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CONCERTED CONFORMATIONAL EXCHANGE PROCESSES IN MOLECULAR ADDUCTS OF ANTIMONY PENTACHLORIDE AND N,N′-ALKYLUREAS

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Abstract—A variable temperature proton magnetic resonance (PMR) study of 1:1 molecular adducts between antimony pentachloride and *sym*-di-, tri- and tetramethylurea, 1-ethyl-, 1-isopropyl- and 1-isobutyl-3-methylurea and N,N′-dimethyl-2-imidazolidone has been carried out. Separate signals ascribed to free and complexed donors were observed at room temperature. In systems of di-, tri- and tetramethylurea the donor–donor exchange became rapid on the NMR time scale at 130°.

At low temperatures the signals from the 1,3-dialkyl- and tetramethylurea adducts separated into two sets revealing an exchange between conformational isomers. The activation parameters for a two-site exchange of each alkylamino group in the ethylmethylurea adduct were determined from a total lineshape treatment of the PMR signals. The two groups gave the same values within the combined uncertainties of the measurements of $\Delta G^{\ddagger}$ (16·0 ± 0·1 kcal mol^{-1}) and $\Delta H^{\ddagger}$ (15·0 ± 0·6 kcal mol^{-1}). From observed population ratios and the results of the total lineshape treatment, the conformational exchange of $SbCl_5$-1-R-3-R′-alkylurea adducts is judged to be a concerted rearrangement of the adduct molecule, consisting of inversion of $SbCl_5$ at the oxygen atom coupled to an interlocked rotation of the alkylamino groups.

INTRODUCTION

NUMEROUS NMR studies of Lewis acid-base systems since 1960 have included attempts to establish relative scales of base strength for electron pair donors and of acceptor strength for electron acceptors, especially metal halides.[1,2] Gore *et al.*[3] have studied the variable temperature PMR study of molecular adducts between $SbCl_5$ and N,N–dimethylformamide, and Gillespie and Hartman[4] have investigated intermolecular exchange reactions in systems of BF_3 and methyl ketones. An intramolecular reorientation was recently observed in a low temperature study of the BF_3-diethyl ketone system,[5] which was interpreted in terms of BF_3 exchange between two equivalent bonding sites at the carbonyl oxygen atom arising from a nonlinear C═O—B bond. The present variable temperature PMR study of molecular adducts between $SbCl_5$ and N,N-alkylureas was undertaken to determine whether an analogous rearrangement could be observed in the urea adducts. Indications of C═O—Sb bond angles less than 180° in $SbCl_5$ adducts in solution have been found from measurements of formation enthalpies for a series of alkyl ketone adducts.[6] To minimize intermolecular associations and solute–solvent interactions, dilute solutions in an inert solvent were used in this study.

RESULTS

In the PMR spectra of all urea–$SbCl_5$ systems studied, separate signals ascribed to the 1 : 1 adduct and donor present in excess were observed at room temperature.* The adduct signals appeared at lower field and their chemical shifts relative to that of the solvent did not change noticeably with temperature or composition of the sample. The results of the experiments are summarized in Fig. 1, except for those involving *i*BMU (see Fig. 3), which gave the following changes in chemical shifts upon adduct formation (ppm): $HNC\underline{H}_3$ (0·40), $N\text{-}C\underline{H}_2$ (0·27), $CH(C\underline{H}_3)_2$ (0·12). The change in chemical shift upon adduct formation is defined as the difference between the chemical shift found for the adduct and that for donor in dilute solution. This procedure was adopted since changes in shift determined from spectra of samples containing adduct with donor in excess did not give reproducible results. The shift of the adduct signals did not change, but the

