A STUDY OF INTERNAL ROTATION IN 2-FURALDEHYDE THROUGH ^{13}C RELAXATION TIMES IN THE ROTATING FRAME

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Carbon-13 relaxation times in the rotating frame were used to study the exchange between unequally populated rotamers of 2-furaldehyde. Calculated free activation energy and activation enthalpy are in good agreement with the results of ^{1}H line shape analysis. Accuracy and reliability of this method in comparison with the line shape analysis is discussed.

Hindered rotation of the aldehyde group in 2-furaldehyde have been already studied by ^{1}H NMR spectroscopy. Dahlqvist and Forsén[1] extracted activation parameters from the line shape analysis of the $H_{(3)}$ and COH proton signals. They noticed that the results obtained using the $H_{(3)}$ signal were systematically lower than those derived from the COH signal. The reasons are not completely clear and were attributed to temperature dependence of chemical shifts of both rotational isomers and/or to an incorrect estimate of other relaxation contributions to the spectral line widths.

Measurement of relaxation times in the rotating frame performed on signals averaged out by fast exchange is a method of choice for the study of exchange processes in the fast exchange region. This method has been used so far for the study of exchange reactions with equally populated states[2]. The aim of the presented paper is the application of this technique to the study of exchange between unequally populated *s-cis* and *s-trans* forms of 2-furaldehyde

s-trans (A) *s-cis* (B)

and the evaluation of advantages and disadvantages of this method in comparison with the commonly used line shape analysis.

THEORY

Methods based on the measurement of transverse relaxation times allow to study the exchange processes in a remarkably wide temperature range above the coalescence temperature. Besides the spin echo method[3], the measurement of relaxation times in the rotating frame $(T_{1\varrho})$ is increasingly used[4-8]. The relationship for the contribution of a fast exchange in the equilibrium to the relaxation time $T_{1\varrho}$ of a signal originated by transition between two states A and B with relative populations p_A and $p_B = 1 - p_A$ and chemical shifts ν_A and ν_B can be obtained from the equation derived by Meiboom[9] and by analogy with relationships valid for the spin echo method[3] as

$$(T_{1\varrho}^{ex})^{-1} = 4\pi^2 p_A p_B (\nu_A - \nu_B)^2 \, \tau_{ex}/(1 + \omega_1^2 \tau_{ex}^2) \, , \tag{1}$$

where ω_1 is the locking field amplitude in rad s^{-1}. The equation (1) holds if

$$|\nu_A - \nu_B| \, \tau_{ex} \ll 1 \, . \tag{2}$$

For the average lifetime τ_{ex} apply the following relationships with the rate constants k_{AB} and k_{BA} for the transition from the state A to the state B and *vice versa*.

$$\tau_{ex}^{-1} = k_{AB} + k_{BA} \tag{3}$$

$$k_{AB} = p_B/\tau_{ex} \tag{4}$$

$$k_{BA} = p_A/\tau_{ex} \, . \tag{5}$$

The value of $T_{1\varrho}^{ex}$ can be determined experimentally from the times $T_{1\varrho}$ and T_1 using the relationship

$$(T_{1\varrho}^{ex})^{-1} = T_{1\varrho}^{-1} - T_1^{-1} \tag{6}$$

in which T_1^{-1} represents the contribution of the fast processes to the relaxation in the rotating frame.

From the relationship (1) it is evident that for $\omega_1^2 \tau_{ex}^2 \gtrsim 1$ is $T_{1\varrho}^{ex}$ linearly dependent on ω_1^2. Therefore, using the measured relaxation time T_1 and the $T_{1\varrho}$ values measured at several amplitudes of the locking field ω_1, it is possible to obtain by the least squares treatment the value of τ_{ex} and one of the two remaining parameters, *i.e.*, either the abundance of both isomers or the difference of their chemical shifts. The second parameter has to be determined from the low temperature measurement when the exchange is slow and does not affect the line shape. Substituting the known values of τ_{ex} and p_B into equation (4), we obtain the rate constant k_{AB}. From the

Eyring equation

$$k_{AB} = \left(\varkappa kT/h\right) \exp\left(-\Delta G_{AB}^{\neq}/RT\right), \tag{7}$$

where $\varkappa$ is put equal to unity, we can calculate the value of $\Delta G_{AB}^{\neq}$. Assuming that the chemical shift difference $\nu_A - \nu_B$ is temperature independent and the product $\omega_1^2 \tau_{ex}^2 \ll 1$, the equation (1) can be rearranged using equation (4) as

$$T_{1\varrho}^{ex} = Ck_{AB}/\left(p_A p_B^2\right). \tag{8}$$

Substituting k_{AB} from the Eyring equation and taking the logarithm we obtain

$$\ln\left(T/T_{1\varrho}^{ex}p_A p_B^2\right) = \ln C' + \Delta H_{AB}^{\neq}/RT, \tag{9}$$

where C and C' include constants and temperature-independent variables. Thus, activation enthalpy $\Delta H_{AB}^{\neq}$ can be calculated from the slope of dependence of $\ln\left(T/T_{1\varrho}^{ex}p_A p_B^2\right)$ on T^{-1}. Activation parameters for the reverse reaction are calculated similarly.

