ing step is the reaction $\mathrm{FePh_2^{++} + Ph \rightarrow FePh_3^{++}}$. Within experimental error the ratio of $k_{\mathrm{diss.}}/k_{\mathrm{form.}}$ was found to be equal to the experimentally determined value of the dissociation constant $K_{\mathrm{diss.}}$ of ferroin.

The dissociation of ferriin was found to be a first order reaction in sulfuric acid solutions. The rate of reaction decreases with increasing sulfuric acid concentration.

MINNEAPOLIS, MINN. RECEIVED JUNE 14, 1948

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Relative Reactivities of Some Substituted Benzyl Fluorides[1]

BY WILLIAM T. MILLER, JR., AND JACK BERNSTEIN[2]

The development of a general method of preparation for the substituted benzyl fluorides[3] made possible the measurement of their relative reactivities. It was considered that such a study would furnish a worthwhile comparison of the replacement reactions of fluorine with those of the other halogens since the reactivity of the benzyl chlorides and bromides have been studied from this point of view by a number of workers. No systematic quantitative measurements on the reactivity of alkyl fluorides have previously appeared in the literature.

The basic reaction pattern for side-chain halides has been elucidated by Ingold[4] on the basis of two general type reaction mechanisms usually termed S_N1 and S_N2 for unimolecular and bimolecular reactions with nucleophilic reagents. Ordinarily hydrolysis or alcoholysis reactions occur by both mechanisms but one or the other may be made predominant by the choice of suitable reactants and the effect of substituents then becomes diagnostic of reaction mechanism.

In the present work the rates of reaction of various substituted benzyl fluorides with sodium ethoxide in 95% alcohol were determined and satisfactory second order rate constants were obtained as shown in Table I. The order found for the effect of the substituent in increasing the reactivity of the side chain fluorine was in general $m\text{-NO}_2 > p\text{-X} > m\text{-X} > p\text{-CH}_3 > \text{H} > m\text{-CH}_3 > o\text{-X}$ in agreement with the order for electron attraction by a substituent,[5] and hence indicated a predominately bimolecular or S_N2 reaction mechanism favored by the withdrawal of electrons. Franzen,[6] who studied the reaction of several substituted benzyl chlorides with sodium ethoxide in absolute alcohol, also observed this reaction to be a second order reaction in which the effect of substituents in increasing the reactivity was $o\text{-CH}_3 > p\text{-X} > p\text{-CH}_3 > m\text{-X} > m\text{-CH}_3 > \text{H} > o\text{-X}$. The effect of halogen substitution is of especial interest since the order for electron release is the resultant of opposing inductive and mesomeric or resonance effects as defined by Ingold.[5] The net result of these effects for benzenoid halogen has been indicated to be in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$ on the basis of evidence from a number of sources.[7] In the meta substituted benzyl fluorides the order of reactivity was found to be exactly as expected, $\text{I} > \text{Br} > \text{Cl} > \text{F}$. In the para series the order was $\text{I} > \text{Cl} > \text{Br} > \text{F}$, the position of the chloro and bromo isomers being reversed due presumably to polarization effects.

The relative reactivities of the substituted benzyl fluorides were also found by determining the per cent. reaction of the fluorides after refluxing in various reagents for a definite length of time. The solvents were alcohol and 1.0 N hydrochloric acid, alcohol and 0.1 N hydrochloric acid, aqueous alcohol, and alcohol and 1.0 N sodium hydroxide. The initial molar concentrations of the benzyl fluorides were maintained approximately the same in all cases to insure comparable results. When acidic solvents were used, there was some loss of hydrogen fluoride, but the loss could not change the order of reactivity since corresponding losses would occur in all cases.

In the reaction with alcohol and 1.0 N sodium hydroxide solution, the observed order of reactivity was $m\text{-NO}_2 > p\text{-X} > p\text{-CH}_3 > m\text{-CH}_3 > \text{H} > m\text{-X} > o\text{-X}$. This order does not follow either the order for electron release or electron withdrawal for the substituents, although it agrees with the order for the effect of substituents determined by Olivier[8] for the reaction of substituted benzyl chlorides with dilute alkali in aqueous acetone. Apparently in this case, reaction was occurring concurrently by both S_N2 and S_N1 mechanisms. This seemed further to be indicated since the reaction of p-chlorobenzyl fluoride with dilute aqueous alcoholic sodium hydroxide yielded

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(1) Presented in part before the Division of Organic Chemistry of the American Chemical Society at Atlantic City, N. J., September 10, 1941. Based on the thesis submitted by Jack Bernstein to the Graduate School of Cornell University in partial fulfillment of the requirements for the Ph.D. degree, June, 1941.

