Barriers to Internal Rotation and Intermolecular Exchange in Vilsmeier–Haack Adducts

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LEWIS ACIDS can react with dimethylformamide (DMF) to give carbonium ions with important electrophilic character,[1] and recently the reaction has been extended to sulphonyl halides.[2]

The structure of these adducts has received great attention[3,4] and Fratiello has studied DMF complexes with $AlCl_3$, $GaCl_3$, and $SbCl_5$.[5] On the basis of n.m.r. investigations we have proved the following formulation[4] for the Vilsmeier–Haack complexes prepared under very mild conditions:

$$[Me_2N-\overset{+}{C}HCl \longleftrightarrow Me_2-\overset{+}{N}=CHCl]OX^- \quad (A)$$
$$X = SOCl,\ POCl_2$$

In some cases (X = SOCl, COCl) the adduct changes to the unique species:

$$[Me_2N\overset{\cdots}{-}CHCl]^+Cl^- \text{ and } CO_2 \text{ or } SO_2 \text{ is evolved} \quad (B)$$

We have studied the barrier to internal rotation around carbon–nitrogen bonds to correlate reactivity and thermodynamic properties. The results are summarized in the Table.

With $POCl_3$, an oily product is obtained, nearly free of DMF and solvent, whereas in the case of $COCl_2$ (V) and $SOCl_2$ (IV) it is possible to isolate a crystalline adduct. These pure compounds were dissolved in chloroform, methylene bromide, and tetrachloroethane in order to investigate the possible solvent effects on the barrier.

The rate constants were calculated by the lines-separation method,[6] before coalescence, and by the narrowing of lines,[7] after the collapse of peaks. The numerical values were tabulated with an I.B.M. 1620 machine and plotted for interpolation.

The adducts (I) and (II) have the structure:

$$[Me_2N\overset{\cdots}{-}CHCl]^+OPOCl_2^- \text{ and } [Me_2N\overset{\cdots}{-}CHCl]^+OSOCl^-.$$

The results confirm that the same complex, $[Me_2\,N\overset{\cdots}{-}CHCl]^+Cl^-$, is obtained either from (II) or (III) when they are heated *in vacuo*. Furthermore the similar values of T_c, ΔF^*, and E_a for (III), (IV), and (V) suggest that CO_2 is almost completely evolved as soon as $COCl_2$ reacts on DMF (III). Consequently, structure (B) is to be retained for (III), (IV), and (V).

We propose the following sequences for the observed phenomena:

$$Me_2N-CH=O + XCl \leftrightarrows$$
$$Me_2\overset{+}{N}\overset{\cdots}{-}CH\overset{\cdots}{-}\overset{-}{O}\cdots XCl \rightarrow$$
$$[Me_2N\overset{\cdots}{-}CHCl]^+\ OX^{-\ddagger} \rightarrow$$
$$[Me_2N\overset{\cdots}{-}CHCl]^+Cl^-$$

‡ for X = COCl, SOCl.

Solvent effects observed on the thermodynamic parameters are not significant. However, on addition of excess DMF to the pure adducts (I), (IV), or (V), the mixture exhibits an intermolecular exchange for the methyl and methine groups of DMF and Vilsmeier complexes (coalescence temperatures are in the range 40—60°).

The electrophilic character of these adducts could be related to double-bond order and π-electron density, but it is probable that these properties are connected (in a rather complex way) with activation energy. Our results show

		Coalescence temperature (±2° K) T_c	Free energy difference (±0·2 kcal. mole^{-1}) $\Delta F^*_{T_c}$	Activation energy (±2 kcal. mole^{-1}) E_a	Solvent
(I)	DMF–$POCl_3$	279	14·3	24·3	$(CHCl_2)_2$
		272	14·1	19	$CHCl_3$
		277·5	14·5	17·2	CH_2Br_2
(II)	DMF–$SOCl_2$	278	14·2	11·7	$(CHCl_2)_2$
		266	13·7	11·5	$CHCl_3$
		267	13·7	9	CH_2Br_2
(III)	DMF–$COCl_2$	260	13·2	16·6	$(CHCl_2)_2$
		262·5	13·4	17·9	$CHCl_3$
(IV)	DMF–$SOCl_2$†	258	13·1	17·2	$(CHCl_2)_2$
(V)	DMF–$COCl_2$†	258	13·1	18	$(CHCl_2)_2$
		249	12·7	16·3	$CHCl_3$

† Gently heated (40—50°) *in vacuo.*

the importance of the anion. It is too soon to draw a correlation between the values of thermodynamic parameters and yields, or rates of electrophilic additions. Work is in progress to clarify the mechanisms involved in these intra- and inter-molecular exchanges.

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