Nuclear Magnetic Resonance Investigations of Carbonium Ion Intermediates. Part IV.[1] Study of the Intermediates involved in the Reaction between Carboxamides and Lewis Acids (Extended Vilsmeier Reaction) by ^1H and ^{13}C Nuclear Magnetic Resonance Spectroscopy †

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Structural and dynamic ^1H and ^{13}C n.m.r. spectroscopy have been used to study the reaction between *N*-substituted carboxamides and Lewis acids. The complex kinetics are explained by the formation of new intermediates and self-condensation compounds whose structure is demonstrated by ^{13}C n.m.r. Hindered rotations around C–N bonds in the starting materials are also measured by ^1H and ^{13}C resonance with a view to discussing the nucleophilicity of carboxamides. A second-order exchange reaction is shown to occur in alkyl-substituted iminium salts and activation parameters are computed.

In the course of our study of the reaction between dimethylformamide (DMF) and oxygenated Lewis acids we have shown, on the basis of n.m.r. arguments,[2] that the electrophilic intermediates of the Vilsmeier–Haack reaction are ionic compounds with the iminium salt structure (1). It has also been proved that in relatively highly concentrated media (*ca.* 1M) the formation of the complexes follows equilibrated second-order kinetics [3] associated with important solvent effects. Moreover the Vilsmeier reagents (1) may be considered good Lewis acids since they react with DMF in the same way as do $POCl_3$ or $SOCl_2$ and undergo nucleophilic attack from halide anions.[4]

$[(CH_3)_2N\overset{...}{-}CHCl]^+B^-$ (1) $R^1{}_2NCOR^2$ (2)

When amides other than DMF are used with Lewis acids in the carbonylation process, it has been shown from a synthetic point of view [5,6] that complications occur. However Brederek *et al.*[5] have succeeded in preparing an amino-ketone by heating a mixture of substituted amides and $POCl_3$. Similarly Janousek and Viehe [7] have obtained malonodiamides from dichloromethylenedimethylammonium chloride and dimethylacetamide (DMA). More recently Linda *et al.*[8] have studied the kinetics of the acetylation of aromatic heterocycles with the dimethylacetamide–phosgene complex. To our knowledge no work has been done on the mechanism of the formation of electrophilic intermediates derived from substituted carboxamides (2) and Lewis acids. Owing to the theoretical and practical interest of this question, in this paper, we shall report structural and dynamic results related to the mechanism of the reaction between carboxamides and Lewis acids.

EXPERIMENTAL

Materials.—The reagents used were carefully dried and distilled twice except for solid amides which were recrystallized.

The reaction of carboxamides (0.01 mol) with Lewis acids (0.011 mol) at 273 K in CH_2Cl_2, $CHCl_2{\cdot}CHCl_2$, or MeCN resulted in the formation of (3) as the chief product, accompanied in the case of (3a and b) by small amounts of the self-condensation product (4). If the temperature was

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[1] Part III, G. Jugie, J. A. S. Smith, and G. J. Martin, *J.C.S. Perkin II*, 1975, 925.

[2] G. J. Martin and M. L. Martin, *Bull. Soc. chim. France*, 1963, 1637.

[3] G. J. Martin and S. Poignant, *J.C.S. Perkin II*, 1972, 1964 (in this reference, the frequency factor *A* is expressed in min^{-1}).

[4] G. J. Martin and S. Poignant, *J.C.S. Perkin II*, 1974, 642.

[5] H. Brederek, R. Gompper, and K. Klein, *Chem. Ber.*, 1959, **92**, 1456.