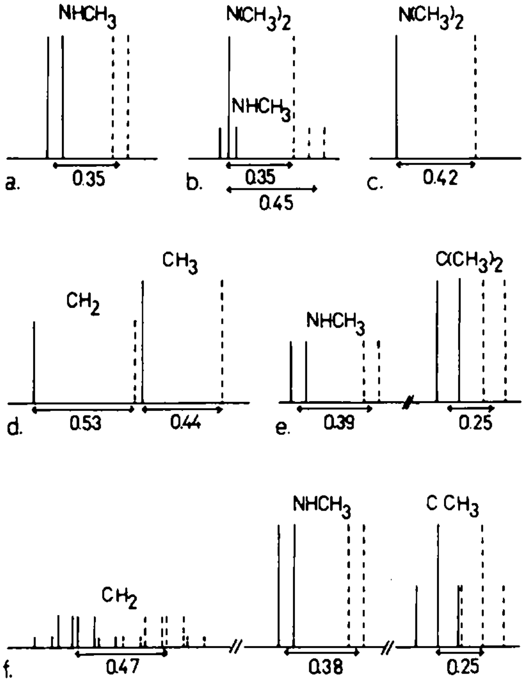

FIG 1. Schematic PMR spectra at 40°C of N,N′-alkylureas and of $SbCl_5$-alkylurea adducts in CH_2Cl_2 solution. Broken lines represent alkylureas and full drawn lines the adducts. The changes in chemical shift upon adduct formation in ppm are indicated. The H_0- field increases from left to right in the schematic spectra. (a) DMU, (b) TrMU, (c) TMU, (d) DMI, (e) iPMU, (f) EMU.

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* The abbreviations given after the structural formula of the donor compounds will be used in the following: $(CH_3NH)_2CO$, DMU; $(CH_3)_2N(CH_3NH)CO$, TrMU; $[(CH_3)_2N]_2CO$, TMU; $C_2H_5NH(CH_3NH)CO$, EMU; i-$C_3H_7NH(CH_3NH)CO$, iPMU; i-$C_4H_9NH(CH_3NH)CO$, iBMU and $\overline{N(CH_3).(CH_2)_2.N(CH_3).CO}$, DMI.

chemical shifts of the excess donor were found to vary between different samples, presumably due to acidic impurities introduced during sample preparation.

At the concentration used in the PMR analyses it was not possible to study the signals from the methine hydrogen in the spectra of the iPMU and iBMU adducts.

The di-, tri- and tetramethylurea adducts were studied at high temperatures in tetrachloroethane solution, and separate signals for free donors and adducts persisted to 130° (60 MHz). At about this temperature, exchange broadening was observed but at the same time irreversible degradative processes started to take place in the samples.

The spin coupling of the NH proton to adjacent Me and methylene protons observed in samples of alkylureas in solution was also seen in the adducts. When traces of, e.g. HCl were added to solutions of alkylureas, the coupling disappeared due to fast proton exchange, whereas the coupling in the adducts in samples containing no unbound $SbCl_5$ seemed to be insensitive to acidic impurities. In samples containing free $SbCl_5$, the NH proton coupling disappeared at about the coalescence temperature of the duplicate set of adduct signals (see below), while with donor present in excess it persisted up to temperatures at which donor–donor exchange began to become rapid.

TABLE 1. PMR SPECTRAL PARAMETERS OF THE LOW TEMPERATURE DOUBLET SETS OF SIGNALS OF THE N,N′-ALKYLUREA-$SbCl_5$ ADDUCTS (CH_2Cl_2 SOLUTIONS)

Donor	Group	Shift separation/ppm	$^3J_{CHNH}$/Hz	T_C/°C
DMU[a]	$NHC\underline{H}_3$	0·111	4·8; 5·3	32 ± 5
EMU[b]	$NHC\underline{H}_3$	0·108	4·6; 5·3	30 ± 3
	$NHC\underline{H}_2^-$	0·29	[c]	[c]
	$CC\underline{H}_3$	0·041	—	20 ± 5
*i*PMU[b]	$NHC\underline{H}_3$	0·130	4·8; 5·2	−5 ± 5
	$C(CH_3)_2$	0·02	—	−20 ± 5
*i*BMU[a]	$NHC\underline{H}_3$	0·12	5; 5	15 ± 5
	$NHC\underline{H}_2^-$	0·34	[c]	22 ± 8
	$C(C\underline{H}_3)_2$	0·07	—	5 ± 5
TrMU[a]	$N(C\underline{H}_3)_2$	0·173	—	0 ± 3
TMU[a]	$N(C\underline{H}_3)_2$	0·107	—	−46 ± 3

