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NMR STUDY OF DONOR EXCHANGE RATES AND BARRIERS TO INTERNAL ROTATION IN $SbCl_5$ ADDUCTS OF SOME CARBONYL-CONTAINING COMPOUNDS

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Abstract—Molecular $SbCl_5$ adducts of N,N-dimethylacetamide, N,N-dimethylethylcarbamate, ethylchloroacetate, 1,1-dimethyl-3-isopropylurea, dimethyl carbonate, 2-oxo-5,5-dimethylhexahydropyrimidine, diethyl ketone and N,N-dimethyltrichloroacetamide in halogenated hydrocarbon solutions have been studied by PMR. The rate-determining step in the donor exchange with donor in excess of the 1:1 donor-acceptor ratio was found to be dissociation of the adduct. By comparing activation enthalpies for adduct dissociation with calorimetric data for enthalpies of adduct formation it was possible to show that the activation enthalpy for the adduct formation process is close to zero. Where applicable, effects of adduct formation on N—C barriers to internal rotation have been measured or estimated. These barriers increase considerably, which implies that coordination takes place at the carbonyl oxygen atom. The N—C barrier to internal rotation in uncomplexed N,N-dimethylethylcarbamate was also determined. Most measurements were evaluated with complete lineshape equations and computer treatment of digitized spectra. A method for the estimation of the magnitude of hidden systematic errors in activation parameters is discussed.

INTRODUCTION

High-resolution NMR spectroscopy provides a very powerful tool for the study of reversible exchange processes. One field of application is intermolecular donor or acceptor exchanges in molecular electron pair donor-acceptor adducts of Lewis acids and bases. Many systems of group III acids and organic bases have so far been studied,[1-6] and in some cases the exchange mechanisms have also been investigated.

In the present paper a study of $SbCl_5$ adducts of some carbonyl-containing compounds is presented. Enthalpies of adduct formation in 1,2-dichloroethane have previously been determined for these systems.[7] The aim of the present work was to investigate whether or not a correlation exists between these enthalpies and activation parameters for donor exchange.

Since some of the donors are amide-type molecules, rates for restricted rotation around the amide bonds could also be studied, and were found to decrease as compared to the unbound molecule. For comparison, the barrier to internal rotation in uncomplexed N,N-dimethylethylcarbamate had to be measured, since only approximate values were available.[8,9] Only three papers in the very active field of amide barriers to internal rotation have previously treated effects of adduct formation.[10-12]

EXPERIMENTAL

The abbreviations given in parenthesis after each name will be used in the text. Preparative and/or purification procedures for N,N-dimethylacetamide[13] (DMA), $(CH_3)_2NCOCH_3$; N,N-dimethylethylcarbamate[14] (DMURET), $(CH_3)_2NCOOC_2H_5$; ethylchloroacetate[15] (MCET), $ClCH_2COOC_2H_5$; 1,1-dimethyl-3-isopropylurea[16] (DMIPU), $(CH_3)_2NCONHCH(CH_3)_2$; dimethyl carbonate[17] (DMCARB), $(CH_3O)_2CO$ have been described previously. Diethyl ketone (DEK), $(C_2H_5)_2CO$ was obtained from Fluka AG and distilled prior to use. N,N-Dimethyltrichloroacetamide (DMTCA), $(CH_3)_2NCOCCl_3$ was synthesized from anhydrous dimethylamine and trichloroacetylchloride in benzene. It was purified by distillation at reduced pressure, followed by fractional crystallization. 2-Oxo-5,5-dimethylhexahydropyrimidine, $CH_2NHCONHCH_2C(CH_3)_2$ was a generous gift from Badische Anilin und Soda Fabrik, Ludwigshafen, Germany. This compound was recrystallized from EtOH and dried under vacuum. DMA, DMURET, MCET and DMCARB were generous gifts from Dr. G. Olofsson, Thermochemistry Laboratory, University of Lund. $SbCl_5$ was obtained from Merck AG and was of chromatographic grade.

