alyses. It is not improbable that the results of such researches might lead to a view of their basic electronic structure totally different from that here presented.[35]

[35] NOTES ADDED IN PROOF.—Dr. S. C. Nyburg of the Department of Chemistry, University College of North Staffordshire (private communication) is at present performing X-ray structural analyses of these complexes. Bridged complexes of V(III) with RCO_2^- groups have been characterized recently by B. Jezowska-Trzebiatowska and L. Pajdowski, *Roczniki Chemii*, **31**, 769 (1957). A stable paramagnetic isomer of bis (N-methylsalicylaldimine) Ni(II) has been reported by C. M. Harris, S. L. Lenzer and R. L. Martin, *Australian J. Chem.*, **11**, 331 (1958).

MURRAY HILL, NEW JERSEY

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WISCONSIN]

Proton Magnetic Resonance Spectra of Malic Acid and its Salts in Deuterium Oxide[1,2]

BY ROBERT A. ALBERTY AND PAUL BENDER

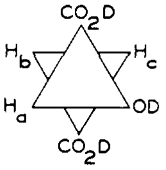
RECEIVED JULY 17, 1958

After exchange with deuterium oxide, malic acid and its salts represent systems of three non-equivalent protons. The structures of the proton magnetic resonance spectra obtained can be approximated quite well by use of the recently developed theories for the case in which one of the chemical shifts is large with respect to the two others and to the three coupling constants. It is possible to identify the chemical shifts with particular protons and the coupling constants with particular pairs by use of high resolution experiments on the monodeuterio-L-malate produced enzymatically. The monodeuterio-L-malate produced by hydrating fumarate by fumarase is that diastereomer in which the protons are gauche when the carboxyl groups are *trans*, as shown earlier by proton resonance experiments on the solid acid. The changes in chemical shifts and coupling constants with concentration and degree of neutralization of malic acid have been studied. Better resolution is obtained when the cation is potassium rather than lithium or sodium.

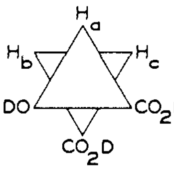
Introduction

The high resolution proton magnetic resonance spectra of simple organic compounds provide a means for determining the positions of deuterium atoms substituted for hydrogen atoms and for analyzing mixtures of the various partially deuterated species produced by exchange or in the course of various reactions. The L-malate formed from fumarate by the action of pig heart fumarase in D_2O contains one atom of deuterium in the methylene group,[3] and proton resonance experiments on the solid acid at −196° show that the two protons are in the gauche position[4] provided that the carboxyl groups are in the *trans* position. A study of the high resolution spectra of malic acid and the enzymatically prepared monodeuterio-L-malic acid and their salts was undertaken in order to provide the basis for the analysis of mixtures of partially deuterated malic acids arising in the acid and base catalyzed hydrations of fumarate.

Analysis of the high resolution spectra of two-spin systems for the case in which the difference in chemical shifts is of the order of magnitude of the coupling constant is well known.[5-7] Analysis of the high resolution spectra for systems of three protons recently has been described in detail[8-10] for the approximation that $|\nu_b - \nu_a| >> |\nu_c - \nu_b|$, $|A_{ab}|$, $|A_{ac}|$, $|A_{bc}|$, where the ν's are the n.m.r. frequencies and the A's are coupling constants. For malic acid the subscripts designate the various protons as indicated by



I



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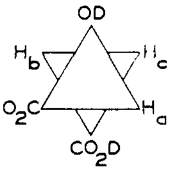

III

According to this nomenclature the monodeuterio-L-malic acid produced enzymatically is represented by H_2D_cM.

Experimental

The carboxyl and hydroxyl protons of recrystallized[11] malic acid and its salts were exchanged out and replaced by deuterons. The dry sample was dissolved in D_2O, the water sublimed out and the process then repeated two times. The sample then was dissolved in 99.5% D_2O, usually to give a concentration of 2 *M*, and sealed in a 5 mm. (o.d.) tube.

