The Barrier to Internal Rotation in Amides

II.* N,N-Dimethyltrichloroacetamide. Experimental Errors in the Evaluation of Rate Constants with the NMR Lineshape Method

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The barrier to internal rotation around the \(-\text{N}-\text{C}=\) bond in \(N,N\)-dimethyltrichloroacetamide (DMTCA) has been studied by the NMR lineshape technique at both 60 and 100 MHz. The exchange rates have been evaluated by an iterative computer program using the complete lineshape.

The activation parameters characterizing the internal rotation in DMTCA were determined to be: \(E_a = 15.7 \pm 0.6\) kcal/mole; \(\Delta H^\ddagger = 15.1 \pm 0.6\) kcal/mole; \(\Delta F^\ddagger = 15.0 \pm 0.1\) kcal/mole, and \(\Delta S^\ddagger = 0.3 \pm 0.6\) e.u.

Sources of error in the application of the NMR lineshape method for the evaluation of rate data are discussed.

The nuclear magnetic resonance (NMR) lineshape method developed by Gutowsky and co-workers\(^2\) has become a powerful tool for the study of moderately rapid reversible chemical exchange processes. It is, however, not until recently that the errors in the rate constants determined by the NMR lineshape technique have been critically discussed.\(^5\) During the course of our studies of the barrier to internal rotation in the \(\text{=C=}-\text{N}\) bond in amides and examines we have undertaken a study of some sources of experimental error in the practical application of the lineshape technique. For the purpose of this investigation we have chosen \(N,N\)-dimethyltrichloroacetamide (DMTCA). For this compound the barrier to internal rotation has previously been determined by both the NMR lineshape \(^6\) and spin-echo methods.\(^6\)

When kinetic data are to be evaluated from exchange broadened NMR spectra it is in general desirable to evaluate the exchange parameters using

* Part I in this series is Ref. 1.
information from the complete spectral lineshape. In recent years the use of iterative computer programs for the fitting of theoretical spectra to experimental ones has become more and more widespread.\textsuperscript{10-12} This approach is fairly straightforward for chemical exchange in relatively simple spin systems where the lineshape depends on a small number of parameters but may become impractical in larger spin systems. The use of approximate equations (cf. Appendix for a collection of some of those most commonly used), relating some features in the experimental NMR spectrum to the exchange rate, may introduce appreciable errors in the final kinetic data, as has been demonstrated by Allerhand \textit{et al.}\textsuperscript{4} This must be kept in mind when activation parameters determined \textit{via} approximate equations are considered.

The use of the complete lineshape in the evaluation of exchange rates is, however, \textit{per se} not necessarily a guarantee for obtaining accurate activation parameters. For example, the NMR lineshape in the case of a nucleus exchanging between two equally populated sites depends, apart from the exchange rate $\tau$, also on the spin-spin relaxation time $T_2$ and on the difference, $\delta \nu$, in Larmor frequency for the nucleus in each site.\textsuperscript{13} The latter two parameters cannot, however, be evaluated from the experimental NMR spectra for all regions of $\tau$, and in practice some extrapolated or interpolated values of these parameters must be assigned. Aside from these difficulties inherent in the lineshape method there may also be other sources of error, for example in the determination of the true sample temperature.

In the present investigation we have studied the influence of errors in $T_2$, $\delta \nu$, and sample temperature on the activation parameters for the restricted rotation in DMTCA as evaluated by iterative computer fitting of the complete lineshape of the proton magnetic resonance (PMR) spectrum. PMR spectra obtained at both 60 and 100 MHz have been used in the evaluation. For comparison activation parameters have also been evaluated from the experimental lineshape by the use of the approximate equations listed in the Appendix.

**EXPERIMENTAL**

\textbf{Materials.} DMTCA was prepared from dimethylamine and trichloroacetyl chloride. The compound was distilled before use (b.p. 86.5°C/6 mm; lit. *b.p. 85.2°C/5 mm*). The spectra were recorded using a sample of neat DMTCA containing 5 % tetramethylsilane (TMS) as internal reference.