[a] At 60 MHz
[b] At 100 MHz
[c] Not determined

At lower temperatures the proton NMR signals of the N,N′-alkylurea adducts separated, *via* an intermediate broadened signal into two sets of signals. However, for the TrMU adduct, the signal from the CH_3NH group remained unchanged down to −80°. Examples of low temperature PMR spectra are shown in Figs 2 and 3, and the shift separations, coupling constants, $^3J_{CHNH}$, and the coalescence temperatures are summarized in Table 1. The results are given for samples containing donor in excess, except for those involving iPMU and iBMU where signals from free donors overlapped the adduct signals. The two sets of signals which appear at low temperatures are obviously indications of an exchange between conformational isomers that has become slow on the NMR time scale. The spectra of the 1-R-3-R′-alkylurea adducts (R≠R′), particularly the

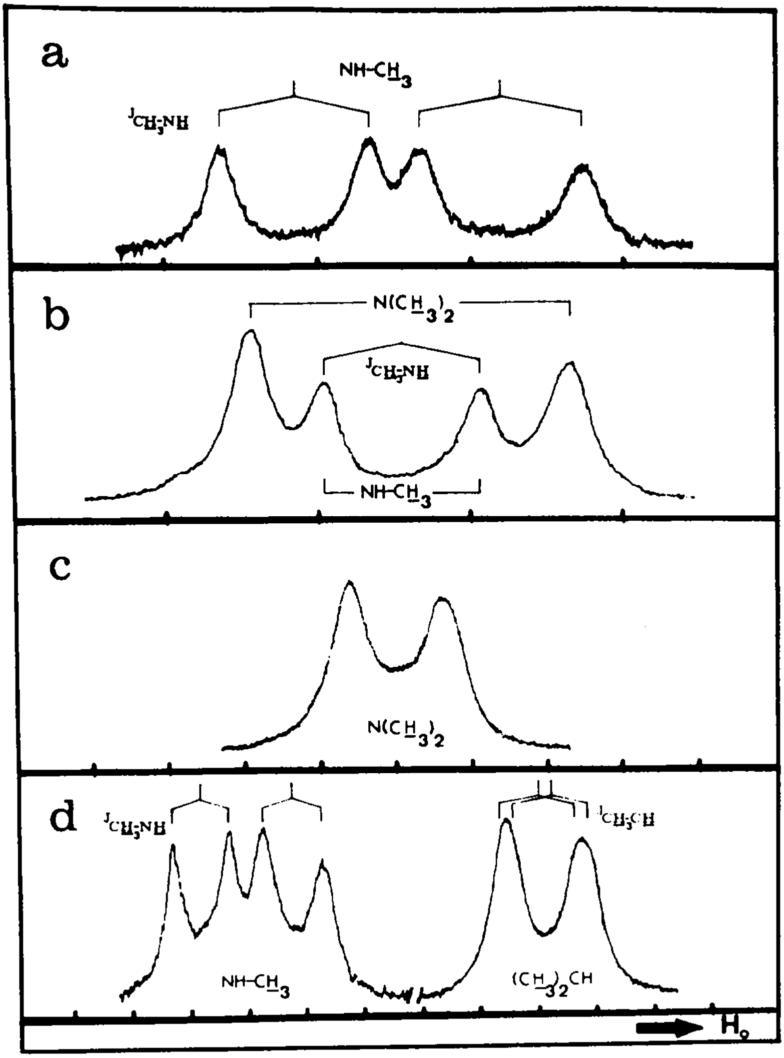

FIG 2. 60 MHz spectra of doublet adduct methyl signals at low temperatures. The marks are at 5 Hz intervals. Notice the changes in horizontal scales. (a) DMU.SbCl$_5$ at 0°. (b) TrMU.SbCl$_5$ at −40°. (c) TMU.SbCl$_5$ at −57°. (d) iPMU.SbCl$_5$ at −55°. The two signals are recorded at different gains. The $(CH_3)_2CH$ splitting is resolved at 100 MHz.

iBMU adduct, contained valuable information for the interpretation of the exchange process.

The two alkylamino groups were assumed to be involved in two-site exchanges $A \rightleftharpoons B$ and $C \rightleftharpoons D$:

$$R_{(A)}NHCOR'NH \rightleftharpoons R_{(B)}NHCOR'NH$$

$$RNHCOR'_{(C)}NH \rightleftharpoons RNHCOR'_{(D)}NH$$

For the moment we leave the molecular details of this process open.

