tion with 1,4-dioxane, which has frequently been used with other halides.[4]

Subsequent study has shown the formation of a 1:1 addition compound by direct reaction of antimony(III) fluoride and dioxane and by reaction in methanol solution. The complex decomposes at 143° into its components and can be used as a mild fluorinating agent.

Experimental

Antimony(III) fluoride was refluxed for 15 minutes with a 14-fold excess of dioxane, filtered and cooled. Alternatively, a mixture of 15 ml. of dioxane (0.17 mole) and 15 ml. of methanol was added slowly to a solution of 19.3 g. (0.11 mole) of the fluoride in 30 ml. of methanol. After brief refluxing the solution was cooled, the crystals removed, and dried in a stream of dry air. Samples were analyzed for antimony by titration with potassium bromate,[5] using Naphthol Blue Black.[6]

Anal. Calcd. for $SbF_3\cdot C_4H_8O_2$: Sb, 45.62. Found: Sb, 45.47, 45.54, 45.57.

The dissociation temperature was found by determining the heating curve of a 14-g. sample in a nickel cell, using copper–constantan thermocouples and a Speedomax recorder. A sharp break occurred at 143°, and a sample heated to 305° showed a break in its cooling curve at 290°, corresponding to the m.p. of the fluoride.

Benzotrichloride was fluorinated by the complex, using the apparatus and procedures given by Henne,[7] maintaining the same fluoride–chloride ratio. Both benzotrifluoride and the chlorodifluoride were formed.

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(4) M. S. Kennard and P. A. McCusker, THIS JOURNAL, **70**, 1039 (1948); C. J. Kelley and P. A. McCusker, *ibid.*, **65**, 1307 (1943).

(5) H. H. Willard and H. Diehl, "Advanced Quantitative Analysis," D. Van Nostrand Publishing Co., Inc., New York, N. Y., 1943, p. 350.

(6) G. F. Smith and R. L. May, *Ind. Eng. Chem., Anal. Ed.*, **13**, 460 (1941).

(7) A. L. Henne in R. Adams, ed., "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 62.

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Ammonium Pentafluorozirconate(IV) and its Monohydrate[1]

BY HELMUT M. HAENDLER AND DEAN W. ROBINSON

RECEIVED APRIL 8, 1953

Ammonium pentafluorozirconate(IV), NH_4ZrF_5, has been reported as one of the intermediate products of the thermal decomposition of ammonium heptafluorozirconate(IV), $(NH_4)_3ZrF_7$.[2] Attempts to grow single crystals of the pentafluorozirconate from solution for X-ray structural studies led to the discovery of its monohydrate. Both compounds crystallize from a solution of zirconium oxide in hydrofluoric acid, to which has been added 75% of the theoretical quantity of ammonium fluoride. The predominant product is controlled by the rate of crystallization. Rapid crystallization favors formation of the hydrate, slow crystallization suppresses it. The monohydrate loses water spontaneously in air of low humidity to become the anhydrous compound. Powder diffraction and Weissenberg photographs of the two compounds are distinctive.

Experimental

All crystallizations were carried out with platinum or polyethylene apparatus. To obtain the monohydrate, the solution was evaporated by heating to incipient crystallization, filtered and cooled. The hydrate crystallized in clusters of clear, colorless, six-sided right prisms. These were separated mechanically from the small crystals of the anhydrous compound, the formation of which could not be prevented completely.

Anhydrous pentafluorozirconate was produced with exclusion of hydrate by allowing the solution to evaporate slowly for 2–3 weeks, or by adding a small amount of ethanol prior to the slow evaporation. This compound crystallized in small, colorless, almost square plates, with truncated faces.

X-Ray diffraction powder photographs were taken of the products obtained by heating the hydrate at 110° and from its spontaneous decomposition in air. They were identical with the pattern of the pentafluorozirconate produced in the thermal decomposition of the heptafluorozirconate.

