández-Alonso, *ibid.*, **100**, 6917 (1978); (c) P. Schuster, *Chem. Phys. Lett.*, **3**, 433 (1969); (d) S. Kato, H. Kato, and K. Fukui, *J. Am. Chem. Soc.*, **99**, 684 (1977); (e) J. E. Del Bene and W. L. Kochenour, *J. Am. Chem. Soc.*, **98**, 2041 (1976); (f) J. E. Del Bene, *Chem. Phys. Lett.*, **44**, 512 (1976); (g) G. Karlström, H. Wennerström, B. Jonsson, S. Forsen, J. Almlöf, and B. Roos, *J. Am. Chem. Soc.*, **97**, 4188 (1975); (h) W. J. Bowma and L. Radom, *Aust. J. Chem.*, **31**, 1649 (1978).

(3) (a) F. J. Marsh, B. G. Thomas, and M. S. Gordon, *J. Mol. Struct.*, **25**, 101 (1975); (b) A. D. Isaacson and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 4453 (1975).

(4) (a) M. Kimura and M. Kubo, *Bull. Chem. Soc. Jpn.*, **26**, 250 (1953) (assumption of equal C–C bond lengths and ring planarity); however, C–O bond lengths are different. (b) A. C. P. Alves and J. M. Hollas, *Mol. Phys.*, **23**, 927 (1972); (c) *ibid.*, **25**, 1305 (1973); (d) H. Simanouchi and Y. Sasada, *Tetrahedron Lett.*, 2421 (1970); (e) *Acta Crystallogr., Sect. B*, **29**, 81 (1973); (f) T. A. Hamor and J. E. Derry, *ibid.*, **29**, 2649 (1973); (g) J. W. Emsley, J. C. Lindon, and D. S. Stephenson, *Mol. Phys.*, **27**, 641 (1974); (h) L. Weller, *Can. J. Chem.*, **50**, 1975 (1972); (i) J. F. Bagli and M. St. Jacques, *ibid.*, **56**, 578 (1978).

(5) (a) R. S. Brown, A. Tse, and R. C. Haddon, unpublished results; (b) Y. Demura, T. Kawato, H. Kanatomi, and I. Murase, *Bull. Chem. Soc. Jpn.*, **48**, 2820 (1975); (c) C. Svenson, J. L. Bernstein, S. C. Abrahams, R. C. Haddon, and F. H. Stillinger, manuscript in preparation. (d) Very recent deuteron quadrupole coupling constant studies on the solution states of the OD species have indicated C_s symmetry for **4**, **5**, and **6**: L. M. Jackman, J. C. Trewella, and R. C. Haddon, to be published.

(6) (a) K. Hafner, H. E. A. Kramer, H. Musso, G. Ploss, and G. Shulz, *Chem. Ber.*, **97**, 2066 (1964); (b) H. M. Pickett, *J. Am. Chem. Soc.*, **95**, 1770 (1973). (c) H. Fuess and H. J. Lindner, *Chem. Ber.*, **108**, 3096 (1975). The OH distances were assigned from the neutron diffraction determination. X-ray diffraction placed the O---O separation at 2.513 Å. It is not clear whether crystal packing forces might distort the H bond from its equilibrium position.

(7) T. D. Thomas and R. W. Shaw, *J. Electron Spectrosc., Relat. Phenom.*, **5**, 1081 (1974).

(8) R. S. Brown and D. A. Allison, *J. Am. Chem. Soc.*, **99**, 3568 (1977).

(9) E. J. J. Grabowski and R. L. Autrey, *Tetrahedron*, **25**, 4315 (1969).

(10) Tropolone was a gift from Professor S. Masamune.

(11) J. W. Cook, A. R. Gibb, R. A. Raphael, and A. R. Somerville, *J. Chem. Soc.*, 503 (1951).

(12) R. C. Haddon, F. Wudl, M. Kaplan, J. H. Marshall, R. E. Cais, and F. B. Bramwell, *J. Am. Chem. Soc.*, **100**, 7629 (1978).

(13) Prepared according to procedures cited in ref 6a.

(14) N. N. Kalinina, V. T. Klimko, T. V. Protopova, and A. P. Skolinov, *J. Gen. Chem. USSR (Engl. Transl.)*, **32**, 2116 (1962).

(15) The spectra of **1a** and **1c** have already been presented in ref 1d.

(16) Each of the materials we have investigated shows at least one low-intensity peak on the high binding energy side of the O_{1s} ionizations. However, in the case of compounds **3a**, **3b**, **4**, and **7** its intensity is low and for that reason has not been included in the data analysis. Its presence is apparent, however, in the spectra of these molecules and we feel that it arises from a shakeup phenomenon (see text and ref 17).

