

TABLE V  
COMPARISON OF OBSERVED AND CALCULATED PRODUCT DISTRIBUTION, MOLES PER 100 MOLES OF CETANE CRACKED

Carbon no.	Obsd. 372° av. 9 runs	Calcd. (372°) (uncorr. for alkylation and poly- meriza- tion)	Alkylation and poly- merization correction	Total (calcd.) corr.
1	0.7 ± 0.2	0	0	0
2	5.1 ± 0.9	0	0	0
3	96.6 ± 8.9	108.6	-22.3	86.3
4	163.1 ± 11.9	136.5	11.1	147.6
5	68.0 ± 6.6	74.8	3.5	78.3
6	18.5 ± 3.5	40.2	5.0	45.2
7	14.1 ± 2.0	7.6	1.6	9.2
8	6.1 ± 0.8	2.8	0.6	3.4
9	1.9 ± .5	0.7	.1	0.8
10	0.5 ± .2 <sup>a</sup>	.6	.1	.7
11	1.3 ± .4	.5	.2	.7
12	2.5 ± .7	.2	.1	.3
13		.6	.0	.6
Total	378.4 ± 36.6 (375.7 ± 10.7) <sup>b</sup>	373.1		373.1

<sup>a</sup> The amount of C<sub>10</sub> observed seems to be out of line with the other products. It is possible that some of its isomers have been hidden in other peaks and are thus not properly accounted for. <sup>b</sup> This sum is an average total over the 9 complete runs rather than the total of the figures in column II.

the bed was necessary and was made in accordance with our previous discussion (paper I) under the assumption that the maximum possible specific activity ratio of a secondary product to the propylene at the bed exit was 2. The observed specific activity ratios reported previously were used. The method by which the cor-

rection was made becomes apparent by examination of the discussion in the first paper of this series.

Propylene is by far the most important product to be considered for alkylation or polymerization since it is not only very reactive but is also present in far the highest concentration of all olefins. The neglect (for lack of tracer data) of other alkylation reactions is expected to give rise to some error in the results but they should still be accurate enough to indicate whether the calculation we have outlined above is a valid approach. The calculated and observed results for 372° are shown in Table V. Details of the calculations can be found in pages 175-194 of the thesis of Van Hook.<sup>1</sup>

The point in least agreement is that for carbon number six. Here the predicted value is more than a factor of two times the observed one. The discrepancy could be rationalized by the hypothesis that carbonium ion cracking is more rapid at this temperature than ion saturation by hydrogen abstraction. Thus since, by the  $\beta$  rule, the 3<sup>+</sup>-*n*-hexyl ion will not crack and would not by the hypothesis saturate as rapidly as the 2<sup>+</sup>-*n*-hexyl ion cracks, the equilibrium between the 2<sup>+</sup> and 3<sup>+</sup> ions would be disturbed and some 3<sup>+</sup>-*n*-hexyl would rearrange to 2<sup>+</sup>-*n*-hexyl which could in turn crack. Such behavior would be an important factor in the determination of the final amount of product only for carbon number six since higher homologs can crack from either position.

In summary, then, one can state that the introduction of temperature sensitive terms into the standard Greensfelder method of calculation of product distributions, and the use of experimental radioactive tracer results to correct for secondary reactions, enables one to obtain fairly good agreement between the observed and calculated distribution for cracking *n*-hexadecane at 372° over a silica-alumina catalyst.

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## Activation Energies for Reorientation Processes in Ferrocene and Some of its Derivatives: A Study of Proton Magnetic Resonance Spectra

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A systematic study of the proton magnetic resonance spectra of ferrocene and some of its typical derivatives has been made over a wide range of temperature (78-300°K.) using a Pound-Knight-Watkins type oscillator and a special cryostat. The line width ( $\delta H$ ) and the second moment ( $\Delta H$ )<sup>2</sup> data have been interpreted to elucidate the reorientation processes of the cyclopentadienyl rings and the influence of the substituents on such processes. Some derivatives with completely deuterated substituents were specially studied to eliminate any contribution to the absorption curves obtained for the protons. In general  $\delta H$  and ( $\Delta H$ )<sup>2</sup> have been shown to increase with increased substitution at corresponding temperatures; the broadening arising from interactions between the protons of the cyclopentadienyl rings and the nuclei of the substituents is also discussed. The plots of  $\delta H$  vs. temperature have been used to evaluate the correlation time  $\tau_c$  at certain temperatures. The magnitudes of the activation energy  $E_a$  for the reorientation processes have been calculated therefrom. These range from 2.3 kcal./mole for ferrocene to 5.0 kcal./mole for diperdeuterioacetylferrocene and are seen to increase with increasing substitution in one or both rings.

