

[CONTRIBUTION FROM THE SUN OIL CO., MARCUS HOOK, PENNSYLVANIA]

A Molecular Orbital Study of Polarographic Oxidation Potentials of Methyl-Substituted Aromatic Hydrocarbons

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Polarographic half-wave oxidation potentials have been determined in acetonitrile vs. a Ag-0.10 N Ag⁺ reference electrode at a rotating platinum electrode for eleven methyl-substituted benzenes and for eight other methyl-substituted hydrocarbons, including naphthalene, 1,3-butadienes, and 9,10-dimethylantracene. In order to test the prediction of the Hückel molecular orbital theory that changes in ionization potential with methyl substitution are proportional to the square of the Hückel coefficients, a plot is made of changes in polarographic oxidation potential vs. the square of the Hückel coefficients. The straight line obtained fits the equation $\Delta E_{1/2(\text{ox})} = 0.798 \sum_r C_{jr}^2 + 0.045 \text{ v.}$ The slope is corrected for comparison with plots of ionization potential by dividing by 0.827. With β_0 taken as -2.1 e.v. , h is -0.46 as compared with -0.54 obtained by plotting ionization potential directly. Considering the crude model for the methyl group used, the Hückel theory accounts reasonably well for the gross observed change. It fails, however, to account for finer details in the oxidation potentials of methyl-substituted toluenes where no contribution to $E_{1/2(\text{ox})}$ is observed for groups substituted *ortho* and *meta*, and a contribution of -0.15 v. is observed per substituent placed *para* to another methyl group.

Introduction

Streitwieser has recently shown¹ that the change in ionization potential with methyl substitution in aromatic hydrocarbons and olefins can be accounted for satisfactorily by the simple HMO (Hückel Molecular Orbital) theory. In this model, the methyl group is regarded as perturbing the carbon to which it is attached, such as to change the coulomb integral α_0 at that position. Equation 1 accounts for this change

$$\alpha_r = \alpha_0 + h\beta_0 \quad (1)$$

by assigning a negative value to h . The effect of a change of α_r , $\delta\alpha_r$, on the energy ϵ_m (eq. 2) of the highest occupied molecular orbital is given by eq. 3.² In

$$\epsilon_j = \alpha_0 + m_j\beta_0 \quad (2)$$

$$\delta\epsilon_j = C_{jr}^2\delta\alpha_r = C_{jr}^2h\beta_0 \quad (3)$$

eq. 3, C_{jr}^2 is the square of the coefficient at the position of substitution r in the j th molecular orbital of the parent hydrocarbon.

The simple HMO theory relates ionization potential to ϵ_m and, as Streitwieser¹ has indeed shown, a plot of change in ionization potential against C_{jr}^2 gives a straight line.

Ionization potentials are rather difficult to measure and there are rather large discrepancies in values obtained by different methods and by different workers using the same method.³ For these reasons, we feel that direct measurement of ionization potential does not provide the best test of eq. 3.

Recently, studies in this laboratory⁴ and elsewhere⁵ have shown a linear relation between polarographic oxidation potential and ionization potential which suggests that changes in solvation energy do not play an important part in the determination of differences in half-wave potentials between compounds. The

(1) A. Streitwieser, Jr., *J. Phys. Chem.*, **66**, 368 (1962).(2) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947).

(3) Examples of the variation of ionization potential with the method of measurement for electron impact, photoionization, and spectroscopic measurements are given in ref. 1.

(4) (a) W. C. Neikam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, **111**, 1190 (1964); (b) J. W. Loveland and G. R. Dimeler, *J. Anal. Chem.*, **33**, 1196 (1961).(5) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

equation which relates oxidation potential ($E_{1/2(\text{ox})}$) to photoionization potential (I) for 35 compounds is

$$E_{1/2(\text{ox})} = 0.827I - 5.40 \text{ v.}^{4a} \quad (4)$$

From this equation, it is apparent that changes in ionization potential will be reflected in proportional changes in oxidation potential; thus, $\Delta E_{1/2(\text{ox})}$ will be a suitable variable with which to test the predictions of the Hückel theory.

The use of polarographic half-wave potentials to test eq. 3 will largely avoid the difficulty of discrepancy between results of various workers.