For various reasons the same solvent could not be used throughout the whole series of experiments. Deuterochloroform and hexadeuterobenzene were obtained from Ciba AG and were 99·5% isotope enriched. The $CDCl_3$ was found by a chromatographic method[18] to contain less than 0·02% water. Dideuterodichloromethane was obtained from Merck AG and 1,1,2,2-tetrachloroethane and dichloromethane from BDH. The latter two compounds were distilled prior to use. All solvents and

donor compounds were pure as judged from NMR spectra. Samples were prepared directly in the NMR tubes by mixing known amounts of donor and $SbCl_5$ solution, while cooling with solid CO_2. These manipulations were done in a polyethylene glove bag (Instruments for Research and Industry) under dry N_2. NMR tubes were sealed with Wilmad polyethylene plugs and stored at dry ice temperatures until spectra were recorded (within 24 h). Only in the case of the DEK adduct was some significant decomposition of the samples noted. All measurements were started at a low temperature and in these samples a violet-brown discoloration was observed at $-10°$. For the temperatures and heating times used it was however judged that the effect on the measured rate constants was not serious, since restoring the low temperature produced almost the same spectra unless the sample had been heated far above the coalescence temperature. The most significant changes were then in the relative integrals of the adduct and free donor signals.

Slow crystallization occurred in some samples at low temperatures, and the sample was intermittently removed from the probe to allow the crystals to re-dissolve.

The samples had the following compositions: DMURET 1·0 M in 50:50 $CDCl_3$-C_6D_6,* DMURET adduct 0·4 M, free donor 0·8 M in 1,1,2,2-tetrachloroethane (0·4/0·8/TCA), DMA adduct 0·4/0·8/TCA, DMTCA adduct 0·30/0·35/CD_2Cl_2, DMIPU adduct 0·3/0·3/CD_2Cl_2, MCET adduct 0·6/0·6/$CDCl_3$, DMCARB adduct 0·6/1·6/$CDCl_3$, 0·6/0·8/$CDCl_3$ and 0·6/0·65/$CDCl_3$, DEK adduct 0·6/0·3/$CDCl_3$ and 0·6/1·2/$CDCl_3$ and 2-oxo-5.5-dimethylhexahydropyrimidine adduct 0·3/0·6/ CH_2Cl_2.

All spectra were recorded with a Varian Associates A-60A spectrometer with a V-6040 temperature controller.

Temperature measurements in all lineshape measurements were made with an internal capillary tube as previously described.[12] For the approximate measurements on the DMA and MCET adducts we used sample substitution with Varian's ethylene glycol sample and a dimethylether-methanol capillary,[16] respectively.

Rate constants were evaluated using complete lineshape equations with temperature corrections on all lineshape parameters as previously described.[12] Systems in which both restricted rotation and donor exchange are present (DMIPU, DMTCA, DMURET and DMA) represent "four-site" exchanges (Fig 2) and both processes affect the lineshape.[19] In the DMIPU case the restricted rotation in the adduct can be treated by the common "two-site" equations, because its rate is well separated from the rates for donor exchange and from the rotation rate in the unbound molecule.

Digitized spectra were processed on a UNIVAC 1108 computer with a series of programs written in this laboratory, built around J. P. Chandler's subroutine STEPIT (Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana, U.S.A.) to obtain the best fit between the observed and calculated spectra. During the course of the present work a new subroutine, SYSERR, was developed and added to the available program package to allow for automatic estimation of errors in the rate constants arising from estimated uncertainties in the interpolated spin-spin relaxation times (T_2) and the extrapolated shift differences ($\delta\nu$). The maximum and minimum possible exchange rates (τ) corresponding to an observed spectrum can be estimated by calculating τ values when the observed and calculated spectra are adjusted to best fit, T_2 and $\delta\nu$ having in turn the following combinations of values: T_2(max), $\delta\nu$(max); T_2(max), $\delta\nu$(min); T_2(min), $\delta\nu$(max); and T_2(min), $\delta\nu$(min). This is done by SYSERR. This calculation also provides a basis for weighting the data pairs (exchange rate/temperature) in a subsequent activation parameter calculation because the relative uncertainties in the exchange rates at different temperatures are obtained.

