

Structure Investigation of Tri-*p*-methoxyphenylmethyl Carbonium Ion

PER ANDERSEN and BERNT KLEWE

Universitetets Kjemiske Institutt, Blindern, Oslo 3, Norway

Crystal data have been obtained from tri-*p*-methoxyphenylmethyl- HCl_2 and -HBr_2 , tri-*p*-methoxyphenylmethyl- ClO_4 , tri-*p*-methoxyphenylmethyl- $\text{HCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{-HBr}_2 \cdot 4\text{H}_2\text{O}$. The two water-containing compounds are isomorphous with rhombohedral unit cells of equal dimensions, where $a = 13.24 \text{ \AA}$ and $\alpha = 118.9^\circ$, space group, $R\bar{3}$. This investigation has given structural information on the carbonium ion, but no information has been obtained about the anions due to statistical distribution of the anion and water.

The molecules tri-*p*-methoxyphenylmethyl- HCl_2 , -HBr_2 , $\text{-HCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{-HBr}_2 \cdot 4\text{H}_2\text{O}$, and -ClO_4 were studied in order to find the most suitable compound for determining the structure of a carbonium ion. The crystal structures of the hydrogendihalogenides containing water of crystallization have been investigated. These compounds were of interest also because no structures containing HCl_2^- or HBr_2^- ions had so far been determined. Tri-*p*-methoxyphenylmethyl- HCl_2 was first prepared by Baeyer and Villinger.¹ Gomberg and Cone,² who also synthesized the perchlorate, carried out the first chemical analysis of the hydrogen dichloride. Sharp,³ who investigated their infrared and ultraviolet spectra, discussed four possibilities for the position of the additional hydrogen molecule and concluded that an HCl_2^- ion was present. Following an infrared investigation of $(\text{CH}_3)_4\text{NHCl}_2$, Waddington⁴ drew attention to the similarity of the spectra of the HF_2^- and HCl_2^- ions. The spectrum strongly suggested a linear ion and a symmetrically situated proton. Chany and Westrum⁵ arrived at the same conclusion from a thermodynamic investigation of $(\text{CH}_3)_4\text{NHCl}_2$. Problems concerning the carbonium ions have been extensively reviewed by Bethell and Gold.⁶ No structure determinations of carbonium ions of the triphenylmethyl type had been carried out when this work started, but Gomes de Mesquita, McGillavry and Eriks⁷ reported in 1959 that a crystal structure determination of triphenylmethyl-perchlorate was in progress. That structure and that of pararosanol perchlorate⁸ have now been refined three-dimensionally.⁹ Structure determinations of another type of carbonium ion, cyclopropenium¹⁰ and cyclobutenium¹¹ ions, have also been published recently.

EXPERIMENTAL

Tri-*p*-methoxyphenylmethane was prepared from anisaldehyde and anisole in a Baeyer's¹² reaction and then oxidized by PbO_2 ¹³ to tri-*p*-methoxyphenylmethanol. On adding gaseous hydrogen chloride to a solution of the alcohol³ in benzene and acetyl chloride the tri-*p*-methoxyphenylmethyl- HCl_3 salt precipitates. By using acetyl bromide and hydrogen bromide instead of acetyl chloride and hydrogen chloride the analogous salt tri-*p*-methoxyphenylmethyl- HBr_3 was obtained. The hydrogen dibromide was more hygroscopic than the corresponding hydrogen dichloride.

When the reactions were carried out in chloroform in an open vessel, needle-shaped red crystals were obtained. Chemical analysis, density measurements and unit cell dimensions showed that the crystals exposed to the atmosphere during crystallization, contained four molecules of water per unit cell. There were some difficulties in obtaining reproducible chemical analyses due to instability. This was particularly true for the hydrogen dibromide.