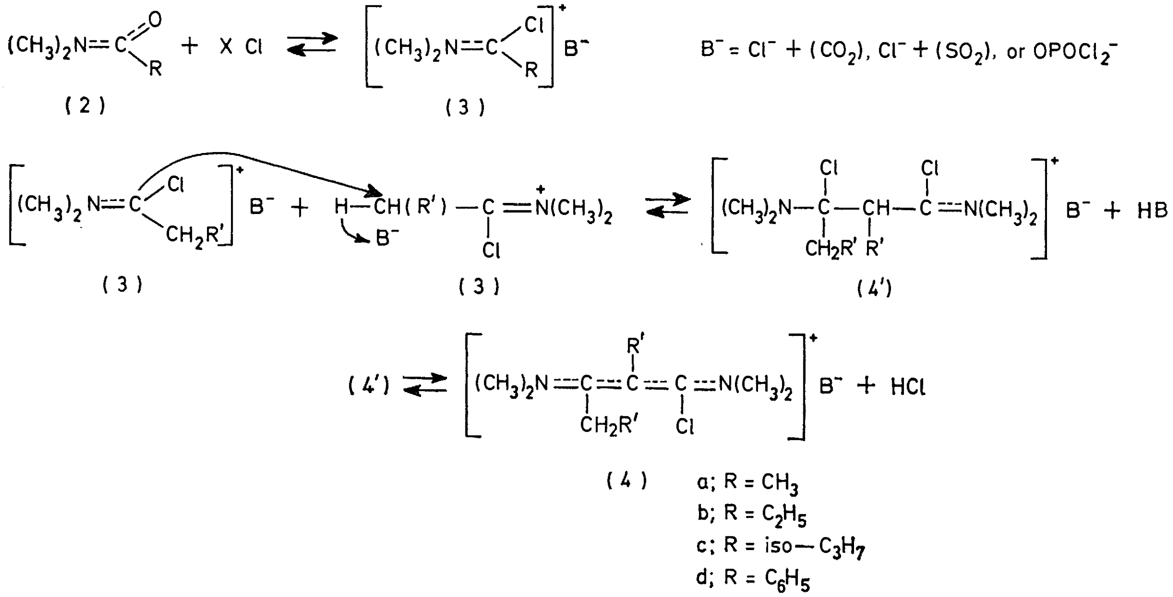
[6] R. Buyle and H. G. Viehe, *Tetrahedron*, 1968, **24**, 4217.

[7] Z. Janousek and H. G. Viehe, *Angew. Chem. Internat. Edn.*, 1971, **10**, 574.

[8] P. Linda, A. Lucarelli, G. Marino, and G. Savelli, *J.C.S. Perkin II*, 1974, 1610.

lowered to 210—220 K ($COCl_2$) the complex (3a or b) was produced almost exclusively (98%). When the reaction was carried out with (2c or d), no self-condensation adduct was formed and (3c or d) was obtained quantitatively. The solvent was evaporated under vacuum and the complexes were obtained as crystals or oils depending on the carboxamide used. Owing to their highly hygroscopic nature the complexes were prepared and transferred to the n.m.r. tubes in air-tight apparatus flushed with dry argon.

The self-condensation adducts (4a and b) were prepared from the reaction of carboxamides (0.01 mol) and $POCl_3$ (0.011 mol) at 330 K or by heating a solution of pure complex (3a or b) in $CHCl_2{\cdot}CHCl_2$. The pure adducts (4a and b) were oily, slightly hygroscopic products which could be diluted in an appropriate solvent and transferred in the n.m.r. tube.



SCHEME Self-condensation of (3) occurs for R = CH_3 and C_2H_5 but not for R = iso-C_3H_7 and C_6H_5 (see text)

Kinetics experiments were performed in an n.m.r. tube following the procedure previously described.[3,4]

Dynamic Magnetic Resonance.—^{13}C Spectra were recorded with a Varian XL 100-12 spectrometer operating at 25.2 MHz and fitted with a Varian 16 K computer. The acquisition time (and pulse delay) was 4 s (0 s) and 0.8 s (3.2 s) in the experiments run to measure $\Delta\nu_\infty$ and $J(^{13}C–H)$, and the coalescence figures, respectively. The spectra were obtained in the proton noise decoupled mode for chemical shift and coalescence studies, but without proton decoupling for $J(^{13}C–H)$ measurements. Most of the $J(^{13}C–H)$ values were also measured with greater accuracy on the proton satellite spectra. The spectrometer was internally locked on 100% [$^2H_6$]DMSO contained in a coaxial cell. Temperatures were controlled by a Varian V 4341 variable temperature accessory carefully checked by means of a thermocouple and readings were taken before and after each run.

RESULTS AND DISCUSSION

Structural Features.—On reacting (2) with $POCl_3$, $SOCl_2$, or $COCl_2$ two major electrophilic intermediates are characterized. The first step gives a complex (3) analogous to (1) and this compound thermally interconverts into a self-condensation product (4) whose structure depends on the nature of R (see Scheme).

