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Inorganic and Organic Onium Salts

by

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ABSTRACT

It has been found that the nitrosonium NO^+ ion absorbs in the infrared anywhere between 2400 cm.$^{-1}$ and 2150 cm.$^{-1}$ The only marked trend is that salts of complex fluoro-acids absorb at higher frequencies than salts of complex chloro-acids. The factors which influence the position of the $N-O^+$ absorption are discussed. Some nitrosonium salts are isomorphous with the corresponding alkali-metal salts and are hence fully ionic. There appears to be little correlation between fully ionic character in the lattice and the position of the NO^+ absorption. Nitric oxide and dinitrogen tetroxide react with β group metal halides to give solid adducts. Infrared spectroscopic examination has shown that these adducts generally contain nitrosonium ions; the nitric oxide generally gives a lower proportion of nitrosonium ion than does dinitrogen tetroxide. It is concluded that complex halo anions are also present.

It has been shown that hexaphenylditin does not undergo marked heterolytic dissociation in nitromethane solution. Triphenyltin fluoroborate can be prepared from solution in organic solvents but much solvent is always carried down with the compound. New salts containing the triphenylmethyl carbonium ion and the SiF_6^{2-} and TiF_6^{2-} anions have been prepared and this cation has been identified in the substance

$Ph_3C^+Br_3^-$. It is found that complex halo anions containing more than one different halogen are not stabilised by the carbonium cations. Organometallic derivatives containing unsaturated linkages appear to be readily protonated in solution in acid; the protonated species are apparently carbonium ions stabilised by co-ordination to the metal. Dyestuff cations of the triphenylmethane dyes are as reluctant to form covalent compounds as the triphenylmethyl group is to form ionic compounds. Covalent comppunds can be prepared using anions derived from weakly basic acids such as HCN. The factors influencing the covalent $\leftrightarrow$ ionic equilibrium are discussed.

The first part of this report has been written up in the same form as it will be shortly submitted to the Chemical Society (London) with a view to publication.

The Infrared Spectrum of the Nitrosonium Ion.

The compounds $NOClO_4$ and $NOBF_4$ have been shown to be isomorphous with the salts NH_4ClO_4 and NH_4BF_4 and to contain nitrosonium, NO^+, ions which have achieved spherical symmetry by rotation.[1] The evidence for the presence of nitrosonium ions in other compounds has been summarised[2] by Addison and Lewis and has involved studies of conductivity, magnetic susceptibility, and Raman spectra; the present report describes the infrared spectra of a series of compounds which, on the basis of their stoichiometry, might be expected to contain the nitrosonium ion. The free nitrosonium ion is generally considered to absorb at about 2300 cm.$^{-1}$; this is to be compared

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[1]. Klinkenberg, Rec. Trav. Chim. 1937, 56, 749.

[2]. Addison and Lewis, Quarterly Reviews, 1958, 9, 115.

with a value of 1700–1900 cm.$^{-1}$ when the NO$^+$ ion is co-ordinated to a metal[3] and of 1050–1200 cm.$^{-1}$ when the NO$^-$ ion is co-ordinated to a metal.[4] The results of the present study are shown in Table 1. There is good agreement between the present results and the Raman spectral measurements which have been previously made on some of these derivatives. With the exception of $2NOCl.SnCl_4$ $NOCl.SbCl_5$, and $2NOCl.PtCl_4$, samples of the adducts between nitrosyl chloride and chlorides tended to give absorption bands in the region of 1800 cm.$^{-1}$ These bands were absent in freshly prepared samples and increased in intensity as the sample was kept. It is considered that these bands are due to the presence of nitrosyl chloride formed by dissociation of the complexes – ClNO absorbs at 1799 cm.$^{-1}$,[5] but there is the possibility of isomeric change in the compounds so that an NO$^+$ group becomes co-ordinated to the metal. In all the examples given in the table there was a strong absorption band between 2150 and 2400 cm.$^{-1}$ It is

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[3] . Lewis, Irving, and Wilkinson, J. Inorg. Nuclear Chem., 1958, 7, 32.

[4] . Griffith, Lewis, and Wilkinson, J. Inorg. Nuclear Chem., 1958, 7, 38.