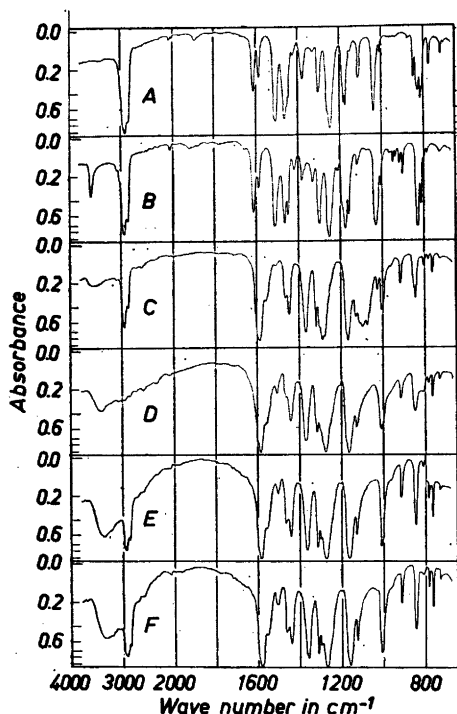


Fig. 1. Infrared Spectra: A. Tri-*p*-methoxyphenylmethane (Nujol). B. Tri-*p*-methoxyphenylmethanol (Nujol). C. Tri-*p*-methoxyphenylmethyl- ClO_4 (Nujol). D. Tri-*p*-methoxyphenylmethyl- HCl_3 (KBr). E. Tri-*p*-methoxyphenylmethyl- $\text{HCl}_3 \cdot 4\text{H}_2\text{O}$ (Nujol). F. Tri-*p*-methoxyphenylmethyl- $\text{HBr}_3 \cdot 4\text{H}_2\text{O}$ (Nujol).

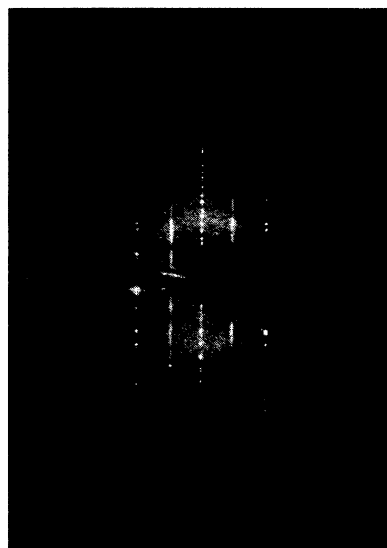


Fig. 2. Tri-*p*-methoxyphenylmethyl- ClO_4 : Oscillation diagram about the *c* axis.

INFRARED AND X-RAY DATA

In order to verify the presence of carbonium ions in the hydrous hydrogen dichloride and hydrogen dibromide crystals, the infrared spectra were recorded and compared with those of the hydrogen dichloride, the perchlorate, the methanol and the methane. The spectra are reproduced in Fig. 1. The compounds assumed to contain carbonium ions gave strong bands close to 1580, 1360, and 1300 cm^{-1} which, according to Sharp,³ are characteristic of the carbonium ion. The broad band at approximately 3400 cm^{-1} in spectra E and F showed the presence of water. Traces of water were also present in the hygroscopic tri-*p*-methoxyphenylmethyl- HCl_2 .

The crystal data were obtained from oscillation and Weissenberg photographs using $\text{CuK}\alpha$ radiation. The following unit cells and space groups were determined:

Tri-p-methoxyphenylmethyl-HCl₂. Orthorhombic unit cell: $a = 34.4 \text{ \AA}$; $b = 8.11 \text{ \AA}$; $c = 29.4 \text{ \AA}$. Systematic absences: hkl , $h + k \neq 2n$; $h0l$, $l \neq 2n$. Possible space groups: $Cmc2_1$, $C2cm$ and $Cmcm$. Density determinations by flotation gave 1.31–1.32 g/cm^3 and the number of molecules per unit cell is 16.

Tri-p-methoxyphenylmethyl-HBr₂. Orthorhombic unit cell: $a = 35.0 \text{ \AA}$, $b = 8.13 \text{ \AA}$, $c = 29.9 \text{ \AA}$. The crystals were very unstable and a complete set of Weissenberg films was not taken. All observations show that the hydrogen dichloride and the hydrogen dibromide compounds are most probably isomorphous. The density was determined as 1.47–1.48 g/cm^3 . The density calculated assuming 16 molecules per unit cell is 1.54 g/cm^3 .

Tri-p-methoxyphenylmethyl-ClO₄. The pattern obtained by oscillation about the needle axis showed that every second layer line was almost continuous with varying intensity (Fig. 2). The zeroth, second, and fourth layer line contained sharp reflections only.

The following crystal data were obtained from an analysis of the sharp reflections. Hexagonal unit cell: $a = 20.5 \text{ \AA}$, $c = 4.21 \text{ \AA}$. There are no systematic absences. The density determined by flotation is 1.41–1.42 g/cm^3 and the number of molecules per unit cell is 3. The possible space groups are $P\bar{3}$ and $P3$, the latter being the most probable because the carbonium ion lacks a center of symmetry. The intensity distribution of the diffuse reflections shows that the disordered structure does not have trigonal symmetry.

Tri-p-methoxyphenylmethyl-HCl₂·4H₂O. Rhombohedral unit cell: $a = 13.24 \text{ \AA}$, $\alpha = 118.9^\circ$. There are no systematic absences. The density was determined by flotation to be 1.26–1.27 g/cm^3 *i.e.* there is 1 molecule per unit cell. The space group is $R\bar{3}$. $R\bar{3}$ can be ruled out since the carbonium ion has no center of symmetry.

