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THE NITRATION OF WEAKLY BASIC SECONDARY AMINES

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It is known that the ease of nitration of aliphatic secondary amines is inversely dependent on their base strengths (1), determined relative to *o*-nitroaniline in acetic acid according to the colorimetric method of Hall and co-workers (2, 3).

A mechanism has been suggested to explain this behavior in terms of an unstable coördination complex of amine and nitric acid, analogous with the comparable unstable complex comprising water and nitric acid which sometimes is called nitracidium hydroxide, and which does not behave as if it were hydronium nitrate. Insofar as this analogy is valid it might be expected that free amine and nitric acid would co-exist in unreactive media in which a weakly basic amine nitrate was dissolved, just as free water and nitric acid are found when equimolecular quantities are dissolved in such media. The behavior of secondary amine nitrates in media both suitable and unsuitable for conversion to nitramines forms the subject of this report.

Although weakly-basic amine nitrates are most useful in such a study, such salts have previously been limited both in number and in type. Most of the few useful salts have been those of α,α'-dicyanodialkylamines. The electron-donating tendency of the cyano nitrogen in such salts may not provide an unambiguous evaluation of the secondary amino linkage at which nitration occurs. For this reason a different type of weakly basic secondary amine was sought, and found, in the preparation of imino-*bis*-2,2,2-trifluoroethane.

The 2,2,2-trifluoroethylammonium chloride required for preparation of the secondary amine was obtained by ammonolysis (4) of 1-bromo-2,2,2-trifluoroethane (5) at 140° for 60 hours with anhydrous ammonia. The inertness of this bromide is evident in the fact that less than 1 % of bromide ion could be detected when the halide was heated at 140° with trifluoroethylamine in ethanol for three days.

When the hydrochloride of trifluoroethylamine was heated to 240° with trifluoroacetamide (6), a good yield of N-2,2,2-trifluoroethyltrifluoroacetamide was formed (7). This compound was converted by use of lithium aluminum hydride (8) in fair yield to imino-*bis*-2,2,2-trifluoroethane.

The *bis*-amine was characterized by conversion to N,N-di-[2,2,2-trifluoroethyl]-N'-phenylurea with phenyl isocyanate. Its base strength in acetic acid was found by titration (1) with perchloric acid (using *o*-nitroaniline as indicator) to be intermediate between imino-*bis*-dimethylacetonitrile and imino-*bis*-methylacetonitrile. This weak basicity was exemplified by failure to form a picrate.

However a nitrate salt could be prepared; it sublimed very readily. An attempt to determine the structure of this salt by single-crystal x-ray diffraction methods was abandoned as unprofitable when it was found to occupy the non-centrosymmetric space group (D_2^2).

When this nitrate salt was treated with acetic anhydride without a chloride catalyst (1, 9), it was converted rapidly to nitrimino-*bis*-2,2,2-trifluoroethane. Its behavior is thus similar to that of the imino-*bis*-acetonitriles, and it has been included with the latter in a study of physical and chemical properties.

In order to relate the physical properties of these salts to the mechanism of their nitration it would be of principal interest to use acetic anhydride as a solvent, but this is impossible because the weakly basic salts are converted rapidly to nitramines in this medium. Therefore the physical properties have been determined in acetic acid (which is the principal component of the medium as nitration approaches completion); the results have been compared in some instances with those in ether, ethanol, and ethanol-water.

The ultraviolet absorption spectra of a series of secondary amine nitrates in these solvents have now been examined in comparison with the base strength of these amines relative to *o*-nitroaniline, as determined by titration with perchloric acid in acetic acid. The data are listed in Table I, together with a redetermination (10) of the wavelength corresponding to maximum extinction for absolute nitric acid in 99.8% acetic acid and in absolute ethanol. Included

TABLE I

RELATIVE BASICITY *versus* U. V. ABSORPTION OF SEVERAL AMINE NITRATES

AMINE NITRATE	REL. BASE STRENGTH IN HOAc	ULTRAVIOLET ABSORPTION			
		Solvent	Molarity	λ_{max} ±10	E_{max}
Abs. nitric acid		HOAc	0.050	2670	9.2
		EtOH	.050	2700	9.2
Imino-*bis*-dimethyl acetonitrile	0.083	EtOH	.037	2700	9.5
Imino-*bis*-2,2,2-trifluoroethane	.140	HOAc	.050	2670	9.3
		HOAc + 2% Ac_2O	.050	2670	
		Et_2O	.050	2680	9.6
		Abs. EtOH	.050	2710	9.3
		97% aq. EtOH	.050	2800	6.2
		65% aq. EtOH	.040	3010	7.2
Imino-*bis*-methylacetonitrile (m.p. 68°)	.182	EtOH	.050	2700	9.2
Imino-*bis*-acetonitrile	.389	HOAc	.030	2670	9.5
		EtOH	.026	2705	9.2
β-Imino-*bis*-propionitrile	.430	HOAc	.010	2950	7.7
Morpholine	.463	HOAc	.050	2960	7.6
		EtOH	.062	3010	6.7
Piperidine	.49	HOAc	.047	2960	8.1
Di-*n*-butylamine	.527	EtOH	.017	3010	6.8
		H_2O	.011	3010	7.7
Diisopropylamine	.675	EtOH	.046	3010	6.6
Diallylamine		HOAc	.032	2960	8.1
Dibenzylamine		HOAc	.040	2960	8.6
Ammonia		HOAc	.050	2950	8.2