The first reference to the possibility of "rotation" of one cyclopentadienyl ring with respect to the other was reported by Woodward, *et al.*<sup>2</sup> These investigators had prepared the diacetyl and dicarboxylic acid derivatives of ferrocene and were considering from the struc-

tural point of view whether the barrier in the way of "rotation" of one ring with respect to the other is sufficient to permit the existence of heteroannular isomers. Richmond and Freiser<sup>3</sup> studied the dipole moments of mono- and diacetylferrocene as a means of obtaining experimental evidence for the free rotation of the cyclopentadienyl rings in ferrocene. The electron diffraction study of ferrocene by Seibold and Sutton<sup>4</sup> indicates that in the vapor state the cyclopentadienyl rings rotate freely about the common orthogonal axis. Molecular orbital treatments<sup>5,6</sup> of ferrocene suggest that no

(1) (a) The author wishes to thank the Research Corporation and the Monsanto Research Laboratory for supporting this work. He is also thankful to Dr. M. Rausch of this Laboratory and Professor R. B. Woodward of Harvard University for supplying some of the derivatives of ferrocene. Any inquiries and requests for reprints after Sept. 1, 1963, should be addressed to this author at Pennsylvania State University, University Park, Pa. (b) Predoctoral research fellowships were made available to this author by the Ethyl Corporation (1961-1962) and the National Science Foundation (Summer 1961). The author is thankful to them for these fellowships.

(2) R. B. Woodward, M. Rosenblum and M. C. Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952).

(3) H. H. Richmond and H. Freiser, *ibid.*, **77**, 2022 (1955).

(4) E. A. Seibold and L. E. Sutton, *J. Chem. Phys.*, **23**, 1967 (1955).

(5) (a) H. H. Jaffe, *ibid.*, **21**, 156 (1953); (b) W. Moffitt, *J. Am. Chem. Soc.*, **76**, 3386 (1954).

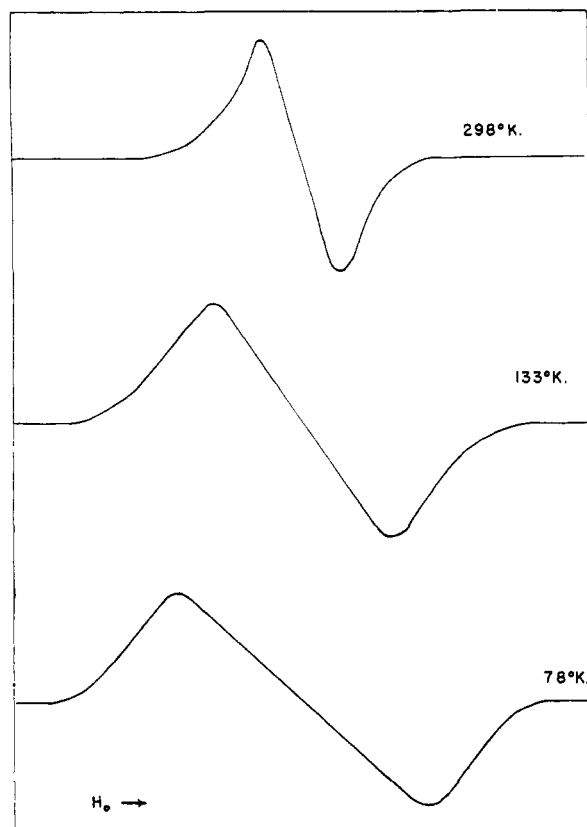


Fig. 1.—Representative proton magnetic resonance absorption curves for acetylferrocene, showing temperature dependence.

