518. *Evidence for the Existence of Hydrogen Dichloride Ions,*
HCl_2^-, *in Organic Compounds.*

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The adducts formed by the action of hydrogen chloride on chlorotri-*p*-methoxyphenylmethane and 9-chloro-9-phenylxanthen have been examined by infrared and ultraviolet spectroscopy. The spectra have been compared with those of the corresponding carbonium salts and are in favour of the adducts' containing carbonium cations and hydrogen dichloride anions. The conditions for formation of carbonium hydrogen dichlorides are discussed and it is suggested that these anions may play an important part in organic reaction mechanisms.

HYDROGEN DICHLORIDE ions, HCl_2^-, are formed by the addition of hydrogen chloride to pyridinium chloride,[1] tetramethylammonium chloride,[2] siliconium chlorides,[3] and cæsium chloride.[4] Since one requirement for the stabilisation of this ion in crystals appears to be a large cation, it was considered possible that carbonium ions might also stabilise it.

The formation of highly coloured adducts by the addition of hydrogen chloride to certain triarylchloromethanes is well known and, from a comparison of the colours of these adducts with the colours of the corresponding perchlorates, Gomberg and his co-workers[5,6] concluded that the adducts contained a " quinocarbonium " grouping, that would now be called a carbonium ion. The present paper describes a spectroscopic study of these adducts.

EXPERIMENTAL

Tri-*p*-methoxyphenylmethane was obtained by Baeyer and Villiger's method;[7] it distilled at 270—280°/10 mm. Its oxidation gave the alcohol;[8] the hydrogen dichloride[5] was obtained by the action of gaseous hydrogen chloride on a solution of the alcohol in chloroform or benzene and acetyl chloride, followed by precipitation with light petroleum (b. p. 60—80°). Purification was effected by re-preparation (Found: C, 65·2; H, 6·0; Cl, 17·5. Calc. for $C_{22}H_{22}O_3Cl_2$: C, 65·2; H, 5·4; Cl, 17·55%). The dichloride was converted into the corresponding chloromethane by passing air through a refluxing benzene solution[5] (Found: C, 72·8; H, 5·1; Cl, 9·3. Calc. for $C_{22}H_{21}O_3Cl$: C, 71·6; H, 5·7; Cl, 9·65%); this chloromethane was obtained as faintly pink crystals, m. p. 161°, and its hydrolysis gave tri-*p*-methoxyphenylmethanol, m. p. 82·5°. The action of a solution of silver perchlorate in ether on an ethereal solution of chlorotri-*p*-methoxyphenylmethane gave tri-*p*-methoxyphenylmethyl perchlorate,[5] m. p. 198° after recrystallisation from chloroform–light petroleum.

Tri-*p*-methoxyphenylmethyl fluoroborate and hexafluorophosphate, both having m. p. 152° (decomp.), were prepared similarly;[9] they were obtained as red crystals but, like other carbonium salts of complex fluoro-acids,[9] did not give consistent analytical results. They were characterised by the weight of silver chloride precipitated during preparation[9] (Found for $C_{22}H_{21}O_3F_4B$: 0·98 equiv. Found for $C_{22}H_{21}O_3F_6P$: 0·96 equiv.).

9-Phenylxanthenol, m. p. 159°, was prepared by the action of phenylmagnesium bromide on xanthone.[10] Other derivatives were prepared as described by Gomberg and Cone[5] and as detailed above for the tri-*p*-methoxyphenylmethyl derivatives. Analyses and melting points recorded were: 9-phenylxanthenyl hydrogen dichloride (Found: C, 69·05; H, 4·7; Cl, 21·0.