also are the spectra in acetic acid of several nitrates of strongly basic amines for which the relative basicities in this medium have not been determined.

With exception to the first four salts listed in Table I all are derived from amines of the "strongly basic" type which are difficult to nitrate in absence of chloride catalyst. The curves for these basic amines have a broad absorption peak at 3010 Å with a maximum molecular extinction coefficient (E_{max}) of about 7.7 in water and 6.7 in absolute ethanol. At shorter wavelengths the curves show steeply-rising end absorption. A slight hypsochromic shift of 50 Å is noted when the solvent is 99.8% acetic acid. These absorption characteristics, which are typical for alkali metal nitrates, ammonium nitrate, and dilute nitric acid (11, 12), indicate that all of the "strongly basic" amine nitrates exist largely in these solvents in the same state as do the inorganic nitrates.

In water-ethanol mixtures the typical absorption of the salts of the first four "weakly basic" amines is exemplified in Table I by imino-*bis*-2,2,2-trifluoroethane nitrate. This absorption is closely similar to that of the "strongly basic" amines. On the other hand, the absorption by nitrate salts of the "weakly basic" amines in ether, absolute ethanol, or acetic acid shows virtual absence of nitrate ion. Instead the absorption maximum at 2710–2670 Å is typical of that for absolute nitric acid in these solvents (10). In one instance the same behavior obtained when 2% of acetic anhydride was included with the acetic acid, although E_{max} tended to increase during the period of measurement. This is probably a consequence of slow nitration owing to the acetic anhydride.

A further contrast between the strongly basic and weakly basic amine nitrates is found in their electrical conductances in acetic acid solution. Thus Table II shows that the conductances of ammonium nitrate and dibutylammonium nitrate are moderately low in this solvent, but are ten- to twenty-fold greater than those found for imino-*bis*-acetonitrile and imino-*bis*-2,2,2-trifluorethane nitrates. The equivalent conductances in acetic acid for nitric acid [in agreement

TABLE II

CONDUCTANCE AT 25°C. IN ABSOLUTE ACETIC ACID

COMPOUND	"CONC'N" mole/litre × 10^3	EQUIV. COND. A
Di-*n*-butylammonium nitrate	6.92	0.272
Ammonium nitrate	10.8	.245
Imino-*bis*-acetonitrile nitrate	6.32	.013
Imino-*bis*-2,2,2-trifluoroethane nitrate	1.43	.014
	1.19	.017
	1.17	.016
	0.69	.022
	.63	.027
	.56	.026
Imino-*bis*-2,2,2-trifluoroethane	1.43	.003−
	.69	.003+
Absolute nitric acid	1.43	.009
	.69	.016
	.50	.019

TABLE III

Freezing Point Lowering in Absolute Acetic Acid

COMPOUND	MOLALITY	ΔT, °C.	MOL. WT. OBS.	FORMULA WT. CALC'D	NO. OF PARTICLES, "i"
Di-*n*-butylammonium nitrate	0.0264	0.089	205	192	0.94
Morpholinium nitrate	.0212	.072	159	150	.94
Ammonium nitrate	.0199	.070	82	80	.98
Imino-*bis*-2,2,2-trifluoroethane nitrate	.0109	.079	121	244	2.05
	.0191	.143	117		
Imino-*bis*-acetonitrile nitrate	.0098	.063	88	158	1.91
	.0177	.128	78		
	.0253	.165	87		
	.0303	.215	80		
Imino-*bis*-acetonitrile	.0373	.136	94	95	1.01
Nitric acid calculated from (15)	.1529	.540	64	63	1.02