Tri-p-methoxyphenylmethyl-HBr₂·4H₂O. The hydrogen dibromide and hydrogen dichloride compounds are isomorphous with equal unit cell dimensions. The density determined by flotation was 1.50–1.52 g/cm^3 , calculated density 1.53 g/cm^3 . The hydrogen dibromide is less stable than the hydrogen dichloride and density changes are possibly caused by loss of HBr.

STRUCTURE DETERMINATION

Attempts have been made to solve the structures of tri-*p*-methoxyphenylmethyl-HCl₂·4H₂O and -HBr₂·4H₂O. The only possible position for the central carbon atom in the carbonium ion is on the main axis requiring a three-fold symmetry of the ion. The period along the trigonal axis is 4.09 Å. If the van der Waals' radius of the benzene ring is assumed to be 1.7 Å, then the maximum twist of the phenyl groups will be approximately 34° assuming *sp*² hybridization of the central carbon atom. Tetrahedral angles at the central carbon atom combined with a twist of the phenyl groups would not be possible. Neither the anion nor water molecules can occupy positions on the main axis and only general positions are available for these groups. The anion must therefore be statistically distributed. The four water molecules may all be statistically distributed or three could be in general positions.

On photographs taken at -110°C of the hydrogen dibromide compound some faint diffuse reflections were observed between the sharp reflections belonging to the lattice. Photographs taken at -80°C did not show these reflections. This indicates movements of one or both of the HBr₂⁻ and H₂O molecules at room temperature. A disordered distribution with anion and water molecules in more or less fixed positions is obtained at a lower temperature. The unit cell dimensions do not depend on the size of the anion and there may be space for a rather free motion of the water molecules or the anion.

Three-dimensional photographic data were collected for tri-*p*-methoxyphenylmethyl-HCl₂·4H₂O at room temperature. Precession and integrating Weissenberg camera, MoK α radiation and multiple film techniques were used. Two-dimensional photographic data (CuK α radiation) were collected at -90°C for tri-*p*-methoxyphenylmethyl-HBr₂·4H₂O with rotation of the crystal about the trigonal axis. Similar data were collected for the chlorine compound at room temperature. The intensities were recorded on a photometer, Lorentz and polarization corrections applied and the intensities placed on an absolute scale by the method of Wilson.

Patterson and sharpened Patterson projections of both compounds along the 4.09 Å main axis gave useful information about the carbonium ion and its orientation. Nothing could be interpreted, however, regarding the anion and water contributions to the maps. A Patterson projection based on the difference between the intensities of the two compounds corrected for unequal thermal damping did not give decisive information about the halogen-halogen and halogen-water distances. The bromine-bromine contribution may range from 2/3 Br-2/3 Br to 1/3 Br-1/3 Br depending on the degree of overlap. Since the halogen-halogen vector was not detected in the Patterson projection, the bromine atoms probably do not overlap. The distribution may be one third bromine atom or even less in each position depending on whether one or more sets of general positions are occupied.

A Fourier projection of tri-*p*-methoxyphenylmethyl-HCl₂·4H₂O along the main axis is shown in Fig. 3. The phases were calculated from the carbonium ion alone using the following molecular parameters: The central bond length 1.50 Å, ring C-C distance 1.40 Å, twist angle of the phenyl groups 30°, C-O

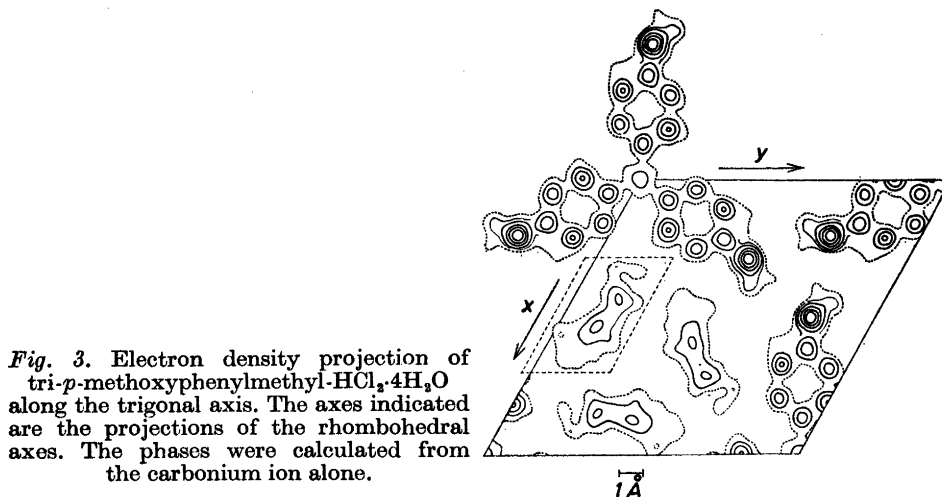


Fig. 3. Electron density projection of tri-*p*-methoxyphenylmethyl-HCl₂·4H₂O along the trigonal axis. The axes indicated are the projections of the rhombohedral axes. The phases were calculated from the carbonium ion alone.

