PHOTOELECTRON SPECTRUM OF MALONALDEHYDE

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The photoelectron spectrum (PES) of malonaldehyde was measured
and assigned in comparison with those of acetylacetone, trifluoro-
acetylacetone, and hexafluoroacetylacetone. The first and the second
bands of malonaldehyde were attributed to the ionizations from the
$b_2\pi$ and the b_1n orbitals, respectively, on the basis of the methyl
and trifluoromethyl substituent effects and the PES result of acetyl-
acetone.

Malonaldehyde is the simplest 1,3-dione compound, and its enol form is espe-
cially interesting because it contains a 6π-electron system and an intramolecular
hydrogen bridge. The present report is concerned with the assignment of the PES of
malonaldehyde.

Experimental and Theoretical

Hydrated sodium salt of malonaldehyde was prepared from tetramethoxypropane.[1]
The salt was acidified with 20% of phosphoric acid. Malonaldehyde was extracted
with diethyl ether, isolated, and was purified by vacuum distillation with chloro-
benzene cold traps three times just before use. Purity was confirmed with NMR
spectra. Reagent grade acetylacetone and hexafluoroacetylacetone were purified
according to Refs. 2 and 3, respectively. Reagent grade trifluoroacetylacetone was
treated with conc. sulfuric acid and distilled in vacuo.

The PES of these compounds were measured using the 584Å helium resonance line
as an excitation source as described in a previous paper.[4] Malonaldehyde was kept
at $0°C$ during the measurement to avoid polymerization.

The CNDO/2 calculations[5] of these compounds were carried out on a FACOM 230-
60 computer at the Institute of Physical and Chemical Research. The geometrical
structure of malonaldehyde was assumed according to Ref. 6. Those of the other
compounds were taken from electron diffraction studies.[7-9]

Results and Discussion

The PES of malonaldehyde is shown in Fig. 1. The vertical ionization poten-
tials, I_v's, of malonaldehyde, acetylacetone, trifluoroacetylacetone, and hexa-
fluoroacetylacetone obtained from the PES are summarized in Table 1. The PES of
acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone were formerly
reported by Evans and coworkers.[10] The PES of acetylacetone was discussed also by
Houk and coworkers[11] and recently by Schweig and coworkers.[12]

The PES of these compounds commonly show the first two bands in the region from
9.0 eV to 12.0 eV well separated from the following bands. On the other hand, the
CNDO/2 calculations predict that the two highest occupied orbitals of these com-
pounds are b_1n and $b_2\pi$ from the top and that these orbitals are well separated in
energy from the following lower energy orbitals. Therefore, the first two bands of
these compounds may safely be ascribed to the ionizations from the b_1n and $b_2\pi$
orbitals, though the order may be uncertain.

The relative intensity patterns of the first two bands of these compounds are
rather similar to one another. This fact may suggest that the first bands of these
compounds correspond to one another and the second ones also to one another, respec-
tively.

The replacement of the two hydrogen atoms of malonaldehyde by two methyl (or
two trifluoromethyl) groups decreases (or increases) the first two I_v's of malon-
aldehyde because of the electron donating (or withdrawing) effect of the methyl (or
trifluoromethyl) groups. From the I_v's of malonaldehyde, acetylacetone, and hexa-
fluoroacetylacetone, the methyl substituent effect in malonaldehyde is estimated to
be -0.33 eV for the first I_v and -0.31 eV for the second I_v per methyl group, and
the trifluoromethyl substituent effect to be +0.48 eV for the first I_v and +0.50 eV
for the second I_v per trifluoromethyl group. By use of these values and the I_v's of
malonaldehyde, the first two I_v's of trifluoroacetylacetone can be estimated to be
9.91 eV and 10.40 eV, and these values are in satisfactory agreement with the exper-
imental values, 9.93 eV and 10.52 eV. This agreement also supports strongly the
assignment that the first bands of these compounds correspond to one another and the
second ones also to one another, respectively. Therefore, malonaldehyde may be
present mainly as the enol form in the gaseous state at room temperature, for
acetylacetone,[7] trifluoroacetylacetone,[8] and hexafluoroacetylacetone[9] exist main-
ly as the enol forms.

According to Schweig and coworkers[12] the 3-methyl substitution effect on the
I_v of acetylacetone is -0.45 eV for the first I_v and -0.17 eV for the second, and
they assigned the first and second PES bands of acetylacetone as the $b_2\pi$ and b_1n
bands, respectively. The 3-methyl substitution effect on the $b_2\pi$ I_v of acetyl-
acetone is estimated to be -0.50 eV using the first order perturbation theory
according to Heilbronner and coworkers[13] and the acetylacetone $b_2\pi$ MO coefficients
given by the CNDO/2 calculation, and this estimated value supports the assignment
about the first two bands of acetylacetone given by Schweig and coworkers.[12]

By combining the assignment of the first two bands of acetylacetone as $b_2\pi$ and
b_1n from the top, with the above conclusion that the first bands of these compounds
correspond to one another and the second ones also to one another, respectively,

the first bands of these compounds may be assigned as the b_2 (like) π and the second bands as the b_1 (like) n, respectively.
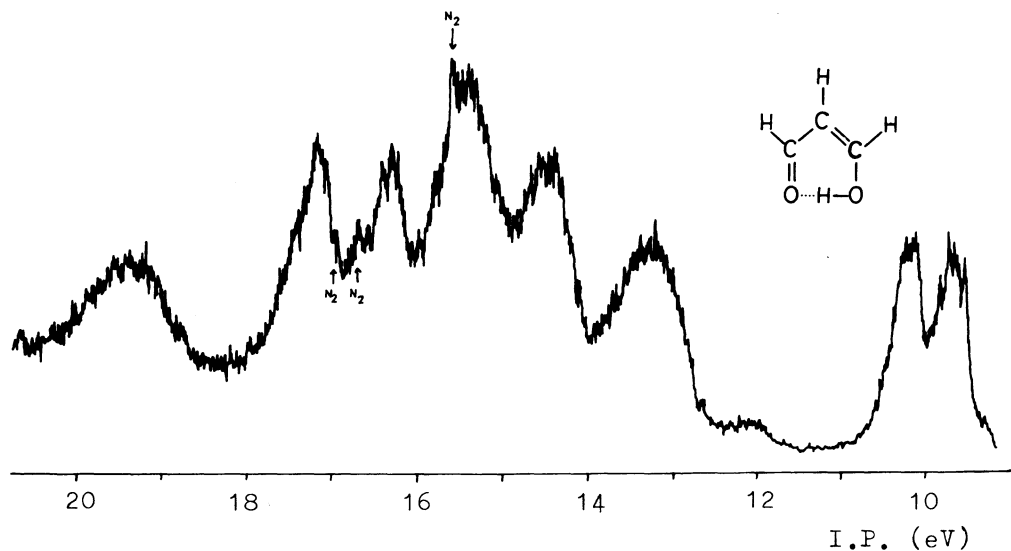

Fig. 1.   Photoelectron spectrum of malonaldehyde.

TABLE 1.   VERTICAL IONIZATION POTENTIALS (I_v in eV) OF MALONALDEHYDE AND ACETYLACETONES[a]

Malonaldehyde	9.76	10.21	13.23	14.41	15.43	16.3	17.2	19.2
Acetylacetone	9.11	9.60	12.7					
Trifluoro-acetylacetone	9.93	10.52	13.27					
Hexafluoro-acetylacetone	10.72	11.21	14.01					

a)   All values are those obtained by the present authors. The values for acetyl-acetones agree with the literature values[10] within the experimental errors.

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