The spectra were observed at a nominal frequency of 40 megacycles using a Varian V-4300 n.m.r. spectrometer equipped with a superstabilizer. The cooling water for the magnet coils was circulated from a thermostat at 25° controlled to ±0.03°. The spectra were recorded with the sample spinning under a variety of experimental conditions. In order to determine chemical shifts with respect to H_2O, small capillaries containing water were placed in the n.m.r. tubes, or ground coaxial tubes[12] were used. The separations of the lines from the water resonance peak were measured using the sideband resonances produced by audiomodulation of the magnetic field.[13] The audio oscillator was checked at intervals with a Hewlett Packard Electronic Counter (Model 524B). By recording sidebands of appropriate spacing and intensity with either the Sanborn or Varian recorders, it was possible to reproduce shifts of the order of 100 c.p.s. with an average deviation of less than 1%.

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[1] Presented at the 133rd meeting of the American Chemical Society in San Francisco, April 16, 1958.

[2] This research was supported by grants by the National Science Foundation and by the Research Committee of the Graduate School of the University of Wisconsin from funds supplied by the Wisconsin Alumni Research Foundation.

[3] H. F. Fisher, C. Frieden, J. S. McKinley McKee and R. A. Alberty, THIS JOURNAL, **77**, 4436 (1955).

[4] T. C. Farrar, H. S. Gutowsky, R. A. Alberty and W. G. Miller, *ibid.*, **79**, 3978 (1957).

[5] E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).

[6] M. K. Banerjee, T. P. Das and A. K. Saha, *Proc. Roy. Soc. (London)*, **226A**, 490 (1954).

[7] W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956).

[8] G. A. Williams and H. S. Gutowsky, *J. Chem. Phys.*, **25**, 1288 (1956).

[9] H. J. Bernstein, J. A. Pople and W. G. Schneider, *Canadian J. Chem.*, **35**, 65 (1957).

[10] H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, THIS JOURNAL, **79**, 4596 (1957).

[11] C. Frieden, R. G. Wolfe and R. A. Alberty, *ibid.*, **79**, 1523 (1957).

[12] J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957).

[13] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 608 (1951).

TABLE I

PROTON MAGNETIC RESONANCE FREQUENCIES AT 40 MC. IN C.P.S. FOR 2 M SOLUTIONS IN D_2O AT 25° MEASURED WITH RESPECT TO H_2O

		K_2M	K_2D_cM	KHM + K_2M	KHM	H_2M + KHM	H_2M	H_2DcM
Exch. protons		−2.8	−1.1	−7.9	−7.3	−9.0	−12.1	−6.2
Methine	1	8.0	9.1	6.7	5.8	3.2	(0.7)	3.9
	2	12.5	18.6	11.6	10.7	8.4	6.0	10.9
	3	16.1		13.7	12.3	9.5	6.8	
	4	20.8		18.8	17.5	14.8	12.1	
Methylene	5	65.8	86.1	61.0	60.5			74.4
	6	70.4	95.4	65.9	64.4	62.5	62.0	81.5
	7	81.2		77.0	75.4	73.6	73.2	
	8	82.6						
	9	85.9		81.8	80.6	78.6	78.8	
	10	90.9		84.4	82.3	80.0	79.4	
	11	98.0		93.0	92.2	90.3		
	12	106.3		100.3	98.9	96.5	95.8	

When concentrations above 2 M were used line broadening was observed which seriously reduced the resolution which could be obtained. Proton magnetic resonance spectra were determined for lithium, sodium, and potassium malate solutions, and the resolution of the spectrum at 2 M was found to be best in the case of the potassium malate. Solutions of lithium and sodium malate have been determined to be more viscous than those of potassium malate[14].

