

Determination of the solubility of fluorine in various solvents*

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Abstract

Fluorine solubility is an important parameter in fluorination reactions, both from the viewpoint of controlling reaction exothermicity and of carrying out reactions homogeneously. Several solvents have been studied in order to define their solubilization ability towards fluorine; some (such as CFCl_3 or $\text{CFCl}_2\text{CF}_2\text{Cl}$) were virtually inert, whilst others (such as CF_3COOH or $\text{CF}_3\text{CH}_2\text{OH}$) were capable of forming hypofluorites with fluorine. Particular additives (such as pentachlorophenol, 2,4-dinitrophenol or 3,5-dichloropyridine) were used in order to favour the formation of hypofluorites or complexes able to increase the amount of dissolved fluorine.

Introduction

Fluorination reactions with elemental fluorine have been studied by many authors and continue to be the subject of extensive research work. The problems connected with the practical utilization of this technology are mainly due to fluorine reactivity, which makes it difficult to control the reaction. The low activation energy and exothermicity of fluorine reactions with aromatic organic compounds result in a very low selectivity.

The reactions can be controlled by working at low temperatures and in a suitable solvent; in this manner products arising from the selective fluorination of aromatic substrates are formed, occasionally in good yields. Indeed, the reaction heat can be rapidly removed by using a solvent and low temperatures. However, due to the low solubility of fluorine in commonly used solvents, reaction occurs mainly at the gas–liquid interface, i.e. in a heterogeneous manner. This can produce local overheating which leads to degradation of the substrate.

The success of the practical utilization of direct liquid-phase fluorination techniques is thus linked to the possibility of promoting fluorine solubilization.

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The usefulness of having some fluorine solubility data is therefore self-evident. The aim of this work was to determine the solubility values of fluorine in various solvents and to search for additives capable of promoting its solubilization through the formation of hypofluorites or other chemical species able to complex fluorine.

Experimental

Materials

Fluorine (99% pure) was purchased from Matheson Co. RM 101, a commercial mixture of perfluoro(2-butyl-tetrahydrofuran) and perfluoro(2-propyl-tetrahydropyran), was supplied by Miteni. The other solvents used were of a commercial grade quality.

General procedures

Experiments were conducted in a 400 ml glass cylindrical reactor, fitted with a mechanical stirrer and an external jacket in which a coolant was circulated in order to keep the reactor at the required temperature.

The required solvent (300 ml) was placed in the reactor; then a flow of fluorine diluted with nitrogen was bubbled through it via a glass pipe. The fluorine flow rate was measured by means of a calibrated flange or calculated by titrating the iodine evolved when the F_2/N_2 mixture was absorbed in an acidic aqueous KI solution for a preset time.

This latter method was used also for determining the amount of absorbed fluorine (i.e. the oxidizing power of the solution); thus, a sample of the solution in which fluorine had been absorbed was immediately discharged from the reactor into an aqueous KI solution, and the evolved iodine titrated.

Alternatively, the solution containing fluorine was treated with a 0.1 N thiosulphate solution, excess thiosulphate being titrated with a 0.1 N iodine solution.

The amount of dissolved fluorine was determined when equilibrium had been achieved, i.e. when the amount of fluorine discharged from the reactor was the same as the amount fed. In some cases, equilibrium was achieved only after some considerable time, or never even achieved, because of the reaction of fluorine with the solvent or the additive. In these cases, the solubility was measured when the amount of fluorine discharged from the reactor remained constant, although in these circumstances it was lower than the amount fed.

Results and discussion

The choice of solvents in which the fluorine solubility was determined depended on their reactivity with fluorine. Experimental data show that $CFCl_3$,

$\text{CFCl}_2\text{CF}_2\text{Cl}$, CHF_2Cl , CHCl_3 and CCl_4 do not react with fluorine, or only sparingly so, at the temperatures used in liquid-phase fluorinations.

On the other hand, the temperatures at which fluorine solubility can be determined in the presence of additives have to be a compromise between the need to operate at the lowest possible temperature and the solubility limits of the additive. It is obviously difficult to find a solvent which reacts very little with fluorine thus enabling low temperatures to be reached, but at the same time keeping in solution an additive capable of forming hypofluorites or complexes with fluorine and the organic substrate undergoing fluorination.

