

1,1,1,3,3,3-Hexafluoropropan-2-ol (HFP) as a Solvent for Electrochemistry[†]

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1,1,1,3,3,3-Hexafluoropropan-2-ol (HFP) is a non-nucleophilic and highly polar solvent with strongly solvating ability toward nucleophiles, especially anionic ones. This combination of properties makes HFP a favourable solvent for electrode reactions in which stabilization of radical cations is required, or where anion participation is not desirable. Examples of successful applications are described for aromatic and heteroaromatic compounds, nitrones, anions, or halogens and halogen-containing compounds. A special case is electropolymerization to give conducting polymers, where the generally lower reactivity of radical cations in HFP leads to qualitatively different behaviour, e.g. formation of a dehydrodimer radical cation from fluoranthene in HFP as compared to the formation of a conducting polymer in acetonitrile.

1,1,1,3,3,3-Hexafluoropropan-2-ol (HFP) is a solvent with exceedingly favourable properties for the generation of persistent solutions of radical cations.^{1,2} The gain of observation time in relation to the previously most favourable solvent, trifluoroacetic acid alone or in admixture with its anhydride, amounts to a factor between 10 and 100. HFP also has been shown to increase the kinetic stability of carbocations by similar factors.³ HFP is strongly polar, in fact the only solvent among ca. 300 which is more polar than water on the Reichardt E_T scale.⁴ It is very weakly nucleophilic and has a strong propensity to solvate anions. It has been used only occasionally as a solvent for electrochemistry,^{5–7} but has then shown strong indications of its usefulness in the study of anodic processes for which it is desirable to stabilize the radical cation. We now describe some further studies of HFP as a solvent for electrochemistry.

Results

General. The solvent properties of HFP are such that polar compounds are easily soluble, whereas nonpolar compounds are difficultly soluble. To take an extreme example of a nonpolar substance for which solubilities are known for a wide range of solvents, C_{60} ,⁸ this compound could be dissolved to a very weakly coloured solution which according to UV spectral analysis con-

tained ca. $5 \mu\text{mol dm}^{-3}$ of C_{60} , provided the extinction coefficient was assumed to be the same as in dichloromethane (solubility $0.36 \text{ mmol dm}^{-3}$). This is the same order of solubility as found in other polar solvents, like ethanol.⁸ Tetraalkylammonium salts were freely soluble in HFP, tetrabutylammonium hexafluorophosphate being an excellent supporting electrolyte for anodic chemistry. This combination had an anodic limit of 2.1 V vs. Ag/AgCl. Alkali metal salts are difficultly soluble in HFP, since HFP solvates cations weakly.¹ On the cathodic side, use was limited by reduction of the proton of the OH group commencing at about 0.4 V vs. Ag/AgCl, meaning that the ferrocinium/ferrocene couple was just barely accessible for measurement.

The reversible potential of the ferrocinium/ferrocene couple in HFP was found to be 0.05 V vs. Ag/AgCl, to be compared with that in dichloromethane, 0.43 V vs. Ag/AgCl.

Aromatic and heteroaromatic compounds. Since HFP does not solvate cations well *per se*, it is not to be expected that radical cations should be stabilized thermodynamically in HFP. The persistency of radical cations in HFP has to be ascribed rather to kinetic factors, above all the low nucleophilicity of HFP itself and the fact that any nucleophilic species accidentally present are so strongly solvated by HFP that their reactivity is vastly attenuated, e.g. by factors of 10^{-8} or less for halide ions in HFP in relation to acetonitrile.¹

Table 1 shows redox potentials $E(\text{ArH}^+/\text{ArH})$ for a

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Table 1. Potentials of ArH^{•+}/ArH redox couples in DCM or HFP, referenced to the ferrocinium/ferrocene system.

