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OXIDATION OF MOLECULAR BROMINE BY URANIUM HEXAFLUORIDE IN ACETONITRILE. PREPARATION AND PROPERTIES OF HEXAFLUOROURANATES(V) CONTAINING POSITIVE BROMINE

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SUMMARY

Molecular bromine is oxidized by uranium hexafluoride in acetonitrile at ambient temperature. The product is formulated on the basis of its spectra, and its brominating and oxidizing abilities as $[Br(C_6H_9N_3)][UF_6]$ in which bromine is bound to an acetonitrile trimer containing C=N bonds.

INTRODUCTION

Recently it has been shown that oxidation of molecular iodine by molybdenum or uranium hexafluorides in acetonitrile leads to the isolation of $[I(NCMe)_2][MF_6]$, M = Mo or U [1]. These compounds are formulated as salts which on the basis of iodine and molybdenum EXAFS studies [2] and their vibrational spectra [1] have cations containing linear N-I-N skeletons. The electrochemical oxidation of Br_2 in MeCN has been observed to occur at +1.6 V vs. Ag^+, Ag [3] and cations of the type $[BrL_2]^+$, L = quinoline [4] or quinuclidine [5] have been structurally characterized. It seemed worthwhile therefore to attempt the analogous oxidation of Br_2 by MoF_6 and UF_6 ($E_{1/2}$ for MF_6, MF_6^- are ca. + 2.3 and 1.60 V respectively [6]) in the hope of preparing $[Br(NCMe)_2]^+$ salts.

We find that although Br_2 is oxidized by UF_6 in MeCN the product does not contain $[Br(NCMe)_2]^+$ as additional reactions involving the solvent occur. No reaction occurs between Br_2 and MoF_6 and this work therefore provides the first example of different behaviour occurring between these two strong oxidizing agents in MeCN.

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RESULTS

Addition of uranium hexafluoride to a frozen solution of molecular bromine in acetonitrile, mole ratio $Br_2:UF_6 \geqslant 3:1$, results in a decrease in the red colour of the solution as the mixture is allowed to warm slowly to room temperature. A pale green solid, empirical formula $C_6H_9BrF_6N_3U$, remains after removal of unchanged Br_2 and MeCN. If excess Br_2 is not used, and if the temperature is allowed to rise too quickly, the solvent is extensively polymerized. The solid can be stored for long periods <u>in vacuo</u> at 273 K, but slow decomposition to give Br_2 as one product occurs. Decomposition is more rapid (observable after 12 h) in MeCN at room temperature.

The presence of the hexafluorouranate(V) anion is indicated both by the solid's electronic spectrum in MeCN [7], and by the observation of ν_1 and ν_3 of UF_6^-, at 619 (Raman) and 515 cm^{-1} (i.r) respectively [8], in the solid's vibrational spectrum. Characteristic bands due to MeCN are not observed in the latter, but strong bands at 1627, 1580, and 1520 cm^{-1} in the solid's i.r spectrum indicate the presence of $>$C=N- groups [9]. The mass spectrum of the solid (Table) is consistent with bromine being bound to CH_3CN oligomers, and supports the microanalytical data in indicating a ratio Br : CH_3CN of 1 : 3.

TABLE

Mass spectrum of $[Br(C_6H_9N_3)][UF_6]$

m/z	Relative intensity	Assignment	m/z	Relative intensity	Assignment
283	3.1	$C_6H_7Br_2N_3$	82	33.6	$C_4H_6N_2$
281	6.1				
279	2.9		67	6.8	C_4H_5N
201	22.4	$C_6H_8BrN_3$	66	2.8	C_4H_4N
203	21.9		54	9.8	C_3H_4N
160	7.1	$C_4H_5BrN_2$			
162	6.8		42	100	C_2H_4N
123	21.5	$C_6H_9N_3$	41	28.9	C_2H_3N
121	5.1	$C_2H_2BrN_2$			
119	5.5				

On the basis of this evidence the solid is formulated as $[Br(C_6H_9N_3)]$-$[UF_6]$.

