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CORRELATION OF KINETIC STUDIES BY NMR AND OTHER METHODS

RATES OF INVERSION OF DOUBLY-BRIDGED BIPHENYLS BY NMR

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Abstract—The rates and the activation parameters have been determined for the inversion of the doubly-bridged biphenyls I and II from change of the line shapes of the NMR spectra at various temperatures in the range from 60° to 200° for I and down to −100° for II. The activation parameters obtained for I both in C_4Cl_6 and DMSO-d_6 are in good agreement with those previously obtained for the racemization of the optically active I by polarimetric measurement. The upper limit of the estimated activation energy for II is compatible with that obtained by the study of the temperature dependence of ESR spectra for the anion radical derived from II.

FROM the exchange averaging of the NMR signals, the rate constant of rate processes can be obtained by applying to the line shape the equations derived from the modified Bloch equation containing a term for the exchange and solved under the condition of the stationary state.[1] One of the most important features of this NMR technique is its utility in studying the rate processes with the rate constant k_1 of the order of $1\text{–}10^4$ sec^{-1},* and the determination of activation parameters of conformational isomerization, valence tautomerization, etc by variable temperature NMR study has now become almost routine.[4] It is to be noticed, however, that the spread in the reported values of $\Delta H\ddagger$, $\Delta S\ddagger$ or $\Delta F\ddagger$ for a given molecule exceeds very often the limit of the experimental error given by individual authors, and some doubts have been thrown on the theoretical interpretation of the so-called Arrhenius parameters obtained by NMR method.[5,6]

We have now succeeded, by comparing the data from the independent methods of the common example of biphenyl inversion in I and II, in demonstrating that the NMR method is dealing with the same physical processes with those observed by the polarimetric and by ESR methods, although correlation is only qualitative in the latter example. These molecules are non-planar and the dihedral angle between the two benzene rings may be regarded 45° and 15°, respectively, in the equilibrium

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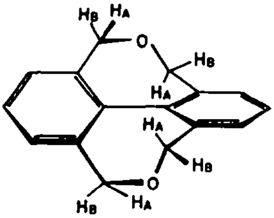
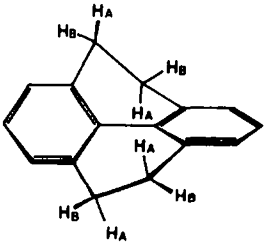
* Classical methods of the kinetic measurements such as weighing or titrating the products or reactants at several times after the start of the reaction are generally applicable only to the reaction with k_1 less than 10^{-1} sec^{-1}. Polarimetric and photometric methods are also included in this category. Such special devices as flow method and flash photolysis have made possible the measurement of faster reactions with k_1 in the ranges $10^{-1}\text{–}10^3$ and ca. 10^6 sec^{-1}, respectively. From this point of view, the NMR method can be said to follow relatively fast reactions. The line separations of NMR spectroscopy are, on the other hand, smaller than those of other spectroscopic methods, hence the latters can follow even faster reactions. For example, the line broadening of the IR bands can provide information on the rate processes with k_1 of the order of 10^{11}.[2] From the line broadening and the coalescence of the hyperfine splitting in the ESR spectra can be obtained information of k_1 of the order $10^4\text{–}10^9$ sec^{-1}.[3]

position.[7,*] The rates and activation parameters of inversion of the optically active I[7] and the anion radical made from II† have already been presented and it is expected from the estimated chemical shifts that NMR spectra of I and II will show transient line shapes due to exchange between H_A and H_B in their magnetic environment at ca. 150° and −90°, respectively. In the present work, NMR spectra of I and II have been examined in the temperature range of 60 to 180°, and 30 to −100°, respectively, and the results used to calculate the activation parameters.



I



II

(I) NMR spectra of I at room temperature in various solvents have already been reported.[7] Methylene parts consist of a typical AB-quartet; at 80° in hexachloro-1,3-butadiene, the quartet centering at 4·30 ppm from the internal TMS has $\delta_{AB} = 19{\cdot}6$ and $J_{AB} = 11{\cdot}3$ c/s. These observations confirm that at these temperatures the biphenyl skeleton in I is fixed non-planar and, due to the relatively long half-life of the inversion,[7] a pair of protons on each methylene group are mutually diastereomeric, thus permitting observation of the separate chemical shifts. As the temperature is raised, the line-width of the AB-signals broadens at first with the outer two lines broadening more rapidly than the two inner lines, the formers soon disappear while the latters gradually coalesce into a broad singlet. Then the remaining single line decreases continuously in width with rising temperature. Some representative experimental curves are shown in Fig. 1.