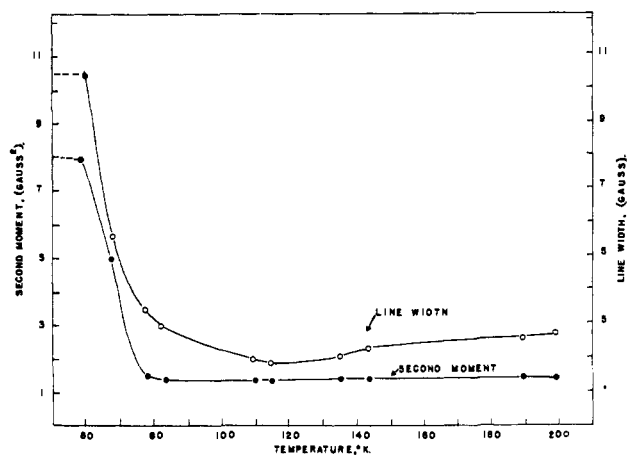


Fig. 2.—Line width and second moment as a function of temperature for ferrocene.

major barrier exists against free rotation of the cyclopentadienyl rings around the orthogonal axis. Preliminary proton magnetic resonance absorption studies of ferrocene by Mulay, *et al.*,<sup>7,8</sup> and by Holm and Ibers<sup>9</sup> also indicate reorientation of the cyclopentadienyl rings. The present study was undertaken to study the proton magnetic resonance spectra of ferrocene and some of its derivatives over a wide range of temperatures and to obtain the activation energies for the reorientation processes in these molecules.

(6) J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.*, **23**, 954 (1955).

(7) L. N. Mulay, E. G. Rochow and E. O. Fischer, *J. Inorg. Nucl. Chem.*, **4**, 231 (1957).

(8) L. N. Mulay, E. G. Rochow, E. O. Stejskal and N. E. Weliky, *ibid.*, **16**, 23 (1960).

(9) C. H. Holm and J. A. Ibers, *J. Chem. Phys.*, **26**, 1753 (1957); **30**, 885 (1959).

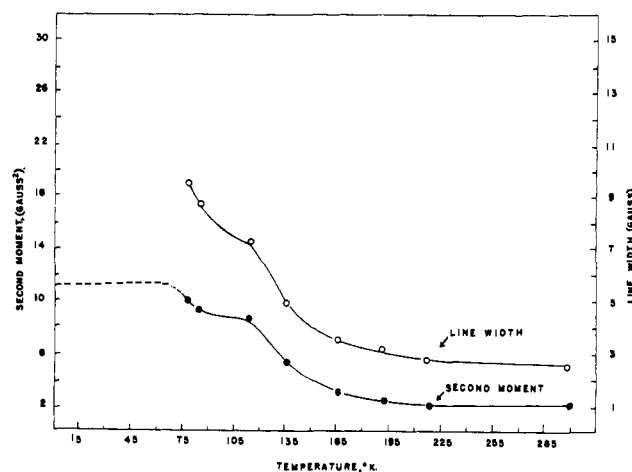


Fig. 3.—Line width and second moment as a function of temperature for acetylferrocene.

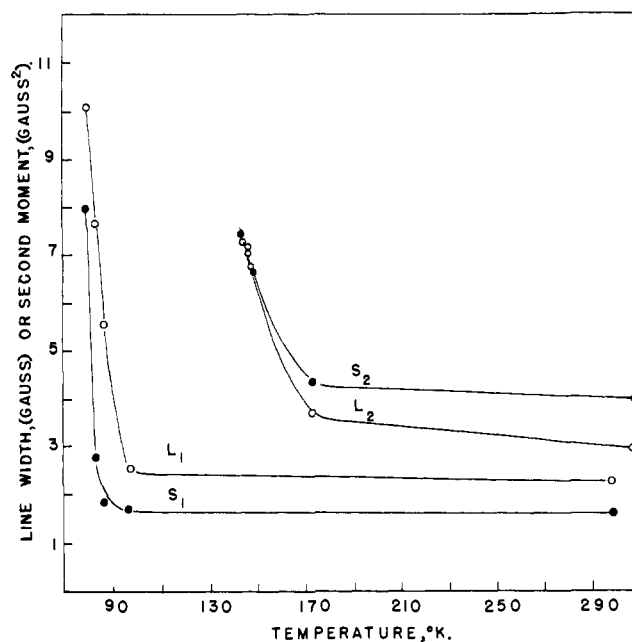


Fig. 4.—Line width ( $L$ ) and second moment ( $S$ ) as a function of temperature for monoperdeuterioacetylferrocene ( $L_1$ ,  $S_1$ ) and for diperdeuterioacetylferrocene ( $L_2$ ,  $S_2$ ).