The ^1H and ^{13}C chemical shifts of both amides and complexes are listed in Table 1. It is interesting to note that the equivalence observed for the $(CH_3)_2N$ protons of some complexes is fortuitous. Well resolved diastereotopy is observed for the corresponding carbon atoms, which makes the study of exchange processes by dynamic carbon resonance possible. The δ values are characteristic of charged species although the replacement of $\cdots C\cdots O$ by $\cdots\overset{+}{C}\cdots Cl$ does not alter the carbon resonance much.[9] A similar trend is shown by the behaviour of the $^1J(^{13}C–H)$ values which are 144—146 Hz for the complexes compared with 138—139 Hz for the amides.[1] A high field shift with respect to $POCl_3$ [$\delta(^{31}P)$ shifts from +3.5 for $POCl_3$ to −6 to −8 p.p.m. for (3) relative to H_3PO_4] is also observed for the phosphorus resonance in the complex; this shift agrees with the anionic nature of the phosphoryl group.

The ^{35}Cl quadrupole resonance studies of the solid compounds confirm the above formulation; the n.q.r. frequencies observed are characteristic of a covalent $C–^{35}Cl$ bond.[1]

The proposed structures of the self-condensation adducts (4) are best supported by the ^{13}C spectra as the ^1H signals provide no definite proof owing to the fortuitous equivalence of the methyl groups: (4a; B = Cl), ^1H $\delta(CH_2Cl_2;\ Me_4Si)$ 3.37 [2 × $N(CH_3)_2$], 2.52 (CCH_3), and 5.29 (CH); ^{13}C $\delta(CDCl_3)$ 42.8 and 43.0 [2 × $N(CH_3)_2$], 20.0 (CCH_3), 90.8 (CH), and 155.3 and 170.5 (CCH_3 and CCl) ($J_{CH} \simeq$ 148 Hz); (4b; B =

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[9] G. Olah, *J. Amer. Chem. Soc.*, 1974, **96**, 884.

TABLE 1

Chemical shifts (in p.p.m. from Me_4Si) of protons and carbon atoms of amides (2) and complexes (3). $\delta(^1H)$ Values are measured at 315 K in CH_2Cl_2 and $\delta(^{13}C)$ values at 305 K in $CDCl_3$. δ(H-3) and δ(C-3) refer to the atom α to C-2

		Amides $\overset{1}{(R^1CH_2)_2}N{-}\overset{2}{C}(O)\overset{3}{R^2}$						Complexes $[\overset{1}{(R^1CH_2)_2}N{=}\overset{2}{C}(Cl)\overset{3}{R^2}]^+X^-$						
R^1	R^2	H-1	H-3	C-1	C-2	C-3	$J_{C\text{-}1,H1}$/Hz	X^-	H-1	H-3	C-1	C-2	C-3	$J_{C\text{-}1,H\text{-}1}$/Hz
H	H ^{c}	2.81 2.91	7.93	31.2 36.2	161.7		139	Cl^-	3.96 ^{a} 4.20	11.10	46.5 ^{b}	166.2		146
								$OPOCl_2^-$	3.86 ^{a} 4.08	10.05	43.3 ^{a} 48.9	165.7		146.5
H	CH_3	2.88 2.97	2.01	34.8 37.8	169.6	21.4	138	$OPOCl_2^-$	3.94 ^{d}	3.10	46.3 47.0	176.2	28.4	145
H	CH_2CH_3 ^{e}	2.92 ^{a} 3.01	2.33	34.6 ^{a} 36.4	172.7	26.4	137	$OPOCl_2^-$	3.89 ^{d}	3.27	46.0 47.6	180.4	32.6	145.5
H	$CH(CH_3)_2$ ^{f}	2.90 3.04	2.80	35.3 37.1	175.6	30.2	137	Cl^-	4.05 ^{b}	3.90	47.2 48.6	184.4	37.0	144.5 146.5
								$OPOCl_2^-$	3.89 3.96	3.80	46.6 48.4	184.1	36.6	146.5 147.5
H	C_6H_5 ^{g}	2.91 ^{a} 3.05	7.4	35.2 39.1	170.4	135.8	139	$OPOCl_2^-$	3.86 4.04	≃7.18	48.5 48.8	172.6	130.0	146
CH_3	CH_3 ^{h}	3.31	2.01	40.1 42.9	170.1	21.4		$OPOCl_2^-$	4.20 ^{d}	3.10	53.3 54.0	176.5	28.3	
CH_3	$(CH_2)_2CH_3$ ^{i}	3.32	2.25	39.8 42.0	171.8	34.6		Cl^-			52.9 54.0	179.7	40.4	
								$OPOCl_2^-$	4.20 ^{d}	3.20	53.6 54.6	180.3	40.9	
$\begin{matrix}CH_3\\C_6H_5\end{matrix}\Big>N$	H	3.24	8.46	31.7	161.5		139	$OPOCl_2^-$	3.86	9.51				