Ammonium ion was determined by distillation from basic solution into boric acid and titration with hydrochloric acid. Zirconium was determined by digestion with sulfuric acid and ignition to the oxide. Water was determined by heating at 110°.

Anal. Calcd. for $NH_4ZrF_5\cdot H_2O$: NH_4, 8.12; Zr, 40.94; H_2O, 8.10. Found: NH_4, 7.64; Zr, 41.15; H_2O, 8.25.

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(1) Research supported by the Atomic Energy Commission and the Research Corporation.

(2) H. M. Haendler, C. M. Wheeler and D. W. Robinson, THIS JOURNAL, **74**, 2352 (1952).

Diazonium Fluoborates as Initiators of Vinyl Polymerization[1]

BY C. S. MARVEL, H. Z. FRIEDLANDER, SHERLOCK SWANN, JR., AND H. K. INSKIP

RECEIVED JANUARY 26, 1953

In some experiments on the electrolytic generation of free radicals for the initiation of polymerization,[2] hydroquinone was added as a "shortstop" immediately after the electrolysis to prevent polymerization during the examination of the mixture. In those runs involving the electrolysis of *p*-bromobenzenediazonium fluoborate, extensive polymerization of acrylonitrile was observed after the addition of hydroquinone, but not before. Tests showed that the sulfuric acid anolyte solution and the fluoborate anion were not responsible for the polymerization. Further study demonstrated that the diazonium fluoborate in the presence of hydroquinone or ferrous ammonium sulfate caused the initiation of polymerization at 30°. In Table I are summarized the results of a number of homopolymerizations and copolymerizations initiated by substituted benzenediazonium fluoborates.

The effect of *p*H on yield and viscosity of polyacrylonitrile is demonstrated in experiments 1–6. Optimum conditions obtain at about *p*H 3. At 0° no polymer was obtained from acrylonitrile even after four days (experiments 7, 8) unless the amount of initiator was doubled over that used at 30° (experiments 9–14), and even with increase of initiator the yield and viscosity were relatively low. The effectiveness of the ferrous-salt activator in promoting polymerization of acrylonitrile at 30° is demonstrated in the 18-hour polymerizations (ex-

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(1) The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

(2) H. Z. Friedlander, S. Swann, Jr., and C. S. Marvel, *J. Electrochem. Soc.*, in press.

TABLE I

POLYMERIZATIONS INITIATED BY SUBSTITUTED BENZENEDIAZONIUM FLUOBORATES[a]