From analysis of spectra of the EMU, iPMU and iBMU adducts equal population ratios, A/B = C/D (or D/C) were found for all three adducts, which shows that the motions of R and R′ are correlated. The population ratios were close to 1 : 1 for the EMU and iPMU adducts, while for the iBMU adduct the ratio was found to be about 0·75 : 1. The population ratios were derived from the total line shape treatment in the case of the signals of the EMU adduct (see below), and by relative area measurements of the spectra in the case of the iPMU adduct. The population ratio for the $(C\underline{H}_3)_2CH$ group in the iBMU adduct was determined by comparison between simulated and observed spectra. Through relative area measurements it was found that the same ratio was applicable to the signals of the $C\underline{H}_3NH$ group.

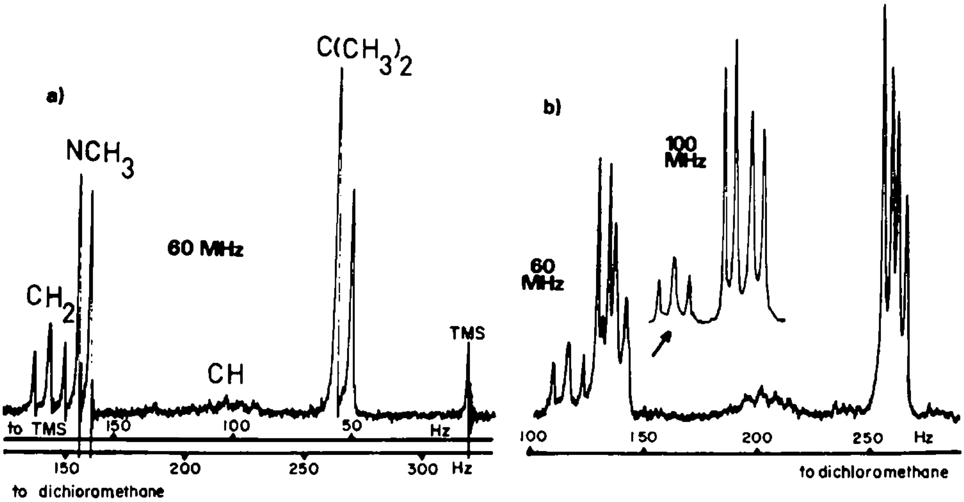

FIG. 3. (a) iBMU at 36° and (b) iBMU . $SbCl_5$ at −25° (in CH_2Cl_2). Spectrum (b) is composed of two equivalent sets of signals with relative intensities of 1 :0·75. The NCH_3 signals overlap one of the CH_2 triplets in (b). The CH_2 signals are triplets due to almost equal spin coupling to the CH and NH protons, the NCH_3 signals are doublets due to spin coupling to NH, and the $C(CH_3)_2$ and CH groups show spin coupling to each other and second order effects due to the small shift difference between them.

For 1-ethyl-3-methylurea a total lineshape treatment of the adduct signals was performed to evaluate rate constants and activation parameters for the exchange process.* The signals from the 1- and 3-substituents were treated separately. Theoretical spectra for various exchange rates between two sites were calculated, and some examples of simulated and experimental spectra are given in Fig. 4a and b. The resulting values, with estimated error limits, are given in Table 2. The two alkylamino groups give the

TABLE 2. ACTIVATION PARAMETERS FOR THE DYNAMIC EXCHANGE PROCESS INVOLVING THE ALKYLAMINO GROUPS IN THE EMU.$SbCl_5$ ADDUCT

	$\Delta G^{\ddagger}$/kcal.mol^{-1}	$\Delta H^{\ddagger}$/kcal.mol^{-1}	$\Delta S^{\ddagger}$/cal.mol^{-1}.K^{-1}
N—$C\underline{H}_3$	16·05 ± 0·10	14·6 ± 0·7	−4·9 ± 2·7
N—CH_2—$C\underline{H}_3$	16·00 ± 0·10	15·4 ± 0·5	−2·0 ± 2·0

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* A total lineshape treatment was not considered meaningful for the iPMU and iBMU adducts due to the small shift separation at slow exchange in the former case and overlapping signals in the latter case.

same results within the combined uncertainties of the measurements. The population ratio found (A/B = C/D) corresponds to $\Delta G_{298} = 0{\cdot}011$ kcal.mol^{-1}. The agreement between calculated and observed spectra was not as good as we have found for other systems presumably due to impurity signals which appeared in the sample after sealing the tube with a flame torch. Their origin was probably traces of pyrolysis products of the solvent. The accuracy in the determination of the rate constants from the $NC\underline{H}_3$ spectra at temperatures near coalescence was therefore probably not better than ± 20 per cent whereas it was probably better than ± 10 per cent for $N—CH_2—C\underline{H}_3$. This was considered in the estimation of errors in the activation parameters given in Table 2.