[a] A single coalesced line is observed at 315 K; the given values are obtained at a lower temperature. [b] Coalescence value. [c] $J(^{13}C\text{–}H\text{-}3)$ (2) 192; $J(^{13}C\text{–}H\text{-}3)$ (3; X = Cl) 231; $J(^{13}C\text{–}H\text{-}3)$ (3; X = $OPOCl_2$) 232.5 Hz. [d] There is a fortuitous equivalence of δ(H-1) in the complex. [e] The parameters of the methyl group (Et) are: (2) δ(H) 1.08, δ(C) 9.2; (3) δ(H) 1.42, δ(C) 9.7. [f] The parameters of the methyl groups (Pr^i) are: (2) δ(H) 1.06, δ(C) 19.5; (3; X = $OPOCl_2$) δ(H) 1.38, δ(C) 19.5. [g] The parameters of the C_6H_5 substituents are: (2) $\delta(C_{\alpha,\beta})$ 126.3—127.6, $\delta(C_\gamma)$ 128.7; (3) $\delta(C_{\alpha,\beta})$ 128.1—128.5, $\delta(C_\gamma)$ 133.9. [h] The parameters of the methyl groups in $N(CH_2CH_3)_2$ are: (2) δ(H) 1.08 and 1.15, δ(C) 12.8 and 14.0; (3; X = $OPOCl_2$) δ(H) 1.52 and 1.53, δ(C) 11.6 and 12.2. [i] The chemical shifts of the CH_3 groups in $N(CH_2CH_3)_2$ are: (2) δ(H) 1.11, δ(C) 12.9 and 14.3; (3; X = $OPOCl_2$) δ(H) 1.50 and 1.52, δ(C) 11.8 and 12.9. The parameters of CH_2CH_3 groups of the propyl substituent are: (2) CH_2: δ(H) 1.62 (CH_2) and 0.95 (CH_3), δ(C) 18.7 (CH_2) and 13.9 (CH_3); (3; X = $OPOCl_2$) δ(H) 1.93 (CH_2) and 1.11 (CH_3), δ(C) 20.9 (CH_2) and 13.3 (CH_3). The results for simple amides are consistent with previously reported data (W. McFarlane, *Chem. Comm.*, 1970, 418; D. E. Dorman and F. A. Bovey, *J. Org. Chem.*, 1973, **38**, 1719).

TABLE 2

Chemical shifts, coalescence temperatures, and free energies of activation for the rotation around the C–N bond in $(R^1CH_2)_2NCOR^2$ in $\cdot CHCl_2\cdot CHCl_2$ (TCE)