The $^{13}C\{^1H\}$ and ^1H n.m.r. spectra of $[Br(C_6H_9N_3)]$ in CD_3CN or EtCN are reversibly, temperature dependent and indicate that several species are present, (Figure). Broad signals are observed at room temperature in the $^{13}C\{^1H\}$ spectrum

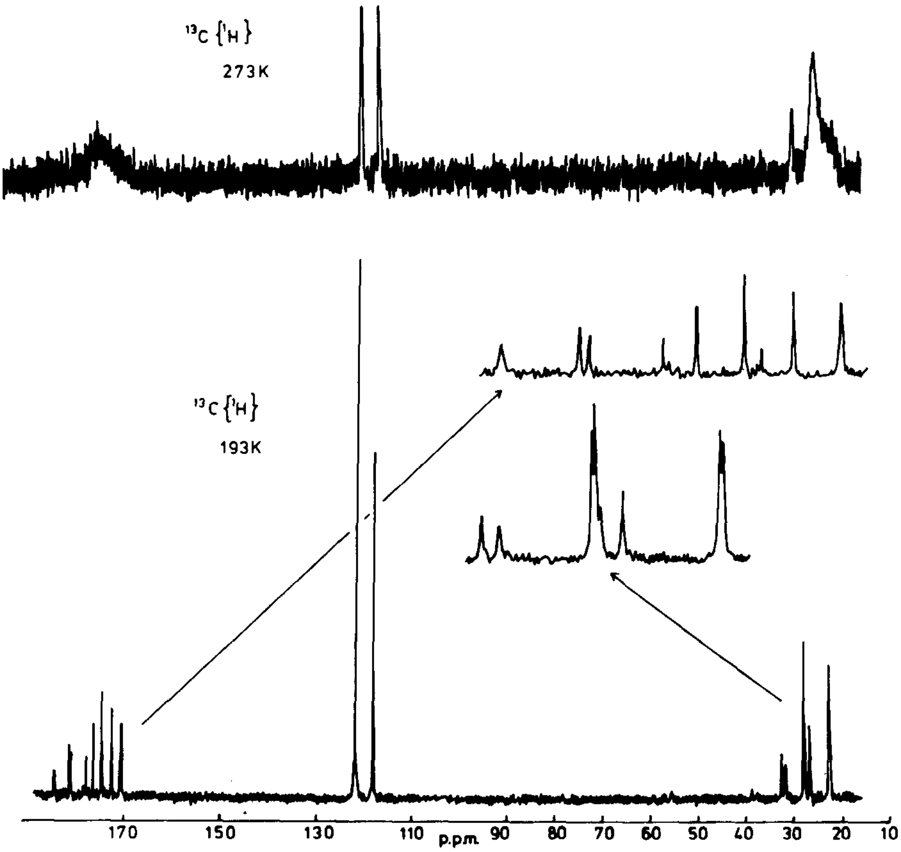


Fig. $^{13}C\{^1H\}$ n.m.r. spectra of $[Br(C_6H_9N_3)][UF_6]$ in $EtCN/CD_3CN$. Signals ca. δ_c=120 p.p.m. are due to solvent cyano-carbon resonances.

but these sharpen on cooling. In the 193 K spectrum six signals in the region δ_c=22.3 to 27.8 p.p.m., and two at δ_c=31.6 and 32.4 p.p.m are assigned to CH_3- and $-CH_2$- groups respectively on the basis of DEPT experiments. Nine signals in the region δ_c=170.5 to 184.7 p.p.m are assigned to $>$C=N- carbons having slightly different environments. For comparison δ_c values for 2,4,6-trimethyl, 1,3,5-triazine are 175.9 ($>$C=N) and 25.4 p.p.m. (CH_3) respectively [10].

In the ^1H spectrum broad signals observed at room temperature sharpen on cooling and at 193 K singlets at δ_H=3.04 and 3.25 p.p.m are assigned to CH_3- groups and at δ_H=4.88 p.p.m to -CH_2-. The spectrum also contains relatively weak resonances at δ_H=14.0 and 14.1 p.p.m assigned to -NH protons.