\textbf{Instrumental.} The NMR-spectra were recorded at 60 MHz using a Varian A60 A spectrometer and at 100 MHz using a Varian HA-100 spectrometer. The 100 MHz spectra were recorded in the frequency sweep mode. Both spectrometers were equipped with a variable temperature probe and a V-6040 variable temperature controller. The shifts were measured with the sideband technique using a Hewlett Packard audio frequency oscillator model 202 and a Hewlett Packard frequency counter model 5512. The resolution of the spectrometers was adjusted so as to always obtain the same linewidth (~0.30 Hz) for the TMS signal.

A Leeds and Northrup model K4 potentiometer bridge was used for the measurement of the thermocouple voltage.

\textbf{Temperature measurement.} The temperature of the sample was obtained from the temperature-dependent shift between the methylene- and OH-signals in a 1:1:1 mixture of CD$_3$OD, (CH$_3$OH)$_n$, and a 5 % solution of HCl in D$_2$O. This solution was kept in a sealed capillary centered in the middle of the sample tube by means of two teflon plugs.
The temperature dependence of the shift between the methylene- and the OH-signals in this "internal glycol thermometer" was calibrated against a precalibrated copper-constantan thermocouple in a separate experiment in the following way. The glycol capillary was centered in the middle of the NMR tube by means of a single teflon plug placed at the bottom of the tube. The tube was filled to a height of about 5 cm with a suitable liquid (for example m-xylene, acetone, dimethylformamide) and placed in the probe of the A-60 A spectrometer. In order to measure at the same time the sample temperature and the chemical shift difference between the methylene- and OH-signals in the glycol capillary, a small precalibrated copper-constantan thermocouple was fixed in the annular space in such a position that it was possible to spin the NMR tube during the calibration. The lower end of the thermocouple was positioned so close to the receiver coil of the spectrometer that the signal intensity was decreased by about 50%. The thermocouple in this position was about 0.5 cm above the receiver coil.

The complete calibration procedure was repeated two to three times, and the reproducibility was of the order of ±0.2°C. The type of liquid surrounding the capillary during the calibration was found to have little or no effect upon the calibration curve.

As the temperature used for the calibrations of the temperature-dependent shift of the "internal glycol thermometer" was measured about 0.5 cm above the receiver coil, the temperature gradient in the probe will introduce systematic errors in the temperatures obtained from these shifts. For this reason we have measured the temperature gradient along the sample tube in the A-60 A probe at a few temperatures (Table 1). At −65°C the temperature above the receiver coil increases by about 0.5°C/cm and at +83°C it decreases by about 0.2°C/cm.

**Table 1.** Temperature gradients above the receiver coil in the A-60 A probe at different temperatures and at a gas flow of 15 SCFH (Standard cubic feet per hour).

<table>
<thead>
<tr>
<th>Distance above the receiver coil mm</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>−65.50 -31.85  -1.40 +39.80 +83.50</td>
</tr>
<tr>
<td>5.0</td>
<td>−65.20 -31.70  -1.25 +39.80 +83.35</td>
</tr>
<tr>
<td>10.0</td>
<td>−65.00 -31.50  -1.10 +39.80 +83.30</td>
</tr>
<tr>
<td>15.0</td>
<td>−64.85 -31.35  -1.05 +39.85 +83.15</td>
</tr>
<tr>
<td>20.0</td>
<td>−64.75 -31.25  -1.05 +39.85 +83.05</td>
</tr>
<tr>
<td>25.0</td>
<td>−64.60 -31.15  -0.90 +39.85 +82.85</td>
</tr>
<tr>
<td>30.0</td>
<td>−64.55 -31.05  -0.85 +39.85 +82.60</td>
</tr>
</tbody>
</table>

The temperatures obtained from the "internal glycol thermometer" will therefore be too high at temperatures below the magnet temperature and too low for temperatures above that of the magnet. A correction for the systematic errors in the temperatures determined by the "glycol thermometer" can be made by measuring the temperature gradients along the y-axis in the probe for each temperature. However, the temperature range encountered in the evaluation of interconversion rates from NMR spectra is usually fairly small (60°C for $E_a$ = 16.0 kcal/mole), and thus the errors in the measured temperatures introduced by the temperature gradient in the probe may be estimated to be less than ±0.2°C if the thermocouple is fixed about 0.5 cm above the receiver coil during the calibration. Furthermore the gas flow through the probe may change from time to time and hence also the temperature gradient. For the reasons mentioned above we have included the systematic errors introduced by the temperature gradient as well as the error in the calibration in the total estimated error (less than ±0.5°C) in our temperature measurements.