		^{13}C (25.18 HMz)			^1H			
R^1	R^2	$\Delta\nu_\infty$/Hz	T_c/K	$\Delta G^\ddagger T_c$/kcal mol^{-1} (TCE)	$\Delta\nu_\infty$(Hz)/ ν_0(MHz)	T_c/K	$\Delta G^\ddagger T_c$/kcal mol^{-1} (solvent)	Ref.
H	H	128	>430		7.7 (60)	392	21.0 (neat) ^{a}	*c*, *d*
					11.3 (100)	400	21.0 (TCE) ^{b}	4
H	CH_3	77.1	376	18.3	6.7	342	18.2 (neat) ^{a}	*c*, *d*
H	C_2H_5	45.6	350	17.4	9.0 (60)	326	17.2 (neat) ^{a}	*d*
					8.7 (100)	330	17.4 (TCE) ^{b}	This work
					5.1 (60)	325	17.5 (TCE) ^{b}	This work
H	$CH(CH_3)_2$	40	340	16.9	13.4 (60)	318	16.5 (neat) ^{a}	*d*
					14.5 (100)	325	16.8 (TCE) ^{b}	This work
					8.4 (60)	320	16.9 (TCE) ^{b}	This work
H	C_6H_5	108	326	15.6	7.3 (60)	293	15.4 (CH_2Cl_2) ^{a}	*e*
					10.2 (60)	285	15.3 (CH_2Br_2) ^{a}	*f*
					13.8 (100)	305	15.7 (TCE) ^{b}	This work
CH_3	CH_3	72.9 CH_2	370.5	18.05				
		26.7 CH_3	353	17.9				
CH_3	$CH_2CH_2CH_3$	50.1 CH_2	345	17.05				
		32.0 CH_3	340	17.1				

[a] $\Delta G^\ddagger$ At 298 K. [b] $\Delta G^\ddagger$ Measured at T_c. [c] I. O. Sutherland, *Ann. Reports N.M.R. Spectroscopy*, 1971, **4**, 203. [d] T. Drakenberg, K. J. Dahlquist, and S. Forsen, *J. Phys. Chem.*, 1972, **76**, 2178. [e] B. E. Matsubayashi and T. Tanaka, *J. Inorg. Chem.*, 1969, **31**, 1963. [f] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, 1962, **66**, 540.

OPOCl$_2$), ^{1}H δ(CDCl$_3$) 2.69 and 3.67 [2 × N(CH$_3$)$_2$], 2.97 (C*H*$_2$CH$_3$), 1.28 (CH$_2$C*H*$_3$), and 2.05 (CCH$_3$); ^{13}C δ 42.8 and 44.9 [2 × N(CH$_3$)$_2$], 28.7 (CH$_2$), 9.7 (CH$_2$CH$_3$), 16.3 (*C*CH$_3$), 115.1 (*C*CH$_3$), and 146.9 and 188.0 (*C*CH$_2$ and CCl). Separate peaks corresponding to the *N*-methyl groups of (4a) cannot be detected in the ^{1}H spectrum but a small difference of chemical shift appears in the ^{13}C spectrum. In the *N*-ethyl analogue of (4a) three signals assigned to the methyls of the ethyl groups are however observed in the aliphatic portion (11—14 p.p.m.) of the ^{13}C spectrum. It may be concluded that the exchange process is fast with respect to the n.m.r. time scale for only one of the NR$_2$ groups of (4a) and its *N*-ethyl analogue; other equivalences are fortuitous. In compound (4b), the (CH$_3$)$_2$N groups show separate ^{13}C lines at 302 K, but the low-field signal splits at 218 K (1M solution in CH$_2$Cl$_2$; $\Delta\nu_\infty$ 75 Hz; ν_0 25.18 MHz). It has been shown [10] that the free enthalpies of activation for the hindered rotation process around the C–N bonds in alkyl- or aryl-substituted cyanines [N$\cdots$C$\cdots$C$\cdots$C$\cdots$N]$^+$B$^-$ are relatively high and both (CH$_3$)$_2$N groups show separate ^{1}H methyl resonances at 310 K. On this basis, a decrease of the charge density delocalisation is proposed for the chlorocyanine system in order to explain the lowering of the rotational barrier around the (CH$_3$)$_2$N–C(C$_2$H$_5$) bond. The observation of diastereotopic methyl groups in the (Cl)C–N(CH$_3$)$_2$ fragment is prevented by the occurrence of intermolecular halogen exchange which proceeds through a relatively low energy pathway. This process appears to be analogous to examples which will be discussed later for complexes (3).