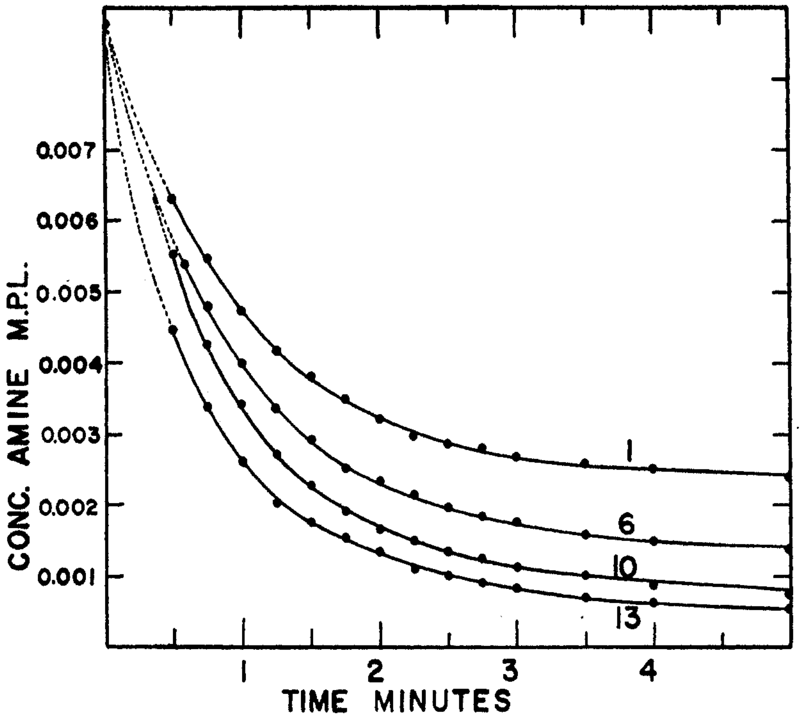
with Kolthoff's values (13)] and for imino-*bis*-trifluoroethane is also recorded. Perhaps fortuitously the sum of amine and nitric acid conductances approximates the values found for the salt.

A notable difference between strongly basic and weakly basic amine nitrates is found in the freezing point depressions for their solutions in acetic acid. These data evaluated by Eichelberger's calculated molal freezing point constant ($k_F = 3.59$) (14) are incorporated into Table III. They show, in agreement with Eichelberger, that ammonium nitrate is slightly associated in acetic acid and, further, that dibutylammonium and morpholinium nitrate behave similarly. On the other hand, imino-*bis*-2,2,2-trifluoroethane nitrate and imino-*bis*-acetonitrile nitrate seem to be bi-particulate in this solvent of low dielectric constant at concentrations where imino-*bis*-acetonitrile is not associated. At these concentrations nitric acid in acetic acid has been reported to be undissociated (15).

These contrasts in light absorption, conductivity, and freezing point depression indicate that strongly basic and weakly basic amine nitrates in acetic acid are functionally different. It is usually assumed that strongly basic amine salts either are ionized or else are hydrogen-bridged ion pairs. Weakly basic amine nitrates cannot be included in either of these categories. Instead they behave in acetic acid (also in ether and absolute ethanol) as free amines and free nitric acid.

We have pointed out previously that the physical properties of solutions of weakly-basic amine nitrates in acetic anhydride could not be determined because they were converted rapidly in this medium to the corresponding nitramines. A kinetic study in the anhydride is thus indicated, but heretofore the available amines were neither sufficiently stable nor amenable to satisfactory analytical determination for utilization of the kinetic approach.

The preparation of imino-*bis*-2,2,2-trifluoroethane has now provided a weakly basic aliphatic secondary amine which is stable. Furthermore its reaction with nitric acid in acetic anhydride can be followed photometrically by observation