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(3) Bernstein, Roth and Miller, THIS JOURNAL, **70**, 2310 (1948).

(4) Ingold and Rothstein, *J. Chem. Soc.*, 1217 (1928); Hughes and Ingold, *ibid.*, 244 (1935). For general type mechanisms for halide replacement reactions see Hughes, *ibid.*, 968 (1946), and references cited.

(5) Ingold, *Chem. Revs.*, **15**, 225 (1934).

(6) Franzen, *J. prakt. Chem.*, [2] **97**, 82 (1919); Franzen and Rosenberg, *ibid.*, **101**, 333 (1920).

(7) Watson, "Modern Theories of Organic Chemistry," 2nd ed., Oxford University Press, London, 1941, p. 101.

(8) Olivier and Weber, *Rec. trav. chim.*, **53**, 869 (1934).

TABLE I

REACTION OF THE BENZYL FLUORIDES WITH SODIUM ETHOXIDE AT 76°

Substituent	Concentration of fluoride, moles per liter	Concentration of NaOEt. moles per liter	Observed values of *K*					Average value of *K*
o-Br	0.2281	0.2150	0.054	0.056	0.056	0.057	0.053	0.055
m-CH_3	.2192	.2163	.095	.090	.090	.087	.089	.090
. . .	.2212	.2139	.097	.096	.093	.098		.095
m-F	.2172	.2138	.097	.097	.096	.099		.097
o-Cl	.2281	.2148	.102	.105	.100	.096	.094	.099
p-CH_3	.2162	.2149	.103	.102	.101	.100	.102	.012
m-Cl	.2259	.2137	.114	.120	.115	.114		.116
m-Br	.2253	.2164	.119	.119	.121	.123	.119	.120
m-I	.2230	.2133	.123	.132	.131	.130	.131	.129
p-F	.2179	.2149	.133	.130	.126	.131		.130
p-Br	.2215	.2141	.138	.144	.146	.143	.143	.143
p-Cl	.2196	.2143	.139	.145	.150	.148		.146
p-I	.2207	.2138	.154	.162	.161	.162	.162	.160
m-NO_2[a]	.2008	.2102	.314	.328	.314	.330		.322
p-NO_2[b]	. . . .	. . . .	. . .					. . .

[a] Solution turned light brown during the heating indicating some side reaction. [b] Reacted very rapidly, but formed very highly colored solution. A solid was isolated which melted above 300°, indicating that the reaction occurring was not a simple replacement of fluorine by ethoxide.

both *p*-chlorobenzyl alcohol and ethyl *p*-chlorobenzyl ether.

The relative reactivity of the substituted benzyl fluorides in aqueous alcohol or aqueous alcoholic hydrochloric acid was found to be *p*-CH_3 > *m*-CH_3 > H > *p*-X[9] > *o*-X > *m*-X > *m*-NO_2 > *p*-NO_2. The order for the effect of substituents is essentially that observed for benzyl chlorides by Olivier,[10] who studied the reaction with aqueous alcohol, and of Bennett,[11] who utilized aqueous acetone. The reaction was indicated as proceeding principally by an S_N1 mechanism. In this reaction, the ionization of the C–F bond is followed by or concurrent with attack by an alcohol molecule and subsequent elimination of a proton since the product isolated from the reaction of *m*-methylbenzyl fluoride with aqueous alcoholic hydrochloric acid has been shown to be ethyl *m*-methylbenzyl ether and not *m*-methylbenzyl alcohol.[3]

A particularly interesting point as regards fluorine chemistry is the marked electron release which may be exhibited by benzenoid fluorine. This is strikingly illustrated by *p*-fluorobenzyl fluoride which was found to be hydrolyzed faster in neutral or acidic aqueous alcohol than benzyl fluoride. Shoesmith and Slater[12] similarly found *p*-fluorobenzyl bromide more readily hydrolyzed by aqueous alcohol than benzyl bromide.