Results

Dipotassium Malate (K_2M).—The proton resonance spectrum of dipotassium malate in D_2O as illustrated in Fig. 1a shows that the three protons are non-equivalent. The average frequencies for a number of spectra are summarized in Table I. This and the following spectra have been analyzed as described by Gutowsky, Holm, Saika and Williams[10] for the approximation that one of the chemical shifts is much larger than the other and the three coupling constants. Of the 14 lines which are possible in this case, two are expected to be weak and have not been observed in any of the spectra. The line to the left of the one due to H_2O in the added capillary is due to protons in the medium which spend a fraction of the time on the malate hydroxyl group.[15] The frequency of this line is markedly dependent upon concentration, and it approaches the H_2O line as the solution is diluted with D_2O. From the relative areas it is apparent that the quadruplet immediately to the right of the H_2O line is due to the methine hydrogen. The two individually symmetrical quadruplets due to the methylene protons are superimposed since $|\nu_b - \nu_c| \cong |A_{ab}|, |A_{ac}|, |A_{bc}|$. In order to analyze the spectrum due to the methylene protons as two individually symmetrical quadruplets with equal separations of the outer lines from the inner lines, it is apparent that the quadruplet numberings must be 5-7-8-11 and 6-9-10-12.[16] The average value of A_{bc} obtained from the separations 5–7, 8–11, 6–9 and 10–12 is 15.3 ± 0.1 c.p.s. This coupling constant is somewhat larger than the value of 12.4 ± 0.6 c.p.s. obtained by Karplus, *et al.*,[17] for the proton–proton coupling in methane.

From the 9–10 separation, which is equal to $2A_+ - A_{bc}$, the value of A_+ may be obtained, and from the 7–8 separation, which is equal to $2A_- - A_{bc}$, the value of A_- may be obtained. The parameters A_+ and A_- are used as shown later in connection with equation 1 to calculate $\nu_b - \nu_c$ and $A_{ab} - A_{ac}$. As a check on these values of A_+ and A_- the quantity $2(A_+ - A_-)$ is obtained from the 2–3 separation. In cases where the results were slightly different the value of A_+ was calculated from the 9–10 separation and the value of A_- was calculated from this value of A_+ and the 2–3 separation. The separation between the centers of the overlapping quartets is equal to $(^1/_2)(A_{ab} +$

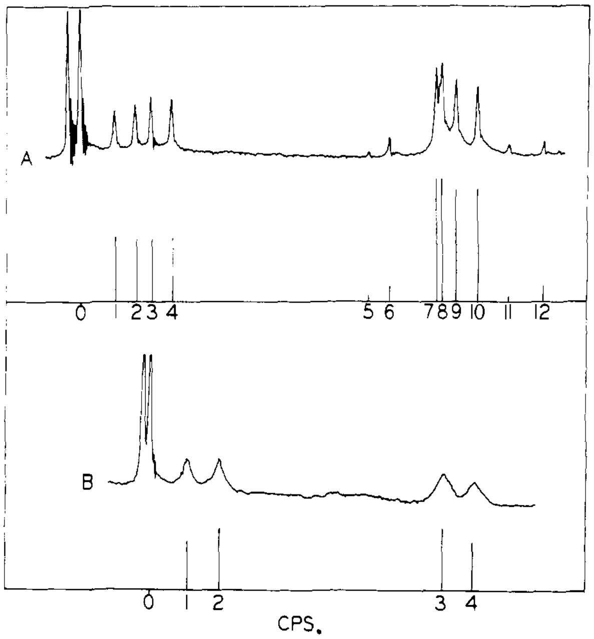

Fig. 1.—Proton nuclear magnetic resonance spectra of: (a) 2 M dipotassium malate and (b) 2 M dipotassium monodeuterio-L-malate in D_2O at 40 Mc. The magnetic field strength increases to the right. The line marked zero is due to H_2O in a small capillary. The vertical lines are located at the frequencies computed from the chemical shifts and coupling constants, and the heights are proportional to the theoretical intensities.

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(14) Personal communication from G. W. Miller.

(15) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(16) The lines 1–12 in the spectra in this paper correspond with lines 1, 5, 2 and 6 in the 1-spin set and 2, 6, 3, 1, 7, 5, 4 and 8 in the 2-spin set, respectively, in Gutowsky, *et al.*[10]

(17) M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957).

