

Ionization of Aqueous Mandelic Acid: Conductance and Thermodynamics

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Introduction

Mandelic acid is a water soluble, moderately weak acid. Its properties are adapted to measurement of its ionization behavior yet almost nothing about it has been reported in the literature to date. It does have some uses in analytical chemistry and in medicine. As part of an ongoing study of the thermodynamics of weak acid ionization we report here conductance measurements on mandelic acid for concentrations between about one millimolar and one-tenth millimolar for a temperature range of 10 to 75 degrees Celsius. The only other report in the literature closely related to our work is one study by Banks and Davies (1) who found mandelic acid to have a pK 3.411 at 25°C measured by conductivity.

Experimental

Solution preparation and measurement procedures were essentially the same as described earlier by Strong, Kinney, and Fischer (15). A set of four conductivity cells was used to obtain conductivities for eight different concentrations. D(-) mandelic acid (D- α -hydroxyphenylacetic acid) was purchased from Sigma Chemical Company as a high purity preparation and was used without further treatment other than drying it over phosphorus pentoxide in a vacuum dessicator at room temperature for several weeks.

Results

Molar conductivities for mandelic acid are listed in Table I for eight concentrations and fourteen temperatures. At the foot of the table molar concentrations at 25°C are listed while molarities at other temperatures were calculated by multiplying each listed concentration by the ratio of the density of water at each desired temperature to the density at 25°C. Calculations indicated that any difference between the density of water and the various solutions was less than 0.01%.

In Table II are presented the derived values of Λ_0 , $pK_a(c)$, and $pK_a(m)$ together with the standard errors calculated from the scatter of the experimental values around the calculated values. The two sets of pK_a values reflect two different standard state choices: (1) an ideal one molar standard state represented by $pK_a(c)$ which is the result of the fact that solution conductivity is a volume property and (2) an ideal one molal standard state represented by $pK_a(m)$ which is the more desirable choice for thermodynamic analysis. The conversion of $pK_a(c)$ to $pK_a(m)$ was done as proposed by Robinson and Stokes

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TABLE I *Mandelic Acid—Molar Conductivities*

Deg C.	$\Lambda_0, \text{cm}^2 \Omega^{-1} \text{mol}^{-1}$									
10	130.99	138.04	143.98	221.32	221.60	231.03	234.72	237.89		
15	143.44	151.15	157.64	242.39	242.72	253.08	257.13	260.56		
20	155.49	163.86	170.95	263.04	263.42	274.74	279.14	282.76		
25	167.15	176.22	184.28	283.27	283.68	295.97	300.70	304.68		
30	178.26	187.97	196.71	302.87	303.33	316.57	321.66	325.95		
35	188.82	199.15	208.56	321.84	322.57	336.55	342.19	346.60		
40	198.79	209.73	220.02	340.02	340.93	355.79	361.82	366.48		
45	208.15	219.69	230.77	357.45	357.76	374.27	379.91	385.61		
50	216.86	229.01	241.33	374.03	374.82	391.95	398.02	403.89		
55	224.91	237.63	251.28	389.79	390.80	408.65	415.23	421.38		
60	232.33	245.71	261.08	404.64	406.58	424.70	431.74	437.97		
65	239.08	253.20	271.53	418.60	421.89	439.77	447.42	453.65		
70	245.30	260.30	281.41	431.63	436.43	453.87	462.33	468.49		
75	250.86	266.84	292.06	443.77	451.05	467.11	476.70	482.45		
$C \times 10^3 @ 25^\circ \text{C}$	1.1705	1.0094	0.8971	0.18103	0.18055	0.14354	0.13278	0.12219		

