

## Species Responsible for the Vibration Band at 2200 $\text{cm}^{-1}$ Observed in the Spectra of Some Systems containing the Acetylium Ion

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**Summary** In contrast to current belief, the doublet at 2300 and 2200  $\text{cm}^{-1}$  observed in the i r spectra of certain acylating media is not due to two different types of acetylium ion, but to the formation of the diacetylacetylium ion (2200  $\text{cm}^{-1}$ ), a trimer of the acetylium ion (2300  $\text{cm}^{-1}$ )

AMONG the many publications concerned with the composition of acylating systems, many<sup>1-5</sup> report the existence of two characteristic i r absorption bands at 2200 and 2300  $\text{cm}^{-1}$ . Numerous suggestions have been put forward to account for these bands, and five species have been proposed. These are shown in Table 1. The idea common to these suggestions is that the two bands belong to the acetylium ion existing in two different forms, and until now, we had adopted this view<sup>6</sup>.

In fact, the only evidence for the structure of the acetylium ion is that proposed by Boer<sup>8</sup> and recently by Weiss and Le Carpentier,<sup>9</sup> who have determined the crystal structures

of  $\text{Ac}^+\text{SbF}_6^-$  and  $\text{Ac}^+\text{AlCl}_4^-$  respectively by X-ray crystallography. In these crystals the acetylium ion is linear and is subject to no interactions other than ionic crystal packing. In their i r spectra, the crystals are characterised by a band at 2300  $\text{cm}^{-1}$ . The latter compound ( $\text{Ac}^+\text{AlCl}_4^-$ ) is the product isolated by Susz and Wuhrmann<sup>10</sup>. These results allow the i r band at 2300  $\text{cm}^{-1}$  to be assigned to a linear acetylium ion subject to no influence from its counter-ion other than weak electrostatic forces.

We now discuss the band at 2200  $\text{cm}^{-1}$  and the structure of the product responsible for this absorption.

The i r spectra of solutions of  $\text{Ac}_2\text{O}$  in  $\text{CF}_3\text{SO}_3\text{H}$  show a doublet at 2300—2200  $\text{cm}^{-1}$  when the concentration of  $\text{Ac}_2\text{O}$  is low (<0.25 mol/mol of  $\text{CF}_3\text{SO}_3\text{H}$ ). At room temperature, the intensity of the 2300  $\text{cm}^{-1}$  absorption diminishes and that of the 2200  $\text{cm}^{-1}$  increases as a function of time, this process is accelerated by the presence of  $\text{CF}_3\text{SO}_3\text{Na}$ . An analogous change of intensity with time is observed with solutions of  $\text{AlCl}_3$  in  $\text{AcCl}$ .

From the system  $\text{AcCl}-\text{AlCl}_3$  we have isolated two crystalline products: one (A) possesses a single band at  $2300\text{ cm}^{-1}$ , and the other (B) a band at  $2200\text{ cm}^{-1}$ .

i.r. absorption at  $500\text{ cm}^{-1}$  are thus consistent with the following structure.



TABLE 1

Previous allocations of the i.r. bands at  $2200$  and  $2300\text{ cm}^{-1}$

	(I) Ac <sup>+</sup> free ion	(II) Ac <sup>+</sup> [MCl <sub>4</sub> ] <sup>-</sup> ion pair	(III) [Ac...MCl <sub>3</sub> ] <sup>+</sup> Cl <sup>-</sup>	(IV) MeC≡O <sup>+</sup>	(V) CH <sub>3</sub> =C=O <sup>+</sup>
Cook <sup>1</sup> .. .. .	2300	2200			
Cook <sup>2</sup> .. .. .	2200		2300		
Bertoluzza <sup>3</sup> .. .. .		2200	2300 <sup>a</sup>		
Cassimatis <sup>4</sup> <i>et. al.</i> .. .. .	Two mesomeric forms were considered			2200	2300

<sup>a</sup> Bertoluzza considered that the crystalline product of formula  $\text{AcAl}_2\text{Cl}_7$  isolated by Peach, Tracy, and Waddington<sup>7</sup> had the structure (III)  $(\text{Ac}\cdots\text{AlCl}_3)^+\text{AlCl}_4^-$ .

TABLE 2. Characteristics of A and B.