EXPERIMENTAL

The measured sample contained distilled 2-furaldehyde, diethyl ether, and deuterated acetone in the volume ratio 3 : 4 : 1. Relaxation times of the carbons $C_{(3)}$ and COH were measured on a JEOL FX-100 FT NMR spectrometer at 25·05 MHz in non-rotating 10 mm sample tubes under proton noise decoupling. Spin-lattice relaxation times were obtained by the inversion recovery method (pulse sequence $5T_1 - 180° - \tau - 90° -$ acquisition), relaxation times $T_{1\varrho}$ using the sequence $5T_1 - 90°_x - \tau_{SL,y} -$ acquisition. Amplitude of the locking field ω_1, applied during interval τ_{SL}, was calibrated using the pulse width required for the inversion of magnetization. Variable temperature controller NM-5471 was calibrated by means of methanol[10] under conditions identical to those of other measurements. This calibration was checked through the melting point determination of several pure compounds (acetone, undecane, 1,4-xylene) contained in capillaries which were placed in the measured sample; the checked parameters were controller temperature readings at their melting points[11]. The error in sample temperature under these conditions should not exceed 1 K.

RESULTS

Room temperature ^{13}C NMR spectra of 2-furaldehyde have been already measured and assigned[12]. Lowering the temperature slows down the rotation; this is markedly observable on the $C_{(3)}$ and COH signals that are gradually broadened and finally split into two signals of unequal intensity corresponding to s-trans and s-cis isomers. Initially it was assumed[1] that the more intense signals are due to the s-cis form. However, this assignment was later reversed on the basis of a nuclear Overhauser effect measurement on the $H_{(3)}$ protons[13].

Thermodynamic parameters of this reaction, *i.e.* ΔG^0_{AB}, ΔH^0_{AB}, and ΔS^0_{AB}, were obtained from the ratios of integral intensities of the $C_{(3)}$ signals of both isomers in the slow exchange region at temperatures 183 K, 189 K, and 195 K (Tab. I). At least three readings of the integral ratio were made and their average was used in calculation. Activation parameters were studied at temperatures 245 K to 286 K. The dependence of $T^{ex}_{1\varrho}$ of an averaged $C_{(3)}$ signal on ω^2_1 (Tab. II) was measured at 245 K. The value $\tau_{ex} = 2\cdot15 \cdot 10^{-4}$ s was calculated from the slope and the magnitude of $T^{ex}_{1\varrho}$ for $\omega_1 = 0$. The value $p_B = 0\cdot194$ at this temperature was calculated from the values of ΔH^0_{AB} and ΔS^0_{AB}. The value $\Delta G^{\neq}_{AB} = 45\cdot7$ kJ mol^{-1} was calculated from equations (4) and (7). The chemical shift difference of the $C_{(3)}$ signals in both isomers, $\left| v_A - v_B \right| = 245$ Hz, was obtained using the regression parameters and known values of p_A and p_B. This value agrees very well with the difference of 241 Hz found at 183 and 195 K.

Activation enthalpy was derived from the slope of the temperature dependence given by equation (9). Relaxation times were measured at $\omega_1 = 1\,000$ rad s^{-1} so that the condition $\omega^2_1 \tau^2_{ex} \ll 1$ was satisfied for all temperatures used except 245 K. Extrapolated value of $T^{ex}_{1\varrho}$ for $\omega_1 = 0$ obtained during the calculation of $\Delta G^{\neq}_{AB}$ was used for this temperature. To confirm the results, all measurements were repeated for the aldehydic carbon. Relaxation times are given in Table II, calculated activation parameters for the direct and inverse reaction are contained in Table III together with the results of the line shape analysis[1]. The reported errors are confidence limits at the 95% confidence level. The error in free activation energy includes the statistical error of the rate constant and the uncertainty of the temperature determination. The error of activation enthalpy was obtained from the statistical error of the linear regression parameters using the equation (9).