However, note in Table I the rather large differences in values of $E_{1/2(\text{ox})}$ obtained by different workers for toluene, *p*-xylene, and the naphthalenes. The present authors used the same experimental procedures as Lund and where checks are possible we are in good agreement. Pysh and Yang, however, used an aqueous calomel reference which we have found to be undependable, and they are in sharp disagreement on many values of $E_{1/2(\text{ox})}$ with Lund and the present authors. Even though the $E_{1/2(\text{ox})}$ values obtained by Pysh and Yang are in many cases in better agreement with the predictions of the HMO theory than our own, we can discover no experimental reason to reject our values as being in error.

Pysh and Yang⁵ have attempted such a test with 11 methyl-substituted benzenes, naphthalenes, and anthracenes, and with 12 methyl-substituted 1,2-benzanthracenes. The agreement with the value for benzenes, naphthalenes, and anthracenes is fair, but with the benzantracenes, it is poor. Streitwieser⁶ has applied this test, with some success, to the change in polarographic reduction potential with methyl substitution in aromatic hydrocarbons.

We report here an additional test with methyl-substituted benzenes, naphthalenes, anthracenes, and butadienes. In addition, we point out a regularity in the oxidation potentials of substituted benzenes which is not explained by the simple HMO theory.

Experimental

Apparatus.—Current-potential curves were recorded by means of a Sargent Model XXI polarograph. Potentials were checked

(6) A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962).

using a General Radio Co., d.c. amplifier and electrometer, Type 1230-A, serial number 1673. Cell resistances were measured with an a.c. conductivity bridge (Industrial Instruments Co., Model RC 16B2). An internal Ag-Ag⁺ (0.10 *N*) reference electrode consisted of 25 cm. of a 16-gauge silver wire coiled to a diameter of 2 cm. Silver ion was added as silver perchlorate in the test solution. This electrode is preferable, as a reference, to a calomel aqueous KCl reference electrode such as was used by Pysh and Yang. Use of the silver electrode in the nonaqueous medium avoids the precipitation problems and uncertainties of liquid junction potential that are associated with aqueous reference electrodes.

The working electrode consisted of a platinum wire 0.5 cm. in length, 0.081 cm. in diameter, with an apparent surface area of 0.125 cm.². This electrode was sealed in a glass tube; mercury was used as a contact to the lead from the polarograph. The silver reference electrode was placed in the cell and the working electrode positioned in the center of the coil. Electrode rotation was controlled at 600 r.p.m. by means of a Sargent synchronous rotator.

Reagents and Material.—Eastman Kodak acetonitrile, practical grade, was used as the solvent. Sodium perchlorate (Fisher Scientific Co.) was dried without further purification at 150° for 24 hr. The dry product was stored over Drierite in a vacuum desiccator.

Silver perchlorate was prepared from sodium perchlorate and silver nitrate according to the method of Lund.⁷

The base solution (0.50 *N* sodium perchlorate in acetonitrile) prepared from the above reagents was found to yield an objectionable residual current at potentials greater than 1.7 v. In fact, a wave with $E_{1/2} = 1.75$ v. was observed. Screening of the solvent and electrolyte showed that the major portion of this wave could be attributed to impurities, possibly nitrate, in the silver perchlorate. Although careful recrystallization from ether-acetonitrile was satisfactory for eliminating the interference, it was found that purification by controlled potential electrolysis of the base solution was more convenient and equally satisfactory. Double-strength base solution was prepared and oxidized at a controlled potential of 1.95 v., using a silver cathode and a platinum anode (3 cm.²). After 3.5 hr., the current on a 100-ml. portion had dropped from 3.8 to 0.35 ma.

Sample Preparation.—The test samples of pure compounds were prepared by weighing the required amount of sample to prepare a 10 mM solution in 25 ml. of acetonitrile. Appropriate dilutions with acetonitrile were then made, so that a final 1:1 dilution with double-strength base solution (1 *M* sodium perchlorate, 0.2 *M* silver perchlorate in acetonitrile) would yield the desired concentration.

Electrode Conditioning.—The conditioning of the electrode can be divided into two steps: (1) initial conditioning after storage and (2) conditioning between runs. Initial conditioning was performed by wiping the electrode with a mildly abrasive tissue (Kim-Wipe) after a complete 0 to 3 v. span of the base solution had been run. The residual current of the blank was then determined in duplicate. Between consecutive runs, the cell and electrode were simply washed with base solution and the electrode was wiped with the tissue.