ArH	E/V in CH ₂ Cl ₂	E/V in HFP	ΔE/V	Ref.
Durene	1.44	1.30	-0.14	
1,9-Me ₂ -dibenzofuran	1.40	1.30	-0.10	5b
Me ₆ -benzene	1.23	1.15	-0.08	
Anthracene	0.98	0.90	-0.08	
4,6-Me ₂ -dibenzofuran	1.40	1.32	-0.08	5b
4,4'-Dimethoxy-1,1'-binaphthalene	0.76	0.69	-0.07	
1,4-Dimethoxybenzene	1.05	0.98	-0.07	
2,4,6,8-Me ₄ -dibenzofuran	1.23	1.17	-0.06	5b
4,4'-Bitoluene	1.25	1.20	-0.05	
1-Methoxynaphthalene	1.03	0.98	-0.05	
2,8-Me ₂ -dibenzothiophene	1.15	1.10	-0.05	5c
Dibenzochrysene	0.90	0.86	-0.04	
2,8-Me ₂ -dibenzofuran	1.32	1.29	-0.03	5b
1,2,3,4,5,6,7,8-Me ₈ -anthracene	0.43	0.40	-0.03	
2,2'-Bidibenzofuran	1.11	1.09	-0.02	5b
2,4,6,8-Me ₄ -dibenzothiophene	1.04	1.02	-0.02	5c
Perylene	0.67	0.66	-0.01	
4-Fluoroanisole	1.43	1.43	0.00	
2,3'-Bidibenzofuran	1.13	1.13	0.00	5b
Dibenzothiophene	1.23	1.24	0.01	5c
3,3'-Bifluoranthene	1.09	1.10 ^a	0.01	
Dibenzofuran	1.47	1.49	0.02	5b
Fluoranthene	1.20	1.22	0.02	
Tris(4-bromophenyl)amine	0.67	0.70	0.03	
2,3-Me ₂ -1,4-(MeO) ₂ -benzene	0.71	0.75	0.04	
3,3'-Bidibenzofuran	1.11	1.15	0.04	5b
4,4'-Dimethoxystilbene	0.62	0.66	0.04	2b
4-Me-2,3,5,6-tetrafluoroanisole	1.76	1.81	0.05	
1,2-Benzodioxole	1.07	1.13	0.06	
2,5-Difluoro-1,4-dimethoxybenzene	1.05	1.12	0.07	
2,2',5,5'-Tetramethoxybiphenyl	0.87	0.95	0.08	
Phenanthrene	1.11	1.26	0.15	
4-Dimethylaminobenzaldehyde	0.74	0.89	0.15	5a

^a For solubility reasons, this measurement had to be performed in HFP: dichloromethane (4:1 v/v).

number of aromatic and heteroaromatic compounds in dichloromethane and HFP, referenced to the internal ferrocinium/ferrocene couple. In most cases the redox potentials refer to chemically reversible or partially reversible processes, where the scan rates have been adjusted to attain conditions for such behaviour. Generally, such reversibility was observed in HFP at scan rates 5×10^{-2} – 10^{-3} of those needed in dichloromethane. The compounds of Table 1 are ordered in increasing potential difference ΔE between HFP and dichloromethane.

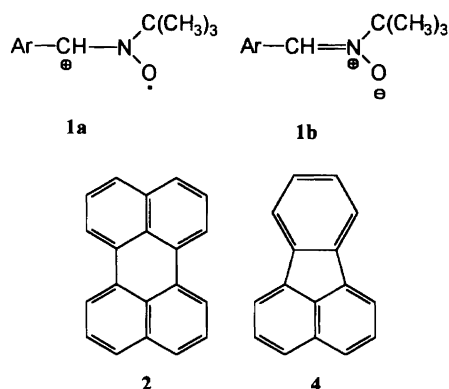
If it is assumed that the effect of the solvent is entirely due to its solvating effect on the radical cation, HFP exerts a weak stabilizing effect on radical cations with extensively delocalized positive charge relative to dichloromethane. These are the systems where $\Delta E < 0$ and which occupy positions in the upper part of Table 1. Systems where the positive charge can be localized onto part of the radical cation, for example at an oxygen or nitrogen atom, show $\Delta E > 0$ and are found in the lower part of Table 1. The strongest effect was noted for a series of α -aryl-*N-tert*-butylnitrones,^{5a} where ΔE was between 0.2 and 0.4 V (Table 2). The structure of a radical cation of this type has been pictured as a dionic