[1] Kaufler and Kunz, *Ber.*, 1909, **42**, 385, 2482; Ephraim, *Ber.*, 1914, **47**, 1828.
[2] McIntosh and Steel, *Proc. Roy. Soc.*, 1904, **73**, 450; 1905, **74**, 320; Herbrandson, Dickerson, jun., and Weinstein, *J. Amer. Chem. Soc.*, 1954, **76**, 4046.
[3] Dilthey, *Ber.*, 1903, **36**, 923; *Annalen*, 1906, **344**, 300.
[4] West, *J. Amer. Chem. Soc.*, 1957, **79**, 4568.
[5] Gomberg and Cone, *Annalen*, 1909, **370**, 142.
[6] Gomberg and West, *J. Amer. Chem. Soc.*, 1912, **34**, 1529.
[7] Baeyer and Villiger, *Ber.*, 1902, **35**, 1197.
[8] Burton and Cheeseman, *J.*, 1953, 832.
[9] Sharp and Sheppard, *J.*, 1957, 674.
[10] Bünzly and Decker, *Ber.*, 1904, **37**, 2933.

Calc. for $C_{19}H_{14}Cl_2$: C, 69·3; H, 4·3; Cl, 21·6%); 9-chloro-9-phenylxanthen (Found: C, 78·7; H, 5·4; Cl, 11·7. Calc. for $C_{19}H_{13}Cl$: C, 77·9; H, 4·5; Cl, 12·1%); 9-phenylxanthenyl perchlorate, m. p. 282° (decomp.); *9-phenylxanthenyl fluoroborate*, m. p. 238° (decomp.) (1·00 equiv. of AgCl); *9-phenylxanthenyl hexafluorophosphate*, m. p. 225° (decomp.) (1·02 equiv. of AgCl).

Silver salts of complex fluoro-acids were prepared as previously described.[11] Cæsium hydrogen dichloride was obtained as needles by the action of hydrogen chloride on a solution of cæsium chloride in hydrochloric acid.[4]

All operations with chlorides and hydrogen dichlorides were carried out in the dry-box.

Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer, with rock-salt or fluorite optics. Mulls were prepared in Nujol or hexachlorobutadiene (in the dry-box if necessary).

Ultraviolet spectra were recorded on a Unicam S.P. 500 spectrophotometer. Chlorine compounds were studied in chloroform solution; reference spectra of carbonium ions were obtained from solutions of the appropriate alcohols in concentrated sulphuric acid.[12] Maxima and minima recorded were:

$(MeO \cdot C_6H_4)_3C \cdot OH$ in H_2SO_4: $\lambda_{max.}$ 494 (ε 114,000), $\lambda_{min.}$ 460 (ε 46,400), $\lambda_{max.}$ 455 mμ (ε 60,700).

$(MeO \cdot C_6H_4)_3C \cdot ClO_4$ in $CHCl_3$: $\lambda_{max.}$ 494 mμ (ε 31,400).

$(MeO \cdot C_6H_4)_3C \cdot HCl_2$ in $CHCl_3$: $\lambda_{max.}$ 490 mμ (ε 978).

9-Phenylxanthenol in H_2SO_4: $\lambda_{max.}$ 450 (ε 5620), $\lambda_{min.}$ 420 (ε 4310), $\lambda_{max.}$ 370 mμ (ε 24,900).

9-Phenylxanthenyl perchlorate in $CHCl_3$: $\lambda_{max.}$ 450 (ε 404), $\lambda_{min.}$ 420 (ε 330), $\lambda_{max.}$ 375 mμ (ε 2420).

9-Phenylxanthenyl hydrogen dichloride in $CHCl_3$: $\lambda_{max.}$ 460 (ε 36·9), $\lambda_{min.}$ 420 (ε 31·5), $\lambda_{max.}$ 380 mμ (ε 210).