Since it has been noted that good linear Arrhenius plots can result although the rate constants may have systematic errors,[20,21] the possible errors in these parameters were accounted for by the following procedure: (i) The activation parameters are calculated *via* τ values based on the "best" estimates (least-squares or other) of $\delta\nu$ and T_2. The τ value-temperature pairs in the calculation are weighted according to their relative uncertainties, as obtained in the SYSERR calculation. This is assumed to lead to the best activation parameters in the least-squares sense. The random error limits of the activation parameters are also obtained in this calculation. (ii) To account for possible hidden systematic errors is the rate constants, arising from error propagation from T_2 and $\delta\nu$ values, the same procedure was repeated, but the rate constants were taken to have that combination of errors (as obtained in the SYSERR calculation) that gives the maximum possible activation enthalpy. The differences between the activation parameters obtained in this calculation and those obtained in calculation 1 are assumed to account for the magnitude of possible hidden systematic errors in the activation parameters. These are then added to the random errors: total error limit of activation parameter $= \pm\sqrt{\{(\text{random error})^2 + (\text{deviation between calculation 1 and 2})^2\}}$. The two error calculations by this approach in the present work are based on linear least-squares values and error limits to 90% confidence for $\delta\nu$ above coalescence and on graphically interpolated values and error limits of $\pm 0{\cdot}1$ s for T_2. No errors in $\delta\nu$ were assumed below the coalescence temperature since $\delta\nu$ can be determined directly from the observed lineshape. Above coalescence almost identical spectra can be calculated with different combinations of $\delta\nu$, T_2 and τ.

Drakenberg *et al.*[21] estimated error limits of activation parameters in a similar way.

Activation parameters were calculated according to the theory of absolute reaction rates and Eq. (1), assuming that the transmission coefficient is unity. Rearrangement of (1) then leads to (2). $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were assumed to be temperature independent and were evaluated *via* (3).

$$k = \frac{\kappa \cdot k_B \cdot T}{h} \exp(-\Delta G^{\ddagger}/RT) \quad (1)$$

$$\Delta G^{\ddagger} = \ln(10) \cdot R \cdot T \cdot (10{\cdot}319 + \log T - \log k) \quad (2)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (3)$$

RESULTS AND DISCUSSION

Table 1 summarizes the observed shift differences between unbound and adduct donor signals. In the preparation of the samples precautions were taken to avoid contamination with water and acidic impurities, since this has been found to affect the

*This solvent mixture was chosen since the two dimethylamino signals are almost shift equivalent in most halogenated hydrocarbon solvents (cf. refs. 8 and 9).

Table 1. Observed PMR shifts between unbound and adduct donor signals at slow donor exchange.

Donor	Group	Shift difference/ppm	t/°C
DMIPU	$(CH_3)_2N$—	0·32	+40
DEK	—CH_2—	0·70	−50
	—CH_3	0·32	−50
DMA	$(CH_3)_2N$—	0·49[a]	+40
	CH_3CO—	0·72[a]	+40
DMURET	$(CH_3)_2N$—	0·42	+10
	CH_3CH_2—	0·70	+10
	CH_3CH_2—	0·17	+10
MCET	$ClCH_2$—	0·75	−80
	CH_3CH_2—	0·30	−80
	CH_3CH_2—	0·52	−80
DMCARB	CH_3O—	0·27	−50
DMTCA	$(CH_3)_2N$—	0·51	−40

[a]Ref. 22

chemical shifts of the PMR signals of the unbound donor. In the presence of hydrogen halides, protonated complexes with the composition $DH^+MX_{n+1}^-$ and $D_2H^+MX_{n+1}^-$ are formed. (MX_n = $SbCl_5$;[22] BF_3.[23]) The $SbCl_5$ adducts also react with water to give ternary complexes of the composition $D{\cdot}H_2O{\cdot}SbCl_5$.[24] The exchange between donor bound in these ternary complexes and unbound donor has been observed to be rapid on the PMR time scale. Varying amounts of impurities in the samples will thus give rise to varying chemical shifts of excess donor, the observed shift being averaged over the unbound donor and ternary complexes.