TABLE II *Mandelic Acid: Limiting Conductance and Ionization Constant*

Temp. °C	Λ_0 $\text{cm}^2\Omega^{-1}\text{mol}^{-1}$	St. Err.	$\text{pK}_a(\text{c})$	St. Err. $\times 10^4$	$\text{pK}_a(\text{m})$	$\sigma\%$
10	296.14	0.34	3.3976	23	3.3975	0.06
15	324.50	0.37	3.3986	22	3.3982	0.06
20	352.66	0.39	3.4020	22	3.4012	0.06
25	380.65	0.42	3.4072	22	3.4059	0.06
30	408.34	0.45	3.4147	22	3.4128	0.06
35	435.92	0.61	3.4247	27	3.4221	0.07
40	462.79	0.70	3.4354	29	3.4320	0.08
45	488.40	0.35	3.4456	14	3.4414	0.04
50	514.36	0.48	3.4591	18	3.4539	0.05
55	539.63	0.65	3.4736	23	3.4673	0.06
60	564.63	1.27	3.4893	42	3.4819	0.11
65	589.06	2.31	3.5057	72	3.4972	0.18
70	612.54	3.58	3.5216	106	3.5118	0.26
75	635.92	5.71	3.5389	160	3.5278	0.39

(13) using $\text{pK}_a(\text{m}) = \text{pK}_a(\text{c}) + \log(\text{H}_2\text{O density})$. The righthand-most column of Table II lists $\sigma\%$, the standard deviation of the experimental lambda values from those calculated and presented as a percentage of lambda zero at each temperature.

Table II shows that the precision of the measurements ranged between 0.05% and 0.1% up to 60°C but deteriorated markedly above 60°C. The decrease in precision seemed to be a consequence of slight leaks of solution along the seal between the platinum electrode leads and the glass of the electrode chamber. These leakage difficulties differed from cell to cell and increased with rise in temperature.

In Fig. 1 $\text{pK}_a(\text{m})$ is plotted as a function of temperature in the lower part of the figure while the Walden product, $\eta_0\lambda_0$, for the mandelate ion is plotted in the upper part of the figure. Vertical bars indicate the calculated standard error at each temperature. For comparison, data for benzoic acid (15) are included in the figure. The continuous curve drawn for mandelic acid has been calculated to give the best fit when each datum is weighted by $1/(\text{standard error})^2$.

Analysis of the conductivity-concentration relation at each temperature was made with a conductance function recently proposed by Fuoss (3) in which

$$\Lambda = [1 - \alpha(1 - \gamma)] [\Lambda_0(1 - \Delta X/X) - \Delta \Lambda_c]$$

where ΔX is the relaxation effect correction generated by the external field X , $\Delta \Lambda_c$ is the electrophoretic effect correction, $1 - \gamma$ is the fraction of the ions that are paired while α represents the fraction of the paired ions that are in contact. This 1978 function differs from the one proposed by Fuoss in 1975 (4) and used in the treatment of the benzoic acid data (15) primarily in the way the dissociation constant enters into the model. In this new model the division between ions and unionized molecules includes the effect of diffusion of the ions out of the Gurney sphere to become free ions that contribute to the flow of charge. However, for mandelic acid the two functions give Λ_0 and pK values that differ by a negligible amount compared to the scatter, 0.05% of Λ_0 and less than 0.001 for pK .

There is just one measurement of pK and Λ_0 reported in the literature by Banks and Davies (1) who found $pK_a(c) = 3.411$ by conductivity at 24.92°C . We have corrected their data to 25.00°C and done a recalculation by the same procedure used for our data and find $pK_a(c) = 3.4062$ and $pK_a(m) = 3.4051$ with a standard error of 0.0010. This is in good agreement with our $pK_a(m) = 3.4059$. Their Λ_0 recalculated is $378.03\text{ cm}^2\Omega^{-1}\text{mol}^{-1}$ with a standard error of 0.26 which is not in terribly close agreement with our $\Lambda_0 = 380.65$. It does seem likely that Λ_0 for mandelic acid would not be much different from that found for benzoic acid where $\Lambda_0 = 381.72$ at 25°C .