Table 2. Potentials of nitrone^{•+}/nitrone redox couples in DCM or HFP, referenced to the ferrocinium/ferrocene system.^{5a}

Nitron	E/V in CH ₂ Cl ₂	E/V in HFP	ΔE/V
4-NO ₂ -PBN	1.48	1.68	0.20
4-CH ₃ O-PBN	0.86	1.18	0.32
4-CH ₃ -PBN	1.05	1.38	0.33
3,4-OCH ₂ O-PBN	0.80	1.13	0.33
α -Phenyl- <i>N-tert</i> -butylnitron (PBN)	1.10	1.48	0.38
4-(CH ₃) ₂ N-PBN	0.28	0.66	0.38
4-F-PBN	1.13	1.54	0.41

aminoxylcarbenium ion with the positive charge localized at the benzylic position (**1a**),⁹ and in this sense a large ΔE is expected. On the other hand, in the case of nitrones the parent compound has a dipolar structure (**1b**), and solvation of the negative oxygen by HFP might in part contribute to the large effect on ΔE .

For oxidation beyond the radical cation stage, HFP did not seem to offer any particular advantages. Perylene (**2**) was chosen as a model for study, since both redox



couples $2^{\cdot+}/2$ and $2^{2+}/2^{\cdot+}$ have been shown¹⁰ to be electrochemically reversible in liquid SO_2 at -40°C at a sweep rate of 200 mV s^{-1} with a difference of 0.70 V between $E_{\text{rev}}(2^{2+}/2^{\cdot+})$ and $E_{\text{rev}}(2^{\cdot+}/2)$. In HFP at 20°C , the $2^{2+}/2^{\cdot+}$ couple became quasireversible only at sweep rates $>2\text{ V s}^{-1}$ and then the difference between $E_{\text{rev}}(2^{2+}/2^{\cdot+})$ and $E_{\text{rev}}(2^{\cdot+}/2)$ was 0.84 V . This behaviour is understandable in view of the strongly electrophilic properties of dications¹¹ and the weak solvating properties of HFP toward cationic species.

Anionic species. The strong solvation of anions X^- by HFP has a profound effect upon the redox potentials $E(\text{X}^{\cdot-}/\text{X}^-)$, as seen from the data reported in Table 3, again ordered in increasing ΔE . For comparison with rate studies, the rate constant ratios for reactions of some anions with tris(4-bromophenyl)aminium ion in acetonitrile and HFP, respectively, have been included.¹ Rate constants are not available for reactions in dichloromethane, but they should be larger than in acetonitrile, if anything.¹² As expected, the potential difference is larger for hard anions like chloride and carboxylate ions than for soft ones, like iodide and trinitromethanide ion.

Reduction of halogens and compounds containing 'positive halogen.' Table 4 lists potentials for the reduction of various oxidants **3**, comprising halogens and an assortment of compounds usually classified as possessing a 'positive halogen' atom. All compounds are seen to be stronger oxidants in HFP, sometimes much stronger.

This is expected in view of the stabilization of anionic species $3^{\cdot-}$ by HFP. The higher oxidizing power explains why these reagents can be used with advantage to generate solutions of persistent radical cations in HFP, particularly iodine chloride^{2b} and phenyliodine(III) trifluoroacetate.¹³

A second important feature for the electrochemistry of most oxidants **3** is the stabilization of halide ions by HFP, which makes the formation of complexed halogens of type X_3^- much less favourable, thus removing the complicating influence of this intermediate in the electrochemical reaction sequence.^{2b}

Electropolymerization. The use of HFP as a solvent for studying the formation of electrically conducting polymers has been briefly commented upon earlier, and applied to dibenzofuran.^{5b} A conclusion of this work was that the reactions involved in electropolymerization seemed to be slower in HFP than in other solvents, as expected from the generally lower reactivity of cationic species in HFP.