[5] . Burns and Bernstein, J. Chem. Phys., 1950, 18, 1669.

considered that this band is characteristic of the nitrosonium, NO^+, ion. Most of the peaks are sharp singlets but some compounds gave shoulders. It has previously been shown[6] that $(NO)(NO_2)S_3O_8$ gives two Raman peaks at 2277 and 2308 cm.$^{-1}$ and the former peak has been considered to be due to the asymmetriel stretching vibration of the NO_2^+ ion which has been rendered Raman active by the ion site symmetry. In view of the analytical figures for the compounds studied in the present work a similar explanation is unlikely to hold for the two bands which are observed in the spectra of some of the compounds. It seems more likely that the splitting of the main band is due to the presence of more than one type of nitrosonium ion in the unit cell.

Most of the compounds prepared were examined by X-ray powder photography and the unit-cell dimensions found are given in Table 2. It was confirmed that nitrosonium fluoroborate, chlorostannate, and chloroplatinate are isomorphous with their potassium analogues - the latter two salts have been briefly mentioned[7] to be isomorphous with their potassium analogues but no cell dimensions were given.

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[6] Gerding and Eriks, *Rec. trav. chim.*, 1952, 71, 773.

[7] Klinkenberg, *Chem. Weekblad.* 1938, 35, 197.

Table I.

Vibrational Spectra of Compounds containing NO^+ Ions.

$NOBF_4$	2387	sharp
$(NO)_2GeF_6$	2391	sharp, shoulder at 2336
$(NO)_2SnF_6$	2342	sharp
$NOPF_6$	2379	sharp
$NOAsF_6$	2340	sharp
$NOSbF_6$	2385	broad, shoulder at 2342
$NOVF_6$	2391	sharp, shoulder at 2328
$NOUF_6$	2333(a)	
$NOMoF_6$	2331(a)	
$NOSO_3F$	2377	broad
$(NO)_2S_2O_7$	2278	sharp, shoulder at 2294
$NOHSO_4$	2340(b) R	
$NOClO_4$	2313(b) R	
$(NO)(NO_2)S_3O_{10}$	2308R (c) 2277R	
$NOAlCl_4$	2242	sharp, shoulder at 2370
	2236(b) R	
$(NO)_2SnCl_6$	2191	broad
$NOSbCl_6$	2189	broad
$NoBiCl_4$	2331	broad
$(NO)_2TiCl_6$	2165	broad
$NOMnCl_3$	2271	broad
$NOFeCl_4$	2200	sharp, shoulder at 2275
$NOCuCl_3$	2271	broad
$NOZnCl_3$	2187	broad
$NOHgCl_3$	2268	broad
$(NO)_2PtCl_6$	2201	sharp

All present work except where marked, all figures in cm.$^{-1}$

R, Raman spectra

(a) Greichman, Smith, Trond, and Ogle, Inorg. Chem., 1962, 1, 61.

(b) Gerding and Houtgraaf, Rec. trav. Chim., 1953, 72, 21.

(c) Gerding and Eriks, Rec. trav. Chim., 1952, 71, 773.

Table 2

Unit Cell Dimensions in Å.

$NOBF_4$	orthorhombic	a = 7.88, b = 5.72, c = 7.40	(a)
KBF_4	orthorhombic	a = 7.83, b = 5.67, c = 7.35	
$NOSO_3F$	orthorhombic	a = 8.59, b = 5.99, c = 7.37	(b)
KSO_3F	orthorhombic	a = 8.56, b = 5.95, c = 7.33	
$(NO)_2SnCl_6$	cubic	a = 10.24	(a)
K_2SnCl_6	cubic	a = 10.14	
$(NO)_2PtCl_6$	cubic	a = 11.27	(a)
K_2PtCl_6	cubic	a = 11.18	

(a) Wyckoff 'Crystal Structures'

(b) Sharp, J.Chem.Soc., 1957, 3761.