Experiment no.	Monomer	Comonomer	Weight ratio, monomer/comonomer	Total monomer(s) weight, g.	Water, ml.	Initiator,[b] g.	Activator,[c] g.	pH[d]	Temp., °C.	Time, hr.	Conversion, %	Inherent viscosity[e]
1	Acrylonitrile	None	...	16.1	40	0.1	0.01	1.0	28	3	5.2	3.80
2	Acrylonitrile	None	...	16.1	40	.1	.01	2.0	28	3	11.9	4.52
3	Acrylonitrile	None	...	16.1	40	.1	.01	3.0	28	3	22.2	5.22
4	Acrylonitrile	None	...	16.1	40	.1	.01	4.0	28	3	20.9	3.30
5	Acrylonitrile	None	...	16.1	40	.1	.01	4.9	28	3	7.0	1.79
6	Acrylonitrile	None	...	16.1	40	.1	.01	5.3	28	3	9.4	1.89
7	Acrylonitrile	None	...	10.0	33	.1	.01	U	0	96	0	..
8	Acrylonitrile	None	...	10.0	33	.2	.01	U	0	96	19	2.01
9	Acrylonitrile	None	...	8.0	30	.1	None	U	30	18	17.5	5.50
10	Acrylonitrile	None	...	8.0	30	.1	0.002	U	30	18	100	7.11
11	Acrylonitrile	None	...	8.0	30	.1	.01	U	30	18	100	7.32
12	Acrylonitrile	None	...	8.0	30	.1	.02	U	30	18	100	5.32
13	Acrylonitrile	None	...	8.0	30	.1	.1	U	30	18	100	5.06
14	Acrylonitrile	None	...	8.0	30	.1	1.0	U	30	18	100	3.33
15	Acrylonitrile	None	...	10.0	40	.1	0.01	U	30	114	100	3.98
16	Acrylonitrile	None	...	10.0	40	.1	None	U	30	114	94	Insol.
17	Methyl acrylate	None	...	10.5	40	.1	None	U	30	114	93	0.47
18	Styrene	None	...	10.0	40	.1	None	U	30	114	75	0.41
19	Acrylonitrile	Butadiene	75/25	20.0	20	.1	0.05	U	30	69	18.5	0.54
20[f]	Acrylonitrile	Butadiene	50/50	20.0	20	.1	.05	U	30	69	24.3	0.61
21	Acrylonitrile	Butadiene	25/75	20.0	20	.1	.05	U	30	69	7.5	0.24
22[g,i]	Acrylonitrile	Butadiene	50/50	20.0	45	.2	.05	U	50	40	29.5	Insol.
23[h]	Acrylonitrile	Butadiene	50/50	20.0	45	[k]	.05	U	50	40	93.5	Insol.
24[i]	Acrylonitrile	Styrene	50/50	20.0	45	.2	.05	U	50	40	31.0	0.47
25	Acrylonitrile	None	...	10	40	.1	None	U	50	15	90	2.97
26	Acrylonitrile	None	...	10	40	.1	0.01	U	50	15	88	3.01
27	Acrylonitrile	None	...	10	40	[k]	None	U	50	15	80	3.97
28	Acrylonitrile	None	...	10	40	[k]	0.01	U	50	15	69	3.70
29	Styrene	None	...	10	40	.1	None	U	50	15	24	0.26
30	Styrene	None	...	10	40	.1	0.1	U	50	15	38	0.18
31	Methyl acrylate	None	...	10	40	.1	None	U	50	15	88	0.45
32	Methyl methacrylate	None	...	10	40	.1	None	U	50	15	100	1.82
33	Vinyl acetate	None	...	10	40	.1	None	U	50	15	0	...

[a] With the exceptions noted, the reaction medium in each experiment consisted of 2 ml. of emulsifier MP-635-S in varying amounts of redistilled water. MP-635-S consists of a mixture of alkanesulfonic acids in the C_{16} range (49.5%), unreacted hydrocarbons (10.3%), sodium chloride (0.86%), sodium sulfate (0.4%), isopropyl alcohol (3%), and the balance water. We are indebted to Dr. S. Detrick, Jackson Laboratory, E. I. du Pont de Nemours and Company, for a generous sample of this material. [b] p-Bromobenzenediazonium fluoborate, except where otherwise indicated. [c] Ferrous ammonium sulfate hexahydrate. [d] Either adjusted with sulfuric acid–sodium acetate, or, in the experiments marked U, unbuffered. [e] In dimethylformamide. [f] Acrylonitrile incorporation in copolymer, from N analysis, 48.7%. [g] Acrylonitrile incorporation 38.2%. [h] Acrylonitrile incorporation 60.5%. [i] Acrylonitrile incorporation 34.8%. [j] Dodecylamine hydrochloride, 2 g., was substituted for MP-635-S as emulsifier in this experiment. [k] p-Methoxybenzenediazonium fluoborate was substituted for the bromo compound as initiator in these experiments; 0.2 g. in experiment 23; 0.1 g. in experiments 27 and 28.