Walden products for the mandelate ion at the various temperatures were calculated. For this calculation the limiting conductance of the hydrogen ion was subtracted from the limiting conductance of mandelic acid to give the limiting anion conductance which when multiplied by the viscosity of water gave the Walden product at each temperature for the mandelate ion. These are assembled in Table III and displayed in Fig. 1 where the vertical bars show the calculated errors derived from the standard error in Λ_0 values. The continuous curve is derived from a cubic polynomial in the temperature that fits the

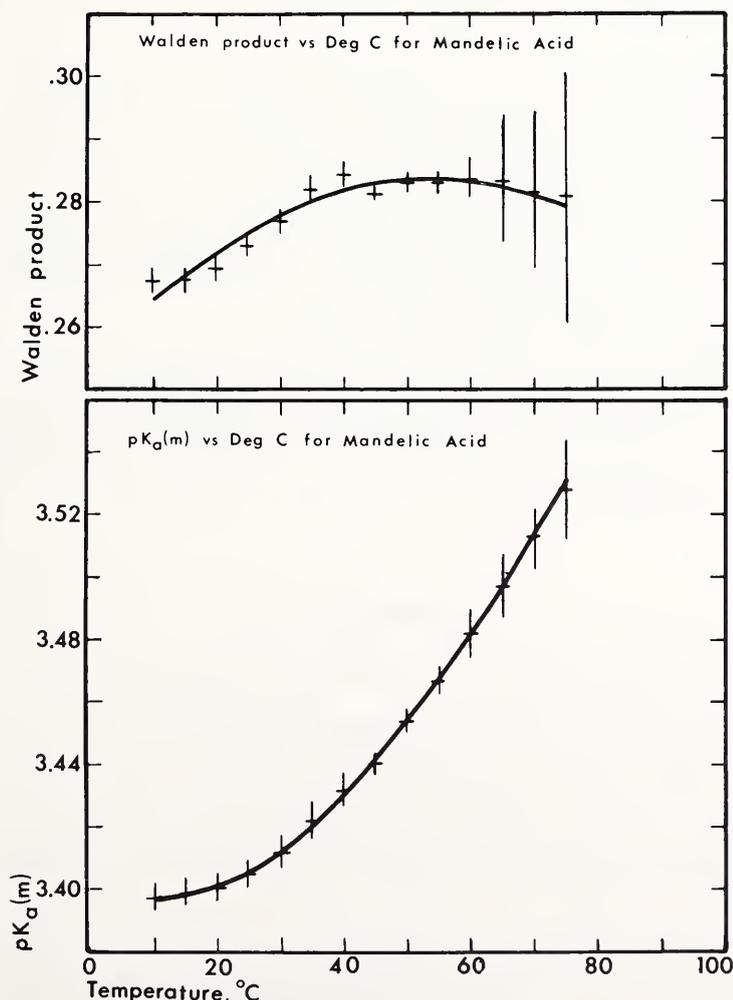


FIGURE 1. Walden Product, $\eta_0\lambda_0^-$, and $pK_a(m)$ for mandelic acid. Vertical bar shows standard statistical error assigned to each datum.

TABLE III *Mandelate Ion: Limiting Conductance and Walden Product*

Temp. °C	$\Lambda_0(\text{obs})$ $\text{cm}^2\Omega^{-1}\text{mol}^{-1}$	Dev. ^a	λ_0^- $\text{cm}^2\Omega^{-1}\text{mol}^{-1}$	Walden Product $\eta_0\lambda_0^-$	Dev. ^b
10	296.14	-0.19	20.32	0.265	0.004
15	324.50	0.08	23.59	0.268	0.004
20	352.66	0.23	27.12	0.272	0.004
25	380.65	0.19	30.86	0.275	0.004
30	408.34	0.07	34.79	0.277	0.004
35	435.92	-0.34	38.89	0.280	0.004
40	462.79	-0.46	43.12	0.281	0.005
45	488.40	0.23	47.46	0.283	0.002
50	514.36	0.10	51.88	0.284	0.003
55	539.63	0.18	56.35	0.284	0.003
60	564.63	0.01	60.84	0.284	0.006
65	589.06	-0.13	65.32	0.283	0.010
70	612.54	0.13	69.77	0.282	0.015
75	635.92	-0.09	74.16	0.280	0.022