**Rate measurements.** The rate of internal rotation around the −C−N− bond in DMTC was obtained by iterative computer fitting of theoretical spectra calculated according to the theory of Gutowsky and co-workers to the experimental spectra. The iterative subroutine in the curve-fitting program was developed by Ingri et al.[14]

for the evaluation of equilibrium constants from potentiometric titration data. This programme finds the "best" set of parameters for each spectrum according to the method of least squares by assuming that the "error square sum" is a second order function. The particular programme used in this investigation allows variation of up to nine parameters at the same time.

The line shape equation pertinent to the present case is a function of the spin-spin relaxation time \( T_1 \), the chemical shift difference (\( \delta \nu \)) between the exchanging protons, and the mean lifetime (\( \tau \)) for the protons in each site. These parameters were determined in the following way above and below the coalescence temperature.

The effective spin-spin relaxation time \( T_1^{\text{eff}} \), in which both the true spin-spin relaxation time and the effect due to the inhomogeneity of the magnetic field are included, was estimated by iterative curve fitting in the limits of fast and slow interconversion. If different values for \( T_1^{\text{eff}} \) were obtained at these limits even though the resolution of the spectrometer was kept as constant as possible throughout the experiment (see experimental section), the values of \( T_1^{\text{eff}} \) at the intermediate temperatures were obtained by linear interpolation between those for the slow and fast interconversion limits. In the temperature region below the coalescence temperature the chemical shift difference between the two \( N-\text{CH}_2 \) groups (\( \delta \nu \)) and the interconversion rate (\( \tau \)) were determined by simultaneous iteration of both of these parameters to obtain the best fit to the experimental spectral line shape. For temperatures above the coalescence point the spectrum contains too little information to allow a simultaneous determination of both \( \delta \nu \) and \( \tau \), and thus only \( \tau \) was varied in the curve fitting procedure. The value of \( \delta \nu \) for each temperature in this region was obtained from linear extrapolation on a plot of \( \delta \nu \) versus sample temperature in the region below coalescence.

In order to estimate the extent to which the activation parameters depend on the errors in the \( T_1^{\text{eff}} \) and \( \delta \nu \) values used in the line shape equation, the mean lifetime \( \tau \) was evaluated not only using \( T_1^{\text{eff}} \) and \( \delta \nu \) values determined as described above, but also with the same value of \( T_1^{\text{eff}} \) at all temperatures. Furthermore, different slopes in the \( \delta \nu \) vs. temperature plot above the coalescence temperature were employed (cf. calculations II, III, and V in Table 2). The interconversion rates for the restricted \( =\text{C}-\text{N}--\text{C}= \)

rotation in DMTCa were also determined from the experimental spectra by the use of approximate equations (cf. eqns. 1-5 in the Appendix).

**Table 2.** A comparison of the activation parameters and the frequency factors for the restricted rotation in the \( =\text{C}-\text{N}--\text{C}= \) bond in DMTCa calculated with different values for the spin-spin relaxation time \( T_1 \) and the peak separation in the absence of exchange, \( \delta \nu \). The errors given in the table are calculated assuming only random errors. (Cf. discussion in the experimental part.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Resonance frequency MHz</th>
<th>( T_1 ) sec.</th>
<th>( \delta \nu ) Hz</th>
<th>log ( A )</th>
<th>( E_\nu ) kcal/mole</th>
<th>( \Delta H^# ) kcal/mole</th>
<th>( \Delta F^# ) kcal/mole</th>
<th>( \Delta S^# ) e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>60 0.24 -0.30</td>
<td>17.80 -16.66</td>
<td>13.3</td>
<td>15.7 ±0.1</td>
<td>15.1 ±0.1</td>
<td>15.0 ±0.1</td>
<td>0.3 ±0.3</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>60 0.24</td>
<td>17.80 -16.66</td>
<td>13.9</td>
<td>16.4 ±0.1</td>
<td>15.9 ±0.1</td>
<td>14.9 ±0.1</td>
<td>3.1 ±0.5</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>60 0.24</td>
<td>17.80 -17.10</td>
<td>14.2</td>
<td>16.8 ±0.2</td>
<td>16.2 ±0.2</td>
<td>14.9 ±0.2</td>
<td>4.3 ±0.6</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>100 0.24</td>
<td>28.60 -27.60</td>
<td>13.3</td>
<td>15.7 ±0.1</td>
<td>15.1 ±0.1</td>
<td>15.0 ±0.1</td>
<td>0.3 ±0.3</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>100 0.24</td>
<td>28.60</td>
<td>13.8</td>
<td>16.3 ±0.1</td>
<td>15.7 ±0.1</td>
<td>15.0 ±0.1</td>
<td>2.4 ±0.4</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) \( T_1 \) for each temperature was obtained by linear interpolation between these values.