Nitrosonium fluorosulphate is isostructural with potassium fluorosulphate, both compounds being isomorphous with potassium fluoroborate.[8] The fluorosulphate is presumably undergoing free rotation in the two salts. The results from powder photography strongly support the presence of an ionic lattice in the four compounds where lattice dimensions were established and, by comparison of infrared spectra, in all the compounds listed in Table 1 In each case the lattice dimensions of the nitrosonium slats are slightly greater than those found for the corresponding potassium salts; it has been estimated that when the nitrosonium ion is in free rotation and is acting as a sphere that the effective radius is 1.40 Å. (cf. K^+1.33 Å)[1]. No nitrosonium salt of a complex fluoro acid other than the fluoroborate is isomorphous with the corresponding potassium salt. Complex halides generally have structures which are based on close-packing of halide ions.[9] The fluoride ion (r = 1.33 Å) is smaller than the nitrosonium ion and the formally asymmetrical ion can probably not attain full spherical symmetry. The chloride ion (r = 1.81 Å) is larger and appears more able to accommodate the nitrosonium ion

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[8] . Sharp, J. Chem. Soc., 1957, 3761.

[9] . Wells, Quarterly Reviews, 1954, 8, 380.

and to allow it to attain spherical symmetry. Nitrosonium fluoroborate and fluorosulphate, which are isomorphous with the potassium salts do not have close-packed structures.

The vibrational frequency of the nitrosonium ions vary widely as has previously been noted by Gerding and Houtgraaf[10] who explain the variation in terms of polarisation of the anion by the cation - such polarisation having also been postulated by Seel[11] and by Burg and McKenzie[12]. In the present work, however, it has been shown that salts which absorb at both the high and low frequency ends of the range are isomorphous with the corresponding potassium salts and are hence unlikely to be appreciably polarised. The only generalisation that it is possible to make about the trends in values of the NO^+ vibrational stretching frequency is that salts of complex fluoro acids tend to give the highest frequency, followed by salts of oxy-acids, followed by salts of complex chloro acids. There is a vague trend in that the salts containing larger anions tend to give lower NO^+ vibrational frequencies than salts of smaller anions.

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[10] Gerding and Houtgraaf, *Rec. trav. Chim.*, 1953, *72*, 21.

[11] Seel, *Z. anorg. Chem.*, 1950, *261*, 75.

[12] Burg and McKenzie, *J. Amer. Chem. Soc.*, 1952, *74*, 3143.

It is apparent that the factors governing the NO^+ vibrational frequency are complex, but it is suggested that both interaction between the nitrosonium ion and the halogens of the complex anion and between the nitrosonium ion and the central metal atom of the anion may be of importance in lowering the frequency of the N-O vibration. This frequency is probably also dependent upon the effect of the charges in the lattice - that is upon the size of the NO^+ ion. Since chlorine atoms are more diffuse than fluorine atoms they might be expected to exert a greater electronic effect at the cation side. There appears to be no correlation between the position of the nitrosonium ion absorption and the stability of the compound.

Complex anions corresponding to those required in the present study have been postulated previously. $NOCl.CuCl$ must be formulated on the present evidence as $NO^+CuCl_2^-$ which would be expected to be diamagnetic. The compound is diamagnetic when first prepared, but becomes paramagnetic on standing. It is possible that there is a change to a nitrosyl complex during this transition[2,13].

[13] Asmussen, *Z. anorg. Chem.*, 1939, **243**, 127.

Experimental

Infrared spectra were measured on mulls in 'Fluorube' grease between calcium fluoride windows It was found that any other mulling agent caused immediate decomposition of the nitrosonium salt as did the use of windows of sodium chloride. All preparations of mulls were carried out in the dry-box. Spectra were measured on a Grubb Parsons Model DB3 spectrophotometer using sodium chloride optics. Each spectrum was referenced against a spectrum of polystyrene.

X-Ray powder photographs were taken in Lindemann glass capillaries using CuK_{α} radiation. Photographs were measured visually but calculation of $\sin^2\theta$ values and indexing of powder lines were carried out on a Ferranti Sirius Computer using programmes developed in these laboratories.

Compounds were prepared by the literature method given in the table. Analysis for nitrogen was carried out by reduction with Devarda's alloy followed by distillation and estimation of the ammonia produced. Chlorine was estimated as silver chloride.