Although the substituted benzyl fluorides fell into a similar order to the substituted benzyl chlorides in their reaction with aqueous alcohol or aqueous alcoholic hydrochloric acid, there was one important difference. The reaction of the benzyl fluorides was catalyzed by the presence of acid, whereas Olivier[8] has observed that the addition of acid did not catalyze the reaction of the chlorides.[13] This catalysis is clearly indicated in Table II. In each case, the per cent. reaction after ten hours in the presence of added 0.93 *N* hydrochloric acid was approximately the same as after one hundred and twenty hours with an equal volume of 0.1 *N* hydrochloric acid. In addition the per cent. reaction after one hundred and twenty hours in the presence of 0.1 *N* hydrochloric acid was usually

TABLE II

PER CENT. REACTION OF BENZYL FLUORIDES WITH AQUEOUS ALCOHOLIC ACID AND BASE

Substituent	1 Alcohol and water[a]	2 Alcohol and 0.101 *N* HCl[a]	3 Ratio of column 2 to 1	4 Alcohol and 0.927 *N* HCl[b]	5 Alcohol and 0.989 *N* NaOH[b]
p-CH_3	84.8	84.0	1.0	95.5	46.9
p-CH_3	6.5[d]	65.7[d]	10.1	. .	. . .
m-CH_3	19.6	67.0	3.4	70.1	37.4
None	7.6	33.4	4.4	41.2	37.1
p-F	10.5	49.6	4.7	60.0	46.9
p-Cl	6.2	21.3	3.4	19.8	51.0
p-Br	5.8	19.3	3.3	16.8	48.8
p-I	5.2	17.8	3.4	16.0	53.0
o-Cl	4.4	13.3	3.0	9.1	36.7
o-Br	2.2	5.7	2.6	5.4	23.9
m-F	3.0	4.7	1.5	4.3	29.0
m-Cl	2.6	4.4	1.7	4.1	30.5
m-Br	2.6	4.2	1.6	3.9	33.1
m-I	2.6	4.0	1.5	3.7	36.2
m-NO_2	1.4	1.4	1.0	2.8	61.2
p-NO_2	1.2	1.4	1.2	3.1	100.5[c]

[a] One hundred-twenty hours reflux. [b] Ten hours reflux. [c] Side reaction occurred as evidenced by darkening of solution. [d] Refluxed for only ten hours since reaction proceeded to completion during one hundred and twenty hour reflux.

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(9) Except for *p*-fluorine.

(10) Olivier, *ibid.*, **41**, 301, 646 (1922); **42**, 516, 775 (1923).

(11) Bennett and Jones, *J. Chem. Soc.*, 1815 (1935).

(12) Shoesmith and Slater, *ibid.*, 214 (1926).

(13) Qualitative observations that the hydrolysis of organic fluorides may be promoted by acids have been made previously. See Swarts, *Acad. roy. Belg., classe sci. Mém.*, 414 (1900), and Henne and Midgley, THIS JOURNAL, **58**, 882 (1936).

greater than in the presence of water and the hydrofluoric acid formed by the reaction. This ratio is shown in Table II, column 3. The degree of catalysis is in the same general order as the degree of reactivity, the more reactive compounds being catalyzed to a greater extent than the less reactive compounds.

TABLE III

REACTION OF BENZYL FLUORIDE WITH SODIUM ETHOXIDE AT 76°

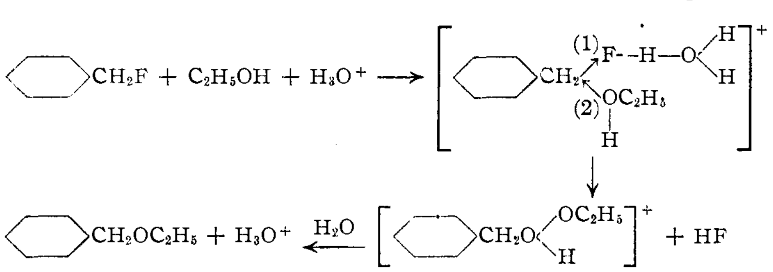
Sample of benzyl fluoride, 2.5145 g. (0.02284 mole); zero concentrations of benzyl fluoride, 0.2212 molar; zero concentration of sodium ethoxide, 0.2139 molar.

Elapsed time, hours	Millimoles of alkali reacted	K	Millimoles of fluoride ion formed	K
..	...	...	...	...
0	0	0	0	0
3.0	0.130	0.097	0.126	0.094
6.0	.242	.096	.249	.099
10.0	.368	.093	.352	.089
20.0	.694	.098	.673	.094

Average value of K determined by acid–base titration: 0.095 mole per liter per hour.

Average value of K determined by fluoride ion titration: 0.094 mole per liter per hour.