\( b \) \( \delta \nu \) for each temperature above the coalescence temperature was obtained from a linear interpolation between these values for \( \delta \nu \).

\( c \) \( A \) is the frequency factor in the Arrhenius equation.

Thermodynamic functions. The activation parameters for the $\equiv C \equiv N \equiv$ rotation in DMTCA were calculated according to the theory of absolute reaction rates, using the Eyring equation (1)

$$k = \frac{1}{\tau} = \frac{xkT}{h} \cdot \exp(-\Delta F^+/RT)$$

written in the expanded form (2)

$$\ln \left( \frac{1}{\tau} \right) = -\frac{\Delta H^+}{RT} + \frac{\Delta S^+}{R} + \ln \frac{xkT}{h}$$

The energy of activation, $E_a$, is obtained from the slope of the plot of $\log(1/\tau)$ versus $1/T$ assuming $x=1$.

RESULTS AND DISCUSSION

The activation parameters for the restricted rotation around the $\equiv C \equiv N \equiv$ bond in DMTCA obtained by different methods of evaluation are summarized in Tables 2, 3, and 4.

A comparison of the activation parameters in Table 2 shows that the $E_a$ and $\Delta H^+$ values obtained using $T_2^{\text{eff}}$ equal to 0.24 sec for all temperatures differ from those calculated with $T_2^{\text{eff}}$ values obtained from a linear interpolation between 0.24 and 0.30 sec by as much as 0.7 kcal/mole (see calculations I and II in Table 2). This shows that even small systematic errors in $T_2^{\text{eff}}$ may cause errors in $E_a$ and $\Delta H^+$ which are larger than the random errors. The use of $T_2^{\text{eff}}$ values obtained by a linear interpolation between the high and low temperature data may of course also be criticized since the variation of $T_2^{\text{eff}}$ may be nonlinear. However, this method makes the determination of $T_2^{\text{eff}}$ most uncertain in the coalescence region where the spectra are quite

Table 3. Comparison of the activation parameters and the frequency factors for the restricted rotation in the $\equiv C \equiv N \equiv$ bond in DMTCA evaluated using the approximate equations 1—5.

<table>
<thead>
<tr>
<th>Method</th>
<th>log $A^*$</th>
<th>$E_a$ kcal/mole</th>
<th>$\Delta H^+$ kcal/mole</th>
<th>$\Delta F^+$ (298°K) kcal/mole</th>
<th>$\Delta S^+$ e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak separation</td>
<td>1</td>
<td>12.0</td>
<td>13.9</td>
<td>13.3</td>
<td>15.0</td>
</tr>
<tr>
<td>Intensity ratio</td>
<td>2</td>
<td>11.2</td>
<td>12.8</td>
<td>12.2</td>
<td>15.0</td>
</tr>
<tr>
<td>Peak broadening</td>
<td>3</td>
<td>16.1</td>
<td>19.2</td>
<td>18.6</td>
<td>14.7</td>
</tr>
<tr>
<td>Peak narrowing</td>
<td>4</td>
<td>14.6</td>
<td>17.6</td>
<td>17.0</td>
<td>15.7</td>
</tr>
<tr>
<td>Peak narrowing</td>
<td>5</td>
<td>12.9</td>
<td>15.1</td>
<td>14.5</td>
<td>15.0</td>
</tr>
</tbody>
</table>

$^a A$ is the frequency factor in the Arrhenius equation.
Table 4. Comparison of activation parameters for the restricted rotation in the \( =\text{C}−\text{N}− \) bond in DMTCA obtained by high resolution and spin-echo methods. The errors for the data obtained in the present investigation are estimated errors (cf. text).