DISCUSSION

Possible structures for the hydrogen chloride adducts are: (1) The proton of the additional hydrogen chloride molecule is co-ordinated to the oxygen atom of the organic molecule, forming an oxonium chloride. (2) The extra hydrogen chloride molecule is loosely held in the organic lattice. (3) The extra hydrogen chloride molecule is co-ordinated to the carbonium ion. (4) The chloromethane is ionised, the extra hydrogen chloride molecule being co-ordinated to the resultant chloride ion. It should be possible to distinguish between these structures by a study of the infrared and ultraviolet spectra. In case (1) the symmetry of the molecule is locally altered, the remainder of the molecule still being similar in shape to the chloromethane: there should then be a change between the spectra of chlorotri-*p*-methoxyphenylmethane and its hydrogen chloride adduct. For cases (2) and (3) the spectra should be very similar to that of the corresponding chloro-methane, the infrared spectrum of both adducts having an extra band due to absorption by the hydrogen chloride molecule. In case (4) the overall symmetry of the molecule has been completely altered and there should be a material change in the infrared spectrum.

Of the various compounds, tri-*p*-methoxyphenylmethane and 9-phenylxanthenol would be expected to have completely covalent character, with approximately tetra-hedral bonding about the central carbon atom. The salts containing carbonium ions (perchlorates, fluoroborates, and hexafluorophosphates) should have approximately planar bonding about the " central " carbon atom:[9] that these salt contain identical carbonium

Anion	ClO_4^-	BF_4^-	PF_6^-
K⁺ or Rb⁺	1075, 1122[13]	1032, 1058[14]	845[9]
$(p\text{-}MeO \cdot C_6H_4)_3C^+$	1100 (diffuse)	1060 (diffuse)	844
9-Phenylxanthenyl	1090	1052	842

ions is shown by the presence of a roughly constant spectrum for each cation with the spectrum of the appropriate anion superimposed. The anion spectra which have been

[11] Sharp and Sharpe, *J.*, 1956, 1855.
[12] Anderson, *J. Amer. Chem. Soc.*, 1935, **57**, 1673.
[13] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[14] Coté and Thompson, *Proc. Roy. Soc.*, 1952, *A*, **210**, 217.

recorded are summarised in the Table which gives $\nu_{max.}$ in cm.$^{-1}$. Fig. 1 shows the relevant infrared spectra. The spectra of chlorotri-*p*-methoxyphenylmethane and 9-chloro-9-phenylxanthen are typical of " tetrahedral " molecules, but on addition of one equivalent of hydrogen chloride the spectra change and become more typical of carbonium structures.

To consider the two series of spectra in turn: for tri-*p*-methoxyphenylmethyl derivatives important changes occur over the region 1600—1200 cm.$^{-1}$. The moderate band at 1610 cm.$^{-1}$ in the spectrum of the chloromethane disappears and is replaced by a very strong band at 1581 cm.$^{-1}$; the strong band at 1507 cm.$^{-1}$ disappears and the relative intensities of the bands at 1460 and 1445 cm.$^{-1}$ are reversed; the 1365 cm.$^{-1}$ band is