### Experimental

The proton magnetic resonance absorption spectra were obtained at a frequency of 21 Mc.p.s. with a broad-line apparatus constructed in this Laboratory, similar to that of Pound, Knight and Watkins.<sup>10-12</sup> The level of oscillation and the field modulation amplitude were maintained small enough to avoid saturation of the absorption signal and to prevent distortion of the resonance line shape. All absorption spectra were obtained from powdered (polycrystalline) samples. It was found convenient to vary the field by passing a current through windings on the poles of a permanent magnet. Thus the microphonic noise arising from a variable condenser in the frequency variation method was eliminated. The line widths of the absorption spectra were measured in gauss from peak to peak of the recorded first derivative curves of line shapes.

The second moments of the absorption curves were obtained graphically by programming Simpson's rule in Fortran<sup>13</sup> for the IBM 1620 computer. At least three absorption spectra whose peaks were symmetrical on both sides of the first derivative line were used in calculating the line widths and second moments. Both halves of the curves were used in computing the second moments as a double check on the values. The average deviations of the results varied from 0 to  $\pm 0.2$  gauss for the line

(10) R. V. Pound and W. D. Knight, *Rev. Sci. Instr.*, **21**, 219 (1950).

(11) G. D. Watkins and R. V. Pound, *Phys. Rev.*, **82**, 343 (1951).

(12) G. D. Watkins, Ph.D. Thesis, Harvard Univ., May 29, 1952.

(13) IBM 1620 Data Processing System Bulletin, J26-4200-2, International Business Machines Corporation, White Plains, N. Y., 1961.

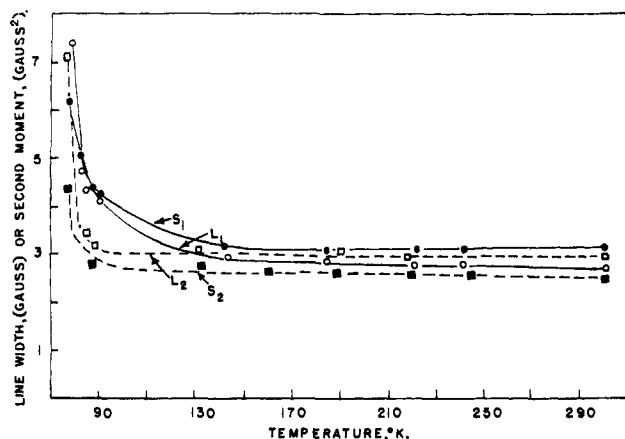


Fig. 5.—Line width and second moment as a function of temperature. Solid lines  $S_1$  and  $L_1$  represent, respectively, the second moment (closed circles) and line width (open circles) data for monocarboxyl ferrocene. Dotted lines  $S_2$  and  $L_2$  represent, respectively, the second moment (closed squares) and line width (open squares) data for diferrocenyl mercury.

widths and from  $\pm 0.1$  to  $\pm 0.8$  gauss<sup>2</sup> for the second moments. A cryostat of a special design<sup>14</sup> was constructed to obtain different temperatures.

To illustrate the temperature dependence of the line shapes, representative absorption curves are shown in Fig. 1 for acetylferrocene. The line widths and second moments of the recorded first derivative absorption curves for the various derivatives of ferrocene are plotted as a function of temperature in Fig. 2 to 5.

### Results and Discussion

**A. Ferrocene.**—The absorption lines for ferrocene throughout the temperature range studied (78–415°K.) were very similar to a liquid-like line shape, indicating the presence of rapid reorientation processes in the molecule. The anomalous narrowing of the absorption line in the region of 115°K. appears to have some bearing on the transition in the crystal structure. It is interesting to note that when crystals of ferrocene in a closed vial are cooled in liquid nitrogen the color changes from orange to lemon-yellow and the crystals explode with the formation of a finely divided yellow powder. The color is reversible and the ferrocene is unchanged chemically. These changes in ferrocene near liquid nitrogen temperature are reminiscent of the well-known second order phase transitions which occur in many crystals and which have previously been related to changes in the line-widths and second moments of their absorption lines.<sup>15</sup>

The anomalous narrowing of the absorption line for ferrocene might be attributed to the conversion of the staggered configuration of the cyclopentadienyl rings in ferrocene to the eclipsed configuration. The staggered configuration represents a state of low energy in which the interactions between protons on opposing rings are less than those in the eclipsed form where the interactions are comparatively larger. The interproton distances would be farther apart in the staggered form than in the eclipsed form. If it is assumed that all the molecules exist in the staggered form below the minimum in the line width *vs.* temperature curve (Fig. 2), then the increase in the line width above 115°K. can be ascribed to the formation of the eclipsed forms of the ferrocene molecule in which the interproton interactions would have increased to the extent where they contribute significantly to the line width.