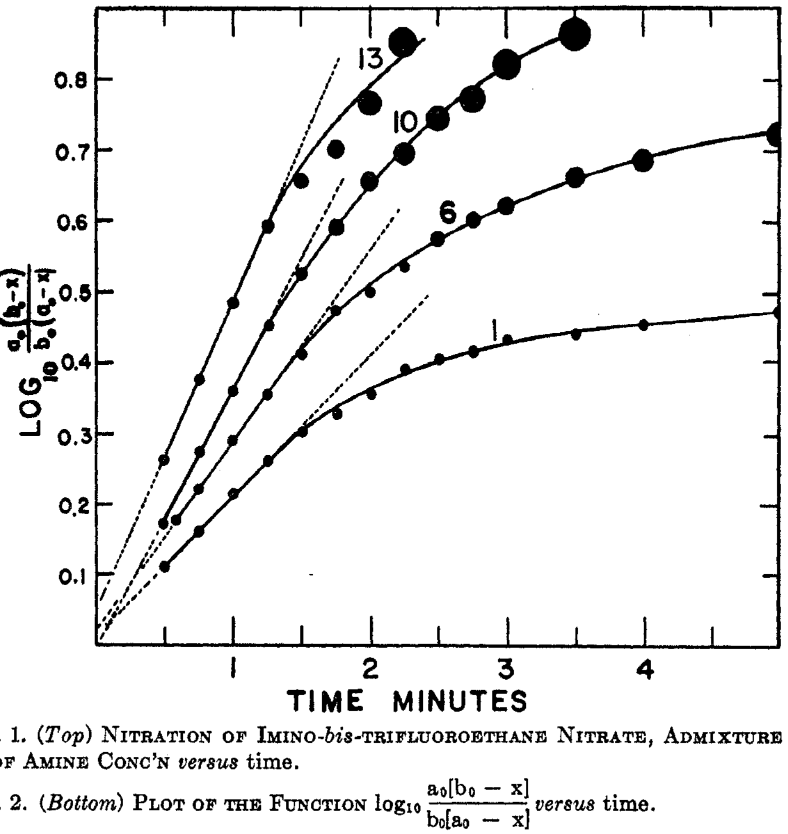


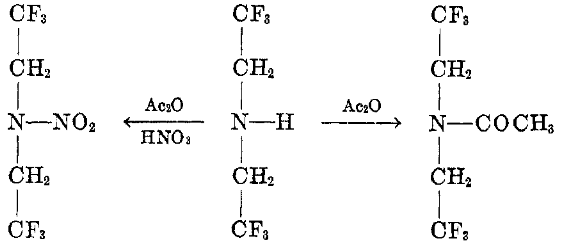
FIG. 1. (*Top*) NITRATION OF IMINO-*bis*-TRIFLUOROETHANE NITRATE, ADMIXTURE AT 25°. PLOT OF AMINE CONC'N *versus* time.

FIG. 2. (*Bottom*) PLOT OF THE FUNCTION $\log_{10} \frac{a_0[b_0 - x]}{b_0[a_0 - x]}$ *versus* time.

of the increase in optical density in the ultraviolet region because of the nitramine which is formed during the reaction. The conversion is rapid (one-half to five minutes) and after the reaction is complete, no further change in optical density occurs.

The rapidity of reaction requires the use of large excesses (200–1200 moles) of acetic anhydride in order that the imino-*bis*-trifluoroethane nitrate will dissolve within 15 to 45 seconds. Since these time intervals represent up to 30% of the total reaction period an extended extrapolation to zero time (as shown by typical experiments in Fig. 1) is required.

The large excess of acetic anhydride is deleterious because it promotes the competing reaction of acetylation. This was demonstrated by determination of unused nitric acid (as nitron nitrate) after the reaction had proceeded to completion according to photometric observation.



$$(CF_3CH_2)_2N{-}NO_2 \xleftarrow[HNO_3]{Ac_2O} (CF_3CH_2)_2N{-}H \xrightarrow{Ac_2O} (CF_3CH_2)_2N{-}COCH_3$$

In consequence it is found that the yield of nitramine is low (30–60%) unless the molar ratio of nitric acid to amine was at least 2:1. Because of the systematic error (low yield *versus* extended extrapolation to zero time) ratios lower than 2:1 have been disregarded in the kinetic study.

Table IV describes the series of experiments wherein the molar ratio of nitric

TABLE IV

NITRATION OF IMINO-*bis*-TRIFLUOROETHANE NITRATE, ADMIXTURE AT 25°.

EXP. No.	[Amine] m.p.l. × 10^4	$\frac{[\text{Total } HNO_3]}{[\text{Amine}]}$	k_2 L.mole^{-1} min.$^{-1}$	% MOLAR YIELD BY E_m AT 2900 Å
1	88	4	17.4	73
2	175	2	15.8	74
3	88	4	17.0	75
4	350	1.5	16.7	81
5	175	2.4	18.7	81
6	88	5.0	17.6	84
7	263	2.0	18.8	86
8	175	3.0	18.9	90
9	88	6.0	17.9	92
10	88	6.0	19.3	92
11	88	8.0	18.2	92
12	88	6.0	19.0	93
13	88	8.0	16.5	94
14	131	4.0	19.0	95
15	88	6.0	18.8	98

acid to amine has been varied from 2 to 8. It may be seen that the yields of nitramine under these circumstances vary from 73–98%. The results of the four typical experiments plotted in Fig. 1 have been re-plotted (Fig. 2) in respect of the function $\log_{10} \frac{a_0[b_0 - x]}{b_0[a_0 - x]}$ *versus* time (where a_0 and b_0 are initial base and acid concentrations and x is the photometrically-determined concentration of nitramine) in order to show that portion of the reaction time interval (30–75 seconds) which is sufficiently linear for calculation of second-order rate constants.

$$k_2 t = \frac{2.303}{b_0 - a_0} \log_{10} \frac{a_0 (b_0 - x)}{b_0 (a_0 - x)}$$

The subsequent curvatures in Fig. 2 are attributed to competitive consumption (pseudounimolecular) of amine in formation of the transparent acetamino-*bis*-trifluoroethane.