The experimental values found for fluorine solubility are reported in Table 1. To date, the only known value for fluorine solubility is for CFCl_3 [2], in which a solubility of 4 mg F_2 in 100 g solution was measured at -75°C . This is in good accord with the maximum value of 7.2 mg F_2 in 100 g CFCl_3 solution measured at -83°C (see Table 1), considering that this latter value was determined with a higher concentration of fluorine in nitrogen. Moreover, as can be seen from Fig. 1, a virtually direct proportionality resulted between temperature and fluorine solubility in CFCl_3 .

The solvent which gave the highest value of fluorine solubility was $\text{CFCl}_2\text{CF}_2\text{Cl}$ (12.5 mg F_2 in 100 g solution). This value was measured at -20°C : it was not possible to use lower temperatures because incipient solidification of $\text{CFCl}_2\text{CF}_2\text{Cl}$ was already observed at -20°C .

Fluorine showed a moderate solubility in RM 101 in comparison with the other solvents used. Moreover, the inertness of this solvent with respect to fluorine made it possible to study the effects of fluorine concentration in

TABLE 1

Fluorine solubility [mg F_2 (100 g solution) $^{-1}$] in various solvents at the reported temperatures ($^\circ\text{C}$) and F_2 concentrations (%v/v) in nitrogen

Solvent	% F_2 (v/v)	Temp. ($^\circ\text{C}$)	Fluorine solubility [mg F_2 (100 g solution) $^{-1}$]
CFCl_3	21	0	1.1
		-35	3.4
		-55	5.1
		-70	6.4
		-85	7.4
$\text{CFCl}_2\text{CF}_2\text{Cl}$	25	20	6.0
		0	7.9
		-20	12.5
RM 101	21	-10	4.3
		-30	6.3
		-70	11.0
CF_3COOH	9	-13	5.4
$\text{CF}_3\text{CH}_2\text{OH}$	6	-30	2.5

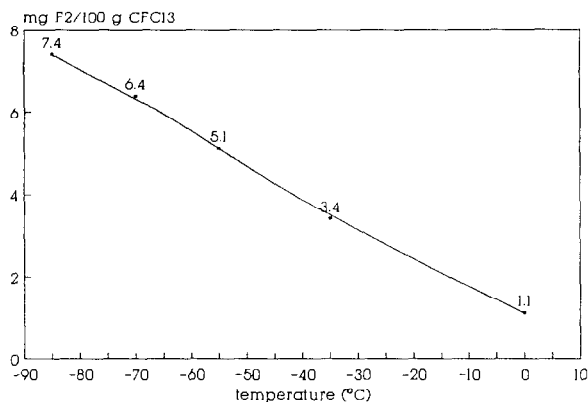


Fig. 1. The change in fluorine solubility [$\text{mg F}_2 (100 \text{ g solution})^{-1}$] with temperature in CFCI_3 .

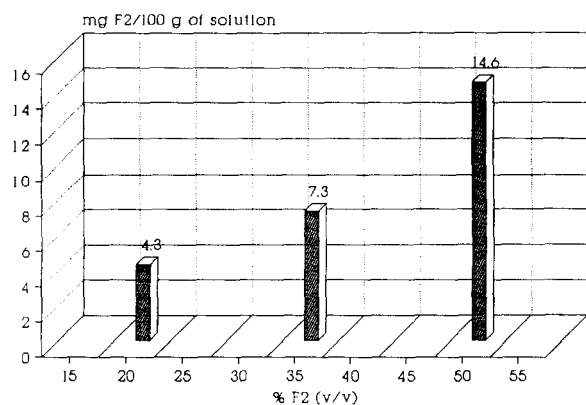


Fig. 2. The change in fluorine solubility [$\text{mg F}_2 (100 \text{ g solution})^{-1}$] relative to the fluorine concentration (%v/v) in the gaseous phase bubbled through RM 101.

nitrogen on its solubilization. The experimental data, measured at -10°C , are reported in Fig. 2; it can be seen that an increase in gaseous fluorine concentration produces a remarkable increase in solubility.