With excess $SbCl_5$ in the sample, the signal of the TMU.$SbCl_5$ adduct remained a singlet down to at least $-100°$. Such a drastic lowering of the coalescence temperature was not observed for the other adducts, but at least in the case of DMU.$SbCl_5$ the coalescence temperature decreased 10 to 15° upon addition of excess $SbCl_5$.

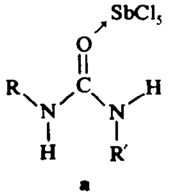
The signals of the DMI adduct remained unchanged down to $-70°$. It was not possible to lower the temperature any further due to the low solubility of the adduct.

DISCUSSION

In principle, either oxygen or nitrogen can act as the electron pair donor atom in urea adducts. It is evident from structural studies of solid $(NH_2)_2COH^+NO_3^-$ and $CH_3NH(NH_2)COH^+NO_3^-$ that the carbonyl oxygen is the most basic atom in urea and N-alkylureas.[7, 8] The changes in the chemical shifts upon adduct formation observed for the N-Me protons are of the same magnitude for alkylureas, dimethylacetamide[9] and dimethylformamide.[10] This supports oxygen coordination in the alkylurea adducts, as $SbCl_5$ is known to coordinate to oxygen in amide adducts. In solid $SbCl_5.HCON(CH_3)_2$, the C=O—Sb angle is 124·5° and Sb lies in the $HCONC_2$ plane on the same side as the formyl hydrogen.[11]

The strong donor–acceptor interaction in the alkylurea adducts, as revealed by for instance the high–ΔH values (~30 kcal.mol^{-1}) for the formation of the adducts in solution,[12] is reflected in the slow donor–donor exchange observed up to 130° in samples containing donor in excess. As can be seen in Fig. 1, the changes in chemical shifts upon adduct formation are roughly the same for equivalent groups in different alkylureas.

The strict correlation between the two alkylamino groups in the 1-R-3-R′-alkylurea adducts shown by the population ratios and by the activation parameters of the EMU adduct is not expected to arise unless the $SbCl_5$ part of the adduct molecule is involved in the conformational exchange. In alkylureas as well as in adducts, two alkyl groups on different nitrogen atoms in a position *trans* to the carbonyl group will encounter steric interference. $SbCl_5$ can for steric reasons be expected to bind preferably at the lone electron pair *cis* to a hydrogen atom. The stable conformers of the 1-R-3-R′-alkylurea adducts can therefore be assumed to be as follows.



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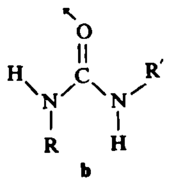