Inspection of Table IV shows a rate constancy averaging 18.0 ±2.2 moles^{-1}. liters•min.^{-1}. Despite this large deviation the constancy seems to justify a description of the reaction as first-order in amine and in nitric acid.

$$\frac{d[\text{nitramine}]}{dt} = k_2[\text{amine}][\text{nitric acid}]$$

Furthermore the table shows, with one exception (Expt. 13), that the lowest of the individual "constants" correspond with the lowest yields of nitramine as estimated photometrically. Although early experiments showed that the presence of acetic acid caused a retardation with consequent low yields of nitramine, the retardations shown as low constants and yields in Table IV are attributed by us to trace contamination with nitrous acid.

The nitric acid used in these experiments originally contained not more than 0.02% of nitrous acid according to the chloramine-T analysis. However this may be expected to increase gradually to about 0.04–0.05% with age. Furthermore a non-evaluable amount of nitrous acid may be generated upon admixture of the reagents at 25°. For this reason a new set of experiments have been carried out in which the reagents were mixed at −50° to −80° and then warmed rapidly to 25°. The results of these experiments are shown in Table V.

We believe that the rate constant (23.2–23.9) obtained (Expts. 16, 21) under conditions of virtual freedom from contamination with nitrous acid is closely representative of the reaction of imino-*bis*-trifluoroethane and nitric acid in large excess of acetic anhydride, especially since the photometric method has been checked by a gravimetric procedure. In the latter method aliquots of reaction mixture (like that of Expt. 16) have been drowned in aqueous sodium acetate, and the unchanged nitric acid then precipitated as nitron nitrate.

Using these improved conditions the effect of additives has been examined. In confirmation of earlier experiments it has been found (Expt. 25) that reaction in 95% acetic anhydride is strongly retarded; the low yield indicates that the calculated constant (in brackets) has no real significance. Likewise the addition of large amounts of either tetraethylammonium nitrate or lithium nitrate so

TABLE V

NITRATION OF IMINO-*bis*-TRIFLUROETHANE NITRATE, ADMIXTURE AT −50 TO −80°

EXPT. No.	[Amine] m.p.l. × 10^4	$\frac{[\text{Total HNO}_3]}{[\text{Amine}]}$	ADDITIONAL SUBSTANCE, m.p.l.	k_2 L.mole^{-1} min.$^{-1}$	% MOLAR YIELD BY E_m AT 2900Å
16	175	2.7	None	23.2	94
17	175	3.0	$NaClO_4$, 84 × 10^{-4}	66.0	102
18	88	5.2	$NaClO_4$, 25 × 10^{-4}	43.7	100
19	175	2.6	$(Et)_4NNO_3$, 13 × 10^{-5}	15.9	74
20	175	3.4	$(Et)_4NNO_3$, 25 × 10^{-4}	(3.6)	46
21	88	5.2	None	23.9	95
22	88	5.4	$LiNO_3$, 13 × 10^{-6}	21.7	93
23	88	5.4	$LiNO_3$, 58 × 10^{-6}	(9.2)	69
24	88	5.0	$LiNO_3$, 51 × 10^{-5}	(4.7)	44
25	88	5.3	5% Acetic acid	12.3	82

retards the rate that calculated constants are meaningless because of competitive acetylation. Nevertheless it is suggestive from the results of Expts. 19–24 inclusive that the reaction is strongly inhibited by the common ion, nitrate. Indeed this is the more probable because of the marked acceleration observed (Expts. 17–18) when sodium perchlorate (which should increase the ionic strength) is added.

These results may be interpreted in terms of the following equations, where R_2NH is imino-*bis*-trifluoroethane

$$R_2NH_2NO_3 \xrightarrow{Ac_2O} R_2NH + HNO_3 \qquad \text{i}$$

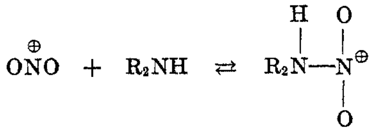
$$2\,HNO_3 + Ac_2O \rightleftarrows N_2O_5 + 2\,AcOH \qquad \text{ii}$$

$$N_2O_5 + Ac_2O \rightleftarrows 2\,NO_2OAc \qquad \text{iii}$$

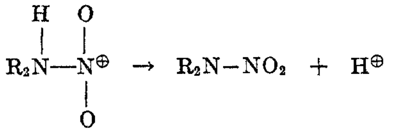
$$N_2O_5 \rightleftarrows \overset{\oplus}{ONO} + \overset{\ominus}{NO_3} \qquad \text{iv}$$

$$\overset{\ominus}{NO_3} + NaClO_4 \rightleftarrows NaNO_3 + \overset{\ominus}{ClO_4} \qquad \text{v}$$

$$NO_2OAc \rightleftarrows \overset{\oplus}{ONO} + \overset{\ominus}{OAc} \qquad \text{vi}$$



$$\overset{\oplus}{ONO} + R_2NH \rightleftarrows R_2\overset{\overset{H}{|}}{N}-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{N}}{}^{\oplus} \qquad \text{vii}$$



$$R_2\overset{\overset{H}{|}}{N}-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{N}}{}^{\oplus} \rightarrow R_2N-NO_2 + H^{\oplus} \qquad \text{viii}$$