TABLE II

SUMMARY OF COUPLING CONSTANTS IN C.P.S. AND CHEMICAL SHIFTS δ FOR 2 M SOLUTIONS IN D_2O AT 25°

	K_2M	K_2D_cM	$KHM + K_2M$	KHM	$H_2M + KHM$	H_2M	H_2D_cM
A_{ab}	9.7 ± 0.2	9.4	8.9	8.5	7.8	7.1	7.1
A_{ac}	3.1 ± .2		3.2	3.2	3.8	4.4	
A_{bc}	15.3 ± .1		15.9	16.4	16.3	17.1	
δ_a	0.360 ± .003	0.362	0.318	0.288	0.225	0.168	0.168
δ_b	2.26 ± .01	2.27	2.09	2.03	1.98	1.98	1.92
δ_c	2.00 ± .01		1.92	1.89	1.85	1.82	

A_{ac}). A second value of $A_{ab} + A_{ac}$ is obtained from the 1–4 separation, and excellent agreement invariably resulted.

The n.m.r. frequencies ν in c.p.s. were measured arbitrarily with respect to the water line. The mean frequency ν_a of the methine proton is obtained from the average of lines 1 and 4 or 2 and 3. The mean frequency ν_{bc} of the methylene protons is obtained from the average of the central frequencies of the two superimposed quadruplets. By use of the values of A_+, A_-, A_{bc}, $A_{ab} + A_{ac}$, ν_a and ν_{bc} the theoretical frequencies may be calculated using the relations of Gutowsky, *et al.*[10] The theoretical frequencies are in excellent agreement with the experimental results. The positions of the theoretical lines in Fig. 1a have been calculated in this way.

In order to calculate the theoretical intensities it is necessary to obtain the values of $A_{ab} - A_{ac}$ and $\nu_b - \nu_c$. These are calculated from the values of A_+ and A_- using the two simultaneous equations[10] which define A_+ and A_-.

$$(4A_{\pm}^2 - A_{bc}^2)^{1/2} = (\nu_b - \nu_c) \pm \frac{1}{2}(A_{ab} - A_{ac}) \quad (1)$$

Interchanging the values of A_+ and A_- simply interchanges the values of A_{ab} and A_{ac} without altering the computed spectrum. Actually the assignment of these two coupling constants to particular pairs of protons could not be done without knowledge of the structure of the dipotassium monodeuterio-L-malate, which is discussed next. We will label the coupling constants correctly and justify the assignment later. The theoretical intensities calculated using the values of the parameters obtained as described above represent the data quite well as shown by the heights of the vertical lines in Fig. 1a, but there is a significant deviation in the intensities of lines 1–4. This discrepancy arises because of the assumption[10] that $|\nu_b - \nu_a| >> |\nu_c - \nu_b|, |A_{ab}|, |A_{ab}|, |A_{ac}|$, and this observation indicates that better values of the chemical shifts and coupling constants could be obtained by extending the treatment to a higher order of approximation.

Since it is found that the sum of the coupling constants is greater than their difference, it is apparent that A_{ab} and A_{ac} have the same sign and this is arbitrarily taken to be positive. The best values of these coupling constants are summarized in Table II.

The values of the frequencies ν_b and ν_c for protons b and c measured in a c.p.s. displacement from the water line were calculated from $(\nu_b - \nu_c)$ as obtained from equation 1 and $\nu_{bc} = (\nu_b + \nu_c)/2$. The values of the chemical shifts are summarized in Table II in field-independent units by use of the definition $\delta = 10^6(H - H_{ref})/H_{ref}$. It should be noted that the chemical shifts for protons *b* and *c* are not given by the centers of the respective quartets. In obtaining the best values of the chemical shifts and coupling constants from 4–6 spectra, it was found better to analyze each spectrum separately and then average the chemical shifts and coupling constants from the various spectra, rather than to average the frequencies of the various lines and then analyze the average spectrum. The indicated uncertainties in the chemical shifts and coupling constants for K_2M are the average deviations for 6 spectra.

The magnitudes of the chemical shifts and coupling constants depend somewhat upon the concentration of K_2M and are slightly different when other cations are used. No corrections for differences in bulk magnetic susceptibility have been made because these differences are believed to be too small to be significant.