The sharp drop in the line width (10.5 to 3.3 gauss) and second moment (8 to 1.7 gauss<sup>2</sup>) over the range 60–80°K. must indicate the commencement of some

(14) The details of this will be published separately. Cf. L. N. Mulay, *Rev. Sci. Instr.*, **28**, 279 (1957).

(15) E. R. Andrew, *J. Chem. Phys.*, **18**, 607 (1950).

considerable motion in the lattice. The reduction can be accounted for by any one of the possible motions about the fivefold axis such as rotation, quantum mechanical tunneling through the potential barrier, and rotational oscillations, although at these low temperatures it is expected that the motion would be restricted to rapid oscillations of fairly large amplitudes. Reorientation of the cyclopentadienyl rings about their fivefold axes at frequencies greater than that corresponding to the rigid-lattice width would reduce the intramolecular contribution (2.4 gauss<sup>2</sup>) to the second moment by three-fourths<sup>16</sup> and the intermolecular contribution (5.6 gauss<sup>2</sup>) by four-fifths<sup>17</sup> of the rigid-lattice value. A second moment of about 1.7 gauss<sup>2</sup> is therefore expected. This agrees well with the observed value of about 1.5 gauss<sup>2</sup>. Clearly these results are consistent with reorientation processes in ferrocene.

Anomalous narrowing of the absorption line was first observed and reported by Mulay, *et al.*<sup>7</sup> Holm and Ibers<sup>9</sup> first refuted this observation in 1957 and then reconfirmed it later in 1959. It is noteworthy that in subsequent work the commencement of the  $\lambda$ -transition observed by Edwards, Kington and Mason<sup>18</sup> in the heat capacity curve of ferrocene coincides with anomalous narrowing of the line width for ferrocene. The  $\lambda$ -transition occurs over the range 125–200°K. and the anomalous narrowing over the range 115–225°K.

**B. Acetylferrocene.**—The introduction of an acetyl group into the ferrocene molecule has a pronounced effect on the line shape which is particularly noticeable over the temperature range studied (78–298°K.). Several of the spectra are shown in Fig. 1 as a function of temperature. The line width and second moment remain fairly constant from room temperature to 210°K. Then they show a gradual increase between 210 and 78°K. Beyond this point they show a steep rise and reach an estimated maximum value at 50°K. The rigid lattice value of the second moment for acetylferrocene was estimated by combining the calculated rigid-lattice values for the methyl group and the ferrocene molecule. Gutowsky and Pake<sup>18</sup> have calculated the rigid-lattice value for a triangular group (CH<sub>3</sub>) of protons to be 21.2 gauss<sup>2</sup>. A weighted average of the two sets of protons in the molecule  $[3/(3+9)] \times 21.2 + (9/12) \times 8$  gives 11.3 gauss<sup>2</sup>. Any decrease in the second moment caused by the removal of a proton in the formation of acetylferrocene is overcome by the interactions between the protons of the acetyl group and those of the cyclopentadienyl rings.

The rather steep descent (Fig. 3) of the line width and second moment for acetylferrocene between 50 and 210°K. can be ascribed to reorientation of the methyl group about its triad axis and of the cyclopentadienyl rings about their fivefold axes of symmetry. Since the methyl group has the smallest moment of inertia in comparison to the substituted and the unsubstituted cyclopentadienyl rings, it is expected that the methyl group will begin to reorient first, then the unsubstituted ring and lastly the substituted ring. Reorientation of the methyl group<sup>16</sup> is expected to reduce its contribution to the second moment (5.3 gauss<sup>2</sup>) by three-fourths of its rigid-lattice value. This gives a value of 7.3 gauss<sup>2</sup>, which is seen to correspond to 128°K. It may be pointed out that the decrease in the second moment from 75° to 110°K. is compatible with the

(16) H. S. Gutowsky and G. E. Pake, *ibid.*, **18**, 162 (1950).

(17) E. R. Andrew and R. G. Eades, *Proc. Roy. Soc. (London)*, **A216**, 398 (1953).

(18) J. W. Edwards, G. L. Kington and R. Mason, *Trans. Faraday Soc.*, **56**, 660 (1960).