^a $\Lambda_0(\text{calc}) - \Lambda_0(\text{obs})$ where $\Lambda_0(\text{calc}) = 237.76 + 5.8747T - 5.3181 \times 10^{-3}T^2 - 2.9910 \times 10^{-5}T^3$

^bUncertainty in Walden product produced by applying all the standard error for Λ_0 listed in Table II to λ_0^- .

observed Λ_0 with an average deviation of 0.17 conductance units. The hydrogen ion conductances used in these calculations are derived from an equation given by Harned and Owen (6) based on the conductivity data for hydrochloric acid of Owen and Sweeton (11). However, these data extend only from 5° to 65° C. To include values beyond 65° C a Λ_0 value at 100° C cited by Quist and Marshall (12) was combined with the transport numbers of Macdonald and Owen (9) to calculate a $\lambda_0^-(\text{H}^+)$ at 100° C of $648 \text{ cm}^2\Omega^{-1}\text{mol}^{-1}$.

With increasing temperature $\eta_0\lambda_0^-$ for the mandelate ion increases at least up to 55° C. For higher temperatures the uncertainties in the data are large enough to preclude any decision as to the pattern although the data suggest that the Walden product goes through a maximum near 55° C. The observed increase is about 7% of $\eta_0\lambda_0^-$ at 10° C.

Discussion

From the variation of $\text{pK}_a(\text{m})$ with temperature it is possible to derive the thermodynamic parameters ΔH° , ΔS° , ΔC_p° , and their variation with temperature. Whether this is practical hinges on the number of data points, the temperature range, and the precision of the data. The most careful considerations of a suitable calculation strategy have been made by Clarke and Glew (2) and by Ives and Moseley (8). Their conclusion is that the proper function to describe the temperature pK relation is $\text{pK} = A + B/T + C\log T + DT + \dots$ where terms after the logarithm term form a power series in T.

For the mandelic acid data the precision and temperature range of the data are sufficiently limited that only the first three terms of the fitting equation are clearly justified. Therefore the Ives and Moseley sigma plot method was used. The resulting equations are:

$$\begin{aligned} \text{pK}_a(\text{m}) &= -37.6882 + 1738.97/T + 14.2508 \log T \\ \Delta G^\circ &= 7956.9 + 65.206T \log T - 172.45T \\ \Delta H^\circ &= 7956.9 - 28.319T \\ \Delta S^\circ &= 144.13 - 65.206 \log T \\ \Delta C_p^\circ &= -28.3 \text{ cal/mole-deg} \end{aligned}$$

The energy units in these equations are calories per mole and the temperatures are Kelvin. The fitting is such that calculated pK values agree with observed values with an average deviation of less than 0.02% or about 1 unit in the third digit to the right of the decimal in the pK values.

TABLE IV *Thermodynamic Parameters for Four Acids at 25° C*

	ACETIC ACID ^a	BENZOIC ACID	GLYCOLIC ACID ^b	MANDELIC ACID
pK _a (m)	4.756	4.1985	3.831	3.4059
ΔG°, cal/mol	6487.	5728.	5226.	4648.
ΔH°, cal/mol	8.7	61.	163.	-486.
-ΔH°/T, cal/mol-deg	-0.029	-0.20	-0.547	1.63
ΔS°, cal/mol-deg	-21.7	-19.0	-17.0	-17.2
ΔC _p °, cal/mol-deg	-29.3	-38.6	-39.9	-28.3

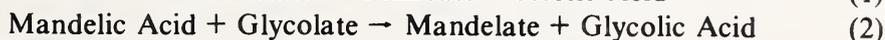
^aHarned and Ehlers (5) data recalculated to give pK_a(m) = -38.1023 + 1909.45/T + 14.7317 log T.