Dipotassium Monodeuterio-L-malate (K_2D_cM).—The high resolution proton spectrum of the dipotassium malate produced by hydrating fumarate in D_2O by use of fumarase is illustrated in Fig. 1b. The spectrum may be analyzed by use of the theoretical result[5] that the separation between the two center lines is $(A^2 + \Delta^2)^{1/2} - A$, where A is the coupling constant obtained from the splitting of either doublet and Δ is the difference between the two chemical shifts. From the value of Δ and the fact that the 4 line spectrum is centered about the average of the two chemical shifts, the values of the two chemical shifts may be calculated. The chemical shifts of $\delta = 0.362$ and 2.27 and a coupling constant of $A = 9.4$ c.p.s. are obtained. The chemical shift of 2.27 may be assigned to the proton (H_b) which is gauche with respect to the methine hydrogen since the n.m.r. experiments[4] on the solid acid showed that there is no H_c. Thus the coupling constant is identified as A_{ab}. The high resolution proton spectrum for this salt makes it possible to identify the 9.7 ± 0.2 c.p.s. coupling constant for K_2M as that for the a and b protons and the chemical shift of 2.27 as that of the b proton. The coupling constants and chemical shifts are summarized in Table II.

It will be noticed in Fig. 1b that the lines are broader than those of the salt which does not contain deuterium. This is because deuterium with a spin of 1 tends to split lines into triplets with coupling constants about $^1/_6$ as large as the corresponding proton–proton coupling constants. However, these lines never were resolved. There also may be some broadening due to the quadrupole moment of deuterium.

Monopotassium Malate (KHM).—The solubility of this substance is somewhat less than 1 M at 25°, but supersaturated solutions are obtained easily and the n.m.r. spectra were run on supersaturated solutions. Since at 25° the ionization constant of acetic acid is 1.75×10^{-5} and the ionization constant of lactic acid is 1.38×10^{-4}, it is to be expected that the first proton removed from malic acid will be that on the carboxyl group nearer the hydroxyl group and that there will be of the order of 10% of the other ionized form. However, since the average lifetimes of the carboxyl protons (deuterons) are short compared with the reciprocals of the n.m.r. frequency shifts, separate spectra for the two ionized forms are not to be expected. As shown by Fig. 2b the spectrum from KHM is intermediate between those from H_2M and K_2M. But it may be seen in Table II that the coupling constants and chemical shifts are not exactly averages of those for H_2M and K_2M.

KHM + K_2M.—The n.m.r. spectrum of an equimolar mixture of KHM and K_2M is intermediate between that of the two constituents as shown by Fig. 2a. This is because the proton equilibria are rapid compared with the n.m.r. frequencies. Assuming that the reaction of M^- with a proton is diffusion controlled, as has been found for several similar reactions by Eigen,[18] the second-order rate constant would be expected to be approximately 10^{11} l. mole^{-1} sec.$^{-1}$ at 25°. Thus at pH 5, HM^- would be formed with a first-order rate constant of 10^6 sec.$^{-1}$. Since the acid dissociation constant of HM^- is 4×10^{-4}, the first-order rate constant for the dissociation of the proton is expected to be about 4×10^7 sec.$^{-1}$. Since these rate constants are much larger than the n.m.r. chemical shifts and coupling constants, these latter are the averages of those for K_2M and KHM. Analogous results have been obtained by Gutowsky and Saika[19] and by Grunwald, Loewenstein and Meiboom[20] for mono-, di- and trimethylamine. The chemical shifts and coupling constants are summarized in Table II.

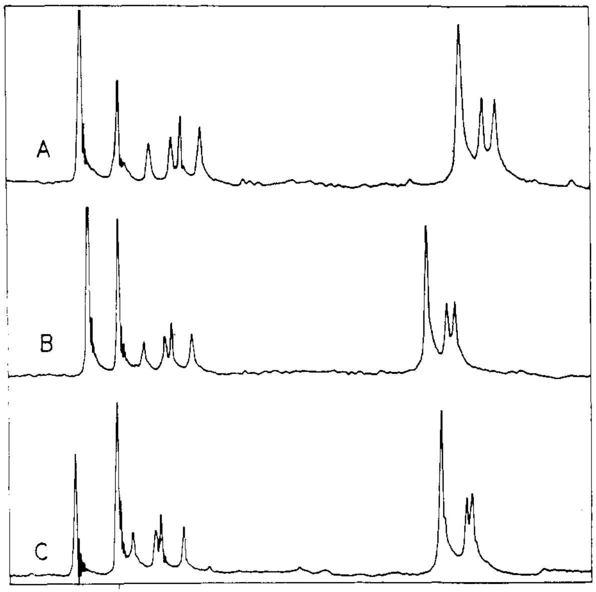

Fig. 2.—Proton nuclear magnetic resonance spectra of: (a) K_2M + KHM, (b) KHM and (c) KHM + H_2M in D_2O at 40 Mc. The sweep speed varied slightly between these various patterns and the magnet was slightly undercycled. The mixtures are equimolar and in each case the total malate concentration is 2 M.