The adduct PMR signal is shifted to low field and the shifts attenuate with increasing distance from the donor site.[25] Conjugative effects and conformational changes modulate these values, and consequently they are not a good measure of donor ability. This can for instance be seen by comparing the values for the dimethylamino signals in DMTCA and DMA in Table 1 with the $-\Delta H$ values for these compounds in Table 2, and analogously for the ethyl signals in DEK and MCET.

Donor exchange process

The mechanism of the exchange process is of fundamental importance for the interpretation of the NMR measurements. Three possible mechanisms have been considered in previous studies on similar systems.[2-5] (D = donor, A = acceptor).

$$DA \rightleftharpoons D + A \qquad \text{(I)}$$

$$DA + D^*A^* \rightleftharpoons DA^* + D^*A \qquad \text{(II)}$$

$$D^* + DA \rightleftharpoons D + D^*A \qquad \text{(III)}$$

The following rate expressions will then be valid for these cases:[26] (τ_{DA} = lifetime of DA, [X] = concentration of X and k = rate constant for the process)

$$\text{(I):} \quad \frac{d[DA]}{dt} = k[DA] \qquad (4)$$

$$\tau_{DA} = \frac{1}{k} \qquad (5)$$

$$\text{(II):} \quad \frac{d[DA]}{dt} = k[DA]^2 \qquad (6)$$

$$\tau_{DA} = \frac{1}{k[DA]} \qquad (7)$$

$$\text{(III):} \quad \frac{d[DA]}{dt} = k[DA]\cdot[D] \qquad (8)$$

$$\tau_{DA} = \frac{1}{k[D]} \qquad (9)$$

By studying the concentration dependence of τ_{DA}, the appropriate rate-determining step can be elucidated. The free donor concentration was varied for the DMCARB and DEK systems and τ_{DA} values for different excess donor concentrations were found equal within experimental error. Therefore exchange process (III) can be ruled out for these systems. Similarly, exchange process (II) can be tested for by varying the adduct concentration,

Table 2. Activation parameters for donor exchanges and literature values for enthalpies of $SbCl_5$ adduct formation.

Donor	$\Delta G^{\ddagger}_{298.2}$/ kcal·mol^{-1}	$\Delta H^{\ddagger}$/ kcal·mol^{-1}	$\Delta S^{\ddagger}$/ cal·mol^{-1}·K^{-1}	$-\Delta H$/ kcal·mol^{-1}
$ClCH_2COOEt$	(10·0)[a]	(13 ± 1)[b]	—	12·80 ± 0·01[d]
$(CH_3O)_2CO$	10·88 ± 0·16	15·7 ± 0·4	16 ± 1·7	15·17 ± 0·03[d]
$(C_2H_5)_2CO$[f]	12·2 ± 0·2	15·6 ± 0·4	11·3 ± 1·6	15·90 ± 0·05[d]
$(CH_3)_2NCOCCl_3$	10·92 ± 0·25	17·2 ± 1·0	21 ± 4	16·10 ± 0·05[e]
$(CH_3)_2NCOOEt$[g]	17·44 ± 0·10	24 ± 1	23 ± 3	22·37 ± 0·03[d]
$(CH_3)_2NCOCH_3$	(21)[c]	(27 ± 2)[b]	—	27·80 ± 0·08[d]

Error limits of activation parameters include random errors only and correspond to a 90% confidence level.

[a]$\Delta G^{\ddagger}_{298}$; [b]Assuming $\Delta S^{\ddagger} = 15 \pm 5$ cal·mol^{-1}·K^{-1}; [c]ΔG_{408}; [d]From ref. 7, 1,2-dichloroethane solution; [e]G. Olofsson, private communication; [f]Combination of rate constants from both methyl and methylene signals; [g]Combination of rate constants from both N- and C-methyl signals.

but practical problems arose when this was attempted for the DMCARB system, which was judged to be best suited for this purpose. Crystallization of adduct in the samples made an increase of adduct concentration almost impossible. Lowering this concentration to 0·15 M gave the puzzling result that although a plot of log τ versus $1/T$ still had the same slope, the exchange rates increased, which is not in agreement with any of the rate-determining steps (I)–(III). Possible rationalizations are that a solvent effect, arising from a decreased concentration of polar molecules, increases the exchange rate* or that exchange-promoting impurities become important at this concentration range. It seems difficult to investigate this fully.