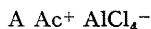
A	I.r. <sup>a</sup> cm <sup>-1</sup>	M.p. °C	N.m.r.	Analysis			Reactions <sup>b</sup>		
				C	H	Cl		Al	
A	2300	85	s, δ 4.12, p.p.m.	Found:	11.5	1.5	66.2	12.9	$\text{A} + \text{H}_2\text{O} \xrightarrow{\text{excess}} \text{AcOH}$ (212 g) (1 mole) $\text{A} + \text{EtOH} \xrightarrow{\text{excess}} \text{AcOEt}$ (212 g) (1 mole) $\text{A} + \text{PhOMe} \xrightarrow{\text{excess}} \text{AcC}_6\text{H}_4\text{OMe}$ (212 g) (0.98 mole)
				Calc. for $\text{Ac}^+\text{AlCl}_4^-$ (M = 212)	11.33	1.43	66.95	12.73	
B	2200	160	Insoluble in inert solvents	Found:	23.9	2.3	48.5	10.5	$\text{B} + \text{H}_2\text{O} \xrightarrow{\text{excess}} \text{AcCH}_2\text{COMe} + \text{CO}_2$ (296 g) (0.80 mole) $\text{B} + \text{EtOH} \xrightarrow{-50^\circ\text{C}} \text{Ac}_2\text{CHCO}_2\text{Et}$ (296 g) (0.97 mole) $\text{B} + \text{PhOMe} \xrightarrow{\quad} \text{Product not identified}$
				Calc. for $(\text{CH}_3\text{CO})_2\text{CHCO}^+\text{AlCl}_4^-$ (M = 296)	24.32	2.36	47.97	9.12	

<sup>a</sup> Both products show a wide band at  $500\text{ cm}^{-1}$  characteristic of  $\text{AlCl}_4^-$ .<sup>10</sup>

<sup>b</sup> The products obtained were characterised by analysis and comparison of their spectra (i.r., n.m.r., m.s., chromatography) with those of commercially available materials, or, in the case of  $\text{Ac}_2\text{CHCO}_2\text{Et}$ , a sample synthesised by another method.<sup>12</sup> The quantities of products formed were estimated directly in the reaction mixture by <sup>1</sup>H n.m.r.

Product A was obtained by allowing equimolar proportions of  $\text{AcCl}$  and  $\text{AlCl}_3$  to react in  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ; after dissolution of the  $\text{AlCl}_3$  the product was precipitated as white crystals by the addition of Freon 113. Product B was obtained from the reaction of  $\text{AlCl}_3$  with a large excess of  $\text{AcCl}$  in the absence of solvent. The mixture evolved  $\text{HCl}$ , and when the band at  $2300\text{ cm}^{-1}$  had disappeared (after 5 to 6 h at room temperature), addition of  $\text{ClCH}_2\text{CH}_2\text{Cl}$  caused B to precipitate as a white solid. The characteristics of A and B are summarised in Table 2.

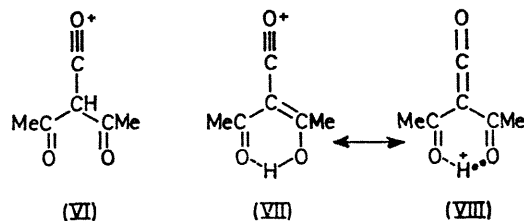
The nature and yields of products obtained from the reaction of a given quantity (212 g) of A with  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , and anisole seem to be consistent with the structure below, especially since the i.r. spectrum shows a band at  $500\text{ cm}^{-1}$  due to the ion  $\text{AlCl}_4^-$ .



The reactions of A with  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , and anisole are quantitative within the limits of experimental error: the nature and yields of these products were studied to compare the reactivities of A and B. The product A is the compound isolated by Susz and Wuhmann and analysed by Weiss and Le Carpentier.

The products obtained from the reactions of B with  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , and anisole show that B does not contain the ion  $\text{Ac}^+$ , but instead the diacetylacetylum ion. The analytical data, the yields of products formed, and the presence of an

The reaction of B with  $\text{H}_2\text{O}$  gave a non-quantitative yield (80%) of product compared with the yield (>95%) obtained from the reaction with  $\text{EtOH}$ . This can be explained by the fact that the latter reaction was carried out under milder conditions ( $-50^\circ\text{C}$ ). Acetylacetone isolated as the product in the first instance arises from the decarboxylation of diacetylacetic acid, a compound that has not been isolated.