Fluoranthene (**4**) has been shown to undergo polymerization in acetonitrile- Et_4NBF_4 with formation of a black conducting deposit,¹⁴ and was therefore selected for a study in HFP. Figure 1a shows the buildup of the polymer in acetonitrile- Bu_4NPF_6 upon repeated cycling of the potential between 0.8 and 1.8 V . The first anodic sweep ($E_{\text{pa}} = 1.63\text{ V}$ vs. Ag/AgCl) leads to the formation of an intermediate with $E_{\text{pc}} = 1.37\text{ V}$, which presumably is the radical cation of an oligomer of fluoranthene. For comparison, CV of an authentic dimer, 3,3'-bifluoranthene, had an ill-defined cathodic peak at ca. 1.5 V and did not form any conducting deposit under similar conditions. Upon cycling, the cathodic peak in Fig. 1a grew slowly, and eventually it became hidden by a broader peak corresponding to what appears to be a wider distribution of several oligomeric species. After the ten cycles shown in Fig. 1a, the electrode was covered by a black deposit which had to be removed by polishing before the next measurement.

In HFP, repeated cycling between 0.5 and 1.4 V (vs. Ag/AgCl) shows a different situation (Fig. 1b). The first anodic sweep ($E_{\text{pa}} = 1.27\text{ V}$) gave an intermediate with a cathodic peak at 1.00 V , and in the second anodic sweep

Table 3. Potentials of $\text{X}^{\cdot-}/\text{X}^-$ redox couples in DCM or HFP, referred to the ferrocinium/ferrocene system.

X^-	E_{pa}/V in CH_2Cl_2	E_{pa}/V in HFP	$\Delta E_{\text{pa}}/\text{V}$	$\log(k_{\text{CH}_3\text{CN}}/k_{\text{HFP}})^a$ (energy difference/eV)	Ref.
I^-	0.19	0.43	0.24		2b
$(\text{NO}_2)_3\text{C}^-$	1.52	1.77	0.25	3.5 (0.21)	
Br^-	0.63	1.04	0.41	8.0 (0.47)	2b
$(\text{CN})_3\text{C}^-$	0.82	1.30	0.53		20
Cl^-	0.63 (AN)	1.42	0.79	7.1 (0.42)	2b
$(\text{PhCOO})_2\text{H}^-$	1.57	~ 2.4	0.9		
$(\text{MeCOO})_2\text{H}^-$	1.28	~ 2.5	1.1	8.9 (0.52)	

^a Rate constants $k/\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ for reaction of X^- with tris(4-bromophenyl)aminium ion (Ref. 1). The value in parentheses represents the corresponding energy difference (in eV).

Table 4. Potentials of 3/3^{•+} redox couples in acetonitrile or HFP, referred to the ferrocinium/ferrocene system.

Compound 3	E_{pc}/V in acetonitrile	E_{pc}/V in HFP	$\Delta E_{pc}/V$	$E_{lim}EPR$	Ref.
Br ₂	0.53	0.77	0.24	1.0	2b
Br ₃ ⁻	0.51	0.77	0.26		2b
I ₂	0.12	0.39	0.27	0.7	2b
Cl ₂	0.44	0.90	0.46	0.9	2b
N-Chlorosuccinimide	-0.75	-0.26	0.49		2b
Cl-C(CN) ₃	-0.02	0.47	0.49	1.1	20
I-Cl	0.44	0.98	0.54	1.2	2b
Cl-C(CN) ₂ CONH ₂	-0.43	0.27	0.70		2b
N-Bromosuccinimide	-0.36	0.58	0.94	1.1	2b
Phenyliodine(III)(OCOCF ₃) ₂	-0.53	0.52	1.05	1.1	