Compound	Reference to preparation	N calc.	N found %
$NOBF_4$	14	12.0	11.6
$(NO)_2GeF_6$	14	11.4	10.9
$(NO)_2SnF_6$	14	9.6	9.3
$NOPF_6$	14	8.0	7.8
$NOAsF_6$	14	6.4	6.1
$NOSbF_6$	14	5.2	5.0
$NOVF_6$	15	7.0	6.2
$NOSO_3F$	14	10.8	10.5
$(NO)_2S_2O_7$	16	10.2	10.0

	Ref. to prep.	N Calc.	Cl calc	N found	Cl found %
$NOAlCl_4$	10, 12	7.0	71.3	6.7	70.6
$(NO)_2SnCl_6$	12, 17	7.2	54.4	6.8	54.0
$NOSbCl_6$	12	3.8	58.3	3.7	58.2
$NOBiCl_4$	18	3.7	37.0	3.6	36.2
$(NO)_2TiCl_6$	17	8.7	66.3	8.2	65.4
$NOMnCl_3$	17	7.3	55.6	7.1	55.0
$NOFeCl_4$	12	6.2	62.3	6.1	62.0
$NOCuCl_2$	12, 13	8.5	43.1	8.3	42.6
$NOZnCl_3$	13, 17	6.9	52.7	6.6	52.0
$NOHgCl_3$	13, 17	4.2	31.6	3.8	30.1
$(NO)_2PtCl_6$	17	6.0	45.5	5.9	45.6

14. Woolf, *J. Chem. Soc.*, 1950, 1053
15. Sharpe and Woolf, *J. Chem. Soc.*, 1951, 798
16. Hart-Jones, Price and Webb, *J. Chem. Soc.*, 1929, 312.
17. Partington and Whynnes, *J. Chem. Soc.*, 1948, 1952; 1949, 3135.

The Interaction of Nitrogen Oxides and Lewis Acids.

The interactions have been carried out both directly and by interaction in a solvent. In all cases the products were examined by infrared spectroscopy and, as far as possible by analysis. This aspect of the work is still under active investigation. The following systems have been investigated:

PF_5/NO. No reaction in petrol at -78° owing to insolubility of nitric oxide in the solvent. Reaction in a bomb gave a very small yield of a white product; it was not possible to obtain infrared data on such a small sample.

PF_5/NO_2. Interaction in a Carius Tube gives an immediate separation of solid. The infrared spectrum shows a strong band at ca. 2300 cm.$^{-1}$ indicating the presence of an NO^+ ion and also strong bands at about 1020 and 1160 cm.$^{-1}$. These latter bands were identified as P-O frequencies and it is considered that there has been interaction to give phosphate or fluorophosphate entities. A weak band at 850 cm.$^{-1}$ indicated the presence of the PF_6^- ion. It is considered that one product of this reaction is $NOPF_6$. The compounds $AsF_5.NO_2$ and $SbF_5.NO_2$ have been reported previously but nothing is known of their structures.

Aynsley, Peacock, and Robinson, Chem. and Ind., 1951, 1117.

PCl_5/NO_2. White solid product. Dissociates to PCl_5 plus NO_2 at room temperature.

PCl_3/NO_2. White solid product. Strong NO^+ absorption with an additional band at 1860 cm.$^{-1}$ This compound appears to be identical with the $P_2O_6NCl_2$ reported to result from the $POCl_3/N_2O_4$ and PCl_3/N_2O_4 reactions.

$SnCl_4/NO$ White product. Weak NO^+ absorption

$SnCl_4/NO_2$ White product. Strong NO^+ absorption

$SbCl_5/NO$ Yellow product. Weak NO^+ absorption

$SbCl_5/NO_2$ Yellow product. Three strong infrared bands at 2200, 2000, and 1850 cm.$^{-1}$. The latter band may be the result of decomposition but the presence of two higher bands suggests that more than one cation is present.

It has been shown that the interaction between nitrogen oxides and boron trifluoride gives $NO^+BF_4^-$ as the major product. The other products are borates. The present work indicates formation of nitrosonium ions in the reactions between nitrogen oxides and non-metal and metal chlorides and fluorides and it is apparent that nitrosonium salts, probably of complex halo-anions, are being formed.

Klement and Woolf, Z. anorg. Chem. 1955, **282**, 149.

Kuhn, 2nd International Symposium on Fluorine Chemistry, Estes Park, Colorado, 1962.

Dinitrogen tetroxide gives higher concentrations of nitrosonium ions than does nitric oxide.

Further studies are necessary to make positive identification of the anions which are present in these nitrosonium salts.

Onium Salts containing predominantly organic or organometallic cations.