—CH<sub>3</sub> group rotation, while both rings of ferrocene are fixed. The reorientation of the unsubstituted ring is expected to reduce its contribution to the second moment by one-half, which corresponds to a value of 3.3 gauss<sup>2</sup> at 190°K. Hence, it is reasonable to expect that the unsubstituted ring commences to reorient between 128 and 190°K. The narrowing observed beyond this temperature (190°K.) may be attributed to the reorientation of the substituted ring.

**C. Monoperdeuterioacetylferrocene and 1,1'-Di-perdeuterioacetylferrocene.**—In order to study the effect of a substituent group on the line shape without the accompanying absorption of the protons, the acetyl hydrogen atoms were replaced by deuterium atoms. The deuterated derivatives were prepared by using perdeuterioacetyl chloride in place of acetyl chloride. The line widths and second moments of both deuterated acetyl derivatives remained fairly constant from room temperature to 90°K. for the mono-derivative and to 160°K. for the 1,1'-derivative (Fig. 4). Only slight differences were noted in the line shapes for all four acetyl derivatives of ferrocene. The rapid rise in the line widths and second moments of the deuterated derivatives is due to the swift decrease in the reorientation rate of the cyclopentadienyl rings whose motion is now expected to be restricted by the added mass of the deuterium atoms, more so than in the case of acetylferrocene. The data indicate that considerably more reorientation is occurring in the monosubstituted derivatives than in the disubstituted one, even at room temperature.

A comparison of line widths and second moments from Fig. 4 with those in Fig. 3 would seem to suggest that the reorientation of rings starts before the reorientation of the corresponding methyl groups, that is at much lower temperatures.

The rigid lattice values of the line widths and second moments of the deuterated acetyl derivatives are expected to be less than those for the protonated derivatives, since the proton-deuteron interactions are negligible compared with proton-proton interactions, due to the smaller magnetic moment of the deuteron. Therefore, the rigid-lattice value for the second moment of the deuterated acetyl derivative should be virtually the same as that for the unsubstituted parent ferrocene, namely 8 gauss<sup>2</sup>, as observed.

**D. Monocarboxylferrocene.**—The second moments for ferrocenemonocarboxylic acid are greater than those for ferrocene alone at corresponding temperatures. This increased broadening can be attributed mostly to the decreased motional narrowing of the absorption line due to the hindrance of the reorientation processes by the carboxyl groups, especially since there is the possibility of hydrogen bonding between the hydroxyl hydrogen atom of one molecule and the carboxyl oxygen of a neighboring molecule. The rigid-lattice values of the line width and second moment for the monocarboxyl derivative of ferrocene are expected to be approximately the same as those for ferrocene since the total absorption in both compounds is due to the same number of relatively isolated protons.

The narrowing of the absorption spectra above 70°K. (Fig. 5) is ascribed to the reorientation of the cyclopentadienyl rings about their five-fold axis of symmetry. Although reorientation of the hydroxyl group (OH) about the C—OH bond of the carboxyl group is not excluded, it alone cannot account for the large decrease in the line width and second moment between 70°K. and 90°K. In fact, reorientation of the isolated proton in the carboxyl group would affect the line shape very slightly.

**E. Diferrocenylmercury.**—The line widths and second moments of diferrocenylmercury remain essentially constant down to 78°K. where they increase rapidly with decreasing temperature and are expected to reach the rigid-lattice values of ferrocene. The values of the second moments for diferrocenylmercury are larger between 298 and 78°K. than the corresponding ones in ferrocene. The line widths for the two compounds over the same temperature range do not differ widely. The preceding two observations may be accounted for from the facts that there is additional broadening due to the mercury-proton interactions which increase the second moment and that the absorption in both derivatives is due to the protons in the cyclopentadienyl rings alone. The larger magnitude of the second moment in diferrocenylmercury also indicates restricted motion about the fivefold symmetry axis of the cyclopentadienyl rings linked by the mercury atom. This is to be expected since the amplitude of reorientation will be highly limited by the bonding between the mercury atom and the carbon atoms in the two rings.