<table>
<thead>
<tr>
<th>Method</th>
<th>( E_a ) kcal/mole</th>
<th>( \Delta H^\ddagger ) kcal/mole</th>
<th>( \Delta F^\ddagger ) (298°K) kcal/mole</th>
<th>( \Delta S^\ddagger ) e.u.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>High resolution (60 MHz)</td>
<td>15.7 ± 0.6</td>
<td>15.1 ± 0.6</td>
<td>15.0 ± 0.1</td>
<td>0.3 ± 2.3</td>
<td>this work</td>
</tr>
<tr>
<td>High resolution (100 MHz)</td>
<td>15.7 ± 0.6</td>
<td>15.1 ± 0.6</td>
<td>15.0 ± 0.1</td>
<td>0.3 ± 2.3</td>
<td>this work</td>
</tr>
<tr>
<td>High resolution (60 MHz)</td>
<td>17.0</td>
<td></td>
<td></td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>Spin echo</td>
<td>14.5</td>
<td>13.5 (^b)</td>
<td>14.9 (^b)</td>
<td>-4.65 (^b)</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>(15.5) (^a)</td>
<td>(14.9) (^a)</td>
<td>(15.0) (^a)</td>
<td>(-0.20) (^a)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Calculated by omitting the points a and b in Fig. 1.

\(^b\) Calculated using the data given by Ref. 6.

broad and the spectral lineshape is therefore also quite insensitive to errors in \( T_2^\text{eff} \). It may therefore be concluded that when a variation of \( T_2^\text{eff} \) with temperature is found this should be taken into account. If for the present case the values of \( T_2^\text{eff} \) measured at the low and high temperature limits are estimated to be accurate to 0.01 sec, an error of ±0.2 kcal/mole would be obtained in \( E_a \) and \( \Delta H^\ddagger \).

In the estimation of the chemical shift difference between the two \( N−\text{CH}_3 \) groups (\( \delta \nu \)) at temperatures above the coalescence point described in the experimental section, it has been assumed that the temperature dependence of \( \delta \nu \) is linear. The chemical shift difference, \( \delta \nu \), is thus for temperatures above the coalescence temperature estimated by a linear extrapolation of the \( \delta \nu \) versus \( T \) plot. The drift in the spectrometer at low temperatures introduces errors in the measured values of \( \delta \nu \) (even though the spectra were run both upfield and downfield), which in turn makes the extrapolation uncertain. We have thus evaluated the activation parameters using different slopes in the extrapolation of the \( \delta \nu \) versus temperature plot. In calculations I and II (Table 2) values of \( \delta \nu \) obtained by extrapolation of the observed temperature dependence of \( \delta \nu \) were used, and in calculation V the value pertinent to the coalescence temperature was used for all higher temperatures. If we estimate that \( \delta \nu \) at temperatures below the coalescence point can be measured within about ±0.2 Hz, this error would then cause an error in \( E_a \) and \( \Delta H^\ddagger \) of about ±0.3 kcal/mole. As the random errors are of the order of ±0.1 kcal/mole, the total error in our determination of \( E_a \) and \( \Delta H^\ddagger \) for the restricted rotation in DMTCA is about ±0.6 kcal/mole.

The errors in the evaluation of the free energy of activation \( \Delta F^\ddagger \) are less sensitive to variations in \( T_2^\text{eff} \) and \( \delta \nu \) (see Table 2), and with the accuracy assumed for these parameters, random errors probably give the largest contribution to the error in \( \Delta F^\ddagger \). The value of \( \Delta F^\ddagger \) determined in the present work can therefore be assumed to be accurate to about ±0.1 kcal/mole. Using the error limits for \( \Delta H^\ddagger \) and \( \Delta F^\ddagger \) estimated above, the error in \( \Delta S^\ddagger \) is calculated to be ±2.3 e.u.