The results obtained from the reactions of B are in fact similar to those reported by Combes,<sup>11</sup> but the interpretation given by Combes is now known to be false. However, it is at present difficult to propose a structure for the diacetylacetylum ion, and we are investigating its n.m.r. spectrum. Nevertheless, we are certain that the species responsible for the band at  $2200\text{ cm}^{-1}$  does not possess any of the structures in Table 1, but is a trimer of the acetylum ion. Bearing

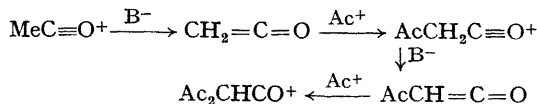
in mind that, in the pure state, the ethyl ester of diacetylacetic acid exists entirely in the enol form,<sup>13</sup> the structures (VI), (VII), and (VIII) for cation of B can be envisaged.

The contribution from the mesomeric keten structure (VIII) provides an explanation for the lowering of the  $\nu\text{C}\equiv\text{O}^+$  frequency by  $100\text{ cm}^{-1}$  with respect to that of the acetylium ion; this effect also explains the  $\nu\text{C}\equiv\text{O}^+$  frequency at  $2190\text{ cm}^{-1}$  in the mesitylium ion.

In  $\text{Ac}_2\text{O}-\text{CF}_3\text{SO}_3\text{H}$ ,  $\text{CF}_3\text{SO}_3\text{Na}$  accelerates the trimerisation of  $\text{Ac}^+$  indicating that the anion must participate in this reaction. This is confirmed by the absence of an i.r. band at  $2200\text{ cm}^{-1}$  in super-acid media where the anions are very poor nucleophiles. We can thus envisage that the first step in the trimerisation reaction involves removal of a proton from  $\text{Ac}^+$  by the anion to form a keten, followed by attack of another acetylium ion giving the acetylacetylium species. Another proton abstraction followed by attack of  $\text{Ac}^+$  leads ultimately to the diacetylacetylium ion (Scheme).

If compound B is left in contact with acetyl chloride for 5 days, a compound is isolated whose structure does not correspond to that of B. Analysis indicates an increase in

the proportion of the organic part (C and H) with respect to the inorganic part (Cl) (calculated for  $\text{Ac}_2\text{CHCO}^+\text{AlCl}_4^-$ : C 24.32; H 2.36; Cl 47.77; found: C 29.7; H 3.4; Cl 27.5%). It appears that there is further polymerisation of the acetylium ion, and a study of this phenomenon, together with an exact structural determination of the complex B will be the subject of a future publication.



SCHEME

These results indicate that the acetylium ion can undergo polymerisation, at least in certain media, and when kinetic studies are made in solutions containing the ion it is necessary to take this fact into account, or to work under conditions where polymerisation is negligible.

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<sup>1</sup> D. Cook, *Canad. J. Chem.*, 1959, **37**, 48.

<sup>2</sup> D. Cook, *Canad. J. Chem.*, 1962, **40**, 480.

<sup>3</sup> A. Bertoluzza, *Estrada dai Rend. Accad. Naz. dei XL, Serie IV*, vol. XX, Rome, 1969.

<sup>4</sup> D. Cassimatis, J. P. Bonnin, and T. Theophanides, *Canad. J. Chem.*, 1970, **48**, 3860.

<sup>5</sup> A. Casadevall, A. Commeyras, P. Paillous, and H. Collet, *Bull. Soc. chim. France*, 1970, 719.

<sup>6</sup> A. Commeyras, A. Germain, and A. Casadevall, Proceedings of the 21st Meeting of the Societ  de Chimie Physique, Paris, Sept. 1970, Gordon and Beach, London.

<sup>7</sup> M. Peach, V. L. Tracy, and T. C. Waddington, *J. Chem. Soc. (A)*, 1969, 366.

<sup>8</sup> F. P. Boer, *J. Amer. Chem. Soc.*, 1966, **88**, 1572; *ibid.*, 1968, **90**, 6706.

<sup>9</sup> J. M. Le Carpentier and R. Weiss, Institut de Chimie de Strasbourg, France, personal communication.

<sup>10</sup> B. P. Susz and J. J. Wuhrmann, *Helv. Chim. Acta*, 1957, **40**, 971.

<sup>11</sup> A. Combes, *Compt. rend.*, 1886, **103**, 814; *ibid.*, 1887, **104**, 109.

<sup>12</sup> A. Spassow, *Org. Synth.*, 1955, **3**, 390.

<sup>13</sup> S. Forsen and M. Nilsson, *Acta Chem. Scand.*, 1960, **14**, 1333; P. Courtot, J. Le Saint, and N. Platzter, *Compt. rend.*, 1968, **267**, 1332.