FIG. 1. *Infrared spectra of*: *A*, *tri*-p-*methoxyphenylmethane*; *B*, *chlorotri*-p-*methoxyphenylmethane*; *C*, *tri*-p-*methoxyphenylmethyl hydrogen dichloride*; *D*, *tri*-p-*methoxyphenylmethyl perchlorate*; *E*, *tri*-p-*methoxyphenylmethyl fluoroborate*; *F*, *tri*-p-*methoxyphenylmethyl hexafluorophosphate*; *G*, *9-phenyl-xanthenol*; *H*, *9-chloro-9-phenylxanthene*; *I*, *9-phenylxanthenyl hydrogen dichloride*; *J*, *9-phenyl-xanthenyl perchlorate*; *K*, *9-phenylxanthenyl fluoroborate*; *L*, *9-phenylxanthenyl hexafluorophosphate.*
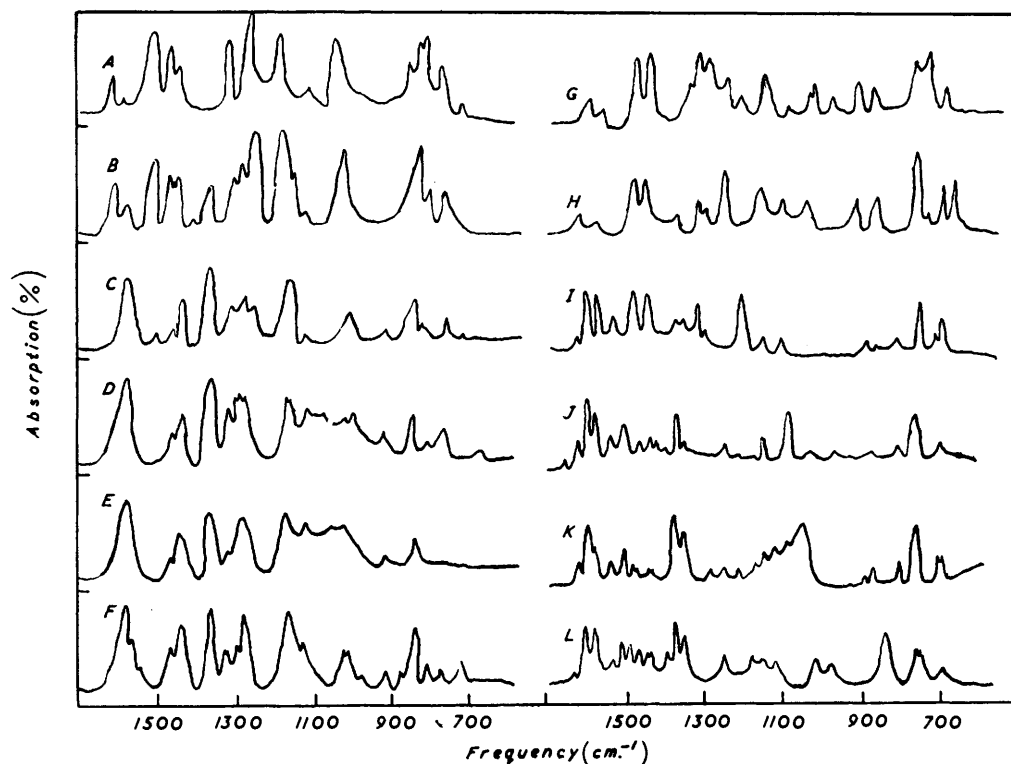
enhanced in intensity and a rather more complicated series of bands appears near 1300 cm.$^{-1}$. The spectrum of the hydrogen chloride adduct closely resembles those of the tri-*p*-methoxyphenylmethyl salts over this region, which contains the skeletal stretching vibrations of the aromatic ring systems.[15] The spectra cannot be completely compared with those obtained for the triphenylmethyl cation [9] since the methoxyl groups give rise to strong absorption in this region;[16] however, strong bands near 1580, 1360, and 1300 cm.$^{-1}$ are typical of carbonium ions.[9] The spectra over the range 1200—650 cm.$^{-1}$ again favour a carbonium structure for the hydrogen chloride adducts. The strongest

[15] Whiffen, *J.*, 1956, 1350.
[16] Briggs, Colebrook, Fales, and Wildman, *Analyt. Chem.*, 1957, **29**, 904.

band in this region is due to the aromatic C–H out-of-plane vibrations,[17] the shift of the peak from 825 to 845—850 cm.$^{-1}$ when the spectra of the covalent compounds are compared with those of the carbonium salts being in accordance with the increased electron-withdrawal from the ring in the latter compounds.[17]

For the 9-phenylxanthenyl derivatives the overall spectrum is more complex, as would be expected for a molecule of lower symmetry. Important changes do, however, occur on passing from 9-chloro-9-phenylxanthen to its hydrogen chloride adduct. The spectrum of the latter approximates to that of a carbonium salt at about 1600 cm.$^{-1}$, where a weak doublet in the " tetrahedral " compound is greatly enhanced in intensity. In its simplicity over the range 1150—650 cm.$^{-1}$ the spectrum is again typical of that from a carbonium salt. However, the presence of a strong doublet at 1485 and 1458 cm.$^{-1}$ in the spectrum of the hydrogen chloride adduct is more typical of the " tetrahedral " type of compound, whilst the strong band at 1205 cm.$^{-1}$ is not typical of either series. It cannot, therefore, be said that the infrared spectrum proves quite definitely a carbonium structure for the