periments 9–14) and in the 114-hour polymerizations (experiments 15, 16). At 18 hours even a trace of ferrous salt caused a sixfold increase in yield, to 100%. At 114 hours, while yields were essentially quantitative both with and without the ferrous salt, only in the experiment that included activator was a soluble, non-cross-linked product obtained. At 50°, however, the activator was not needed, either with p-bromobenzenediazonium fluoborate (experiments 25, 26) or with the corresponding p-methoxy compound (experiments 27, 28). For other monomers the diazonium fluoborate was sufficiently effective to bring about polymerization in the absence of activator. Thus styrene (experiments 18, 29, 30) formed a polymer in fairly good yield provided the reaction time was of sufficient duration, while for methyl acrylate either prolonged reaction time (experiment 17) or increase in temperature (experiment 31) was effective. In the copolymerizations (experiments 19–24), it is noteworthy that replacement of the p-bromodiazonium salt by the p-methoxy salt resulted in a threefold increase in yield (experiments 22, 23); both products, however, were insoluble.

In general we found that the aryldiazonium chlorides were not effective initiators, although some small amounts of polymer were obtained in a few runs.

Our experiments lead us to believe that the polymerization at 30° is initiated by free radicals produced by the reduction of the diazonium fluoborate by either the hydroquinone or the ferrous ammonium sulfate. At 50° there is apparently enough decomposition of an aqueous solution of the fluoborate to give the free radicals necessary for initiation of polymerization. Apparently neither of these conditions produces a large concentration of radicals, for only easily polymerizable monomers seem to give polymers. It is of course known[3] that aryldiazonium salts initiate polymerizations of a variety of monomers in alkaline media, but they have apparently not been used for this purpose primarily in acid media.[4]

Experimental

Each of the polymerizations recorded in Table I was accomplished by either shaking (28 and 30° runs) or tumbling (0° and 50° runs) the indicated reaction mixture for the designated period, preliminary experiments having shown no differences in the products from these operations.

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[3] J. M. Willis, G. Alliger, B. L. Johnson and W. M. Otto, Lecture before Division of Rubber Chemistry, American Chemical Society Meeting, Buffalo, New York, October 29, 1952.

[4] After this note had been accepted for publication W. Cooper published a note in *Chemistry and Industry*, No. 17, p. 407, April 25, 1953, describing the use of *p*-nitrobenzenediazonium *p*-chlorobenzenesulfonate as an initiator for the polymerization of methyl acrylate and acrylonitrile in 2.5 *N* hydrochloric acid solution.

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N-Acetylimesatins and Related Compounds

BY FEDERICO PARISI

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In the course of researches carried out some years ago at the University of Fribourg (Switzerland) on the constitution of the products of the reaction of indigo with benzoyl chloride,[1] it was supposed that imesatins were obtained by the degradation of the products of benzoylation with aromatic amines.

This supposition has since been found to be erroneous, although the possibility of the formation of an imesatin by the treatment of Dessoulavy's compound with ammonia is still being studied.

This note will serve to record the preparation of several N-acetylimesatins and of two derivatives of N-chloroacetylisatin.

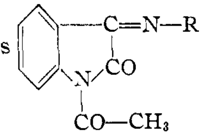
The N-acetylimesatins can be prepared by the action of the corresponding amines on N-acetylisatin (prepared according to J. Büchi[2]) in absolute alcohol without the use of catalysts.

For example: 0.01 mole of N-acetylisatin, 0.02 mole of amine and 30 ml. of absolute alcohol are heated under reflux on the water-bath for an hour, cooled and allowed to stand in the refrigerator to complete the separation of the solid. The product is collected, washed with cold alcohol and then with ether and recrystallized from an appropriate solvent (often glacial acetic acid). It may be necessary to allow the liquid to stand for some days in the refrigerator in order to complete the crystallization. In Table I are given the properties of the substances prepared.

Acetylization of imesatins with acetic anhydride does not produce the corresponding N-acetylimesatins but yields resinous substances.

