Lubrication under Extreme Conditions

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Preparation and Properties of Aromatic Fluorocarbons

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THE LACK OF materials capable of withstanding extreme temperatures and pressures as well as high-energy radiation is a serious problem in the design of present-day aircraft and space vehicles. Since available plastic and rubberlike materials cannot withstand temperatures above several hundred degrees, they have only limited applications for high temperature usage.

Polyphenyl is one of the most thermally stable polymers known. However, this material loses hydrogen at temperatures above 500° C. Presumably, totally fluorinated aromatic substances would have still greater thermal and oxidative resistance. This concept is tentatively confirmed from studies of a perfluoropolyphenyl derivative prepared some years ago in this laboratory (*15*). Although the polymer exhibited good thermal stability, even above 500° C., its physical properties were undesirable because it was high melting, infusible, and brittle. Production of a substance with more desirable properties requires development of new methods of synthesis and study of the products.

PREPARATION AND PROPERTIES

Recent methods for the synthesis of hexafluorobenzene, C_6F_6(*2, 12, 13, 16, 17*), in reasonably good yields and quantities have greatly accelerated progress in the field of research on completely fluorinated aromatic materials. Only six "true" aromatic fluorocarbons are known to date. These compounds and their properties are summarized in Table I, along with their hydrocarbon analogs. The total number of possible pure aromatic fluorocarbons is almost as great as that of the aliphatic fluorocarbons. As in the case of aliphatics, perfluoroaromatics have higher vapor pressures and lower boiling temperatures than the corresponding hydrocarbon analogs. An exception, however, is hexafluorobenzene itself, which has about the same boiling point as benzene. In perfluorinated structural isomers very small differences in boiling points are usually found—e.g., perfluoroxylene and perfluoroethylbenzene (*12*)—but melting points appear to be a function of symmetry.

The physical properties of fluorinated benzenes are given in Table II. Unlike the effect of fluorine substitution in aliphatic hydrocarbons, replacement of one hydrogen by fluorine in benzene raises the boiling point only a few degrees, from 80° to 85° C. (*9*). The boiling point also rises about 5° C. when one hydrogen atom replaces a fluorine atom in hexafluorobenzene (*10, 11*). For the intermediate substituted fluorocarbons, structural isomerization has a profound effect upon boiling points. The lowest boiling aromatic compound known is 1,3,5-trifluorobenzene (76° C.) (*12*), while the 1,2,4-isomer (*9*) and the 1,2,3-isomer (*13*) boil at 88° and 93° C., respectively.

As with all fluorocarbons, the density increases and the refractive index decreases with increasing fluorine content. Surface tension data (*9*) on most of the fluoro-hydroaro-

Table I. Properties of Aromatic Fluorocarbons and Hydrocarbons

Compound	Boiling Point, ° C.	Melting Point, ° C.	n_D^{20}	γ_{20}, Dynes/Cm.	d_4^{20}	References
C_6F_6	80	5.5	1.3781	22.6	1.610	(*2, 12, 13, 16, 17*)
C_6H_6	80	5.5	1.5011	28.88	...	(*14*)
$C_6F_5CF_3$	103	...	1.3680	...	1.7660	(*8, 12, 17*)
$C_6H_5CH_3$	110	−95	1.4969	28.0	0.8669	(*14*)
$C_6F_5CF_2CF_3$	114	...	1.3620	...	...	(*12*)
$C_6H_5CH_2CH_3$	136	−93.9	1.4980	29.2	0.8669	(*14*)
p-$C_6F_4(CF_3)_2$	117	...	1.3610	...	...	(*12*)
p-$C_6H_4(CH_3)_2$	138.3	13.2	1.4958	28.37	0.8610	(*14*)
$(C_6F_5)_2$	...	68	...	...	...	(*12*)
$(C_6H_5)_2$	254	68	...	...	1.180	(*14*)
$C_{10}F_8$	...	86	...	...	...	(*12*)
$C_{10}H_8$	218	80	...	28.8	1.145	(*19*)