The use of solvents capable of forming hypofluorites, such as CF_3COOH and $\text{CF}_3\text{CH}_2\text{OH}$, surprisingly led to low values for the fluorine solubility, with results comparable with the values measured in inert solvents (see Table 1). Thus, in trifluoroethanol a solubility of only 2.5 mg F_2 in 100 g solution was measured at -30°C ; however, it should be pointed out that the amount of fluorine discharged from the reactor was only 16% of the amount fed. This means that in the experimental conditions employed fluorine reacted with the alcohol. Prager and Thompson [3] have reported the synthesis of $\text{CF}_3\text{CF}_2\text{OF}$ by reaction of fluorine with trifluoroethanol at 0°C . Thus it might be possible that in our experimental conditions hypofluorite was formed and, due to its low boiling point (-50°C), was carried away from the reactor

by the gaseous flow, thereby keeping the oxidizing power of the solution at a low and constant value.

It should, however, be stressed that the amount of fluorine fed into trifluoroethanol was only 6% of the amount required theoretically for complete conversion of the alcohol into $\text{CF}_3\text{CF}_2\text{OF}$.

In trifluoroacetic acid, the fluorine solubility is practically the same as in CFCl_3 . Measurement in pure acid was made at -13°C with a fluorine concentration of only 9% v/v in nitrogen. Rozen and coworkers appear to rule out the possibility that the oxidizing power derived by flowing fluorine through trifluoroacetic acid or its solution in CFCl_3 [4], or through solutions of acetic acid [5], is due to the species $\text{CF}_3\text{COOF}^\cdot$ or $\text{CH}_3\text{COOF}^\cdot$: instead they consider that this is due only to the dissolved fluorine. On the other hand, we have observed that the fluorination reactions of aromatics in CFCl_3 or in $\text{CFCl}_3/\text{CF}_3\text{COOH}$ mixtures follow very different courses, with much higher yields of monofluorinated products in the latter. This should provide indirect confirmation of the formation of $\text{CF}_3\text{COOF}^\cdot$, which might transfer fluorine in a subsequent fluorination reaction.

Table 2 lists the values of the fluorine solubility measured after adding small amounts of compounds to the solvents which, because of their acidity (pentachlorophenol or dinitrophenol) or the presence of a nitrogen atom, were considered capable of forming hypofluorites or complexes with fluorine.

The influence of these additives on the fluorine solubility also depends, as can be seen, on the solvent used. With pentachlorophenol, the highest solubility was obtained on using chloroform as a solvent; lower values were obtained with CFCl_3 and CCl_4 . However, the concurrent effect of temperature must not be neglected; hence, the higher solubility value measured in CFCl_3 , over that achieved in CCl_4 , may be ascribed to a much lower temperature. The marked influence of chloroform on the solubility can be attributed to

TABLE 2

Fluorine solubility [mg F_2 (100 g solution) $^{-1}$] in the presence of additives at the reported additive concentration (% by weight), temperatures ($^\circ\text{C}$) and fluorine concentrations (% F_2 v/v) in nitrogen

Additive	% by weight	Solvent	% F_2 (v/v)	Temp. ($^\circ\text{C}$)	Fluorine solubility [mg F_2 (100 g solution) $^{-1}$]
none	—	CFCl_3	21	-70	6.6
pentachlorophenol	5.2	CFCl_3	10	-75	12.7
pentachlorophenol	3.0	CHCl_3	12	-25	78.0
pentachlorophenol	2.4	CCl_4	9	-20	6.0
2,4-dinitrophenol	2.6	CHCl_3	9	-45	107.0
3,5-dichloropyridine	3.8	CFCl_3	12	-78	276.0
3,5-dichloropyridine	3.8	CFCl_3	12	-40	222.0
CF_3COOH	5.4	CFCl_3	14	-60	6.0
CF_3COOH	5.4	CFCl_3	14	-30	3.8

its greater polarity favouring hypofluorite formation and its solubilization in the presence of fluorine.

The decisive effect of pentachlorophenol on the fluorine solubility in CFCl_3 is clear on comparing the value measured in the presence of this additive with that obtained in pure CFCl_3 ; the solubility practically doubles, even though the fluorine concentration was less by almost one-half. The highest solubility value in chloroform, however, was measured in the presence of 2,4-dinitrophenol; this may be ascribed to the greater acidity of this latter compound and also to the lower temperature.

