

A Study of the Combination of Unsaturated Perfluorocarbon Binder and Perfluoroammonium Salt*

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Synopsis

A composite of poly(perfluorobutadiene) and perfluoroammonium hexafluoroarsenate has been developed that can be used as an efficient source of fluorine atoms because the salt does not react with the polymer. This point has been demonstrated by showing that no more than trace amounts of NF_3 , which is formed in most reactions of perfluoroammonium salts, are formed by heating the composite to $120^\circ C$ or by maintaining the composite at $80^\circ C$ for four days. The small amount of NF_3 that is formed can be explained as resulting from reactions with trace impurities.

INTRODUCTION

The objective for the investigation is to show that perfluoroammonium hexafluoroarsenate dispersed in poly(perfluorobutadiene) as a binder is sufficiently stable for the combination to be used as a source of fluorine atoms. The preparation of various perfluoroammonium salts ($NF_4^+AsF_6^-$, $NF_4^+SbF_6^-$, and $NF_4^+BF_4^-$) has been reported by several methods.¹⁻⁴ Thermal decomposition of these salts generates fluorine at 200° to $250^\circ C$ in vacuo.¹⁻³ These perfluoroammonium salts are stable in dry air at ambient temperature, but all react rapidly with moisture and with organic substances, except the perfluorocarbons.

This work studied the stability of a composite of poly(perfluorobutadiene) and perfluoroammonium hexafluoroarsenate under moderate pressure and heat and as a function of time at ambient temperature.

EXPERIMENTAL

Starting Materials

Polyperfluorobutadiene containing high 1,2-moieties was prepared by a method previously described.⁵⁻⁷ The bulk polymer was extracted with *n*-hexane and hexafluorobenzene. The hexafluorobenzene-soluble fraction was freeze dried and used for this investigation. The molecular weight was determined as 8500 by intrinsic viscosity measurement in octafluorotoluene at $90^\circ C$. The previously

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reported relationship between intrinsic viscosity and molecular weight of poly(perfluorobutadiene) was used.^{8,9}

The salt containing the perfluoroammonium cation NF_4^+ studied was NF_4AsF_6 , which was prepared by a method previously described; the purity of the salt was reported as 95%.¹

Mixture of Perfluoroammonium Salt and Binder

A combination by weight of one part of freeze-dried white-powdered poly(perfluorobutadiene) (0.70 g) and four parts of powdered white perfluoroammonium salt (NF_4AsF_6 , 95% purity, 2.78 g) was mixed in the dry box with a spatula in an alumina mortar until well blended, then ground with an alumina pestle. The powders cohered into flat, solid lumps without any observable evolution of fume or change of color. The while solid mixture (3.48 g) was transferred to a Teflon evaporating dish and divided into portions for various studies under moderate pressure and heat and as a function of time at ambient temperature.

Studies of the Composite Under Moderate Pressure and Heat

Preparation of a 3–4 g Pellet Sample of the Mixture Under Moderate Pressure.

The major portion of the above blended solids (3.2 g) was loaded into a metal press between two fitted 1-in.-diameter Teflon sheet disks and pressed at ambient temperature to an estimated pressure of 10,000 psi for 10 min in the dry box to make a fused round (1-in.-diameter and $\frac{1}{8}$ -in.-thick) pellet. The pellet remained intact when the top and bottom Teflon sheet disks were peeled off and the pellet was lifted and dropped into a Teflon beaker. Moderate finger pressure had to be exerted to break the pellet. The exterior surface of the pellet turned brown (probably caused by the method of cleaning the Teflon disks and the inside of the metal press), while the interior of the pellet remained white.

Infrared Analysis of Gaseous Composition of the Pellet Sample at Ambient Temperature. The Teflon beaker, which contained the 1-in.-diameter pellet, was placed into a bed of lead shots at the bottom of a Pyrex reaction vessel (400 ml) which was fitted with an O-ring and metal cap containing a $\frac{1}{4}$ -in.-o.d. outlet and a closed valve. Then the assembled reaction vessel, which contained 1 atm of nitrogen, was removed from the dry box and attached to an evacuated metal manifold. Gas evolution was measured by a Pennwalt Wallace and Tiernan gauge (0–1550 mm with an accuracy of 0.15 mm Hg).

No change of gas pressure (1 atm) in the reaction vessel was detected for $5\frac{1}{2}$ days at ambient temperature. However, the IR spectrum of the gaseous composition showed up two weak absorption peaks, one at 905 cm^{-1} , indicating the presence of trace NF_3 , and one at 1030 cm^{-1} , indicating SiF_4 .^{10,11} The trace amount of SiF_4 indicates the presence of a trace amount of fluorine or HF which attacked the Pyrex reaction vessel to give SiF_4 . The surface of the pellet was light gray.

Infrared Analysis of Gaseous Composition of the Pellet Sample upon Heating.