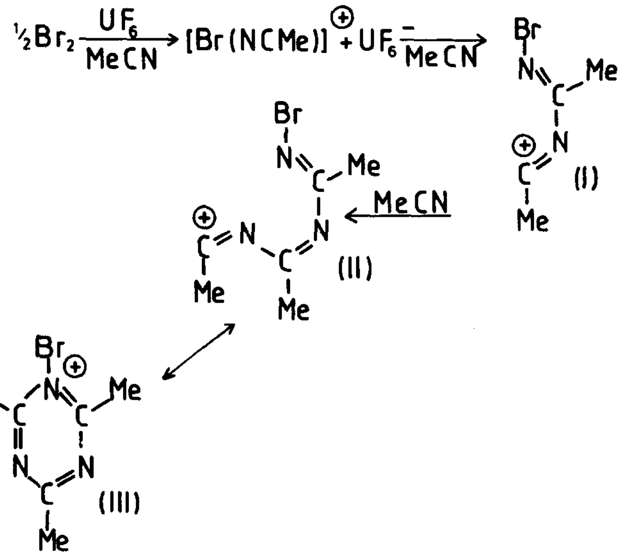
Since there is no evidence for the presence of -CH_2Br or $>$NH groups in the i.r. spectrum of $[Br(C_6H_9N_3)][UF_6]$, the presence of -CH_2- and $>$NH signals in the n.m.r. spectra is considered to be due to slight decomposition of the compounds catalysed by trace moisture.

Two properties which are characteristic of the $[I(NCMe)_2]^+$ cation in MeCN are its ability to iodinate activated benzene derivatives at room temperature and its oxidizing ability, for example towards the copper(I) cation and nitric oxide [1]. Similar behaviour is observed for $[Br(C_6H_9N_3)][UF_6]$. Toluene, anisole, and 9-methylanthracene are brominated under mild conditions, mixtures of products being observed in each case. Tetra-bromination appears possible for toluene and anisole ; in the case of 9-methylanthracene the products appear to contain a dibromo-derivative and 1,2-bis(9-anthryl)ethane. In corresponding iodinations using $[I(NCMe)_2]^+$ I_2 is formed also, but Br_2 was not observed in the present case except in the 9-methylanthracene reaction where a radical cation intermediate may be involved [11].

The solvated copper(I) cation, $[Cu(NCMe)_4]^+$, NO, and I_2 are all oxidized by $[Br(C_6H_9N_3)][UF_6]$ in MeCN at room temperature and the reaction stoichiometries suggest strongly that bromine is in the +1 oxidation state. The products from the first two reactions are Br_2 and $[Cu(NCMe)_6]^{2+}$ or NO^+ ; material containing C=N- groups is also present as a component of the product mixtures. The product from the oxidation of I_2 is not $[I(NCMe)_2]^+$ but appears to contain iodine bound to an MeCN oligomer. However the product decomposes readily to give I_2 in solution even at low temperature and this precluded detailed examination.

DISCUSSION

The oxidation of molecular bromine in acetonitrile differs from that of molecular iodine under similar conditions in two respects. Firstly, oxidation occurs only with the thermodynamically stronger oxidizing agent, uranium hexafluoride ; secondly, the cation formed cannot be described simply as $[Br(NCMe)_2]^+$. A possible structure for the cation and the pathway by which it could be formed are given in the Scheme.



Scheme. Reaction Pathway proposed for the oxidation of Br_2 by UF_6 in MeCN.

It appears that Br^+ is too electrophilic to exist as a simple cation solvated by the relatively weak ligand MeCN, and we propose that oligomerization of MeCN occurs to give species represented by (I) and (II) (Scheme). The isolation of a salt containing $[Br(C_6H_9N_3)]^+$ is rationalized by the ring closure of (II) to give the cation (III) in which the positive charge would be expected to be delocalized.

In order to account for the temperature dependent n.m.r. spectra it is necessary to postulate the existence of an equilibrium in solution between cyclic(III) and acylic(II) forms of the cation. The latter is capable of existing in several conformations, for example planar, syn or anti with respect to the central C=N bond, hence restricted rotation among these could account for the complex $^{13}C\{^1H\}$n.m.r spectrum observed at 193 K (Figure). Other explanations, for example the formation of species with $\overline{C=N-C=N}$ four membered rings, are possible but are less attractive.