distance 1.42 Å and C—O—C = 110°. A part of this projection is reproduced in Fig. 4a together with the same part of the hydrogen dibromide projection (Fig. 4b). One third of a chlorine atom was placed in the peak positions and included in the calculation of the phases. The resulting Fourier map is shown in Fig. 4c where the new maxima A, B and C indicate possible water molecule positions. Least squares refinements with various combinations of water positions resulted mostly in *R* values between 20 and 25 %. Refinements of the bromine compound, however, gave consistently higher *R* values. The possibility that the water molecules were linked to the oxygen atoms of the methoxy groups by hydrogen bonds was also investigated, but least squares refinements did not result in reasonable coordinates and angles.

The primary purpose of this investigation was to obtain structural information about the carbonium ion, but the statistical distribution of the anion

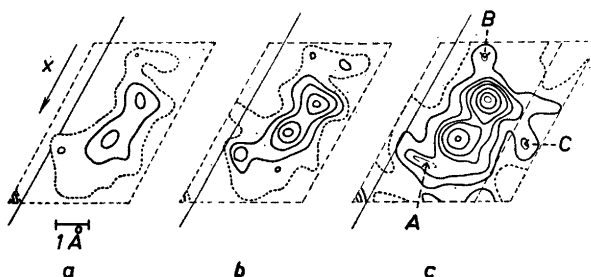


Fig. 4. a. A part of the electron density map shown on Fig. 3. b. The corresponding part of the electron density map of tri-*p*-methoxyphenylmethyl-HBr₂·4H₂O. c. The same part of the electron density map of tri-*p*-methoxyphenylmethyl-HCl₂·4H₂O with halogen included in the phase calculations. Arrows indicate the maxima A, B, and C.

and water prevented accurate determination of the molecular parameters of the cation. The reliable information obtained in this investigation is that the central bonds are coplanar or nearly so, and that the phenyl groups are twisted approximately 30° out of the plane. This is in good agreement with the results for triphenylcarbonium-perchlorate and pararosaniminperchlorate.⁷⁻⁹ It is unlikely that more accurate molecular parameters can be obtained for the present compounds and the work has been discontinued. It was not possible from this X-ray study to find out whether the anion is in the form HX_2^- , $2X^- \cdot H_3O^+$, or $X^- \cdot HX$. The isomorphism of the compounds tri-*p*-methoxyphenylmethyl- HCl_2 and $-HBr_2$ shows that if a HCl_2^- ion is present as proposed from the spectroscopic³ data, then a similar HBr_2^- ion exists as well.

Acknowledgement. The authors wish to express their thanks to Mag. Scient. Else Augdahl for recording the infrared spectra.

REFERENCES

1. Baeyer, A. and Villiger, V. *Ber.* **35** (1902) 3031.
2. Gomberg, M. and Cone, L. H. *Ann.* **370** (1909) 192.
3. Sharp, D. W. A. *J. Chem. Soc.* **1958** 2558.
4. Waddington, T. C. *J. Chem. Soc.* **1958** 1708.
5. Chang, S. and Westrum, Jr., E. F. *Nucl. Sci. Abstr.* **16** (1962) Abstr. No. 2995; Chang, S. *Diss. Abstr.* **23** (1962) 455.
6. Bethell, D. and Gold, V. *Quart. Rev. (London)* **12** (1958) 173.
7. Gomes de Mesquita, A. H., MacGillavry, C. H. and Eriks, K. *Am. Cryst. Ass. Annual Meeting, 1959*, Program and Abstracts.
8. Eriks, K. and Koh, L. L. *Am. Cryst. Ass. Annual Meeting, 1963*, Program and Abstracts.
9. Eriks, K., Koh, L. L., Gomes de Mesquita, A. H. and MacGillavry, C. H. *Nordisk Strukturkemikermöte, 1964*, Abstracts; Gomes de Mesquita, A. H., MacGillavry, C. H. and Eriks, K. *Acta Cryst.* **18** (1965) 437.
10. Sundaralingam, M. and Jensen, L. H. *J. Am. Chem. Soc.* **85** (1963) 3302.
11. Bryan, R. F. *J. Am. Chem. Soc.* **86** (1964) 733.
12. Baeyer, A. and Villiger, V. *Ber.* **35** (1902) 1197.
13. Burton, H. and Cheeseman, G. W. H. *J. Chem. Soc.* **1953** 835.

Received January 15, 1965.