(a) Preparation of triaryl tin compounds.

Although $Ph_3\overset{+}{M}$ (M = C, Si, Ge, Sn, Pb) derivatives are known for M = C (see section b of this report) and the Ph_3Si^+ ion has recently been prepared in the salt $Ph_3Si\ SbF_6$ there is little evidence on Ph_3Sn^+ cations. From a consideration of the infrared spectra of the compounds $Me_3SiOOCH_3$, $Me_2Si(OOCCH_3)_2$, $MeSi(OOCCH_3)_3$, $Si(OOCCH_3)_4$, $Me_3SnOOCCH_3$, $Me_3SnOOCH$, Me_3Sn chloroacetates, $Me_3SnOOCC_6H_5$, Me_3Sn halides, $Me_2Sn(OOCCH_3)_2$, $Me_2Sn(OOCH)_2$, Me_2Sn halides, MeSn halides it has been concluded that the silicon derivatives are covalent but that the tin compounds contain methyl tin cations. The Me_3Sn cation is considered to be planar and the Me_2Sn cation

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G. A. Olah, private communication.

R. Okawara, D. E. Webster, and E. G. Rochow, J. Amer. Chem. Soc., 1960, 82, 3287.

linear. Trimethyl lead carboxylates are also considered to contain planar cations.

R. Okawara and H. Sato, J. Inorg. Nuclear Chem., 1961, 16, 204.

The compounds R_3SiCl react with silver perchlorate to give trialkyl and triaryl silicon perchlorates but the evidence on bonding in these compounds is not complete as, although they react in solvolytic reactions as if they were ionic their infrared spectra are not definite in favouring either a covalent or an ionic structure. Trimethyl tin fluoroborate

U. Wannagat, F. Brandman, W. Liehr, and H. Niederprum, Z. anorg. Chem., 1959, 302, 1085.

has been described as resulting from the reaction between tetramethyl tin and boron trifluoride.

Burg, J. Amer. Chem. Soc., 1961, 83, 2667.

In the present work it was desired to obtain evidence on the dissociation of the derivatives $Ph_3M{-}MPh_3$ (M = C, Si, Ge, Sn, Pb). Work was carried out on the stannane derivatives as these are the most stable. There is previous evidence for dissociation in all of these derivatives. The hexaphenylethanes are dissociated homolytically in solution to triarylmethyl radicals. The hexa aryl disilanes do not appear to be dissociated in solution and no free radicals can be detected.

Sidgwick 'The Chemical Elements and their Compounds'

A. J. Petro and C. P. Smyth, J. Amer. Chem. Soc., 1957, 79, 6147.

It is postulated that Ph_3Si radicals are present as reactive intermediates in radical induced reactions of Ph_3SiH. Hexaphenyldigermane is not dissociated in solution but hexaphenylditin and hexaphenyldiplumbane appear from molecular weight determinations to be dissociated in solution. Magnetic susceptibility studies rule out the presence of free radicals and the only other possibility is heterolytic dissociation.

$$Ph_3Sn - SnPh_3 \rightleftharpoons Ph_3Sn^+ + Ph_3Sn^-$$

This has been questioned on the basis that the Ph_3Sn^+ cation would be expected to be coloured by analogy with the colour of the triphenylmethyl cation, but this reasoning is suspect as the orbitals which would be used in forming the Ph_3Sn^+ ion are very different from those used in forming the Ph_3C^+ ion and in fact the Ph_3Si^+ ion is colourless. By use of a Wayne-Kerr Universal Conductivity Bridge the present work has shown that the heterolytic dissociation of hexaphenylditin in nitromethane is not detectable and is certainly less than 1%. Since the solutions of hexaphenyldilead show changes in colour with change in temperature it would be worthwhile to make similar measurements on such solutions.