A slight wandering of the residual current is observed between 0 and +0.5 v. This wandering, which varies slightly from run to run, is probably caused by oxidation of the platinum electrode in the presence of trace amounts of water to give a thin layer of platinum oxide. The current drops to a few microamperes above 0.7 v. until decomposition of the solvent or electrolyte takes place. Thus, the electrode appears to condition itself during a run. The apparent self-conditioning of the electrode in acetonitrile is undoubtedly responsible for the good reproducibility observed, *viz.*, 0.02 v.

The current-potential curve for the base solution was determined daily. This was required, since at potentials greater than 1.7 v. moderate corrections for the blank were required.

The half-wave potential, $E_{1/2}(\text{ox})$, and the peak currents, i_p , were measured geometrically. The cell resistance never exceeded 100 ohms and was usually about 80 ohms; therefore, corrections for *IR* drop were unnecessary.

Duplicate experiments show reproducibility to be in the order of 0.02 v. for $E_{1/2}(\text{ox})$.

(7) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

Results

Table I lists the oxidation potentials ($E_{1/2}(\text{ox})$) of the compounds studied along with the sum of the coefficients squared of the positions of substitution in the

TABLE I
COMPARISON OF DIFFERENCE IN OXIDATION POTENTIAL
WITH HÜCKEL MOLECULAR ORBITAL COEFFICIENTS

No. in Fig. 1	Compound	$E_{1/2}(\text{ox}), \text{v.}$ vs. Ag- 0.1 <i>N</i> Ag ⁺	$\Delta E_{1/2}(\text{ox}), \text{v.}$	$\sum C_{jr}^2$
1	Benzene	2.08
		2.00 ^{a,b}
2	Toluene	1.98	0.10	0.333
		1.68 ^a	.32 ^a	
		1.93 ^b	.07 ^b	
3	<i>m</i> -Xylene	1.58	.50	0.500
		1.61 ^a	.39 ^a	
4	<i>o</i> -Xylene	1.57	.51	0.500
		1.59 ^a	.41 ^a	
5	<i>p</i> -Xylene	1.56	.52	0.667
		1.47 ^a	.53 ^a	
6	1,3,5-Trimethylbenzene	1.55	1.53	0.500
		1.50 ^a	0.50 ^a	
7	1,2,3-Trimethylbenzene	1.58	.50	0.500
8	1,2,4-Trimethylbenzene	1.41	.67	.750
9	1,2,3,5-Tetramethylbenzene	1.43	.65	.750
10	1,2,3,5-Tetramethylbenzene	1.29	.79	1.000
11	Pentamethylbenzene	1.28	.80	1.000
12	Hexamethylbenzene	1.16	.92	1.000
13	Naphthalene	1.34
		1.24 ^a
		1.31 ^b
14	1-Methylnaphthalene	1.24	0.10	0.180
		1.13 ^a	.11 ^a	
15	2-Methylnaphthalene	1.22	.12	0.069
		1.15 ^a	.09 ^a	
16	2,3-Dimethylnaphthalene	1.08	.26	0.138
		1.05 ^a	.19 ^a	
17	2,6-Dimethylnaphthalene	1.08	.26	0.138
		1.06 ^a	.18 ^a	
18	2,7-Dimethylnaphthalene	1.12	.22	0.138
19	1,3-Butadiene	2.03
20	2,3-Dimethyl-1,3-butadiene	1.83	0.20	0.376
21	2-Methyl-1,3-butadiene	1.84	0.19	0.138
22	Anthracene	0.84
		.79 ^a
		.84 ^b
		.65	0.19	0.388
23	9,10-Dimethylanthracene	.57 ^a	0.22 ^a	
		.65 ^b		

^a Ref. 5. ^b Ref. 7.

highest occupied molecular orbital ($\sum_r C_{jr}^2$). In order to calculate $\sum_r C_{jr}^2$ for the case of methyl-substituted benzenes consideration was given to the degeneracy of the two highest filled orbitals of the parent hydrocarbon benzene (eq. 5 and 6).⁸ The highest occupied orbital

$$\Psi_{E_{1a}} = \frac{1}{\sqrt{12}} (2\phi_0 + \phi_1 - \phi_2 - 2\phi_3 - \phi_4 + \phi_5) \quad (5)$$

$$\Psi_{E_{1b}} = \frac{1}{2} (\phi_1 + \phi_2 - \phi_4 - \phi_5) \quad (6)$$

$$E_{E_{1a}} = E_{E_{1b}} = \alpha + \beta \quad (7)$$

(either $\Psi_{E_{1a}}$ or $\Psi_{E_{1b}}$) was selected as the one which

(8) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, p. 449.

gave the highest value to $\sum_r C_{jr}^2$ for the compound in question.