**F. Activation Energies for the Reorientation Processes in Ferrocene and Some of its Derivatives.**—The barrier hindering reorientation can be estimated if it is assumed that the reorientation is an activated process given by

$$\tau_c = \tau_0 \exp(E/RT) \quad (1)$$

where  $\tau_c$  is the correlation time for the reorientation process,  $\tau_0$  is a constant and  $E$  is the activation energy. This is based on the theory of rate processes.<sup>19</sup> Values of  $\tau_c$  can be obtained from the relation between the correlation time and the line width given by Gutowsky and Pake<sup>16</sup>

$$\tau_c = [\alpha\gamma(\Delta H)]^{-1} \tan [(\pi/2)(\Delta H^2 - V^2)(U^2 - V^2)^{-1}] \quad (2)$$

where  $\alpha$  is an arbitrary shape parameter which has the value unity for a gaussian line shape,  $\gamma$  is the nuclear magnetogyric ratio,  $\Delta H$  is the line width at which  $\tau_c$  is to be determined,  $U$  is the line width for the rigid-lattice and  $V$  is the line width after completion of the motional narrowing. Thus a knowledge of  $U$  and  $V$  permits the calculation of  $\tau_c$  directly from the line width data in the region of the motional narrowing under the assumption of  $\alpha = 1$ .

The constant  $\tau_0$  is found by fitting the calculated values of  $\tau_c$  to Eq. 1. A typical calculation of the correlation time and activation energy is illustrated here for the line width observed at 68°K. in ferrocene. The magnetogyric ratio for the proton has a value of  $2.68 \times 10^4$  radians per sec. per gauss. Substitution of the values for the line width at 68°K. (5.5 gauss), the rigid-lattice line width (10.5 gauss), the line width at the end of the motional narrowing (3.3 gauss) and the magnetogyric ratio into eq. 2 gives for  $\tau_c$  a value  $2.7 \times 10^{-6}$  sec. at 68°K. In order to determine the value of  $\tau_0$ , several other values of  $\tau_c$  are calculated at various temperatures within the line-width transition region over which the motional narrowing occurs. The line-width values were found by extrapolating the curve for line-width vs. temperature to the rigid-lattice value and interpolating the line widths at selected temperatures. These values are substituted into eq. 1 to give a series of equations which can be solved simultaneously to obtain constant  $\tau_0$ . The value is found to be  $1.2 \times 10^{-13}$  sec. for ferrocene. Substitution of the calculated values for  $\tau_0$  and  $\tau_c$  into eq. 1 gives a value of 2.3 kcal. per mole for the activation energy of the reorientation processes which cause the narrowing of the line shape. This process is probably the reorientation of the cyclopentadienyl rings about their fivefold axis of symmetry since

(19) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 548.

TABLE I

CORRELATION TIMES AND ACTIVATION ENERGIES FOR REORIENTATION PROCESSES IN FERROCENE AND SOME OF ITS DERIVATIVES

Compound	Correlation time		Activation energy, kcal./mole
	$\tau_c$ , sec.	$\tau_0$ , sec.	
I Ferrocene	68°K., $2.7 \times 10^{-6}$	$1.2 \times 10^{-13}$	2.3
	78°K., $1.0 \times 10^{-6}$		
II Diferrocenylmercury	75°K., $4.4 \times 10^{-6}$	$4.8 \times 10^{-16}$	3.1
	80°K., $1.2 \times 10^{-6}$		
III Monocarboxylferrocene	75°K., $6.5 \times 10^{-6}$	$4.1 \times 10^{-17}$	3.9
	80°K., $1.3 \times 10^{-6}$		
IV Monoperdeuterioacetylferrocene	78°K., $1.9 \times 10^{-6}$	$1.6 \times 10^{-17}$	4.1
	82°K., $1.3 \times 10^{-6}$		
V Acetylferrocene	(63°K., $4.3 \times 10^{-6}$ )	$9.6 \times 10^{-19}$	3.7) <sup>a</sup>
	69°K., $3.4 \times 10^{-7}$		
VI Diperdeuterioacetylferrocene	132°K., $1.3 \times 10^{-6}$	$6.0 \times 10^{-16}$	5.0
	135°K., $1.1 \times 10^{-6}$		

<sup>a</sup> This represents the component for the reorientation processes in the CH<sub>3</sub> group alone.

this type of motion would require the least amount of energy. This situation may be compared to the pure rotational spectra in the infrared which are observed at very long wave lengths in ferrocene.<sup>20</sup> The correlation

times  $\tau_c$  at various temperatures, the constants  $\tau_0$  and the activation energies for the motional processes which narrow the line shape are given in Table I for the cases which permitted such calculations.