The exchange broadening of the two interacting nuclear spin resonance signals has been written down by Alexander,‡ and under slow-exchange limit at low temperature the observed change in line-width is correlated to the half-life by Eq. (1);

$$\tau = \frac{1 \pm J_{AB}/\sqrt{(\delta_{AB}^2 + J_{AB}^2)}}{\pi(w - w_0)} \qquad (1)$$

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[*] The racemization rates of (−)-I are 2·12 and 10·7 (10^4 sec^{-1}) at 10·1 and 23·3°, respectively, and obey the equation, $k = 10^{12\cdot1} \exp(-20{\cdot}4/RT)$.

[†] M. Iwaizumi and T. Isobe, *Bull. Chem. Soc. Japan* **38**, 1547 (1965) observed, in the ESR spectra of the anion radical of II formed in 1,2-dimethoxyethane by action of sodium, two kinds of proton hyperfine coupling constants of the ethylene groups at −81°; $a_{H_A} = 3{\cdot}81$ and $a_{H_B} = 0{\cdot}79$ gauss, while at 23° they are averaged to the apparently equivalent protons. From the observation they estimated that the rate of inversion in II-anion radical is much slower than 10^6 sec^{-1} at −81°, and that E necessary for inversion is ca. 4 to 5 kcal/mole.

[‡] S. Alexander, *J. Chem. Phys.* **37**, 967 (1962). Note that δ and J are in unit of radian/sec, and the relative chemical shifts between H_A and H_B are put to be 2δ. Note also that Alexander's τ is equal to twice the τ of Gutowsky *et al.*[8]

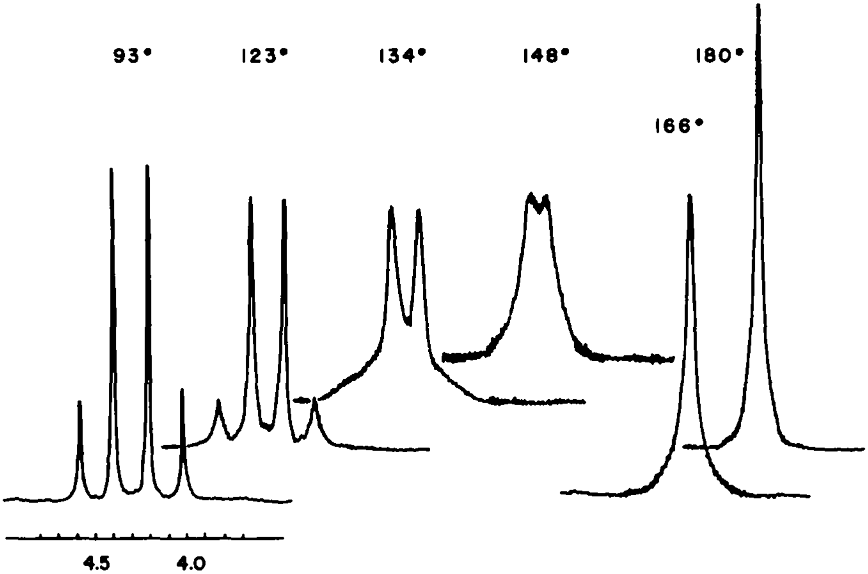

FIG. 1 NMR spectra of CH_2 protons of I in C_4Cl_6 at various temperatures.

where the plus and minus signs are used for the outer and the inner lines of the AB-quartet, respectively, and where w and w_0 are taken to represent line-width in the presence and in the absence of exchange, respectively. At the very point of coalescence of the AB-quartet signal, τ_C is given by Eq. (2), provided natural line-width in the absence of exchange is negligible.[9, 10] The half-line τ_C obtained at the coalescence

$$\tau_C = \frac{\sqrt{2}}{\pi\sqrt{(\delta_{AB}^2 + 6J_{AB}^2)}} \tag{2}$$

temperature may involve a few per cent of systematic error due to the approximation used to derive Eq. (2),[11] but is rather reliable since this is where the greatest spectral changes take place and so easily and precisely determined. Above the coalescence temperature, the width of the coalesced singlet relative to that at $\tau = 0$ can again be used to calculate τ from Eq. (3).*

$$\tau = \frac{2(w - w_0)}{\pi\delta_{AB}^2} \tag{3}$$

Eqs (1) to (3) were employed to calculate the exchange life-time listed in Tables 1 and 2. The reciprocals of these data are identical with the rate constants k_1 for the inversion.† Arrhenius plots of which are shown in Fig. 2. Activation parameters thus obtained are listed in Table 3, and are in quite a good agreement within the experimental error with those reported by Mislow *et al.*[7,‡] This is the first example

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* Derived from Eq. (1) in Ref. 10 under $T_2\,\delta_{AB}^2 \gg 1$ and $T_2^2\,\delta_{AB}^4 \gg J_{AB}^2$. T_2 was equated to $1/\pi w$.[12]

† It should be noted that rate of racemization is twice that of inversion and, therefore, log A (racemization) = log A (inversion) −0·303.