$\Delta S^{\ddagger}$ is derived from the difference between $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ values. The $\Delta G^{\ddagger}$ value depends on the expression used when evaluating the rate constant from τ_{DA}. Positive activation entropies were obtained regardless of which of the expressions (5), (7) or (9) was used to evaluate k. A positive $\Delta S^{\ddagger}$ is expected for step (I) but not for (II) (or (III)). Therefore, the dissociative step (I) is considered to be rate determining in the systems studied. This has also been found to be the case in other similar systems.[4,5]

Literature values for the enthalpy change for the process $SbCl_5$(soln) + Donor(soln) → $SbCl_5$·Donor (soln) in 1,2-dichloroethane solution and observed activation parameters for the reverse process as measured in the present work are summarized in Table 2. The close agreement between the enthalpy for adduct formation and the activation enthalpy is illustrated in Fig 1. Some observations on $SbCl_5$-N,N′-alkylurea adducts[12] have been reconsidered in view of the results in the present work and have been included in Fig 1 with the assumption that $\Delta S^{\ddagger}$ for the donor exchange is similar in magnitude (10–20 cal.mol^{-1}.K^{-1}) to values for the systems where it could actually be measured. This assumption has also been applied to the MCET and DMA rate data. It is probably not possible to determine $\Delta H^{\ddagger}$ for the alkylurea adducts, in ref. 12, due to decomposition of the adduct at the required temperatures. Activation parameters for the MCET adduct are difficult to measure with certainty due to a complicated overlap of $-CH_2-$ and $-CH_2Cl$ signals. The difficulties in properly accounting for the DMA adduct spectra are discussed below.

Solvent effects may be significant for enthalpies of adduct formation as well as for activation parameters. However, similar solvents were used, and it is unlikely that the general trend, as illustrated in Fig 1, can be changed due to these effects. The close agreement between $-\Delta H$ and $\Delta H^{\ddagger}$ leads to the conclusion that $\Delta H^{\ddagger}$ for the process $SbCl_5$ + D → $SbCl_5$·D must be close to zero.

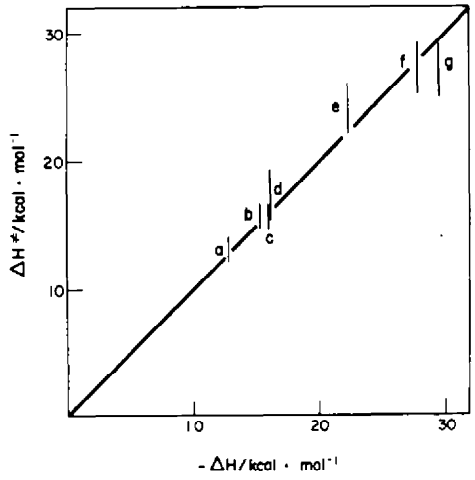


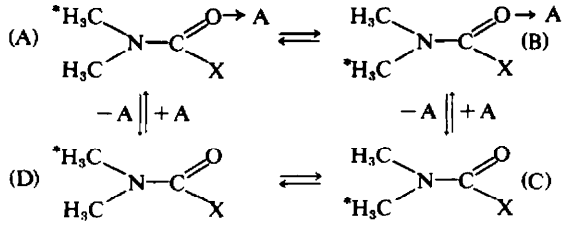
Fig 1. Enthalpies of adduct formation and observed or estimated activation enthalpies for adduct dissociation. The solid line corresponds to $\Delta H^{\ddagger} = 0$ for adduct formation. Where the activation enthalpies are measured (b-e) and not estimated (a, f, g) estimates of realistic error limits of those parameters have been made and combined with the random errors. (a) MCET (b) DMCARB (c) DEK (d) DMTCA (e) DMURET (f) DMA (g) tetramethyl- and 1,3-dimethylurea (from refs. 12 and 33).