No attempt has been made to interpret the retarding effect of nitrous acid. It seems reasonable to relate the second-order kinetics to the interaction of free amine and nitronium ion despite the conclusion of Chédin and Fénéant (16). These authors concluded from Raman spectral studies that although equilibria ii and iii are shifted largely to the right in a large excess of acetic anhydride, equilibria iv and vi are also shifted so strongly to the left that nitronium ion is nondetectable. However nitrations which are demonstrably ionic in nature are not uncommon in media where nitronium ion cannot be detected by spectroscopic means (17). In the present instance the retardation by added nitrates and the acceleration by sodium perchlorate are to be expected if these salts force equilibria iv and v to the left and right respectively.

Reaction vii is specified as rate-controlling but none of the evidence in this report supports the existence of the ammononitronium ion which would justify the inclusion of equation viii. One may predict that such an intermediate will be encountered during nitration of an amine which is more electron-donating than imino-*bis*-trifluoroethane but less electron-donating than dibutylamine. Coordinated nitronium salts will not be unexpected since tertiary amines seem to form complexes with dinitrogen pentoxide (18) and acetyl nitrate (19, 20).

EXPERIMENTAL[1]

2,2,2-Trifluoroethylamine hydrochloride. A mixture of 135 g. (8.0 moles) of anhydrous ammonia, 90 g. (0.55 mole) of trifluoroethyl bromide (5), and 6 g. (0.04 mole) of sodium iodide was maintained at 130–140° for 60 hours in a steel pressure vessel. The volatile products were fractionally distilled at low temperature to remove excess ammonia, and then converted to the hydrochloride salt. Qualitative tests showed that this salt was contaminated with ammonium chloride.

Anal. Calc'd for $C_2H_5ClF_3N$: Cl, 26.7. Found: Cl, 28.4

This analysis indicates that the salt was contaminated with 5.5% of ammonium chloride. On this basis the crude yield, 64 g., was 80%.

N-2,2,2-Trifluoroethyltrifluoroacetamide. A powdered mixture of 40.5 g. (0.282 mole based on 5.5% ammonium chloride content) of crude 2,2,2-trifluoroethylammonium chloride and 32.0 g. (0.282 mole) of trifluoroacetamide was heated at 240° for one hour in a sealed glass tube, and then extracted with a total of 125 cc. of ethyl ether. Distillation of the extracts at 760 mm. yielded 54 g. (98%) of a fraction b.p. 143–144°, m.p. 51–53°. Sublimation at 8 mm. and 40° gave the constant melting point 51.3–52.3°. The compound is soluble in dilute sodium hydroxide and is reprecipitated by acids.

Anal. Calc'd for $C_4H_3F_6NO$: C, 24.6; H, 1.55; N, 7.2.
Found: C, 24.5; H, 1.57; N, 7.5.

In general we have been unable to obtain satisfactory analysis of nitrogen (Dumas) for any of these substances of high fluorine content.

Imino-bis-2,2,2-trifluoroethane. Into a three-necked flask fitted with a mercury-sealed stirrer and an efficient reflux condenser protected by an atmosphere of nitrogen was placed 500 cc. of an etherous solution, which by analysis (21, 22) contained 19.4 g. (0.51 mole) of lithium aluminum hydride. N-2,2,2-Trifluoroethyltrifluoroacetamide (50.0 g., 0.256 mole) dissolved in 200 cc. of dry ether was added over 45 minutes. The resulting sludge was refluxed for 9 hours and then hydrolyzed by the slow addition of 40 cc. of ice-water followed by 300 cc. of 30% sodium hydroxide. The etherous solution of the product was distilled at one atmosphere up to 100°, dried over barium oxide and distilled to yield 32.9 g. (73%) of a fraction b.p. 82.0–82.5° (761 mm.). Fractionation through an efficient column gave material of constant refractive index n_D^{20} 1.3013, b.p. 82.0° (761 mm.).

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[1] All melting points have been corrected against reliable standards.

A volatile nitrate salt was obtained by treating a 4% etherous solution of the amine slowly with exactly one equivalent of 99% nitric acid at −30°. The partially-soluble product was isolated in 94% yield by the cautious vacuum evaporation of the solvent. The salt sublimes rapidly at 140° (760 mm.) or 60° (10 mm.).

Anal. Calc'd for $C_4H_6F_6N_2O_3$: C, 19.7; H, 2.48; HNO_3, 25.8.