DISCUSSION

As seen from Table III, free activation energy calculated from the relaxation of $C_{(3)}$ is practically identical with the value obtained from the measurement on the alde-

TABLE I

Thermodynamic parameters for the interconversion of the rotational isomers of 2-furaldehyde

$\Delta G^0_{AB,T}$, kJ mol^{-1}			ΔH^0_{AB} kJ mol^{-1}	ΔS^0_{AB} J mol^{-1} K^{-1}
183 K	189 K	195 K		
2·9328	2·9180	2·9162	3·18	1·4

hydic carbon. The difference in measured activation enthalpies is a result of small contribution of scalar relaxation to the relaxation time $T_{1\varrho}$ of the aldehydic carbon

TABLE II

Temperature and locking field dependent relaxation times (in s) of the $C_{(3)}$ and COH carbons of 2-furaldehyde

Relaxation time	T, K	ω_1, rad s^{-1}	Carbon	
			$C_{(3)}$	COH
T_1	245	—	4·55	4·75
$T_{1\varrho}$	245	1 000	0·0121	0·158
$T_{1\varrho}$	245	3 000	0·0185	0·224
$T_{1\varrho}$	245	5 000	0·0266	0·326
$T_{1\varrho}$	245	7 000	0·041	0·477
$T_{1\varrho}$	245	10 000	0·069	0·74
T_1	252·5	—	5·79	6·77
$T_{1\varrho}$	252·5	1 000	0·0277	0·326
T_1	260·5	—	6·70	8·00
$T_{1\varrho}$	260·5	1 000	0·0530	0·634
T_1	269	—	8·45	9·34
$T_{1\varrho}$	269	1 000	0·110	1·11
T_1	277	—	9·35	10·8
$T_{1\varrho}$	277	1 000	0·190	1·96
T_1	286	—	11·5	—
$T_{1\varrho}$	286	1 000	0·381	—

TABLE III

Activation parameters for the interconversion of the rotational isomers of 2-furaldehyde (in kJ . . mol^{-1})

	From relaxation times[a]		From lineshape analysis[b]	
	$C_{(3)}$	COH	$H_{(3)}$	HCO
$\Delta G^{\neq}_{AB,T}$	45·73 ± 0·36[c]	45·65 ± 0·36[c]	45·09 ± 0·96[d]	45·76 ± 0·84[d]
$\Delta G^{\neq}_{BA,T}$	42·83 ± 0·35[c]	42·75 ± 0·35[c]	42·66 ± 1·00[d]	43·33 ± 0·84[d]
$\Delta H^{\neq}_{AB}$	49·9 ± 1·9	48·2 ± 2·0	47·10 ± 0·88	49·15 ± 0·71
$\Delta H^{\neq}_{BA}$	47·2 ± 1·9	45·4 ± 2·0	42·71 ± 0·88	44·76 ± 0·71

[a] This work; [b] from ref.[1]: the errors given are average deviations, assuming random errors only; [c] at $T = 245$ K; [d] at $T = 216$ K.

at higher temperatures. Values of T_1 and $T_{1\varrho}$ are then relatively close and the value of $T_{1\varrho}^{ex}$ calculated according to equation (6) contains a larger error. Because of this, the result obtained from the $C_{(3)}$ signal is more reliable.

Agreement with the results of the line shape analysis[1] is very good. The values arising from the analysis of the ^1H signal of the COH group are more close. Some differences between the measured data are due to different values of ΔH_{AB}^0 and ΔS_{AB}^0 used in the calculation of p_A and p_B. These values are difficult to obtain reliably since the available temperature interval of slow exchange is narrow and because of low accuracy of NMR signal integration. However, agreement between the calculated chemical shift differences of both isomers and the results of low temperature measurement indicates a good estimate of thermodynamic parameters. When the values $\Delta H_{AB}^0 = 4\cdot40\,\text{kJ mol}^{-1}$ and $\Delta S_{AB}^0 = 9\cdot09\,\text{J mol}^{-1}\,\text{K}^{-1}$ published by Dahlqvist and Forsén[1] are used for the calculation of the $C_{(3)}$ chemical shift difference, the value 222 Hz is obtained. Since the directly measured difference in the slow exchange region is by 19 Hz higher, the last mentioned values are probably less accurate.

From the above given results it is evident that the study of kinetics of exchange processes by means of relaxation times is more complicated and more time demanding than the line shape analysis. On the other hand, the line shape analysis requires extrapolation of the chemical shift difference, the relative population of both forms and the line width in the absence of exchange obtained from the values in the slow exchange region. The method based on the relaxation times requires extrapolation of one parameter only (either $|v_A - v_B|$ or p_A/p_B) and is therefore more reliable.

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