(17) (a) T. A. Carlson, "Photoelectron and Auger Spectroscopy", Plenum Press, New York, 1975, Chapter 5; (b) S. Pignatoro, R. Di Marino, G. Distefano, and A. Mangini, *Chem. Phys. Lett.*, **22**, 352 (1973); (c) D. T. Clarke, D. B. Adams, I. W. Scanlan, and I. S. Wooley, *ibid.*, **25**, 263 (1974); (d) U. Gelius, C. J. Allan, D. A. Allison, H. Siegbahn, and K. Siegbahn, *ibid.*, **11**, 224 (1971).

(18) (a) A. H. Lowry, C. George, P. D. Antonio, and J. Karle, *J. Am. Chem. Soc.*, **93**, 7399 (1971); (b) J. Powling and H. J. Bernstein, *ibid.*, **73**, 4353 (1951); (c) A. Schweig, H. Vermeer, and W. Weidner, *Chem. Phys. Lett.*, **26**, 229 (1974); (d) L. Zamir, B. S. Jensen, and E. Larsen, *Org. Mass Spectrom.*, **2**, 49 (1969).

(19) Preferential shakeup has been observed in other systems which detracts intensity from one ionization relative to another. See ref 17d and (a) P. M. Plaskin, J. Sharma, S. Bulusu, and G. F. Adams, *J. Electron Spectrosc. Relat. Phenom.*, **6**, 429 (1975); (b) D. P. Spears, H. J. Fischbeck, and T. A. Carson, *ibid.*, **6**, 411 (1975).

(20) It may well be that shakeup occurs from every oxygen ionized in these molecules, but some of the events have low probability and therefore the peaks from such merge into the background. We see an increasing slope to the high binding energy side of the main ionizations in every spectrum but no clearly discernible peaks.

(21) The O_{1s} binding energy for tropolone has been reported previously as a broad peak (fwhm = 2.7 eV) centered at 532 ± 0.2 eV and interpreted as arising from inequivalent oxygens, but it appears as if the spectrum was obtained in the solid form: D. J. Olszanski, T. J. Anderson, M. A. Neuman, and G. A. Melson, *Inorg. Nucl. Chem. Lett.*, **10**, 137 (1974).

(22) FT IR spectra run on dilute solutions of **4** in tetrachloroethylene showed no significant differences between 25 and 100 °C. If these data are applicable to the gas phase then at 50 °C **4** must be completely intramolecularly H bonded.

(23) S. T. Yoffe, P. V. Petrovsky, Ye. I. Goryunov, T. V. Yershova, and M. I. Kabachnik, *Tetrahedron*, **28**, 2783 (1972).

(24) Because of the high acidity of the malonaldehyde (pK_A = 4.46),[1e] it is most likely that OH for OD exchange occurs very rapidly so that the actual species at the outset of the CH exchange experiment is HCOCH=C(H)-(OD).

(25) At 25 °C, kinetic isotope effects commonly lie in the range of k_H/k_D = 5–8:

L. Melander, "Isotope Effects on Reaction Rates", Ronald Press, New York, 1960, Chapter 4.
(26) Even if there is no primary isotope effect (i.e., $k_{-1} = k_{-2}$) expression 3 reduces to

$$\frac{-d[\mathbf{9a}]}{dt} = \frac{d[\mathbf{9b}]}{dt} = \frac{k_1[\mathbf{9a}][EtOD]}{2} = k_{obsd}[\mathbf{9a}]$$

(27) For β-methoxyacrolein (**7**) the formyl and hydroxyvinyl protons appear at δ 9.43 and 7.45, respectively (vide supra).
(28) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969, Chapter 7.
(29) We find that this exchange process is not strictly first order in malonaldehyde, since, as the concentration of MA is reduced, the coalescence temperature is increased, so that very dilute solutions show considerable broadening of the terminal C-H signals even at 25 °C. Small quantities of acid, Hünigs base, and even solid Na_2CO_3 added to the NMR solution reduce the coalescence temperature and thus the exchange process must be very sensitive to trace catalysis by both acid and base.