H_2M + KHM.—The n.m.r. spectrum of an equimolar mixture of H_2M and KHM is intermediate between that of the two constituents as shown by Fig. 2c. Although lines 7 and 8 are not resolved and lines 5 and 11 are so weak that it is difficult to detect them, all three chemical shifts and coupling constants may be calculated. The values of these constants, which are summarized in Table II, permit us to calculate the values of the chemical shifts and coupling constants for malic acid on the assumption that the values for the equimolar mixture are averages. This calculation indicates that $A_{ab} = 7.1$ c.p.s. and $A_{ac} = 4.4$, and $\delta_b = 1.95$ and $\delta_c = 1.81$ would be expected for the H_2M. These values are in reasonable agreement with the parameters obtained directly from the H_2M spectrum.

Malic Acid (H_2M).—The proton resonance spectrum of malic acid in D_2O is illustrated in Fig. 3a. One component of the quadruplet due to the methine hydrogen is obscured by the line due to H_2O in the added capillary. Superficially this spectrum might be interpreted as characteristic of a three proton system with two of the protons magnetically equivalent. When analyzed on this basis it gives a coupling constant between the two kinds of protons of 5.7 c.p.s. However, this interpretation is not consistent with that just given for H_2M + KHM or the spectrum of H_2D_cM which gives a coupling constant for the gauche protons of 7.1 c.p.s. When H_2M solutions are studied at higher concentrations and at higher RF intensities, lines 6 and 12 are found symmetrically arranged around the methylene line at higher field and this methylene line is split slightly. The other methylene line showed no indication of resolution.

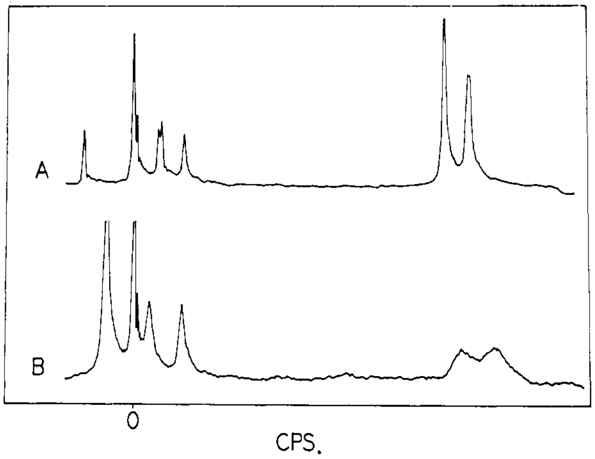

Fig. 3.—Proton nuclear magnetic resonance spectra of: (a) 2 M malic acid and (b) 2 M monodeuterio-L-malic acid in D_2O at 40 Mc.

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[18] M. Eigen and J. Schoen, *Z. Elektrochem.*, **59**, 484 (1955).

[19] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

[20] E. Grunwald, A. Loewenstein and S. Meiboom, *ibid.*, **27**, 641 (1957).

Lines 5 and 11 could not be detected at 40 Mc. but were detected at 60 Mc.[21]

Sufficient information is available in the spectrum at 40 Mc to calculate the three coupling constants and chemical shifts. The separation between lines 6 and 9 is the same as that between lines 12 and 10 and is equal to A_{bc}. The value of A_+ may be calculated from the 9-10 splitting and then A_- calculated using the 2-3 splitting. The coupling constants obtained in this way are summarized in Table II and are in satisfactory agreement with those for the enzymatically prepared monodeuteriomalic acid. The theoretical frequencies and intensities are in excellent agreement with experiment. The frequencies of the spectral lines are the same within experimental error at 1 and 2 M but are all reduced by about 0.6 c.p.s. at 4 M.