*A small change in $\Delta G^{\ddagger}$ corresponds to a relatively large change in τ_{DA}.

Effects of adduct formation on barriers to internal rotation

The exchange scheme in Fig 2 is applicable to the amide systems studied. A detailed assignment of all four N-methyl signals at slow exchange is necessary if the rate constants for restricted rotation and donor exchange are not vastly different. This is true unless the two unbound amide N-methyl signals or the two adduct N-methyl signals have very similar shifts. Fortunately, in the DMIPU case the rate constants are quite different, in the DMURET case the two signals from the unbound donor have almost equal shifts and in the DMTCA case the two adduct N-methyl signals have very similar shifts.

Only one compound, DMIPU, could be studied without complications from exchange between



X = $-CCl_3$, $-OC_2H_5$, $-CH_3$ or $-NHCH(CH_3)_2$

Fig. 2. Exchange scheme for adducts of amide type molecules.

adduct and unbound donor. The coalescence temperature for restricted rotation about the amide bonds in this compound was found to increase 80° upon adduct formation with $SbCl_5$. The activation parameters and results from the study of amide barriers to internal rotation are summarized in Table 3.

For the DMTCA adduct (Fig 2), the exchanges (B) ⇄ (C) and (D) ⇄ (A) are the fastest, followed by (C) ⇄ (D). Therefore the exchange rate for (A) ⇄ (B) cannot be measured. For the DMURET system the donor exchanges (B) ⇄ (C) and (D) ⇄ (A) are slower than the restricted rotation in the free molecule, (C) ⇄ (D). Therefore the restricted rotation in the adduct molecule, (A) ⇄ (B) can be followed up to the point (60°) where the donor exchanges become fast or the PMR time scale. Since the donor exchange rate can also be measured from the ethyl PMR signals it could be judged with certainty that the restricted rotation in the adduct was still slow at 60°, since no contribution from this N—C rotation could be detected in the dimethylamino signal lineshape. Therefore this barrier must be at least 2·5 kcal.mol^{-1} higher than in the unbound molecule.

The full lineshape equations for the DMA system are more complicated since the spin-spin couplings are non-negligible, especially in the adduct PMR signals.[22] However the observations that the same relative order of exchange rates as in the DMURET system appears in this case and that $\Delta G^{\ddagger}_{T_c}$ for restricted rotation in the adduct is higher by an amount of at least 3 kcal.mol^{-1} as compared to the unbound molecule could be made with no lineshape calculations.

The significant increases of the torsional barrier to internal rotation in the adducts can be rationalized in terms of the electron withdrawing power of the acceptor molecule and O-coordination. The combined effect is an increased double-bond character of the amide bonds.

$\Delta S^{\ddagger}$ for the restricted rotation increases from −4 to +7 cal.mol^{-1}. K^{-1} on going from DMIPU to its adduct. A possible rationalization may be that in the very crowded adduct molecule steric interactions cause the entropy of the transition state to be higher than that of the ground state.

The measurements of adduct amide barriers in the present paper have been made with the presumption that the only two forms of amide present in the samples are unbound and adduct amide. Gore *et al.*[10] and Matsubasui and Tanaka[11] assumed in their studies of amide barriers that the only amide species in their samples was adduct amide. The latter two studies were made on samples having donor-acceptor ratios close to 1 and smaller than 1, respectively. In the latter two cases only one N-methyl doublet will be observed in the NMR spectrum at low temperatures. The coalescence of this doublet at increased temperatures is then of course due to an increased rate of rotation around the N—C bond, but the τ value corresponding to an observed lineshape is not necessarily equal to the rotation rate in the *adduct*. The occurrence of small concentrations of amide molecules in other forms than simple adduct may be of importance for the exchange rate between the two rotamers. Assuming that i types of amide molecules are present with fractions p_i, and that their rotamer exchange rates are given by τ_i, the apparent exchange rate (τ_m) as measured from the N-methyl PMR signal lineshape will be given by the expression (10).