Triphenyltin chloride reacts with silver fluoroborate in ether or benzene to give a precipitate of silver chloride and, on removal of excess of solvent, a gummy material

J. Curtice, H. Gilman, and G. S. Hammond,
J. Amer. Chem. Soc., 1957, 79, 4754.

containing fluoroborate ions. It is impossible to remove the final traces of solvent from these materials and it is certain that there is extensive solvation of the triphenyl tin cation by organic solvents. It is suggested that such solvation also occurs in the hexaphenylditin derivatives - for example by a charge transfer a mechanism between solvent benzene and the phenyl groups. Such solvation would explain the anomolous molecular weights of solutions of the hexa-aryl di-tins. Triphenyltin fluoride does not react in a solvent or under a pressure of boron trifluoride to produce triphenyltin fluoroborate. In other studies it has been shown that although tetraphenyltin and boron trifluoride

Sharp and Winfield, unpublished observation

react to give phenyl boron difluoride, the solid product is triphenyltin fluoride and not the fluoroborate. This lack of reactivity of triphenyltin fluoride is attributed to the high lattice energy of this compound.

(b) Carbonium Salts.

The existence of carbonium salts is now well established

Sharp and Sheppard, J. Chem. Soc., 1957, 674.

and it has previously been shown that triaryl methyl carbonium ions may be readily prepared by the reaction

$$Ar_3CCl + AgX \longrightarrow AgCl + Ar_3CX$$

where X is the anion of a very strong acid. During recent work it has been shown that silver salts of dibasic acids are soluble in organic solvents - previous work in this field had been confined to salts of mono-basic acids - and accordingly it has been possible in the present work to prepare triphenylmethyl hexafluorosilicate and hexafluorotitanate, both bright yellow compounds containing the planar propeller-like triphenylmethyl cation. Triphenylmethyl-hexafluorosilicate is appreciably soluble in toluene and the solvent appears to solvate the carbonium cation. The older literature contains many references to what appear to be perhalides of carbonium ions. $Ph_3CBr....Br_5$ has now been shown to contain a triphenylmethyl cation - the colour of the anion obscures the characteristic colour of the cation - but it is relatively unstable and tends to lose bromine under vacuum.

Moss and Sharp, unpublished observations.

Schmidlin "Das Triphenylmethyl"

In previous work it has been shown that it is doubtful whether the adducts $Ph_3CX.BY_3$ (X and Y = F, Cl, or Br) contain discrete mixed haloborate anions although they certainly contain triphenyl methyl cations. If the reaction is carried out with excess BY_3 such that BY_3 is a stronger

Kemmitt and Sharp, J. Chem. Soc., in publication

Lewis Acid than BX_3 (the order of Lewis Acids strength is $BF_3 < BCl_3 < BBr_3$) there is complete displacement of the more weakly acidic BX_3. In the present work these observations have been extended to the use of Lewis Acids other than boron halides. Ph_3CCl reacts with PF_5, AsF_5, and SbF_5 to produce Ph_3CPF_6, Ph_3CAsF_6, and Ph_3CSbF_6 respectively. There is complete displacement of chlorine from the compounds and no evidence for the formation of mixed halo anions. SiF_4 appears to be very weakly acidic and does not interact with Ph_3CCl or Ph_3CF in toluene although triphenylmethyl-hexafluorosilicate has been prepared (see above).

Attempts have been made to stabilise carbonium ions by co-ordination to transition metal ions. Strong evidence was found to support the view that in strongly acidic media - where carbonium ions would be expected to be formed - that there is reaction. The products are extremely reactive and will have to be examined in solution by nuclear magnetic resonance spectroscopy. As this technique was not available during the present contract - it is now - this could not be carried out and the present work was confined to qualitative observations of the type of reaction.

Compound	Acidic medium	Reaction
$C_7H_8Mo(CO)_3$	$HF + BF_3 + CO$	gives $Mo(CO)_6$ plus partially fluorinated polymer
$C_7H_8Mo(CO)_3$	HF	red compound becomes yellow
$C_4H_6Fe(CO)_3$	HF	gives polymer and yellow liquid.
$(\pi\text{-}CH_3C_5H_4)Mn(CO)_3$	$HF + BF_3 + CO$	yellow colour changes to dark green. A yellow compound can be isolated.
$Fe(CO)_5$	HF	yellow changes to red

It is apparent that there is a very wide range of reactions of this type which can be investigated. The reaction detailed above for the preparation of molybdenum hexacarbonyl from cycloheptatriene molybdenum tricarbonyl appears to be one of the first examples of the formation of a true carbonyl under strongly acidic conditions. All of the above reactions are considered to give compounds in which a proton has been added to the organic part of the molecule to give what is effectively a carbonium ion attached to the metal.