‡ See footnote on p. 2378 and Ref. 7.

TABLE 1. EXPERIMENTAL LINE-WIDTHS AND EXCHANGE LIFE-TIMES FOR I IN HEXACHLORO-1,3-BUTADIENE

Temp	*w* for inner lines[a]	*w* for outer lines[a]	*w* for coalesced line[b]	
93°	0·95	1·25		0·87
100°	1·15	2·00		0·39
104°	1·25	2·35		0·31
123°	2·45	4·75		0·10$_6$
129°	2·95	11·75		0·058
134°	4·25			0·046
140°	6·50			0·028
154°[c]			7·00	0·013$_3$
166°			4·15	0·0056
180°			3·50	0·0046
200°			2·25	0·0025

[a] Data treated by Eq. (1)
[b] Data treated by Eq. (3)
[c] The coalescence temp.

TABLE 2. EXPERIMENTAL LINE-WIDTHS AND EXCHANGE LIFE-TIMES FOR I IN DIMETHYL-d_6 SULFOXIDE

Temp	*w* for inner lines[a]	*w* for outer lines[a]	*w* for coalesced line[b]	
64°	0·75	0·75		
80°	0·85	1·20		1·27
91°	1·00	1·45		0·64
102°	1·10	1·70		0·45
111°	1·40	3·05		0·22
121°	2·00	6·0		0·10$_4$
133°	4·50			0·038
141°	6·8			0·024
147°[c]				0·013$_7$
160°			4·35	0·0062

[a] Data treated by Eq. (1)
[b] Data treated by Eq. (3)
[c] The coalescence temp.

TABLE 3. ARRHENIUS PARAMETERS FOR THE INVERSION OF I

Solvent	E (kcal/mole)	log A
C_4Cl_6	19·9 ± 0·5	12·0 ± 0·3
$Me_2SO\text{-}d_6$	21·1 ± 0·6	12·2 ± 0·4

of an activation energy for inversion of a biphenyl which has been determined independently by polarimetric and by NMR methods for the same compound.*

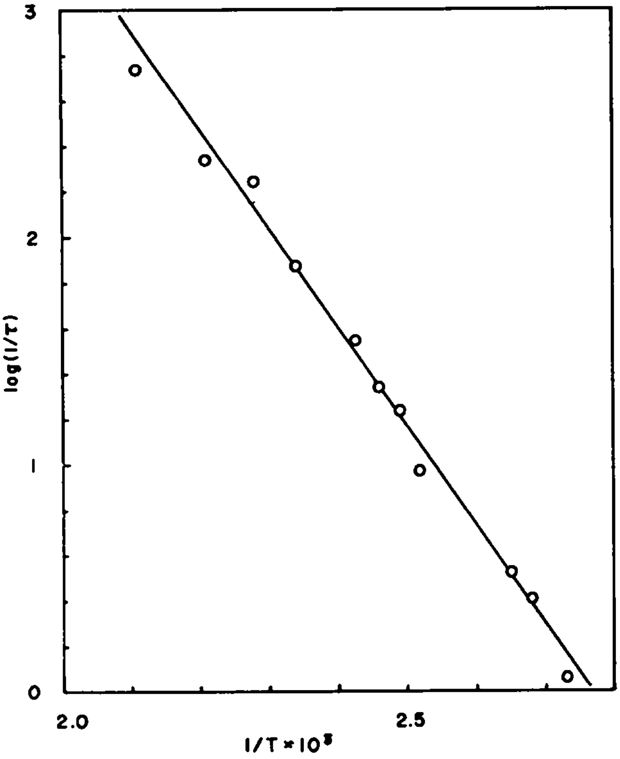

FIG. 2 Plots of log $(1/\tau)$ vs $1/T$ for the inversion of I.