$$\frac{1}{\tau_m} = \sum_i \frac{p_i}{\tau_i} \tag{10}$$

Eq. (10) is valid only if the intermolecular exchange of amide molecules between the different

Table 3. Amide barriers to internal rotation

Molecule	$\Delta G^{\ddagger}_{298.2}$/ kcal.mol^{-1}	$\Delta H^{\ddagger}$/ kcal.mol^{-1}	$\Delta S^{\ddagger}$/ cal.mol^{-1}.K^{-1}	Error est.	Ref.
$(CH_3)_2NCOOEt$	15·50 ± 0·06	14·1 ± 0·6	−4·6 ± 2·0	S	this work
$SbCl_5$ adduct	(>18)[a]	[b]	[b]	—	this work
$(CH_3)_2NCOCCl_3$	15·0 ± 0·1	15·1 ± 0·6	0·3 ± 2·3	S	23
$SbCl_5$ adduct	[c]	[b]	[b]	—	this work
$Me_2NCONHiPr$	9·7 ± 0·1	8·2 ± 0·2	−4·4 ± 1·0	R	16
$SbCl_5$ adduct	13·1 ± 0·1	15·3 ± 0·5	7·2 ± 1·5	S	this work
$(CH_3)_2NCOCH_3$	18·1 ± 0·1	18·3 ± 0·1	0·7 ± 1·0	R	27
$SbCl_5$ adduct	(>21)[d]	[b]	[b]	—	this work

Error estimation: R; random errors to a 90% confidence level.
S; including estimate of maximum systematic errors.
[a]ΔG_{330}; [b]Not accessible; [c]Exchange rate not greater than in unbound molecule; [d]ΔG_{408}

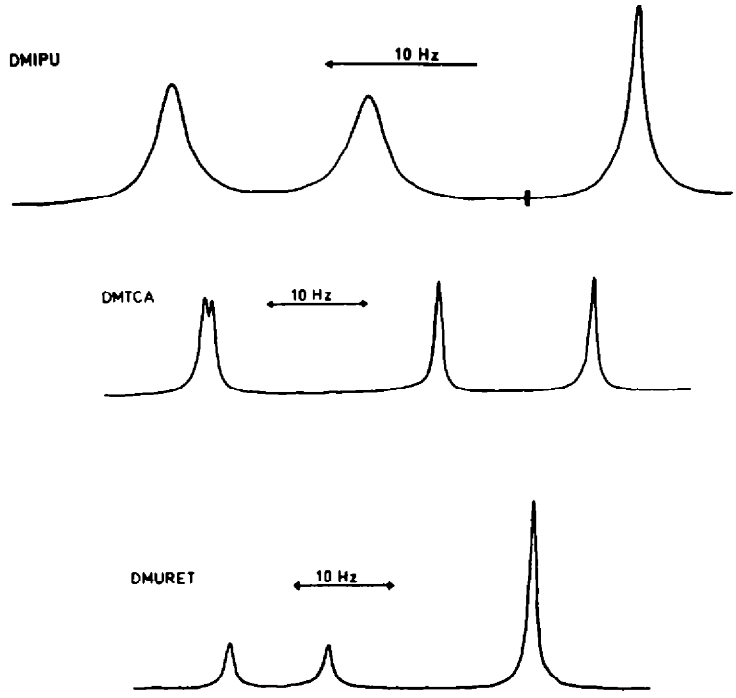


Fig. 3. Some examples of slow exchange spectra of the amide-type molecules studied. The field strength increases from left to right. The two signals at low field correspond to (A) and (B) in Fig. 2 and two (one) at high field to (C) and (D). The DMIPU spectrum was recorded at −35° and the (A) ⇄ (B) exchange leads to broadening of these signals at this temperature. The DMTCA spectrum was recorded at −70° and the DMURET spectrum at −9°.