TABLE I

N-ACETYLIMESATINS



R	Crystallized from	M.p., °C.	Nitrogen, % Calcd.	Found
C_6H_5	AcOH	177–178	10.61	10.59
1,2-$C_6H_4CH_3$	AcOH	185–186	10.07	10.13
1,3-$C_6H_4CH_3$	AcOH	169–170	10.07	9.91
1,4-$C_6H_4CH_3$	AcOH	176–177	10.07	10.07
1,2-C_6H_4OH	*i*-Pr_2O	169–170	10.00	9.89
1,4-C_6H_4OH	Ph·CH_3	194–195	10.00	9.83
1,4-C_6H_4COOH	AcOH	224 (dec.)	9.09	8.94
1-$C_{10}H_7$	AcOH	170–171	8.92	9.01
2-$C_{10}H_7$	AcOH	189–190	8.92	9.03
$C_5H_5N_2$[a]	AcOEt	169–170	20.00	19.82
C_3N_2NS[b]	AcOEt	184–185	15.50	15.41

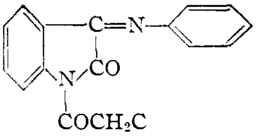
[a] 4-Methylpyrimidyl. [b] 2-Thiazolyl.

Derivatives of N-chloroacetylisatin have also been prepared using aniline according to Huntress.[3] In absolute alcohol as for N-acetylimesatins, N-chloroacetylphenylimesatin (I) was obtained. After crystallization from acetic acid it has m.p. 146°.

Anal. Calcd. for $C_{16}H_{11}N_2O_2Cl$: N, 9.38; Cl, 11.88. Found: N, 9.57; Cl, 11.71.

On the other hand, 0.01 mole of chloroacetylisatin refluxed with 0.02 mole of aniline in 10 ml. of pyridine for five minutes yields after cooling and diluting with an equal volume of water, half a volume of acetic acid and 8 ml. of concentrated hydrochloric acid (without passing the change point of congo red) a resinous precipitate. When stirred for some time this precipitate redissolves in the liquid leaving only a small residue. The filtrate from this, made alkaline with ammonia, gives a yellow precipitate of phenylglycylisatin (II) soluble in mineral acids, in concentrated alkalies and in ethyl alcohol. Crystallized from acetic acid, it has m.p. 197°.

Anal. Calcd. for $C_{16}H_{12}N_2O_3$: N, 9.99; Cl, nil. Found: N, 10.16; Cl, absent.



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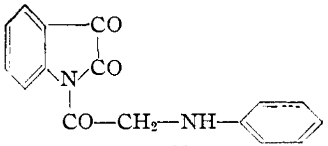

II

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[1] H. de Deisbach and coll., *Helv. Chim. Acta*, **16**, 148 (1933); **17**, 113 (1934); **19**, 1213 (1936); **20**, 132 (1937); **23**, 469 (1940); **24**, 158 (1941); **26**, 1869 (1943); **31**, 724 (1948); **32**, 1214 (1949).

[2] J. Büchi and H. Humi, *Helv. Chim. Acta*, **32**, 1806 (1949).

[3] E. H. Huntress and J. Bornstein, THIS JOURNAL, **71**, 745 (1949).

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Polarography of Tripositive Antimony and Arsenic. Cathodic Reduction of Antimonous in Strong Hydrochloric Acid and Anodic Oxidation of Arsenite and Stibnite in Strong Sodium Hydroxide

BY G. P. HAIGHT, JR.[1]

RECEIVED DECEMBER 17, 1952

The polarography of arsenic and antimony in acid solutions has been investigated by Lingane,[2] Kolthoff and Probst[3] and Bambach[4] who have shown that the tripositive state of each element is generally reducible while the pentavalent states are reduced only in very strong hydrochloric acid. Waves in 1.5 *M* HCl and in 1 *M* HCl plus 1 *M* tartaric acid have been found suitable for simultane-

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[1] Chemistry Department, University of Kansas, Lawrence, Kansas.

[2] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

[3] I. M. Kolthoff and R. L. Probst, *Anal. Chem.*, **21**, 753 (1949).

[4] K. Bambach, *Ind. Eng. Chem., Anal. Ed.*, **14**, 265 (1942).