In Fig. 1, a plot is given of $\Delta E_{1/2(\text{ox})}$ vs. $\sum_r C_{jr}^2$. The least-squares line is drawn through only those points obtained in this laboratory (open circles), although some of the data of Pysh and Yang are included in the figure (filled circles). The least-squares line is

$$\Delta E_{1/2(\text{ox})} = 0.798 \sum_r C_{jr}^2 + 0.045 \text{ v.} \quad (8)$$

Theoretically, the line should pass through the origin; however, the intercept value of 0.045 v. is well within the range of scatter of points in Fig. 1, and we are inclined to accept the least-squares value rather than to force the data to fit theoretical predictions.

Table II shows the result of subtracting the oxidation potential of *m*-xylene from that of other methyl-substituted benzenes (column II) and in column IV of

TABLE II
EFFECT OF *para* SUBSTITUTION ON $E_{1/2(\text{ox})}$ FOR
METHYLBENZENES

No.	Compound	I $E_{1/2(\text{ox})}$, v.	III No. CH ₃ groups	
			II 1.58 v. - I CH ₃ group	IV II/III
1	<i>m</i> -Xylene	1.58 1.61 ^a	0.00	0
2	<i>o</i> -Xylene	1.57	.01	0
3	<i>p</i> -Xylene	1.56 1.47 ^a	.02 .14	0 1
4	1,3,5-Trimethylbenzene	1.55	.03	0
5	1,2,3-Trimethylbenzene	1.58	.00	0
6	1,2,4-Trimethylbenzene	1.41	.17	1
7	1,2,3,5-Tetramethylbenzene	1.43	.15	1
8	1,2,4,5-Tetramethylbenzene	1.29	.29	2
9	Pentamethylbenzene	1.28	.30	2
10	Hexamethylbenzene	1.16	.42	3
Average 6-10 = 0.15			6-10 = 0.15	

^a Ref. 6.

dividing column II by the number of methyl groups substituted *para* to another methyl group. The average value of this calculation for compounds numbered 6 through 10 is 0.15 v.

Discussion

The least-squares line of Fig. 1 is quite reasonable, considering the crude model of the effect of the methyl group used, but it does not exhibit the improvement over plots against ionization potential that is expected from a consideration of the accuracy of the $E_{1/2(\text{ox})}$ values; *i.e.*, ± 0.02 v. In this regard, it should be noted that the oxidation potentials for 1-methylnaphthalene and 2-methylnaphthalene vary in the same direction as their ionization potentials (7.46, 7.95, e.v.) but in an opposite sense to the square of the Hückel coefficients. The same effect is noted with 2,3-dimethyl-1,3-butadiene and 2-methyl-1,3-butadiene where the ionization potentials are 8.72 and 8.87 e.v., respectively. We suggest that these deviations can no longer be ascribed to error in the value of ionization potential¹ and that the reasons must be sought in the model used for the effect of the methyl group or in the values of the Hückel coefficients.

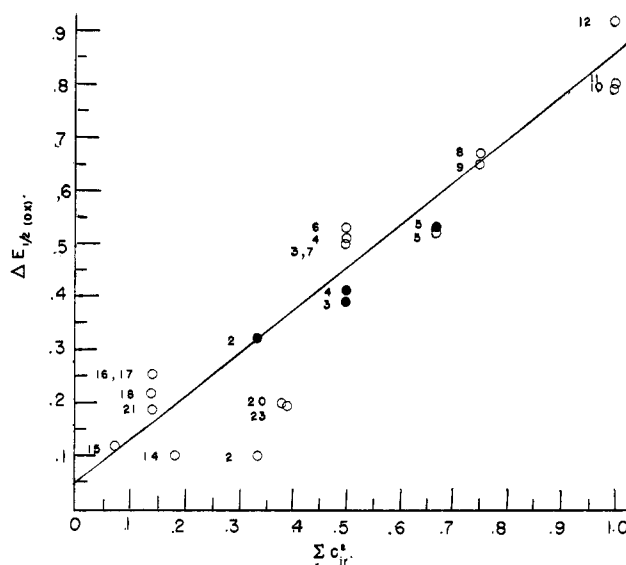


Fig. 1.—Plot of change in polarographic half-wave oxidation potential between methyl derivatives and the parent hydrocarbon ($\Delta E_{1/2(\text{ox})}$) against the sum of the squares of the Hückel coefficients at the position of methyl substitution in the highest occupied molecular orbital ($\sum_r C_{jr}^2$): Pysh and Yang, ●; our data, O. The least-squares curve is drawn through our data only. Numbers refer to compounds listed in Table I.