species is rapid. It is reasonable to assume that this condition is fulfilled in systems where only one set of N-methyl signals is observed. Since amide adducts have low dissociation constants* the free amide concentration is extremely small if the donor-acceptor ratio is less than 1. However, some preliminary measurements on samples of DMURET·$SbCl_5$ adduct with excess $SbCl_5$ indicate that the τ_m values are much smaller than can be expected from estimates of dissociation constants and τ_f values for unbound and adduct DMURET. The only possible explanation is that a small fraction of a third species exists, with a very low N—C barrier. A possible molecule of this kind is an A(DA) adduct with one A coordinating to the oxygen atom and the other to the nitrogen atom. This adduct could very well be weak enough to be in fast exchange with free A and DA, exist to a small fraction and have a very low N—C barrier. Matsubasui and Tanaka[11] studied some benzamide-metal halide adducts and observed increased barriers relative to unbound benzamide for some metal halides, and decreased barriers for others. These results were interpreted O- and N-coordination, respectively. It is possible that this rationalization is in error and that the correct one is that the different metal halides give more or less strong A(DA) adducts. A distinction between these two alternative interpretations can be made by studying samples with donor in excess. This problem will be further investigated.

The situation is similar in the case of excess donor, and the four-site exchange scheme in Fig 2 applies to this situation. Since the τ_f values for unbound amide and adduct amide may differ by more than a factor 10^3 at the same temperature, even a small concentration of unbound amide can give a significant contribution to the total rotamer exchange rate. This may be of importance in samples with donor-acceptor ratios close to 1, as for instance in the study by Gore *et al.*[10]

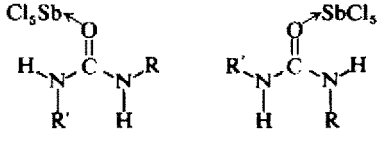
Small fractions of N-coordinated DA-adduct in the samples in equilibrium with O-coordinated DA-adduct may give a contribution to the rotamer exchange in samples of any composition. In any case, the adduct amide barriers quoted in the present paper and in previous studies are certainly not higher than the "true" adduct amide N—C barriers.

Since the effects on the barriers to internal rotation are considerable it is possible to raise barriers too low to be studied in the unbound molecule to an observable value and thus obtain an estimate of

*For example, the dissociation constants for the DMA and DMURET $SbCl_5$ adducts are too low to be measured by calorimetric methods.[7]

the former barrier. One such example is tetramethylurea, where the amide barrier is too low to permit a measurement by NMR.[28] The $SbCl_5$ adduct of this molecule has been studied by NMR[12] and a restricted conformational exchange with t_c around $-50°$ was actually observed. At the time of the study sufficient evidence that this was due to restricted rotation was not available. The possibilities that $SbCl_5$ exchange between two preferred bond directions at the carbonyl oxygen[29] is the rate determining step or that $SbCl_5$ actually coordinates to nitrogen and that the spectra observed[12] are due to exchange between the two nitrogen atoms seem now to have been ruled out. The latter possibility is unlikely in view of a study of ^{15}N-labeled 1,3-dimethylurea adducts[30] and the former seems unlikely since the adduct of the cyclic dialkylurea analog 2-oxo-5,5-dimethylhexahydropyrimidine ($CH_2NHCONHCH_2C(CH_3)_2$) shows no intramolecular exchange in NMR spectra down to at least $-70°$. In ketones the former exchange is also much faster.[29]

It seems however that the possibility of two preferred bond directions at the carbonyl oxygen is still of importance, in particular for 1,3-dialkylurea adducts. In the unbound compounds there are four possible conformations of amide groups, of which at least two have been observed for 1,3-dimethylurea at low temperatures in MeOH.[31] In the less polar solvent $CHFCl_2$, probably only one conformation exists to a measurable extent, which may be the reason why no lineshape changes due to restricted rotation can be observed by PMR in that solvent even at $-120°$.[32] However, in the $SbCl_5$ adducts this conformational preference is altered and the two preferred conformations are the following:[12]



The arguments above suggest that restricted rotation around the amide bonds is the rate-determining step for exchange between these two conformers.

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