Table II. Properties of Fluorinated and Nonfluorinated Hydrocarbons

Compound	Boiling Point, ° C.	Melting Point, ° C.	n_D^{20}	γ_{20}, Dynes/Cm.	d_4^{21}	References
C_6H_6	80.	5.5	1.5011	28.88	0.879	(*14*)
C_6H_5F	84.8	-41.0	1.4646	27.71	1.024	(*4*)
$C_6H_4F_2$-1,4	88.5	-13	1.4422	27.05	1.1684	(*4*)
$C_6H_3F_3$-1,2,4	88.0	-34	1.4228	26.2	...	(*4*)
$C_6H_3F_3$-1,3,5	75.5	5.5	1.41403	27.16	1.277	(*5*)
$C_6H_3F_3$-1,2,3	93	...	...	26.1	...	(*3*)
$C_6H_2F_4$-1,2,3,4	95	...	1.4092	25.3	1.399	(*22*)
$C_6H_2F_4$-1,2,3,5	83	-48	1.4038	23.99	1.393	(*6*)
$C_6H_2F_4$-1,2,4,5	88	4	1.4074	24.9	1.4256	(*4, 15*)
C_6HF_5	84.8	> -15	1.3931	...	...	(*23, 27*)
C_6F_6	80	5.5	1.3781	22.6	1.610	(*2, 13, 16, 17*)
			Aliphatic Compounds			
n-C_7F_{16}	82.51	-51.29	1.2602	13.19	1.7318	(*20*)
n-C_7H_{16}	98.43	-90.6	1.3876	20.26	0.6837	(*14*)
n-C_6F_{14}	57.11	-86.05	1.2515	11.92	1.6995	(*28*)
n-C_6H_{14}	69.0	-94.3	1.3753	18.43	0.6603	(*14*)

matics are shown in Table II. The surface tension decreases with an increase in the number of fluorine atoms. The effect of total fluorination on surface tension in the aromatic series is less than with perfluoroheptane (*20*) and perfluorohexane (*28*). No viscosity data are available at this time.

Generally, these perfluorinated compounds do not support combustion, are miscible with most organic solvents, and do not react with cold concentrated acids or bases. Hot concentrated acids will convert pendant trifluoromethyl groups to carboxylic acids (*15, 18*) after prolonged treatment as shown by the reaction

$$C_6F_5CF_3 \xrightarrow[+2H_2O-3HF]{H_2SO_4\text{ cat.}} C_6F_5CO_2H$$

but will not attack the fluorines attached to the ring. On the other hand, hot alkalies will atack the ring fluorines and cause replacement. This reaction

$$C_6F_6 \xrightarrow[-KF]{+KOH} C_6F_5OH$$

is the basis for the preparation of many of the new compounds already reported in the literature.

Some derivatives of aromatic fluorocarbons are listed in Table III. The trend in physical properties follows those mentioned previously for the parent compounds, with the exception of pentafluorophenol (*24*). In this case the boiling point is lowered considerably. It has been shown that intramolecular hydrogen bonds are formed between the ortho-fluorine atoms and the hydroxyl group. This is also apparent in the amino derivative. The pentafluorophenol is more acidic than ordinary phenol and its acidity approaches that of acetic acid (*10*).

Table III. Properties of Aromatic Fluorocarbon Derivatives

	C_6F_5R		C_6H_5R[a]		
R	Boiling point, ° C.	Melting point, ° C.	Boiling point, ° C.	Melting point, ° C.	References
F	80.0	5	80	5	(*2,13, 16, 17*)
CL	122	...	132	...	(*17*)
Br	135	...	156	...	(*9, 16, 23*)
I	161	...	180	...	(*9, 23*)
CO_2H	...	103	...	121	(*18, 23*)
OH	143	39	189	42	(*10, 24*)
OCH_3	138	...	156	...	(*10, 24*)
NH_2	156	34	184	...	(*11, 21*)
CH_3	109	...	110	...	(*21*)
		Miscellaneous			
$(C_6F_5)_4Si$	...	247	...	233	(*29*)
$(C_6F_5)_3P$	...	114	...	79	(*29*)

[a] Reference (*12*).

The melting points of tetrakis(pentafluorophenyl) silane and tris(pentafluorophenyl) phosphine (*29*) are rather high in comparison to their hydrocarbon analogs. An examination of a Fischer-Hershfelder model of the former suggests that rotation about the carbon-silicon bond is hindered by the ortho-fluorine atoms. Hence, rotation of a phenyl group in this compound would require the cooperative action of adjacent phenyl groups and would account for the higher melting point.

In tris(pentafluorophenyl) phosphine the increase in melting point is even greater than in the silane, and factors other than mere symmetry must be invoked. However, an additional possibility exists as a result of the extra electron pair on the phosphorus atom. The inductive effect of the fluorinated phenyl groups may decrease the electron density on the phosphorus to such an extent that an appreciable dipole is produced, which may lead to greater intermolecular attraction.

THERMAL STABILITY

The stringent and often conflicting requirements for attaining a combination of high thermal stability and plasticity in a material severely restrict the number of conceivable molecular structures. Linear, flexible molecular chains with a large number of possible configurations and strong chemical bonds between all the atoms are needed for the desired properties. A structure approaching this ideal is poly(perfluorophenylene)ether. From model studies it is evident that this substance can exist both in a linear and in a coiled form. Incorporation of various isomers into the chain would increase the possibility of these materials forming amorphous solids having lower pour points. Conversely, poly(perfluorodiphenyl)siloxane has a bulkier structure with considerable steric hindrance between the pendant pentafluorophenyl groups. Hence, this polymer cannot be coiled without bond scission.