The factors which influence the ionisation in an Ar_3CX entity are as follows. The process is

$$Ar_3C:X \longrightarrow Ar_3\overset{+}{C} + X^-$$

and will favour the production of ions if the C-X bond is weak. Thus ionisation will occur more readily in iodides (C-I bond strength 66.5 K.cals.) than in fluorides (C-F bond strength 107.0 K.cals.). As is shown in all of its reactions triphenylfluoromethane is much less reactive than the other triphenylmethylhalides. The value of the bond strength will be greatly dependent upon the presence of electron attracting or electron repelling groups substituted into the aryl rings and hence the ionic or covalent nature of the Ar_3CX molecule will depend upon the substituent in the ring systems. The effect of substituents is also allied to the stability of the carbonium ion and, in general, electron-releasing substituents tend to stabilise the carbonium ion whilst an electron-withdrawing substituent stabilises the covalent model. The actual stability of the carbonium ion is composed of two terms, the resonance energy of the completely conjugated system and the reorganisation energy required to rearrange the tetrahedral Ar_3C entity to a planar propeller-like form. The actual anion affects the equilibrium through its basicity. Anions derived from very strong acids are reluctant to assume a

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Pauling, 'Nature of the Chemical Bond'.

Blicke, J. Amer. Chem. Soc., 1924, 46, 1515.

covalent form whilst anions derived from acids of more normal strengths are reluctant to assume an ionic form.

The final decision as to whether a triarylmethyl derivative is covalent or ionic is a balance of all of these factors. Thus triphenylchloromethane is covalent but on successive substitution of electron-releasing *p*-methoxy groups into the rings the compound becomes ionic on substitution of the fourth methoxy group. Tri-p-methoxy-chloromethane is covalent but if the basicity of the anion is increased slightly by formation of the HCl_2^- ion an ionic derivative results.

Lund, *J. Amer. Chem. Soc.*, 1927, 49, 1346.

The present work is designed to provide further evidence on the actual factors which delinate the boundary between ionic and covalent compounds.

Sharp, *J. Chem. Soc.*, 1958, 2558

The experiments have been carried out using three dyestuff cations:- Malachite green, phenylbis-*p*-N-dimethyl-aminophenylmethyl; Brilliant green, phenylbis-p-N-diethyl aminophenylmethyl; Crystal violet, tris-p-N-dimethylamino-phenylmethyl. These dyestuffs are normally obtained in the form of their chlorides which are coloured and contain carbonium ions. The experiments are designed to prepare covalent derivatives by the use of anions derived from weakly basic acids. In each case the compounds prepared have been analysed and studied by infrared spectroscopy. Salts of all three cations have been studied but they all follow the same pattern and results will be given in detail for Malachite green only.

Anion

silicotungstate. - Yields dark green complex. The infrared spectrum is similar to those of the ionic carbonium salts but there are some differences. It is considered that the large cation is forming some complex with the anion but the nature of the interaction is not yet understood.

phosphomolybdate. - Very similar to silicotungstate. Complex formation.

fluoroborate. - Ionic salt formed

perchlorate. - Ionic salt formed

cyanide. - Light green compound formed. The infrared spectrum is closely similar to that of the leuco base rather than that of the chloride or fluoroborate. It is considered that this is a covalent cyanide.

azide, thiocyanate, cyanate, fluoride	Formation of derivatives which, from their colours are probably covalent but which appear to undergo rapid polymerisation and became sticky so that consistent infrared spectra cannot be obtained.

From the present results it is clear that providing that anions of weakly basic acids are used the dyestuff cations will form covalent compounds. Further work is necessary to find the actual detailed conditions required for covalent and ionic character.

Annex

1. Personnel utilised during the reporting period were:

D. W. A. Sharp	(part time)
J. Thorley	full time
Ali Mohammed	full time

There were no changes in research policies during the period of this Contract.

Dr. D. W. A. Sharp visited the United States during the period of this Contract and the sum of $400 was agreed to be paid to him by contract amendment to enable him to visit Redstone Arsenal and Piccatinny Arsenal.

2. Research personnel say 4000 man hours
+ 200 man hours Dr. Sharp
Total 4200 man hours.

Estimated expenses for materials $1450

No important property has been acquired during the contract period at direct contract expense.