FIG. 2. *Ultraviolet spectra of*: A, *tri-p-methoxyphenylmethanol in conc.* H_2SO_4; B, *tri-p-methoxyphenylmethyl perchlorate in* $CHCl_3$; C, *tri-p-methoxyphenylmethyl hydrogen dichloride in* $CHCl_3$; D, *9-phenylxanthenol in conc.* H_2SO_4; E, *9-phenylxanthenyl perchlorate in* $CHCl_3$; F, *9-phenylxanthenyl hydrogen dichloride in* $CHCl_3$.
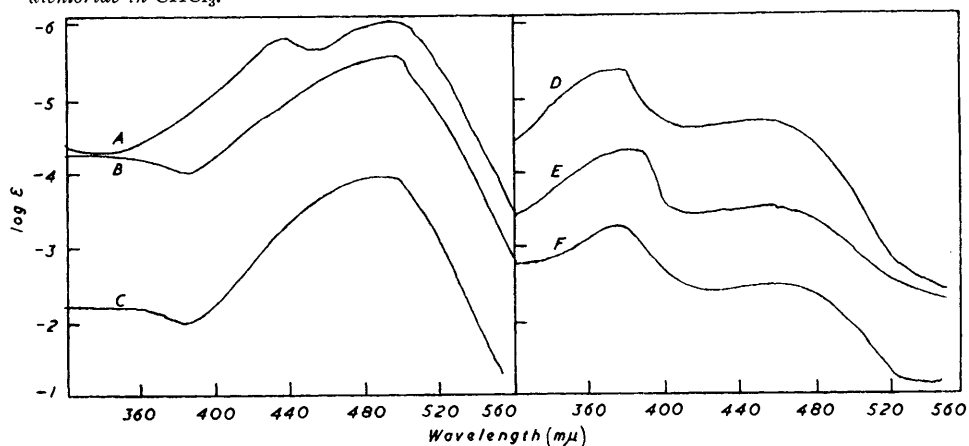
hydrogen chloride adduct of 9-chloro-9-phenylxanthen in the solid state, although much of the evidence favours this structure.

Further proof of the structure of these adducts could, in principle, be obtained from the infrared absorption of the HCl and HCl₂⁻ groupings. Hydrogen chloride absorbs [18] at 2886 cm.$^{-1}$ and very recently Waddington [19] has shown that the hydrogen dichloride ion in tetramethylammonium hydrogen dichloride absorbs at 1180 and 1565 cm.$^{-1}$. For cæsium hydrogen dichloride we have confirmed the presence of a band at 1180 cm.$^{-1}$ but could not find a band at 1565 cm.$^{-1}$. However, in the hydrogen chloride adducts of the chloromethanes, aromatic absorption would obscure any band at 1565 cm.$^{-1}$, and a band at 1180 cm.$^{-1}$ in the spectrum of a tri-p-methoxyphenylmethyl salt would also be obscured. It is possible that the 1205 cm.$^{-1}$ band in the spectrum of 9-phenylxanthenyl hydrogen dichloride is due to absorption by the HCl₂⁻ ion. The infrared spectrum of tri-p-methoxyphenylmethyl hydrogen dichloride over the range 3000—2500 cm.$^{-1}$ is almost identical with that of tri-p-methoxyphenylmethyl perchlorate and there can be no free hydrogen chloride in the lattice.