Nucleophilic attack at the cyano-carbon of an organic nitrile is enhanced greatly by coordination of the cyano-nitrogen to an electrophilic centre. For example aqueous base hydrolysis of MeCN to acetamide is 2 x 10^6 faster for $[(H_3N)_5Co(NCMe)]^{3+}$ than for free MeCN [12]. Nucleophilic attack on coordinated nitriles has also been exploited for synthesis, for example in the formation of 5-methyltetrazole by nucleophilic attack of N_3^- on $[(H_3N)_5Co(NCMe)]^{3+}$ [13], and in the preparation of a tridentate bis(amidine) aminomethyl malonate chelate complex initiated by nucleophilic attack of CN^- on $[(H_3N)_5Co(NCMe)]^{3+}$ [14]. The reaction pathway postulated in the present work is directly analogous, with Br^+ acting as the electrophilic centre for coordination.

If the reaction conditions are not carefully controlled, or if the reaction is carried out in EtCN, polymerization of the solvent is more extensive and a well-defined product is not isolated. This situation is similar to that encountered in reactions between binary fluorides and Cu^I trimethyl phosphite complexes in MeCN where solvent polymerization occurs, apparently initiated by the CH_3^+ cation [15].

The structures proposed for the cation are unusual but its chemical behaviour is not dissimilar from those of other N-bromo compounds, for example N-bromo succinimide [16], which contain electrophilic bromine. The species formed by the anodic oxidation of Br_2 in MeCN has been suggested to be $[Br(NCMe)_n][Br_3]$, n = 1 or 2. The anion was identified by its electronic spectrum but no direct evidence for the cation's structure was presented [3]. The brominating properties of the cation could be accounted for equally well by the structure suggested in the present work.

EXPERIMENTAL

Unless indicated below procedures for purification of reagents, manipulation of products, and spectroscopic measurements were as those described previously [1]. Bromine (B.D.H. AnalaR) was degassed and dried over P_2O_5, then vacuum distilled three times over fresh P_2O_5. Mass spectra were obtained using a Kratos MS12 spectrometer. ^1H and $^{13}C\{^1H\}$ n.m.r. spectra were obtained using a Bruker WP200JY at 200 (^1H) or 50 MHz (^{13}C). Chemical shifts (δ p.p.m) are reported with respect to CD_3CN at δ_c1.3 and CHD_2CN at δ_H1.93 and are positive to higher frequency. ^1H n.m.r. spectra of brominated organics were obtained using a PE R32 spectrometer at 90 MHz (δ_H with respect to Me_4Si).

Preparation of $[Br(C_6H_9N_3)][UF_6]$

A solution of Br_2 (2.0 mmol) in MeCN (5 cm^3) was prepared *in vacuo* and UF_6 (*ca*. 0.7 mmol) added to the frozen solution by vacuum distillation. On warming the mixture to room temperature its dark red colour changed to a pale red. Removal of volatile material left a pale green solid. Analysis: Found: C, 12.9; H, 1.7; Br, 14.5; F, 20.3; N, 7.4; U, 43.1%. $C_6H_9BrF_6N_3U$ requires C, 13.0; H, 1.6; Br, 14.4; F, 20.5; N, 7.5; U, 42.9%. Its vibrational spectrum consisted of the following bands: i.r. ν_{max}, 3160m, 2985s, 2940s, 2890s, 2604m, 1850w, 1627s, 1580s, 1520s, 1455s, 1435m, 1420m, 1380m, 1370m, 1335s, 1305m, 1028s, 950m, 740m, 605s, 515s, 440m, 365m, 290m cm^{-1}. Raman: $\Delta\nu$, 2954w, 1464w, 1414m, 1358w, 1166w, 1058s, 1033m, 964w, 679w, 619s, 606m, 575m, 373w, 337w cm^{-1}.

Reactions of $[Br(C_6H_9N_3)][UF_6]$ in MeCN.

(a) With Nitric Oxide.