The empirical relations shown in Table II suggest that substitution in xylene *ortho* or *meta* to a methyl group has little effect on $E_{1/2(\text{ox})}$. However, substitution *para* decreases $E_{1/2(\text{ox})}$ by 0.15 v. per methyl group placed *para* according to eq. 9 where n is the

$$E_{1/2(\text{ox})} = 1.58 - n(0.15) \text{ v.} \quad (9)$$

number of methyl groups added *para* to other methyl groups. For example, in hexamethylbenzene, n is 3; therefore, $E_{1/2(\text{ox})}$ is predicted to be 1.13 v. as compared to 1.16 v. experimental.

The reality of this effect seems firmly established by reference to the data of Table II where the only exception is *p*-xylene. However, comparison of the data of Pysh and Yang for *m*-xylene and *p*-xylene gives a value for the decrement of $E_{1/2(\text{ox})}$ more in accord with our findings for other substituted benzenes, *viz.* 0.14 v., and it may be that our value of $E_{1/2(\text{ox})}$ for *p*-xylene is in error. We have no explanation for the constant decrement of $E_{1/2(\text{ox})}$ value for increasing *para* substitution by methyl groups at this time, and offer it now as an empirical regularity.

In order to calculate $h\beta_0$ from the slope in Fig. 1, we must correct $\Delta E_{1/2(\text{ox})}$ for the effect on the ionization potential attributed to the fact that the ionization is occurring at the electrode solution interface; *i.e.*, the gas-phase ionization potential is apparently lowered by adsorption and solution effects.¹⁰ This correction is accomplished by dividing the slope of eq. 8 by the slope of eq. 4 and yields a value of 0.96.⁹ If β_0 is taken as -2.1 e.v.,^{10,11} the value of h is -0.46 , which compares favorably with the value -0.54 found by plotting ionization potential directly against $\sum_r C_{jr}^2$.¹

(9) This introduces the large uncertainties found in values of ionization potentials into our scheme and it is used only to obtain a comparison of values of h .

(10) A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959).

(11) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

Conclusions

The HMO theory applied to the effect of methyl substitution on polarographic oxidation potential accounts reasonably well for the observed decrease in oxidation potential with increased methyl substitution.

However, it fails in explaining the finer details, namely, the apparent lack of inductive effect when methyl groups are substituted *ortho* or *meta* in xylene and the constant 0.15-v. change in oxidation potential per group substituted *para*.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

A Nuclear Magnetic Resonance Study of the Protolysis Kinetics of Glycine¹

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The exchange of protons between the amino group of glycine and aqueous solvent has been investigated by means of its effect upon the proton high resolution n.m.r. spectrum of the methylene group. The mean lifetime, τ , between exchanges of protons in the NH_3^+ group was measured at room temperature as a function of glycine concentration and of hydrogen ion concentration. Similar studies were made of the glycine methyl ester. Several mechanisms contributing to the exchange proved to be separable by means of the changes in τ with pH and glycine or ester concentration, and rate constants were obtained for the reactions. A brief comparison of these results with those obtained for other amino acids and for simple amines indicates that the proton-exchange mechanism for positively charged amino groups in strongly acidic solutions are the same for the several types of such systems studied so far.

Introduction

This paper deals primarily with the exchange of protons between the amino group of glycine and the aqueous solvent, as measured by nuclear magnetic resonance techniques. For glycine, it proved possible to measure the exchange rates over an extended range of concentrations. Thereby, we have obtained a better picture of the exchange reactions than was possible in the case of the closely related amino acid sarcosine.³ The general approach and results of the present work, including the interpretation, follow those for sarcosine and provide confirmation of the previously proposed exchange mechanism. The study of glycine covers the exchange of amino protons of the hydrochloride at pH < 1.8 and of the zwitterion at pH > 2.7, as well as the exchange at intermediate pH where both of these ionic species are present at an appreciable concentration in the solution. A similar study was made in strongly acidic solutions, with pH < 2.2, for the methyl ester of glycine hydrochloride, and comparison of the two sets of results is useful in their analysis.