Formation of Products.—The reaction of substituted amides (2) (0.5—1.5M) with POCl$_3$ shows two striking kinetic features which are summarized in reactions (1)—(4). It is interesting to note the similarity in behaviour between the formation of (3c and d) from (2c and d) and POCl$_3$ and the reaction of DMF with POCl$_3$ in relatively dilute media (*ca.* 10^{-2}—10^{-3}M).[4,11] In both processes evidence of an intermediate in the formation of complex (1) or (3) is given by the kinetic behaviour. The new intermediate (3′c and d) is probably structurally related to that intervening in the dilute DMF case.

$$\text{(2a and b)} + \mathrm{POCl_3} \rightleftharpoons \text{(3a and b)} \qquad (1)$$

$$\text{(3a and b)} + \text{(3a and b)} \rightleftharpoons \text{(4a and b)} \qquad (2)$$

$$\text{(2c and d)} + \mathrm{POCl_3} \rightleftharpoons \text{(3′c and d)} \qquad (3)$$

$$\text{(3′c and d)} \rightleftharpoons \text{(3c and d)} \qquad (4)$$

In this respect we have also noted that if DMA is reacted with POCl$_3$ at low concentration, the molecular pathway may be assumed to be (5). Another intermediate (3′a), possibly analogous to (3′c and d) is detected. The steric hindrance in the amide portion of (2c and d) as well as the high dilution of the reagents is thought to be responsible for this common kinetic behaviour. A complete structural and kinetic investigation of the different steps involved in the formation of the products is under study.

$$\text{(2a)} + \mathrm{POCl_3} \rightleftharpoons \text{(3′a)};\ \text{(3′a)} \rightleftharpoons \text{(3a)};\\ \text{(3a)} + \text{(3a)} \rightleftharpoons \text{(4a)} \qquad (5)$$

We think that the 5 × 10^3-fold rate decrease reported [8] for acetylation relative to formylation of 2-methoxythiophen cannot be entirely explained by the structures of the complexes. The influence of self-condensation of the Vilsmeier reagent (3a) prepared from DMA, on the kinetics of thiophen acetylation must be considered since the rate of consumption of the reaction by self-condensation is not substantially less than its rate of formation. The nature of the anion B$^-$ (Cl$^-$ or OPOCl$_2$$^-$) has little effect on these rates.

From our previous results on the kinetics of the reaction between DMF and POCl$_3$ in CH$_2$Cl$_2$ ($k_{273\mathrm{K}}$ *ca.* 4 × 10^{-3} l mol^{-1} s^{-1})[3] and the present data for DMA and POCl$_3$ in the same solvent ($k_{273\mathrm{K}}$ 1.5 × 10^{-4} l mol^{-1} s^{-1}), it may be concluded that DMA is only slightly less reactive to POCl$_3$ than DMF. From another point of view it can be stated [4] that the Vilsmeier reagents [*i.e.* (1) and (3a)] are better Lewis acids than POCl$_3$ itself.

With regard to structure, n.q.r. data [1] have shown that hyperconjugation might be important in alkyl derivatives of the Vilsmeier reagents; this is in agreement with the potential ability of (3a) to give (4a) *via* R$_2$N–C(Cl)=CH$_2$.

Rotational Barriers around C–N *Bonds.*—Only scattered results concerning the rotational barriers around the C–N bonds of *NN*-disubstituted carboxamides are available. Since the non-equivalence of the carbons in the (CH$_3$)$_2$N groups is relatively important, we have measured the chemical shifts at low temperature ($\Delta\nu_\infty$) and determined the coalescence temperatures in order to establish the free activation energies (Table 2).

The values of the free activation enthalpies obtained from the ^{13}C and ^{1}H spectra are quite consistent. With a view to minimizing solvent effects, which are often important for solutions of amides in protic solvents,[12] some barriers have been measured in the same solvent (CHCl$_2$·CHCl$_2$) for both ^{1}H and ^{13}C n.m.r. In the case of *NN*-diethylamides ^{13}C n.m.r. in the noise decoupled mode avoids the complexity of a line shape analysis of the exchanging proton multiplets and offers the possibility of calculating two rate constants for the same process at the coalescence temperature. It is worth noting that the higher the free activation enthalpy for rotation the higher is the rate of complex formation or halogen exchange.

The rotational barriers in complexes (3) are certainly higher than in the amides. The coalescence phenomena observed for the (CH$_3$)$_2$N groups are not first-order processes and may be attributed to halogen exchange.

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[10] M. L. Filleux, D. Le Botlan, A. Reliquet, and F. Reliquet, *Org. Magnetic Resonance*, 1974, **6**, 471.

[11] S. Alunni, P. Linda, G. Marino, S. Santini, and G. Savelli, *J.C.S. Perkin II*, 1972, 2070.