A mixture of $[Br(C_6H_9N_3)][UF_6]$ (0.54 mmol) in MeCN (5 cm^3) was allowed to react with excess NO at room temperature. Br_2, identified by its electronic spectrum, λ_{max}= 390nm, was immediately liberated. Removal of volatile material left a pale green solid (0.265 g; required for complete reaction to $NOUF_6$ + $C_6H_9N_3$ 0.273 g). Its i.r. spectrum contained bands due to NO^+, $\nu(NO)$ = 2330 cm^{-1} [17], UF_6^-, ν_3 = 520 cm^{-1} [8], and at 1620, 1575 and 1520 cm^{-1} assigned to ν (C=N).

(b) With tetra-kis(acetonitrile)copper(I)hexafluorophosphate

$[Br(C_6H_9N_3)][UF_6]$ (0.18 mmol), contained in a frangible glass ampoule, was added to $[Cu(NCMe)_4][PF_6]$ (0.18 mmol) and MeCN (5 cm^3) in an evacuable Spectrosil cell. The ampoule was broken, the electronic spectrum of the solution recorded, and $[Cu^{II}]$ was determined as 0.0375 mol dm^{-3} (required for complete oxidation of Cu^I 0.036 mol dm^{-3}). A similar reaction using an excess of the Cu^I salt yielded a blue-green solid whose i.r. spectrum contained bands assigned to coordinated MeCN, PF_6^-, UF_6^- and at 1620, 1565 and 1530 cm^{-1} assigned to C=N- groups. Br_2 was detected in the volatile fraction.

(c) With Molecular Iodine

Aliquots (5.0 cm^3) of a standard solution of I_2 in MeCN (2.13 x 10^{-3} mol dm^{-3}) were transferred in a glove box to dried, evacuable Spectrosil cells and weighed portions of $[Br(C_6H_9N_3)][UF_6]$ (4.8 - 0.95 x 10^{-5} mol) contained in frangible glass ampoules were added. Absorbances of I_2 at 460 nm were determined, the ampoules broken and the spectra of the products obtained. In most solutions λ_{max} shifted to ca. 400 nm due to Br_2 formation but in the reaction where the bromine salt was 0.95 x 10^{-5} mol, I_2 unreacted was estimated as 0.65 x 10^{-5} mol (expected for complete reaction 0.59 x 10^{-5} mol). A mixture of I_2 (0.2 mmol) and $[Br(C_6H_9N_3)][UF_6]$ (0.2 mmol) in MeCN (5 cm^3) was allowed to react at room temperature and gave a pale brown solid after removal of unreacted I_2, Br_2 and MeCN. Its i.r. spectrum was similar to that of $[Br(C_6H_9N_3)][UF_6]$ containing bands at 515 cm^{-1} assigned to UF_6^- [8] and at 1620, 1575, and 1510 cm^{-1} assigned to $\nu(C{=}N)$. Major peaks (m/z) in its mass spectrum with their assignments were 249, $C_6H_8IN_3^+$; 168, $C_2H_3IN^+$; 167, $C_2H_2IN^+$; 166 C_2HIN^+ and 127 I^+. The solid decomposed readily at room temperature giving I_2 as one product. Its $^{13}C\{^1H\}$ nmr spectrum in CD_3CN contained signals at δ_c=28.9 and 28.7 p.p.m assigned to CH_3- groups.

(d) With Aromatic Compounds.

Aliquots (2cm^3) of a standard solution of $[Br(C_6H_9N_3)][UF_6]$ in MeCN (0.2 mol dm^{-3}) were added to toluene, anisole, and 9-methylanthracene (3.5 - 5.5 mmol) in the glove box. Free Br_2 was observed only in the latter reaction. After hydrolysis the organic products were extracted with petrol and the solids isolated. No attempt was made to separate the components of the mixtures formed nor to optimise yields, but examination of the mixtures by mass spectrometry and ^1H n.m.r. spectroscopy gave the following results: anisole, bromination of the aromatic ring occurred to give products that included $C_6HBr_4(OMe)$ and $C_6H_2Br_3(OMe)$; toluene, bromination of the aromatic and the methyl group occurred, with the incorporation of up to five Br atoms; 9-methylanthracene, formation of a dibromo-derivative and oxidation to give an anthracene dimer.

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