Monodeuterio-L-malic Acid (H_2D_cM).—The proton spectrum of the acid produced by the action of pig heart fumarase on fumarate is illustrated in Fig. 3b. This two proton spectrum was analyzed in the same way as that for K_2D_cM. A coupling constant $A_{ab} = 7.1$ c.p.s. and chemical shifts $\delta_a = 0.168$ and $\delta_b = 1.92$ are obtained. It is possible to denote particular protons by the subscripts since the position of the deuterium atom is known from n.m.r. experiments on the solid acid.[4] As in the case of K_2D_cM the proton spectrum is not as sharp as that for the undeuterated compound.

The coupling constant for enzymatically prepared monodeuterio-L-malic acid has also been measured by Krasna,[22] who in addition prepared the diastereomeric monodeuterio-D-malic acid with the protons in the opposite position. The coupling constants for these compounds are in satisfactory agreement with those reported here.

Discussion

The fact that different values are obtained for the H_a–H_b and H_a–H_c coupling constants does not indicate slow internal rotation[23] since it is now understood that non-equivalence can arise in other ways.[10,24,25] Because of the asymmetry of the H_2M or $M^=$, A_{ab} and A_{ac} would, in general, vary differently with angle of rotation and could have different average values even if conformations I, II and III were equally probable and the rate of interconversion was very fast. The rate of interconversion of various ionized forms is fast since otherwise intermediate spectra would not be obtained for mixtures like $H_2M + KHM$ and $KHM + K_2M$.

The carboxyl groups are expected to spend a large fraction of the time in the *trans* position (conformation I), especially in the divalent salt. Thus protons a and c are *trans* and protons a and b are *gauche*, or nearly *cis*. The *cis* and *trans* F^{19}–F^{19} and H^1–F^{19} coupling constants have been determined for halogenated olefins,[26] and it was found that the *trans* coupling constants are larger than the *cis* coupling constants. These assignments are opposite to those for malic acid, but quite different orbitals are involved in the two cases.

The relative magnitudes of the *cis* and *trans* coupling constants for malate are also different from those of the acetyl derivatives of glucose, galactose, xylose and arabinose.[27] For these compounds 2 and 3 times larger coupling constants are obtained when hydrogens on neighboring carbon atoms are in axial orientations than when one or both of the hydrogens are in equatorial orientation. It is recognized that the present results may be made consistent with these other observations if it is assumed that the conformation of the acid in solution differs from that for the solid. Such a change would require that A_{ab} be interchanged with A_{ac}, and δ_b with δ_c in the previous discussion. The present assignment is made on the assumption that the *trans* configuration for carboxyl groups is most probable in solution.

With knowledge of the chemical shifts and coupling constants for various protons in D_2M, K_2M and various mixtures the proton spectra of the various partially deuterated compounds may be predicted on the basis of the assumption that the electronegativity of hydrogen and deuterium are the same. Preliminary tests of these predictions indicate that they are borne out quite well. The identification of these partially deuterated malates, which would otherwise be much more difficult, is of interest in the interpretation of the acid and base catalyzed fumarate–malate transformation.[28]

Acknowledgments.—The authors are indebted to Professor H. S. Gutowsky and Professor John Roberts for advice concerning this research and to Mr. Wilmer Miller for providing the enzymatically prepared monodeuterio-L-malic acid.

MADISON, WISCONSIN

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[21] Experiment at 60 Mc. by courtesy of Varian Associates.

[22] A. I. Krasna, personal communication.

[23] J. J. Drysdale and W. D. Phillips, THIS JOURNAL, **79**, 319 (1957).

[24] P. M. Nair and J. D. Roberts, *ibid.*, **79**, 4565 (1957).

[25] D. L. Graham and J. S. Waugh, *J. Chem. Phys.*, **27**, 968 (1957).

[26] H. M. McConnell, C. A. Reilly and A. D. McLean, *ibid.*, **24**, 479 (1956).

[27] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, THIS JOURNAL, **79**, 1006 (1957).

[28] This research is to be described in a future publication.