[12] T. Drakenberg, *Tetrahedron Letters*, 1972, 1743.

Halogen Exchange in Complexes (3).—We have shown that halogen exchange takes place when Vilsmeier reagents are dissolved in acetonitrile or in halogenated solvents.[4] The kinetics of this process were studied by line shape analysis of the ^1H resonances. However this phenomenon is not detectable in (3a and b) by ^1H n.m.r., due to the fortuitous equivalence of the peak positions of the amino-groups. Coalescence features are observed by dynamic ^{13}C n.m.r. which provides a good tool for studying exchange processes when diastereotopic protons cannot be differentiated.[13,14] The results for (3d) dissolved in acetonitrile are shown in Table 3; the exchange reaction follows second-order kinetics but the process is considerably slower than for (1). If we assume a non-planar conformation[15] for (3d), the decrease of the electrophilicity of the iminium carbon atom, and therefore the rate of nucleophilic substitution, may be explained by steric hindrance rather than by a purely charge delocalisation effect.

TABLE 3

Kinetics data for Cl^- exchange in $[(CH_3)_2N\cdots C(Cl)\text{-}C_6H_5]^+Cl^-$ in MeCN (^1H n.m.r. 60 MHz). T_c 293, 295, and 298 K at 0.39, 0.18, and 0.092M, respectively. $\Delta\nu_\infty$ 10—10.2 Hz. E_a 12.5 ± 1 kcal mol^{-1}; log A/l mol^{-1} s^{-1} *ca.* 11. The τ values are obtained by a total line shape analysis

T/K	[Complex]/M	τ/s	$10^{-2}k$/ l mol^{-1} s^{-1}	$\Delta G^‡T_c$/kcal mol^{-1} ±0.2
308	0.39	0.005	5.0	14.2
	0.18	0.010		
	0.092	0.018		
302	0.39	0.011	2.1	14.4
	0.18	0.023		
	0.092	0.034		
293	0.39	0.035	0.65	14.7
	0.18	0.065		
	0.092	0.108		
291	0.39	0.061	0.3	15.0
	0.18	0.088		
	0.092	0.136		

When the solvent used is CH_2Cl_2 instead of MeCN, the behaviour previously reported[4] is observed again; the life time τ of a methyl group decreases when the concentration of complex (3d) decreases (Table 4).

TABLE 4

Value of τ_{CH_3-N} for (3d) dissolved in CH_2Cl_2; $\Delta\nu_\infty$ 7.2 Hz (60 MHz; ^1H) and T_c 290 and 285 K for concentrations 0.7 and 0.32M respectively

[(3d)]/M	τ/s 302 K	τ/s 289 K
0.7	0.021	0.053
0.32	0.011	0.030

The variation of the coalescence temperature on increasing the concentration of the complex is good proof that a first-order internal rotation process does not occur. The participation of chlorine atoms from the solvent molecules in intermolecular exchange and the ion-pair constitution of the salt can explain this behaviour.

It must be emphasized that iminium salts (3) are highly hygroscopic compounds and we have checked to what extent chlorine anions arising from hydrolysis of the complexes contribute to the exchange reaction. For 0.35M-(3d) in MeCN, the coalescence temperature (^1H n.m.r.) increases from 293 (no hydrolysis) to 313 K (10% hydrolysis). Finally, it is rather difficult to rationalize the role of Cl^- in partially hydrolysed mixtures since the anion HCl_2^- may exist in such media. The ^1H signal of this species[16] appears at δ 14.6 in a solution (0.4M) of the dimethylbenzamide complex prepared with $COCl_2$ in CH_3CN.

[5/523 *Received*, 17*th March*, 1975]

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[13] J. B. Stothers, 'Carbon 13 N.M.R. Spectroscopy,' Academic Press, New York, 1972, p. 420.

[14] M. L. Filleux, N. Naulet, J. P. Dorie, G. J. Martin, J. Pornet, and L. Miginiac, *Tetrahedron Letters*, 1974, 1435.

[15] G. J. Martin and M. L. Martin, *Progr. N.M.R. Spectroscopy*, 1972, **8**, 176.

[16] F. Y. Fujiwara and J. S. Martin, *J. Chem. Phys.*, 1972, **56**, 4091.