Characterization of the Chemical Ionization Condensation Products for the Benzyl Acetate System Using Mass-Analyzed Ion Kinetic Energy Spectrometry

D. Cameron and R. G. Cooks*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received October 5, 1978*

Abstract: The condensation products resulting from chemical ionization (isobutane reagent gas) of benzyl acetate were characterized using mass-analyzed ion kinetic energy spectrometry (MIKES). These spectra, which provide structural information often lacking in studies on ion–molecule reactions, were obtained by subjecting selected ions to collision-induced dissociation. The benzyl acetate condensation product $C_{14}H_{11}^+$ (179^+) was shown to have the protonated anthracene structure by the identity of its MIKE spectrum with that of the authentic ion, while the $C_{14}H_{13}^+$ (181^+) ion was shown to have a MIKE spectrum identical with that of the 2-benzylbenzyl cation generated from the substituted benzyl alcohol. Other ions in the series $(C_7H_7{\cdot}(C_7H_6)_n\text{-}H_2)^+$ as well as in the $(C_7H_7{\cdot}(C_7H_6)_n)^+$ series gave spectra which were consistent in detail with the disubstituted phenyl and fused-ring ion structures proposed by Meot-Ner, Hunter, and Field. Both of these classes of ions show characteristic modes of fragmentation, particularly phenyl–methylene bond cleavages with hydrogen transfer. The protonated dimer of benzyl acetate sampled here is, at least in part, a covalent polyether rather than the proton-bound dimer previously proposed. The ion is formed by nucleophilic addition to the protonated acetate and dissociates by simple cleavages with successive losses of acetic acid to yield 241^+ ($C_{16}H_{17}O_2^+$) and 181^+ ($C_{14}H_{13}^+$). The latter is a key intermediate in the formation of the higher condensation products. The observed formation of $C_{14}H_{13}^+$ from the protonated dimer represents a parallel pathway to its formation from the benzyl ion and neutral benzyl acetate as observed in a time-resolved CI study. The key results uncovered by application of MIKES to this system are (1) ion structures have been clarified and (2) the kinetic scheme has been extended.

Chemical ionization mass spectrometry (CIMS) has become a widespread technique both in chemical analysis and in the study of ion–molecule reactions, although much of the complex chemistry in the chemical ionization source is still not well understood.[1-4] One area of ion–molecule chemistry of current concern is that of condensation or polymerization type reactions.[1,5-7] These investigations, in which both positive and negative ion reactions have been studied, are complicated by the paucity of structural information about the product ions.

Using mass-analyzed ion kinetic energy spectrometry (MIKES)[3,8,9] in conjunction with collision-induced dissociation (CID),[9,10] it is possible to probe the structure of these polymeric ions. The MIKES technique has been used extensively in ion structural analysis under several names[3,9-15] and determinations as detailed as the site of protonation have been made.[16] A unique feature of the present study is the interpretation of the chemistry of a system using results from conventional low-energy ion–molecule reactions in conjunction with high-energy MIKES data. The benzyl acetate system was chosen because (1) the system has been the subject of a detailed time-resolved CIMS study,[1] (2) a large number of product ions are generated, (3) an intriguing unassigned metastable peak has been reported.[1]

Experimental Section

All the data reported here were obtained using the MIKES instrument,[8] a reverse-geometry mass spectrometer fitted with a chemical ionization (CI) source. Benzyl acetate, contained in a capillary tube, was introduced via the solid probe into the CI source. Isobutane was used as the reagent gas at a source pressure of approximately 0.5 Torr and a source temperature of 425 K. N_2 was used as the collision gas at an indicated pressure on a Bayard-Alpert gage of 3×10^{-5} Torr. The ion accelerating voltage was 6 kV.

MIKE spectra were obtained by mass selecting ions of interest, having these ions undergo a high-energy collision with the target gas, and then measuring the kinetic energies of the fragment ions by scanning the potential applied to the electrostatic analyzer. An energy resolving slit width of 0.75 mm was used. Spectra are calibrated in terms of ion kinetic energy as a fraction of E, the kinetic energy of the main ion beam, and in terms of fragment ion masses. A typical spectrum was recorded in 7 min, while selected areas of the spectrum were rescanned more slowly to check individual mass assignments.

2-Benzylbenzyl alcohol was prepared by reducing α-phenyl-*o*-toluic acid with lithium aluminum hydride in anhydrous diethyl ether.[17] The isobutane mass spectrum of the alcohol revealed very little protonated molecular ion, the major ions being 181^+ $[(M + H)^+ - H_2O]$ and 179^+ $[(M + H)^+ - H_2O - H_2]$.

Benzyl-d_3 acetate was prepared from acetyl-d_3 chloride and benzyl alcohol.[18] It had an isotopic purity of d_3 (97%), d_2 (2.9%), d_1 (0.44%) as determined by electron impact mass spectrometry.

Results and Discussion

1. Protonation and Alkylation of Benzyl Acetate. The reactions of benzyl acetate (BzOAc) in CI using isobutane reagent gas are given in Scheme I. Reaction 1 is an example of the well-known CIMS process, simple protonation of the sample molecule by the reagent ion. The work by Meot-Ner, Hunter, and Field[1] suggests that the formation of $C_7H_7^+$ (reaction 2) occurs in competition with the simple protonation

0002-7863/79/1501-3162$01.00/0