^bNims (10) data recalculated to give pK_a(m) = -54.5736 + 2630.22/T + 20.0379 log T.

The thermodynamic parameters at 25° C are given in Table IV. Some useful comparisons can be made between mandelic acid and related substances such as acetic acid (5), glycolic acid (10), and benzoic acid (15). For the first two we recalculated the pK(T) function by the sigma plot method. However, neither the acetic acid nor the glycolic acid data extend over a wide enough temperature range nor are represented by enough data points to be entirely satisfactory for calculating thermodynamic parameters from curve fitting.

Comparison of mandelic acid with these other three related acids can best be made on an entropy plot as described by Strong and Halliwell (14) Fig. 2 is such a plot with ΔS°, the standard entropy change for the system, on the abscissa and -ΔH°/T, the standard entropy change for the environment, on the ordinate. Diagonal dotted lines indicate constant pK values since $R \ln 10 \text{pK} = -\Delta G^\circ/T = -\Delta H^\circ/T + \Delta S^\circ$. The circles locate the experimental temperatures. Dashed lines connect points at the same temperature for the different acids.

The striking relation among the selected acids revealed by Fig. 2 is that acetic, benzoic, and glycolic acids ionize with little difference in -ΔH°/T anywhere within the temperature range studied. By contrast mandelic and glycolic acids differ in ionization mainly in -ΔH°/T while differing little in ΔS°. It is convenient to compare two contrasting acid-base reactions in relation to the data



These will be referred to as symmetric reactions.

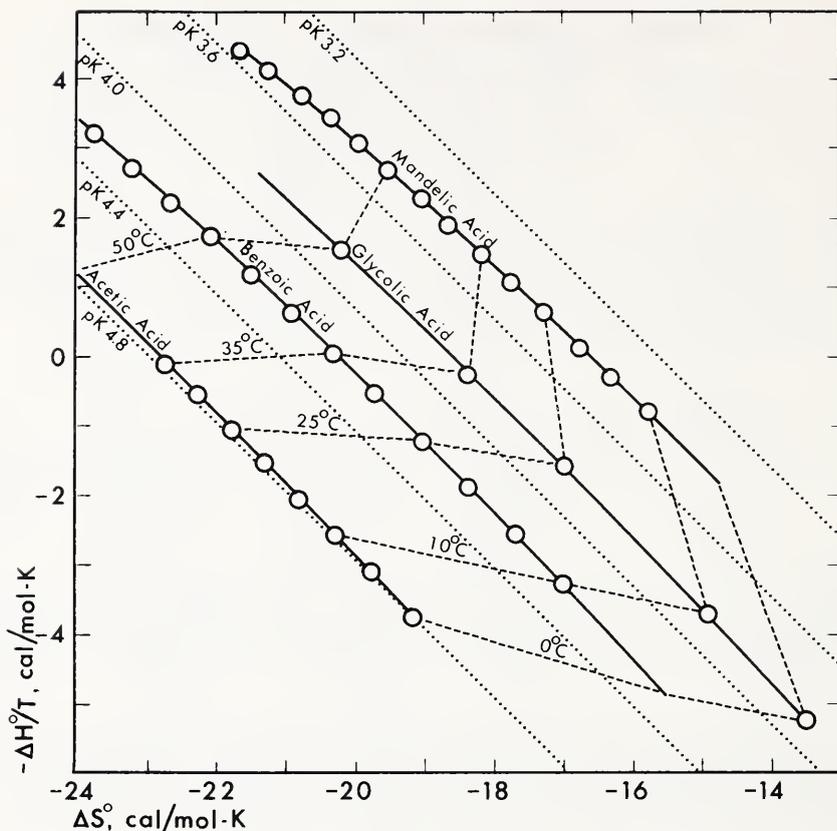


FIGURE 2. Entropy plot for the ionization of four acids in water. The continuous solid curves are calculated from the equations that best fit $pK_a(m)$ vs. T . Each dotted line indicates a constant pK_a ranging from 3.2 on the right to 4.8 on the left. Circles correspond to the experimental temperatures and the dashed lines connect points of the same temperature for the four acids.