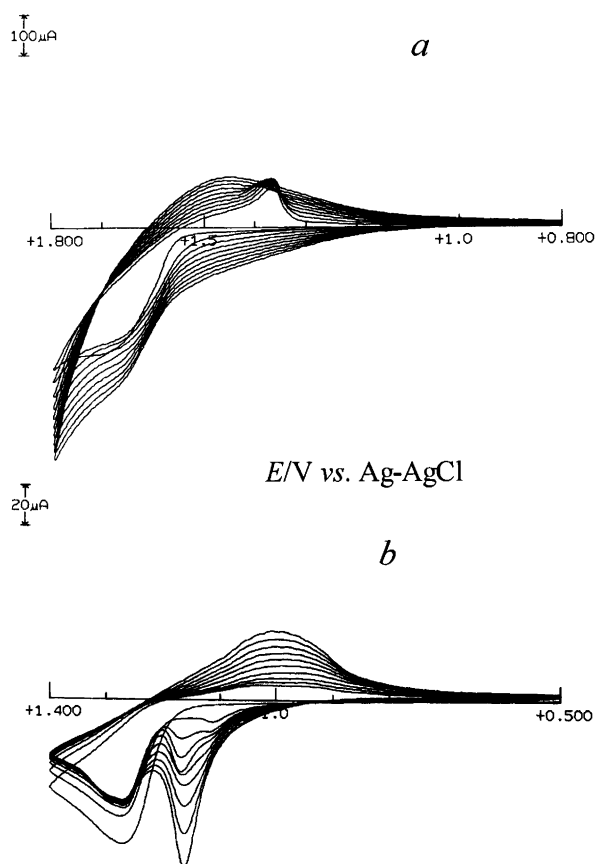


Fig. 1. Repeated CV scans of (a) an acetonitrile-Bu₄NPF₆ (0.15 mol dm⁻³) solution of fluoranthene (8.0 mmol dm⁻³) at 0.8 V s⁻¹ and (b) an HFP-Bu₄NPF₆ (0.15 mol dm⁻³) solution of fluoranthene (satd., ~2 mmol dm⁻³) at 0.4 V s⁻¹.

a small peak at 1.12 V appears. This E_{pa} matched that of 3,3'-bifluoranthene (Table 1; note that the CV of this compound had to be performed in HFP containing 20% of dichloromethane because of its low solubility in neat HFP). Continued cycling removed the cathodic peak at 1.12 V and replaced it with one at 1.17 V, presumably due to precipitated 3,3'-bifluoranthene radical cation salt. However, no visible deposit was apparent after the run, and no polishing of the electrode was necessary between runs.

Conclusions. As solvent for electrochemistry, HFP has some unique advantages due to two of its most characteristic properties, namely its low nucleophilicity and its ability to render nucleophilic species unreactive by hydrogen bonding. This makes HFP especially useful for the study of organic redox systems where radical cations are involved, for example in anodic electropolymerization. Also inorganic systems involving anionic species may be studied with advantage in HFP, since complicating effects of ligation can be eliminated.

The solvent most closely mimicking the properties of HFP seems to be liquid SO₂,^{10,15} which has a wider potential window and can be used for the observation of multicharged species under reversible conditions. Its main disadvantage is the need for special cell equipment for measurement at low temperature (typically in the range -20 to -50 °C) and internal removal of the last traces of water by superactive alumina.¹⁰ HFP can be used as received at room temperature and down to its freezing point, -5 °C.

Experimental

Materials and methods. 3,3'-Bifluoranthene,¹⁶ 4-methyl-2,3,5,6-tetrafluoroanisole¹⁷ and 2,2',5,5'-tetramethoxybiphenyl¹⁸ were prepared according to literature methods. Chlorotricyanomethane was prepared by an improved method.¹⁹ All other substrates were of commercial origin or available from earlier studies. HFP and dichloromethane were of Merck UVASOL[®] quality.

Cyclic voltammetry was performed by the BAS-100 instrument in dichloromethane-Bu₄NPF₆ or HFP-Bu₄NPF₆ (0.15 mol dm⁻³) at a Pt button electrode of 2 mm² surface area. The reference electrode was an Ag/AgCl electrode, and iR compensation was applied. In HFP the ferricinium/ferrocene couple had $(E_{pa} + E_{pc})/2 = 0.05$ V vs. Ag/AgCl at a sweep rate of 100 mV s⁻¹.

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