The above light-gray pellet was then heated to 120°C (248°F). At this temperature, a slow rate of gas evolution was detected, which was identified as NF_3 and SiF_4 by IR analysis. After 2 hr at 120°C , the pellet was cooled to 100°C for 2 hr, and the gas evolution stopped. On further cooling to 80°C and maintaining at 80°C for four days, a trace amount of NF_3 and SiF_4 was again detected in the gas phase (see blank in Table I).

TABLE I
Infrared Absorbance of the Composite^a as a Function of Time

Sample	Cumulative time, hr	Absorbance ^b	
		$A(\text{NF}_3)$ at 905 cm^{-1}	$A(\text{NF}_4^+)$ at 1157 cm^{-1}
Mixture ^a	0.0	0.236	c
	17.5	0.299	c
	24.5	0.299	c
	99.0	0.137	c
	157.2	0.111	c
Blank ^d	0.0	0.193	0.344
	7.8	0.274	0.340
	32.3	0.230	0.297
	127.3	0.263	0.295

^a 4/1 by weight of NF_4AsF_6 /poly(perfluorobutadiene).

^b $A = \text{Absorbance} = \log_{10}(1/T) = \log_{10}(I_0/I)$, where T is transmittance and I_0 and I are the intensities of radiant energy of a given wavelength incident on the sample and emergent from the sample, respectively.

^c Absorbance at 1157 cm^{-1} for NF_4^+ is masked by the broad C—F band of poly(perfluorobutadiene).

^d NF_4AsF_6 .

No dimensional change of the 1-in. diameter pellet was observed at the end of the heat treatments.

Infrared Analysis of Pellet Sample After Heat Treatment. At the end of the heat treatments, 5 mg of solid mixture from the heat-treated, light-gray, 1-in. diameter pellet has dispersed in 350 mg optical-grade KCl in the dry box, pressed into a disc, and placed in an enclosed IR cell between AgCl windows. The IR spectrum of the heated sample closely resembled that of the untreated sample; a small increase in moisture content indicated a slow leak in the reaction vessel during the thermal stability study.

Spectroscopic Analysis of the Composite as a Function of Time

The composite (4/1 by weight of NF_4AsF_6 /poly(perfluorobutadiene); 5 mg) was dispersed in 300 mg optical-grade KCl, pressed into a transparent disc, and placed in an enclosed IR cell with AgCl windows under anhydrous conditions. Table I shows the results of IR absorbances of the mixture and the blank (neat NF_4AsF_6) as a function of time at ambient temperature.

RESULTS AND DISCUSSION

Since most reactions of perfluoroammonium salts generate nitrogen trifluoride (NF_3) as a product, and since NF_3 is very stable¹⁰ and easily detectable¹¹ by its strong characteristic absorption peak at 905 cm^{-1} , $d[\text{NF}_3]/dt$ should be a sensitive indicator of the rate of decomposition. Although perfluoroammonium cation NF_4^+ also shows a strong characteristic peak at 1157 cm^{-1} , this absorbance is masked by the strong broad C—F absorbance of poly(perfluorobutadiene). Thus, the NF_4^+ absorbance is not useful for compatibility studies of the perfluoroammonium salt with the perfluorocarbon binder.

Because of their reaction with trace impurities, NF_4^+ salts generally form detectable quantities of NF_3 when pressed into an optical disc with KCl. The

NF₃ thus formed possesses a finite lifetime before it can be diffuse to the surface and escape. Hence, measurement of $d[\text{NF}_3]/dt$ under these conditions can provide useful comparison of the rate of decomposition with the rate of NF₃ diffusion. The latter is expected to be much smaller than the rate of NF₃ formation, which indicates reaction of the perfluoroammonium salt.

In Table I, the observed decrease in optical density for NF₃ in the mixture NF₄AsF₆/poly(perfluorobutadiene) is thus interpreted to indicate that the mixture is essentially stable. Although the results from a neat NF₄AsF₆ blank study did not show a similar $-d[\text{NF}_3]/dt$, the essentially constant NF₄⁺ optical density value and the lack of detectable reaction products (i.e., ClF₃) indicate the stability of NF₄AsF₆ with respect to KCl, the ingredient in the optical disc. In studying the compatibility of perfluoroammonium salt, it is essential to consider the blank (the neat NF₄⁺ salt alone) as the baseline to properly interpret the compatibility data.

For the 1-in.-diameter pellet sample [3.2 g of 4/1 by weight NF₄AsF₆/poly(perfluorobutadiene)], the detection of trace amounts of decomposition products such as NF₃ in the gaseous composition at the end of the experiment is not surprising because of trace contaminants. The result correlates with the detection of NF₃ for neat solid NF₄AsF₆ in the absence of poly(perfluorobutadiene). From the absence of significant NF₃ formation, we can conclude that the perfluoroammonium salt NF₄AsF₆ is stable with poly(perfluorobutadiene) at 80°C. There is also no dimensional change in the 1-in. pellet after heat treatments.

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