Hepler and Wooley (7) have described a way of interpreting such symmetric reactions. Enthalpy and entropy changes are divided into an internal part which refers to the interaction of the charged ions only and an external part which refers to the interaction of the acid and base with solvent. Thus

$$\Delta H^\circ = \Delta H_i + \Delta H_e$$

$$\Delta S^\circ = \Delta S_i + \Delta S_e$$

Generally for symmetric reactions $\Delta S_i = 0$. Hepler and Wooley suggest that

$$\Delta H_e = \beta \Delta S_e + \gamma \Delta H_i$$

where it is usually found that $\beta \approx T$ and γ is a constant related to solvent and temperature. For reaction (1) $\Delta H^\circ = 0$ therefore $\Delta H_i = -\Delta H_e$. The question of whether ΔH_e or ΔH_i is negative can be approached by considering ΔC_p° which is negative ($-39 + 29 = -10$ cal/mol-deg) for reaction equation (1). A negative ΔC_p° implies a decrease in molecular motion which points to increased hydration for the benzoate-acetic acid pair compared to their conjugates. It is then reasonable to assume that increased hydration is accompanied by decreased enthalpy or $\Delta H_e < 0$. Therefore $\Delta H_i > 0$ so that the attraction by acetate ion for a proton is less than by benzoate ion. It must then be that it is increasing hydration which drives the reaction by raising the entropy of the system. The entropy rises because water molecules initially tied into the water structure gain some freedom of motion on transfer to the acid-ion system.

In the mandelic acid-glycolate system $\Delta C_p^\circ = -28 + 40 = +12$ cal/mol-deg. In line with the Hepler-Wooley analysis ΔH_e is proportional to ΔH_i . Since $\Delta C_p^\circ > 0$ it is reasonable to assume that hydration decreases as the reaction proceeds and that $\Delta H_e > 0$. Therefore we conclude that $\Delta H_i < 0$ and sufficiently large to yield $\Delta G^\circ < 0$.

In summary benzoic acid transfers a proton to acetate ion as a consequence of increased hydration. Mandelic acid transfers a proton to the more electrically attractive glycolate ion.

Of the four acids discussed here Walden products for a range of temperatures are available only for benzoate and mandelate ions thus far. Strong, Kinney, and Fischer concluded that the Walden product for the benzoate ion did not change significantly (<4%) with increasing temperature. It now appears that the mandelate ion has a Walden product that increases some with increasing temperature. This can be taken to indicate that the mobility of the mandelate ion increases with temperature by an amount that is greater than that determined solely by the increasing fluidity of the solvent. Therefore the hydrodynamic volume of the mandelate ion decreases as the temperature increases which implies that solvation decreases with increasing temperature. Furthermore this implies that solvation of the glycolate ion also decreases with increasing temperature but no conductance data are available to verify such a conclusion.

Further work is underway to improve the precision and extend the temperature range of the pK data.

Conclusion

Mandelic acid has been found to have a $pK_a(m)$ of 3.406 at 25°C and to decrease slightly in acidity as the temperature rises. Compared to glycolic acid with a pK of 3.831 the greater acidity of mandelic acid is due to a smaller attraction for positive charge by the mandelate ion compared to the glycolate ion which favors ionization of mandelic acid. The Walden product for the mandelate ion increases with increasing temperature up to about 55°C but beyond that temperature it may decrease slightly although the precision of the present data is inadequate to be sure about the decrease.

Curiously the substitution of a phenyl group seems to have different consequences when acetic and benzoic acids are compared than when glycolic and mandelic acids are compared. The implications of this difference are not yet clear.

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