As far as the solvents are concerned, the activation parameters are rather insensitive to the solvent. The solvents used in the present work were chosen in consideration of the solubility and the temperature range that may be used, and cover nearly both extremes with respect to the dielectric constant and the polarity which characterize the solvent property. It follows, therefore, that the above statement is rather general. The insensitivity is surely an indication that there is no strong

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* Lately the rates of racemization in 2,2′-dimethylbiphenyl (III) have been measured at around −30°.[13] From the activation parameters, k_{rac} at 100° is calculated to be about 150 sec^{-1}. W. L. Meyer and R. B. Meyer, *J. Am. Chem. Soc.* **85**, 2170 (1963) have measured the rate of inversion in 2,2′-bisacetoxymethylbiphenyl (IV) by NMR, and their data are used to calculate the rate of inversion at the coalescence temperature (94°) to be 69 sec^{-1}. If the steric strain in the transition state for inversion may be regarded similar in III and IV because in the most favourable path for inversion in the latter only the non-bonded interaction between α-methylene groups need to be considered effective, it is worthwhile to compare the activation parameters between III and IV. When the latter rate constant is doubled,† the agreement with the former value is satisfactory. The comparison may offer another example in which the rates from independent sources are directly compared.

† See footnote† p. 2379.

solvent-solute interaction in I. This is not unreasonable on considering the non-polarity of I. In conclusion the present study does not necessarily guarantee the general applicability of the NMR method of kinetics, but affords strong support for its validity as far as the solvent effects are small. The numerical discrepancy often encountered in the NMR method is probably due to the temperature dependence of δ_{AB} and T_2 (line-width not associated with the observing exchange process) which are usually assumed to be unaltered within the temperature range used by individual authors. These notorious temperature dependences are most likely the consequence of some kind of solvent effect.*

(II) If 4.5.9,10-tetrahydrodropyrene is fixed as shown in II, the ethylene part of the NMR spectrum should be composed of A_2B_2-multiplet in which δ_{AB} is expected to be ca. 10 c/s by analogy of 6 c/s found in 9.10-dihydro-4,5-dimethylphenanthrene.[10] Even at −90° under 100 Mc/s, the signal at 2·85 ppm from internal TMS in carbon disulfide is singlet, and there is no indication of the line-broadening. The lack of splitting suggests that the inversion of the biphenyl skeleton must be fairly rapid. The lower limit of the rate constant at this temperature is calculated to be 20 $\sec^{-1}$, and consequently the upper limit of the activation energy $E = 8$ kcal/mole on assuming normal frequency factor of 10^{12}.[15] The result is compatible with that given by Iwaizumi *et al.*,† but the present example is not adequate for further numerical discussion.‡

EXPERIMENTAL

Materials. The samples of I and II were prepared according to the literature and their physical constants agreed well with those in the literature.[6]

Spectral measurement. The NMR spectra of I were obtained on a JNM 3H-60 spectrometer (Japan Electron Optics Laboratory Co. Ltd) operating at 60 Mc/s, equipped with a two sample system NMR control and a variable temp probe accessory. The temp was read from the micro-voltage in the thermocouple mounted on the inside wall of the probe insert according to the calibration curve, and the reading accurate to ±2·0°. The spectra of II were recorded on a Varian HA-100 spectrometer operating at 100 Mc/s. Temps were measured by examining the Me and OH signal separation of a MeOH sample as prescribed in the manual catalogs. Approximately 10% W/V solns were employed containing enough TMS as well as

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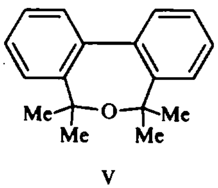
* Even the dipolar tetramethyloxepin (V) suffers from little solvent effect.[14] But the phenomenon may be attributed to the steric effect of the Me groups which make the solvation of the dipolar center less effective.



V

It may also be argued that, due to a wide temp range for studying the temp dependence of the NMR spectra, the assumption that the activation parameters are constant throughout the range is no longer valid. At the present, however, the extent of this factor is not clear.

† See footnote p. 2378.

‡ The activation energy of inversion for II has been calculated to be 7–8 kcal/mole as the sum of the eclipsing energy of the ethylene groups, torsional strain due to the opening of the internal angle and π-delocalization energy in the transition state.[7] The observed value 4–5 kcal/mole* is much lower than the calculated, but the activation energy for inversion in II is not necessarily common for the neutral molecule and its anion radical.

p-cymene in the case of high-temp measurements to make the reference signals of comparable intensity to those of CH_2 resonances investigated. For the line-width measurements, radiofrequency power level was held at around 0·05 m gauss to avoid saturation of any signal. The usual sweep rate was 1 c/s. In all cases w's were measured by sweeping each resonance 3 times in turn without altering any controls. Since the line-width in the absence of exchange w_0 is determined practically by the inhomogeneity of the magnetic field, it was read directly from the width of the TMS and $(CH_3)CH$— signal of *p*-cymene added as the internal references. It was observed to have a full line width at half-height of 0·75 c/s at all temperatures at the sweep rates employed.

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