Found: C, 19.8; H, 2.71; HNO_3, 15.4 (as nitron nitrate).

The salt is readily hydrolyzed even by moist air. It is soluble to the extent of several percent in acetic acid and ethyl ether.

Crystallographic examination. The crystals of nitrate salt used for this purpose were obtained by slow sublimation at 40° (760 mm.). This process gave flat plates with cleavage along (100). The refractive index (by immersion) of 1.35 corresponds to the a axis but the other two indices (1.42 and 1.44) were not related to the crystal morphology.

Because of volatility and hygroscopacity the crystals were enclosed in gelatine capsules while zero, first, and second layer Weissenberg photographs were obtained. The cell is orthorhombic (a = 14.47 ± 0.02 Å; b = 16.69 ± 0.02 Å; C, 5.68 ± 0.005 Å) with b and c axes in the plane of the plate. Rotation about [013] and $[0\bar{1}3]$ gave identical face diagonals with spacings of 23.79 ± 0.09 Å, in agreement with the calculated value of 23.85 Å. Since the crystal density was found in 1,2-dibromoethane-carbon tetrachloride to be 1.76 there must be six molecules per unit cell. The only systematic extinction is that of (001) except when $l = 2n$. This is consistent with the space group D_2^2 (P_{2221}).

N,N-di-[2,2,2-trifluoroethyl]-N'-phenylurea. An equimolar mixture of 1.13 g. of imino-*bis*-2,2,2-trifluoroethane and 0.74 g. of phenyl isocyanate was heated in a sealed tube at 95° for 15 hours. The crystals which formed at 25° were filtered from a small amount of liquid, and weighed 1.67 g. (89%), m.p. 112–114°. Two crystallizations from di-*n*-butyl ether raised the melting point to 115.5–116.3°, weight 1.40 g. (75%).

Anal. Calc'd for $C_{11}H_{10}F_6N_2O$: C, 44.0; H, 3.36; N, 9.33.

Found: C, 44.2; H, 3.48; N, 9.52.

Nitrimino-bis-2,2,2-trifluoroethane. Imino-*bis*-2,2,2-trifluoroethane nitrate (3.66 g., 0.015 mole), was added at 15° over 15 minutes to a solution of 0.72 cc. (0.017 mole) of 99% nitric acid and 7.2 cc. (0.075 mole) of acetic anhydride prepared at 5°. The resulting solution was maintained for 30 minutes at 15°, 2 hours at 25°, and then was drowned in 100 cc. of ice and water. This was extracted with a total 60 cc. ether. The extracts, washed acid free with aqueous sodium bicarbonate and dried over calcium chloride, were fractionally distilled, finally at a pressure of 8 mm. to yield 2.84 g. (84%) of liquid, b.p. 43–45°, m.p. −1–2°. Low temperature crystallization from dichloromethane (4 cc. per g.) raised the melting point to 0.0–1.1°. This material gave a strong green Franchimont nitramine test (23) when diethylaniline was used, and a negative Liebermann nitrosamine test.

Anal. Calc'd for $C_4H_4F_6N_2O_2$: C, 21.3; H, 1.78.

Found: C, 21.3; H, 1.69.

Determination of basicity. The titrations were carried out essentially as described previously, in 99.8% acetic acid. All amine salts used in these determinations were crystallized to constant melting point.

Absorption spectra. The determinations were made with a Beckman Spectrometer Model DU using slit widths of 0.5–1 mm. The absolute ethanol was prepared by the method of Bjerrum and Lund (24) under nitrogen. The acetic acid contained 0.23% water according to titration with Karl Fischer reagent. Ethyl ether was purified from sodium benzophenone. The absolute nitric acid was prepared by vacuum distillation from sulphuric acid and was colorless.

Freezing point depressions. Freezing point curves were determined in a simple Beckmann apparatus protected by a positive pressure of dry nitrogen. The anhydrous acetic acid was prepared by the method of Eichelberger and LaMer (25). It melted at 16.63° and according to titration with Karl Fischer reagent contained less than 0.003% water.

Electrical conductivities. The measurements were carried out at 1000 cycles using lightly platinized platinum electrodes. No precautions were taken against polarization errors.

The specific conductivity ($K = 2.9 \times 10^{-8}$ mho) of the purified acetic acid was subtracted from the observed conductivities.

X-ray diffraction pattern of imino-bis-trifluoroethane hydrochloride. The hydrochloride, prepared from the amine with hydrogen chloride in ether was examined in Cu, K_α radiation (Ni filtered). Relative intensities [I/I_1] in Å are: [10] 3.65; [8] 3.44; [6] 2.48; [5] 5.01; 4.74; [4] 3.01, 2.70, 2.12; [3] 3.32, 3.17, 2.62, 2.37, 2.26, 2.19, 1.59, 1.58, 1.55; [2] 1.94, 1.34; [1] 4.28, 4.03, 3.81, 1.81, 1.73, 1.40, 1.37, 1.31, 1.25.