The correlation times given in Table I are seen to decrease with increasing temperature. This is to be expected if the reorientation is an activated process; that is, the reorientation rate increases as thermal energy is absorbed from the surroundings by the reorienting group. The activation energy for reorientation of the unsubstituted cyclopentadienyl ring (Cp) has its smallest value in the ferrocene molecule where steric and potential hindrances to the reorientation processes are most likely to be at a minimum in comparison to the substituted rings. In diferrocenylmercury where two ferrocene molecules are linked by a mercury atom the activation energy for the unsubstituted Cp ring is larger than that in ferrocene, indicating the restriction of the reorientation process by the steric and potential barriers imposed by the mercury atom. It is seen from Table I that the activation energy increases systematically in going from compounds I to IV, that is, from ferrocene to diperdeuterioacetylferrocene.

(20) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958).

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## The Enthalpy of Interaction of 9-Methyladenine and 1-Methylthymine in Water<sup>1,2</sup>

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The solubility of 9-methyladenine and 1-methylthymine has been determined in pure water and in water solutions of the second compound over a temperature range of 20–40°. An enhancement of solubility is noted when mixed solutions are used. The enhancement is interpreted as a direct consequence of the interaction of these compounds in water. Simple theoretical considerations enable one to estimate the enthalpy of interaction from the solubility measurements. A value of  $-7.3 \pm 0.2$  kcal./mole for complex formation is found. This value suggests that purine-pyrimidine interactions in nucleic acids are somewhat stronger than previous rough guesses of  $-5 \pm 2$  kcal./mole of complex.

### Introduction

The helical ladder structure of naturally occurring deoxyribonucleic acid is a consequence of purine and pyrimidine base pairing.<sup>3</sup> The stability of this configuration is dependent primarily upon the energy of interaction between the base pairs. Little experimental data exist for the energy of interaction of nucleic acid base pairs. The aqueous solvent system virtually eliminates the determination of low concentrations of a hydrogen bond complex by spectroscopic techniques. Calorimetric measurements have been made by Sturdevant, Rice and Geiduschek on the acid denaturation of DNA,<sup>4</sup> but these total heat effects must be interpreted in the light of ionization, base pair interactions and electrostatic charge interactions.<sup>5</sup> In order to delineate the magnitude of these effects, accurate information is first needed on the heats of interaction of the base pairs. The estimate used by Rice, Wada and Geiduschek for an average enthalpy of formation (per base pair) of  $5000 \pm 2000^6$  calories points out the desirability for more refined experimental determinations.

(1) This work was supported by the Division of General Medical Sciences, Public Health Service.

(2) Part of a thesis submitted by D. B. Martin in partial fulfillment of a Master of Science Degree, University of Colorado, 1962.

(3) J. D. Watson and F. H. C. Crick, *Nature*, **171**, 737, 964 (1953).

(4) J. M. Sturdevant, S. A. Rice and E. P. Geiduschek, *Discussions Faraday Soc.*, **25**, 138 (1958).

(5) S. A. Rice, A. Wada and E. P. Geiduschek, *ibid.*, **25**, 130 (1958).

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We have studied the model system base pair of 9-methyladenine (9-MA) and 1-methylthymine (1-MT). In these compounds the methyl group takes the place of the ordinary deoxyribose attachment. The relatively low solubility in water of these derivatives almost precludes a direct calorimetric and activity coefficient study. However, the solubility of these compounds in water and in solutions of each other does provide a route for the measurement of heats of interaction in water. A related technique has been used in estimating enthalpy of interaction of urea with the peptide groups of diketopiperazine.<sup>7</sup> However, the low solubility of the purine and pyrimidine base compounds required a more sensitive measuring technique than had been previously employed.

**Theory.**—The heat of solution  $\bar{H}_2 - H_2^S$  is related to the equilibrium solubility of the compound in terms of the temperature derivative of the solubility  $S_2$ , expressed for experimental convenience in terms of weight per cent, and a concentration derivative of the activity coefficient  $\gamma$  at the given temperature of saturation. Williamson<sup>8</sup> gives various forms of this relation. For our purposes we shall write

$$\bar{H}_2 - H_2^S = -R \left( \frac{\partial \ln S_2}{\partial (1/T)} \right)_{\text{sat}} \left[ 1 + \left( \frac{\partial \ln \gamma}{\partial \ln w_2} \right)_T \right] \quad (1)$$

where  $w_2$  represents the weight per cent concentration

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