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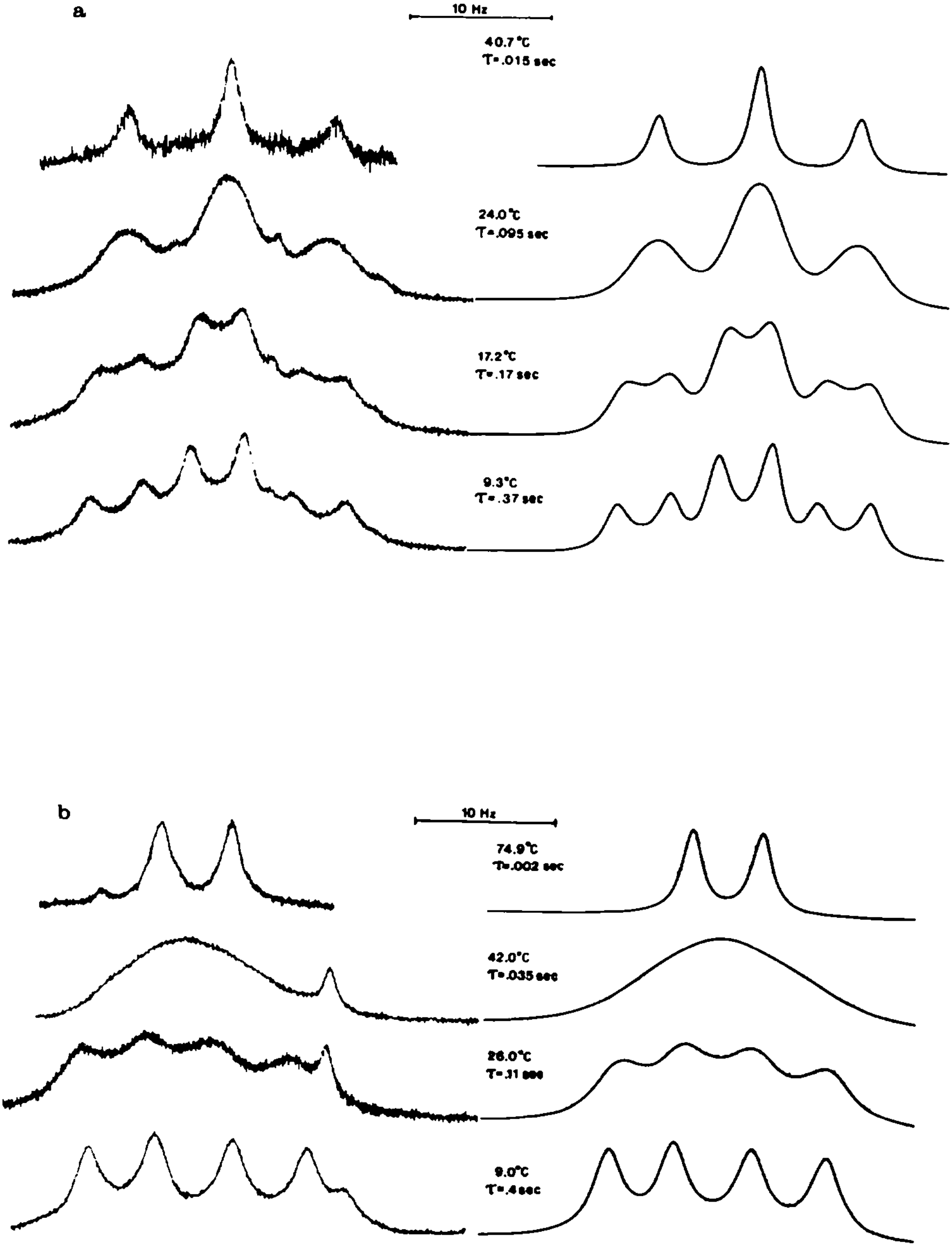

FIG 4. Examples of experimental and calculated 100 MHz spectra of the EMU.SbCl$_5$ adduct at various temperatures. (a) $C\underline{H}_3CH_2$, (b) $C\underline{H}_3$—NH. The additional signals are discussed in the text.

The interconversion of conformer **a** to conformer **b** will then entail a synchronous change of positions for $SbCl_5$ and the two alkyl groups and can accordingly be described as a concerted rearrangement of the adduct molecule, consisting of the inversion of the $SbCl_5$ moiety at the carbonyl bond coupled to an interlocked rotation of the alkylamino groups.

The evidence for the nature of the conformational exchange in the tri- and tetramethylurea adducts is not as conclusive as in the case of the 1,3-disubstituted urea adducts. The separation of the TMU adduct signal into two equally intense singals below $-46°$ is probably due to a slowed down exchange (on the NMR time scale) of $SbCl_5$ between two equal bonding sites, i.e. between two lone electron pairs of the oxygen atom. Asymmetric bonding at the C=O bond will give rise to magnetically non-equivalent dimethylamino groups in the adduct molecule.

In the low-temp. spectra of the TrMU adduct, only the $N(CH_3)_2$ signal is doubled. For this adduct an interpretation of the exchange process in terms of an increased rotational barrier about the C(O)—N bond is a likely possibility. Slow rotation of the $N(CH_3)_2$ group in trimethylurea has been observed at temperatures below $-95°$.[13] The barrier to internal rotation about the C(O)—N bond in dimethylformamide has been observed to increase upon adduct formation,[3] and increased conjugation across the N—C(O)—N moiety can also be expected in the alkylurea adducts.