The use of the approximate eqns. 1—4, given in the Appendix, for the evaluation of $E_a$ and $\Delta H^\pm$ results in values of these parameters which differ from those determined from the total lineshape by several kcal/mole (Table 3). However, eqn. 5 of the Appendix gives values in good agreement with those obtained by the complete lineshape fitting method.

The present investigation shows that the use of the complete lineshape fitting method in the evaluation of $E_a$, $\Delta H^\pm$, and $\Delta S^\pm$ from exchange broadened NMR spectra may result in relatively large errors in these activation parameters unless care is taken to obtain accurate values of $T_2^\text{eq}$ and $\delta v$ at each temperature studied. The uncertainty in the activation parameters may otherwise become so large that no significant conclusions may be drawn from the data. If, however, only a rough estimation of a barrier is needed it is advisable to evaluate $\Delta F^\pm$ since this parameter can be determined quite accurately even with the use of approximate equations.

A comparison between the rate constants from the present study and corresponding data from earlier spin-echo and high resolution studies shows reasonably good agreement (see Table 4). This statement holds in particular if two values in the spin-echo data and one value in the high resolution data are disregarded. It appears that the two deviating spin-echo values (cf. points a and b in Fig. 1) are even in poor agreement with the rest of the spin-echo data. The deviating rate constant in the high resolution study (point c in Fig. 1) is at variance with the rest of the rate data in that work. Good agreement between the activation parameters in the present investigation and those calculated from rate data given in Ref. 6 may be obtained if the points a and b in Fig. 1 are excluded (cf. Table 4).

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**Fig. 1.** A plot of $\log 1/\tau$ vs. $10^9/T$ for DMTCA. Points a and b are omitted in the calculation of $E_a$ from the spin-echo data (see text and Table 4).
- Present work, 100 MHz; △ present work, 60 MHz; ○ Allerhand et al., spin-echo;
- ▽ Fryer et al., 60 MHz; solid line: $E_a = 15.7$ kcal/mole, $\log A = 13.3$. 

APPENDIX

The evaluation of exchange rates from exchange broadened NMR spectra is often performed by measuring some characteristic parameter of the experimental spectrum, such as the peak separation (eqn. 1), the ratio of the

\[ \tau = \frac{\sqrt{2}}{\pi \sqrt{(\delta v)^2 - (\delta v_e)^2}} \]  \hspace{1cm} (1)  

maximum height to the central minimum (eqn. 2),

\[ \tau = \frac{\sqrt{2} V r + \sqrt{r^2 - r}}{\pi \delta v} \]  \hspace{1cm} (2)  

or the half width of the signals (eqns. 3–5), and using approximate equations relating these parameters to the exchange rate.

\[ \tau = \frac{1}{\pi (\delta v_{1/2} - \delta v^0)} \]  \hspace{1cm} (3)  

\[ \tau = \frac{2(\delta v_{1/2} - \delta v^0)}{\pi (\delta v)^2} \]  \hspace{1cm} (4)  

\[ \tau = \frac{2(\delta v_{1/2})}{\pi[(\delta v)^4 + 2(\delta v \delta v_{1/2})^2 - (\delta v_{1/2})^4]^{1/2}} \]  \hspace{1cm} (5)  

In these equations the symbols are defined as follows:

\( \tau \) = the mean lifetime for exchanging protons in each site in the absence of exchange.

\( \delta v \) = the peak separation in the absence of exchange.

\( \delta v_e \) = the peak separation at intermediate exchange rates.

\( r \) = the ratio of the peak maximum to the central minimum.

\( \delta v_{1/2} \) = the linewidth at half of the maximum signal intensity.

\( \delta v^0 \) = \( 1/\pi T_2 \)

\( T_2 \) = the spin-spin relaxation time.

Eqns. 1–3 can be used for calculation of exchange rates in the region between the slow exchange limit and the coalescence point, and eqns. 4 and 5 can be used for exchange rates between the coalescence point and the fast exchange limit.

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