Kinetic studies. (*A*). *Reagents. Acetic anhydride* was purified by treatment with chromic anhydride (3 g. per liter) at 70°. The chromium salt should be added slowly in order to avoid violent reaction. Repeated fractional distillation gave a fraction containing 1.1 ± .2% of acetic acid, with optical transmission at 2900 Å of 66% for 1 cm. of light path.

Nitric acid was prepared for the first 15 experiments by vacuum distillation from sulphuric acid and according to titration with base contained 99.9–100.0% of acid. The nitrous acid content according to titration with chloramine-T (using sodium acetate buffer) (26) was less than 0.018%. This nitrous acid content was decreased in the acid used in the last 10 experiments by rapid aspiration at one-half atmosphere with dry nitrogen for one hour just prior to the kinetic experiments. According to titration with base this acid contained 99.8–100.0% HNO_3; titration with chloramine-T after one day in darkness at +4° showed that it contained less than 0.001% of nitrous acid.

(*B*). *Admixture of nitric acid and acetic anhydride.* During the first 15 experiments the nitric acid was weighed into the acetic anhydride at 25° about 30 to 45 minutes before reaction with the nitrate salt. During the last 10 experiments the nitric acid was cooled to −30°, then added dropwise to acetic anhydride at −80°. After thorough admixture it was thermostatted for ten minutes and then transferred directly to the spectrophotometer cell at 25°. Duplicate aliquots were analyzed for nitric acid content by the nitron procedure.

(*C*). *Spectroscopic analysis.* The photometric rate determinations were carried out in 1-cm. tightly-stoppered quartz cells in a Beckman Model DU spectrometer fitted with a cell compartment maintained at 25.0 ± .1° by an air-bath. After the absorption cell containing a weighed amount of amine nitrate had been brought to this temperature the nitric acid–acetic anhydride mixture was added and the whole was stirred so that the initial reading could be taken within 30 seconds. Subsequent readings were taken at 15-second intervals. The slow dissolution of the salt made the initial time of reaction difficult to ascertain, so all rates have been calculated from that portion of the reaction which occurred 30 seconds after the initial mixing.

The opacity of the acetic anhydride prevented photometric measurement at the peak, *ca.* 2250 Å, of the nitramine absorption curve. At a longer wavelength (2900 Å) the extinction coefficient ($E_m = 37.7$) of the nitramine varied less than 1% over a concentration range of 0.01 to 0.025 *molar*. Assuming additivity of optical densities the absorption of the reaction medium was cancelled by use of the same medium in the comparison cell of the spectrophotometer.

The correction of the optical density for the absorption due to unchanged amine nitrate could only be made approximately since rapid nitration prevented a direct determination of the initial extinction coefficient. The approximate value ($E_m = 5.3 \pm 1$) was obtained by extrapolation of the optical densities to the time when about half of the salt had dissolved in the medium. This value is identical ($E_m = 5.3$) with the extinction coefficient for imino-*bis*-trifluoroethane nitrate in acetic acid.

The nitramine yields calculated from final optical densities at 2900 Å were checked in three cases by precipitation as nitron nitrate of the nitric acid which was vacuum-distilled from the completed reaction. Thus recovered nitric acid was found to correspond to nitramine yields of 33, 22, and 65% in experiments, wherein the yields calculated from the optical density were found to be 39, 28, and 67% respectively.

Gravimetric kinetic procedure. A 40-ml. separatory-funnel was fitted with a wide-bore stopcock plug, which drained acetic anhydride at about 2 ml. per sec., and with two interchangeable stoppers. One of these was solid, the other being hollow. The hollow stopper was fitted with a standard-taper cap and was used for weighing of the amine nitrate sample. The kinetic procedure was effected by adjusting the separatory-funnel with the required nitric acid-acetic anhydride mixture to 25°, then quickly replacing the solid stopper by the hollow one containing the weighed amine nitrate at 25°. The assembly was shaken for 20 seconds, then 4-ml. aliquots were withdrawn at 30-second intervals into tared flasks containing 10 ml. of 1% sodium acetate in 1:1 water-ethanol. After the weight of aliquot was determined it was evaporated under 10 mm. pressure, and the residue was dissolved in 8 ml. of water. After addition of 0.1 ml. of 20% sulfuric acid the solution was treated with a calculated excess of a 10% solution of nitron in 95–5 water-acetic acid. The precipitate was filtered, washed with 15 ml. of iced water, and dried at 100° (10 mm.) for one hour. Tests with authentic weighed samples show that 98–99.5% of the nitric acid is estimated by this method.

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