EXPERIMENTAL

Materials

1-Ethyl-3-methylurea was synthesized from methylamine and ethylisocyanate in C_6H_6. 1-Isopropyl-3-methylurea and 1-isobutyl-3-methylurea were synthesized in the same way, using methylisocyanate and the corresponding amines. To our knowledge the latter compound has not previously been reported. A m.p. of +43° (uncorrected) was found for the iBMU sample and the samples of EMU and iPMU had m.ps in agreement with literature. Tetramethylurea (Schuchardt) was fractionally distilled at reduced pressure. The samples of trimethylurea and N,N′-dimethyl-2-imidazolidone are described in ref 12. 1,1,2,2-Tetrachloroethane was fractionally distilled before use. The following substances, which were commercially available, were not further purified: *sym*-Dimethylurea (Fluka AG), MeOAc (BDH) and CH_2Cl_2 (Fluka AG, spectroscopic grade). All substances were dried with 4A Molecular Sieves before use. They were judged to be pure from PMR analyses. $SbCl_5$ (Merck), chromatographic grade, was used without further treatment.

Samples

The samples were prepared directly in the PMR tubes by mixing (under cooling) known amounts of donor with $SbCl_5$ in solution. The concentration of the adduct in the samples was 0·5 mol.l.^{1} in the studies of EMU, iPMU and iBMU, and 0·3 mol.l.^{1} for the other ureas. They contained in addition either 0·1 mol.l.^{1} of $SbCl_5$ or 0·3 mol.l.^{1} of the donor in excess. The sample used for the lineshape study initially contained 0·95 mol.l.^{1} of EMU:$SbCl_5$ and a small excess of $SbCl_5$. This excess was scavenged by the addition of MeOAc, since with free $SbCl_5$ present in the sample the rate of NH proton exchange became similar to the rate of the exchange process under study, and if the donor was present in excess an unacceptable overlap between signals of adduct and free donor occurred. Only the DMI adduct showed limited solubility in CH_2Cl_2 at low temp. The concentration of the samples containing only donor compound was 0·3 mol. l.^{1}. The PMR tubes were sealed with Wilmad Glass Co. polyethylene plugs, except in the lineshape study where the tubes were permanently sealed with a flame torch.

Apparatus and measurements

NMR spectra were obtained using Varian A-60A, XL-100 and HA-100 NMR spectrometers equipped with variable temperature probes and V-6040 temperature controllers.

For the temperature measurements in the study of EMU–$SbCl_5$, an internal capillary tube containing benzyl alcohol and CH_2Cl_2 was used. The temperature-dependent shift difference between the —CH_2— and

—OH PMR signals had been precalibrated using standard techniques.[14, 15] The estimated accuracy was better than ±0·4°. All other temperatures were taken from the V-6040 dial and are believed to be accurate to ±3°. The solvent signal was used as internal PMR shift reference instead of TMS, which was found to decompose in samples containing $SbCl_5$. The chemical shifts were determined directly from the calibrated charts.

Lineshape measurements and calculations

Theoretical spectra for a two-site spin exchange process were calculated from the equation of Gutowsky, McCall and Slichter[16] and were plotted by means of a UNIVAC 1108 computer equipped with a Calcomp 563 plotter. The parameters in the equation were in this case (i) τ_j, the mean life time of the spins at the site j, (ii) p_j, the spin population at the site j, (iii) $T_2^{eff}{}_j$, the effective spin–spin relaxation time at the site j, (iv) $\Delta\nu$, the chemical shift difference for the spins at the two sites, and (v) J_{jp}, the spin–spin coupling constants characterizing the spin couplings of the spins at site j with other spins p. In the evaluation of these parameters a visual comparison of theoretical and experimental spectra was made. Values of T_2^{eff} and J were determined at the slow and fast exchange limits. The J's were found to be temp. independent and could hence be taken as constants, while the T_2^{eff}-values at low and high temp. were not the same, and a linear interpolation was performed to find the T_2:s at intermediate temp. $\Delta\nu$ and p_j could only be evaluated at temps below the coalescence point and linear extrapolations were performed to obtain the high-temp. values. At temp. below coalescence, the τ-values could be evaluated simultaneously with p and $\Delta\nu$, and at higher temps τ was determined at fixed values of all of the other parameters.

The free energy, enthalpy and entropy of activation values were calculated from the theory of absolute reaction rates, assuming the transmission coefficient to be unity.

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