Experimental Details and Data Reduction

The high-resolution proton magnetic resonance spectra used in the rate studies were obtained with a Varian Associates HR-60 spectrometer operating at 60 Mc./sec. The temperature of the probe and sample was $23 \pm 1^\circ$. The pH measurements were made at the same temperature with either a Beckman or a Radiometer pH meter, both with an expanded scale. The glycine and the glycine ester used in preparing the aqueous solutions were obtained commercially from Nutritional Biochemical Corporation. HCl was added to the solutions as needed to adjust the pH to the desired values.

In principle, the rate of proton exchange between the solvent H_2O and the NH_3^+ group in, e.g., $\text{NH}_3^+\text{CH}_2\text{COO}^-$ could be determined most directly from the effects of the exchange upon the proton absorption of the NH_3^+ group itself. However, the amino proton absorption could not be detected with the usual operating conditions of the spectrometer, most probably because of a large line width due to the large N^{14} and H^1 splitting and its partial

averaging by the proton-exchange reactions and by the short N^{14} T_1 , the short T_1 being a result of the N^{14} nuclear quadrupole interactions.⁴ Nevertheless, the proton exchange produces major resolvable changes in the CH_2 group proton resonance, as shown in Fig. 1.

In the most acidic solutions, the amino group exists as other than NH_3^+ to a negligible extent, the proton exchange is slow, and the spectrum of the methylene group consists of a quartet because of the splittings produced by the three protons of the NH_3^+ group (Fig. 1A). In *less acidic* solutions, the exchange rate increases and the methylene quartet broadens and collapses into a single line which narrows further with increasing exchange rate (Fig. 1B). It should be noted that at these low pH values the exchange is *inhibited* by the acid.

The mean lifetime, τ , between events which exchange a proton from the NH_3^+ group was calculated from the observed line shape of the methylene group, using theoretical curves based upon the "classical" treatment of chemical and spin-exchange effects in high-resolution n.m.r. spectra.⁵⁻⁷ The "classical" treatment was devised and applied initially⁸ to cases such that $\tau^2\delta^2 \gg 1$, where δ is the frequency difference in radians/sec. between two sets of electron-coupled nuclei, one of which is undergoing exchange. However, in our glycine studies δ is a relatively small frequency difference, namely the chemical shift of ~ 200 c.p.s. (at 60 Mc./sec.) between the NH_3^+ and CH_2 group protons.⁸ The coupling constant J between these two groups of protons is ~ 6 c.p.s. The coalescence of the CH_2 quartet occurs as $J\tau$ becomes smaller than unity. So there is a range of τ 's which can be obtained from the exchange averaging of the quartet and which satisfy the condition $\tau^2\delta^2 \gg 1$. However, for shorter τ 's which do not meet this condition a quantum correction should be made.⁹ This correction, as calculated by Alexander,¹⁰ is $[1 + (1 + 9\tau^2\delta^2)^{-1}]$ for a quartet. Therefore, the short τ 's obtained "classically" were corrected by setting their numerical values equal to $\tau[1 + (1 + 9\tau^2\delta^2)^{-1}]$ and solving for τ , which is now the true value.

The proton-exchange processes also affect $\tau_{\text{H}_2\text{O}}$, the mean lifetime of protons in water molecules. Values for $\tau_{\text{H}_2\text{O}}$ were obtained from the observed exchange-broadening of the water line, by means of the relation shown in eq. 1.

(4) W. B. Moniz and H. S. Gutowsky, *ibid.*, **38**, 1153 (1963).

(5) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *ibid.*, **21**, 279 (1953).

(6) N. S. Gutowsky and A. Saika, *ibid.*, **21**, 1688 (1953).

(7) E. Grunwald, A. Loewenstein, and S. Meiboom, *ibid.*, **27**, 630 (1957).

(8) This value was measured by decoupling the N^{14} from the protons in a double resonance experiment.

(9) I. Solomon and N. Bloembergen, *J. Chem. Phys.*, **25**, 261 (1956); J. Kaplan, *ibid.*, **28**, 278 (1958).

(10) S. Alexander, *ibid.*, **37**, 924, 962 (1963); **38**, 1787 (1963); **40**, 2741 (1964), erratum.

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(2) On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel. Some preliminary experiments on this problem were performed at the Institute in association with Dr. S. Meiboom.

(3) M. Sheinblatt, *J. Chem. Phys.*, **36**, 3103 (1962); **39**, 2005 (1963).