Thus, of the possible structures considered, infrared spectra definitely favour the

[17] Bellamy, *J.*, 1955, 2818; Kross, Fassel, and Margoshes, *J. Amer. Chem. Soc.*, 1956, **78**, 1332.
[18] Meyer and Levin, *Phys. Rev.*, 1929, **34**, 44.
[19] T. C. Waddington, personal communication.

carbonium hydrogen dichloride postulate. Further evidence for this formulation for the adducts was sought by a study of the ultraviolet spectra of solutions but this work can only be considered complementary to the infrared results since the species present in solution are not necessarily those present in the solid state. Fig. 2 shows the ultraviolet spectra of solutions of the hydrogen chloride adducts in chloroform and compares them with those of the alcohols in concentrated sulphuric acid and solutions of the carbonium perchlorates in chloroform: the last two solutions are both expected to contain carbonium ions. In the positions of maxima and minima (for details see p. 2559) these spectra confirm the existence of carbonium ions in the solutions of the hydrogen chloride adducts, but in the intensity of absorption there are some unexplained discrepancies.

The existence of these salts containing hydrogen dichloride ions, HCl_2^-, gives rise to many interesting speculations since the only previous example of such an adduct has been the hydrogen difluoride ion, HF_2^-, where it has been postulated that the electronegative fluorine gives rise to a very strong hydrogen bond.[20] However, there is reason to suppose that the formation of such adducts is not even confined to hydrogen fluoride and chloride, the many highly coloured adducts of triarylmethyl salts with acids [21] indicating that the formation of such " bianions " is quite widespread.

Only those triarylchloromethanes which contain a large number of electron-releasing groups attached to the ring systems appear to form stable hydrogen dichlorides. Thus chlorotriphenylmethane forms an adduct with hydrogen chloride which decomposes at —45°,[22] and on substituting p-methoxyphenyl groups for phenyl it is only with chlorotri-p-methoxyphenylmethane that a stable, crystalline hydrogen dichloride can be isolated. Lund [23] considers that the chloromethanes are themselves ionised when there are four or more methoxyl groups attached to the ring systems, and chloromethanes which form hydrogen dichlorides certainly have an easily ionised C–Cl bond.

Since hydrogen chloride catalyses some organic reactions it is likely that carbonium hydrogen dichlorides take part in the reactions as intermediates, *e.g.*, in the isomerisation of camphene hydrochloride.[24, 25] Hydrogen dichloride ions may also occur in reactions where hydrogen chloride is used as a condensing agent. For the reaction between *tert.*-butyl chloride and toluene, the proton-transfer mechanism proposed [26] was similar to that suggested by Sprauer and Simons [27] for the hydrogen fluoride-catalysed reaction. A possible mechanism for the latter involved an intermediate *tert.*-butyl cation but it was rejected on the ground that such carbonium ions had not been shown to exist. Since Olah and Kuhn [28] have shown the existence of complexes such as $C_6H_6Et^+BF_4^-$, formed by interaction of benzene, ethyl fluoride, and boron trifluoride, it seems possible to postulate intermediates such as $PhMe\cdot Bu^+HCl_2^-$ formed by interaction of toluene, butyl chloride, and hydrogen chloride.

[20] Pauling, " The Nature of the Chemical Bond," 2nd edn., Cornell Univ. Press, New York, 1940.
[21] Schmidlin, " Das Triphenylmethyl," Enke, Stuttgart, 1914.
[22] Meyer, *Ber.*, 1908, **41**, 2576.
[23] Lund, *J. Amer. Chem. Soc.*, 1927, **49**, 1346.
[24] Bartlett and Pöckel, *ibid.*, 1938, **60**, 1585.
[25] Bartlett, " Organic Chemistry, an Advanced Treatise," Vol. III, Gilman (Editor), Wiley, New York, 1953, p. 66.
[26] Simons and Hart, *J. Amer. Chem. Soc.*, 1944, **66**, 1309.
[27] Sprauer and Simons, *ibid.*, 1942, **64**, 648.
[28] Olah and Kuhn, *Nature*, 1956, **178**, 1344.