Before attempting the preparation of these large molecules, thermal stability data (*29*) were acquired from small model compounds containing various structures. The thermal stabilities of the compounds studied appear to be in the following order:

$$(C_6F_5)_2 \geqq C_6F_6 \geqq (C_6H_5)_2 > (C_6H_5)_4Si >$$
$$(C_6F_5)_4Si \geqq (C_6F_5)_3P > (C_6H_5)_3P >$$
$$(C_6F_5)_3PO$$

This order is based on thermal stability experiments conducted in glass. Even so, perfluorodiphenyl is unchanged when kept for 1 hour at temperatures below 575° C. Hexafluorobenzene is known to yield perfluorodiphenyl at 800° C. (*2*). The presence of fluorine atoms decreases the stability of the silane, but apparently increases the stability of the phosphine derivatives. However, fluorophosphine oxide is less stable than triphenylphosphine. These phenomena appear to be connected with the pair of coordinating electrons on the phosphine. Trends in results obtained suggest marked differences in bond strengths of the Si—C and P—C bonds in these compounds.

RADIATION STABILITY

Work on the radiolysis of hexafluorobenzene (*7*) has shown that in the presence of high-energy radiation, the major products are larger molecules, analogous in nature and quantity to those found from the irradiation of benzene. Thus, aromatic fluorocarbons appear to have the same high order of radiation resistance as aromatic hydrocarbons. It has also been observed that in certain perfluoropolyphenyls (*15*) considerably less fragmentation of molecules occurs on electron impact (*1*). The latter observation is reminiscent of benzene itself, and contrasts strongly with the extensive fragmentation of saturated fluorocarbons in the mass spectrometer (*19*).

LUBRICATION

Since these perfluoroaromatics have only recently become known, no data are available as to their performance as lubricants or additives. However, some information is available regarding Kel-F oils (*26*). In practical tests, under ordinary conditions, it was determined that fluorocarbon oils perform as well as petroleum oils in so far as lubrication and wear are concerned. From viscosity-temperature curves (*30*), the slopes of the aliphatic fluorocarbon curves are rather steep as compared with those of the silicones or mineral oils, indicating greater changes in viscosity as the temperature increases. Aromatic hydrocarbons, in general, also tend to have steep slopes. It is very likely that aromatic fluorocarbons will, in their viscosity-temperature relationships, be similar to aromatic hydrocarbons. It would be presumptuous at this time, however, to disqualify aromatic fluorocarbons as lubricants when they offer the attractive properties of high thermal, radiation, and hydrolytic stability, as well as resistance to oxidation.

Of special interest in this regard are, again, the perfluorophenylene ethers. Attempts to synthesize the simple perfluorodiphenyl ether were unsuccessful. However, poly(perfluorophenylene)ethers of small molecular weight have been prepared (*25*) by the thermal decomposition of phenolic salts. These materials range from tacky gums to hard brittle glasses with softening temperatures below 50° C. Various para- or meta-linked ethers are suitable by themselves or as additives for extreme-temperature lubricants where frictional temperatures often rise to 500° C., at which temperature conventional oils break down.

PRESENT STATUS OF FLUOROAROMATICS

Unfortunately, there has been no commercial source for hexafluorobenzene. Although this has undoubtedly tended to retard progress in aromatic fluorocarbon chemistry, remarkable progress has been made during the past 5 years on the syntheses and reactions of these materials. Over 100 new aromatic fluorocarbons and derivatives have been prepared and identified, and evaluation of their properties is under way.

A study of the derivatives of hexafluorobenzene is as interesting as that of their parent materials, and many of them have been synthesized by basic attack on hexafluorobenzene. Pentafluoro compounds of phenol, anisole, aniline, and toluene have been prepared (*10, 11, 21, 24*). Still others have been made via the Grignard reagent, pentafluorophenylmagnesium bromide (*9, 23*). This reagent can add, couple, or exchange, and therefore represents a potent tool for synthesis. By this method perfluorodiphenyl, pentafluorostyrene, tetrakis(pentafluorophenyl) silane, and tris(pentafluorophenyl) phosphine were synthesized. Many more different types of derivatives may also be made available by this route.

Aromatic fluorocarbons have not been used extensively to date, primarily because they were not available. However, as techniques and methods of synthesis improve, these materials should find new and useful applications.

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