The influence of 3,5-dichloropyridine was particularly marked; the measured values of fluorine solubility were much higher than those obtained using pentachlorophenol under virtually the same conditions. The significant solubilization of fluorine with this additive is related to the presence of a basic nitrogen atom favouring the formation of complexes. It is well known [6] in fact that pyridine reacts with fluorine at -80°C in CFCl_3 to form a pyridine/ F_2 adduct which decomposes at temperatures higher than -2°C with the formation of a red-brown oil containing fluoropyridine.

No data are available on the oxidizing power of pyridine solutions in solvents capable of solubilizing this pyridine/ F_2 adduct. Experiments carried out to determine fluorine solubility in trifluoroethanol in the presence of pyridine have demonstrated that the pyridine/ F_2 adduct is soluble in this solvent.

Thus, on bubbling a flow of 8% F_2 in nitrogen through a solution of 14% pyridine in trifluoroethanol at -40°C until 43% of the amount of fluorine required to complex all the pyridine had been fed, a solubility value of 1830 mg F_2 in 100 g solution was measured. The overall fluorine present

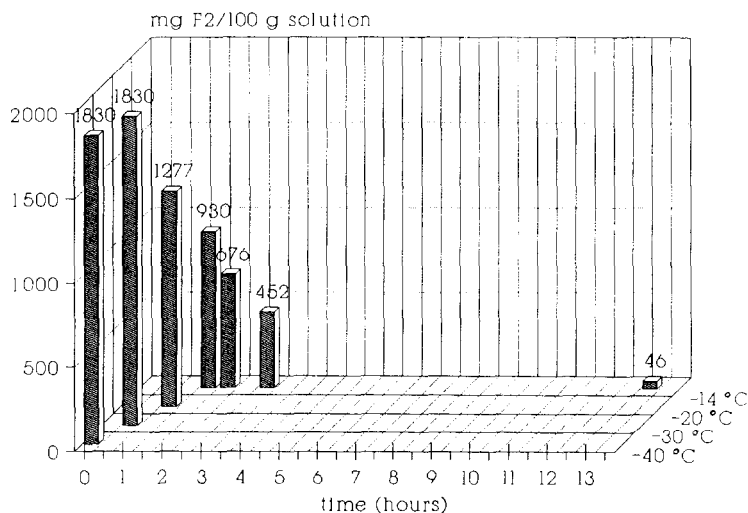


Fig. 3. The change in fluorine solubility [$\text{mg F}_2 (100 \text{ g solution})^{-1}$] with time and temperature in a 14% pyridine solution in trifluoroethanol.

was 60% of the amount fed. A gradual temperature increase in the solution led to a violent reaction, very probably due to adduct decomposition. The change in fluorine solubility with time and temperature is shown in Fig. 3. It can be seen that as time and temperature increase the fluorine solubility remains unchanged until $-30\text{ }^{\circ}\text{C}$; then it begins to decrease gradually. On maintaining the temperature at $-14\text{ }^{\circ}\text{C}$, the amount of dissolved fluorine after 13 h drops to 46 mg F_2 in 100 g solution.

Finally, it must be pointed out that the use of trifluoroacetic acid as an additive does not improve the fluorine solubility; in fact, as can be seen from Table 2, the solubility determined in CFCl_3 in the presence of CF_3COOH was comparable with that measured in pure CFCl_3 at the same temperature.

Conclusions

The measured solubility data demonstrate that fluorine is only very sparingly soluble in inert solvents. Hence fluorination reactions carried out in these solvents lead to rapid degradation of the substrate because the reaction occurs heterogeneously. In the solvents capable of forming hypofluorites, such as CF_3COOH or $\text{CF}_3\text{CH}_2\text{OH}$, the observed low solubility of fluorine is probably due to removal of the hypofluorite by the nitrogen flow.

In the presence of additives capable of forming hypofluorites or complexes with fluorine, very interesting solubility values were observed. In some cases the dissolved amount of fluorine, i.e. the oxidizing power of the solution, reached very high values. These particular solutions could presumably be used to carry out selective fluorination reactions of aromatic substrates.

It should be stressed, nevertheless, that considerable difficulties have been encountered in finding solvents and additives with suitable solubilization powers, polarities, stability and solubility so as to achieve fully the likely results required.

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