The marked acid catalysis of the reaction with aqueous alcohol may be attributed to the formation of a hydrogen bond between the fluorine atom and the hydronium ion. The much smaller ability of the other halogens, as compared with fluorine, to form hydrogen bonds is consistent with the failure of acid to catalyze the reaction of the other benzyl halides with aqueous alcohol. Since the benzyl fluorides appear to react with aqueous alcohol according to an S_N1 mechanism, the solvated proton most probably catalyzes the reaction by forming a hydrogen bond with the fluorine, thereby causing step 1 as shown below to occur more readily since the bond energy of the C–F bond would be decreased.



Since this is the rate controlling step, the speed of the reaction is increased. The use of a more concentrated acid should increase the rate of reaction. A comparison of columns 2 and 4 in Table II shows this to be the case. Finally, the greater the electron density around the fluorine atom, the greater will be its acceptor properties and therefore the more marked the catalysis. This is supported by the experimental observation that the effect of the substituents upon catalysis is in the order $CH_3 > H > X > NO_2$ which is the general order for electron release to the side-chain. In this case, also, the effect of a substituent in the para position is greater than a substituent in the meta position, since the electromeric effects are greater from the para position and the electron release to the side chain under the influence of hydronium ion is therefore greater.

The above discussion of the effects of substituents upon reactivity has been limited essentially to substituents in the para- and meta-positions. The effect of substituents in the *ortho* position is more complicated because of the close proximity of groupings and steric and direct electrostatic effects have been postulated. The ortho substituted benzyl fluorides showed deviations from the order of reactivity predicted on the basis of electron release or electron withdrawal in general similar to those found in the case of the benzyl chlorides.

In addition to determining the relative reactivities of the substituted benzyl fluorides it was desired to compare the reactivity of the benzyl fluorides, as a class, with the reactivity of the benzyl chlorides and bromides. A quantitative comparison was not feasible in most cases, since the benzyl fluorides reacted, in general, much less rapidly than the chlorides. Ingold[14] has observed that benzyl fluoride reacts less rapidly than benzyl chloride with boiling 10% potassium carbonate solution or with boiling alcoholic sodium ethoxide. The rate constant for the reaction of benzyl fluoride with sodium ethoxide in 95% ethyl alcohol (Table I) was found to be 0.095 mole per liter per hour at 76°. Franzen[6] reported the rate constant for the reaction of benzyl chloride with sodium ethoxide in absolute alcohol to be 6.4 moles per liter per day at 30°, corresponding to a value of 0.25 mole per liter per hour at 30° or approximately 50 times as reactive as benzyl fluoride assuming as a basis for comparison that a rise of 10° doubled the reaction rate.

One of the most widely used reactions of determining relative reactivities of halogen compounds is the reaction with sodium or potassium iodide in acetone. The low reactivity of the benzyl fluorides made this reaction not feasible for rate-studies. The reaction of excess *p*-nitrobenzyl fluoride with sodium iodide had proceeded to only 7.3% after one hundred and forty-four hours, and no observable reaction was noted with *p*-chlorobenzyl fluoride under similar conditions. Conant[15] had observed that the reaction of *p*-nitrobenzyl chloride at similar concentrations at 25° had proceeded to 69% in 0.583 hour and that the reaction of *p*-chlorobenzyl chloride at 25° had proceeded to 72.2% in one and one-half hours. Although the rate of reaction

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[14] Ingold and Ingold, *ibid.*, 2249 (1928).

[15] Conant, Kirner and Hussey, THIS JOURNAL, **47**, 488 (1925).

was much lower for the benzyl fluorides, the order for the substituents was the same as for the benzyl chlorides, p-NO_2 > p-Cl.

Also in the reaction with aqueous alcohol, the benzyl fluorides reacted much slower than the benzyl chlorides. After one hundred and twenty hours of reflux in aqueous alcohol, 7.6% of benzyl fluoride had reacted, while Olivier found after two hours of reflux 85% of benzyl chloride had reacted.[10] Similarly, after ten hours of reflux, 6.5% of *p*-xylyl fluoride had reacted while after fourtenth hours 98.3% of *p*-xylyl chloride had reacted.[10] It should be noted that due to the acid catalysis of the reaction of benzyl fluorides with aqueous alcohol, and the failure of acids to catalyze the reaction of benzyl chlorides, it is possible that at sufficiently high acid concentrations a benzyl fluoride, for example, *p*-xylyl fluoride, would react more rapidly than the corresponding *p*-xylyl chloride. However, in all the replacement type reactions actually studied, the benzyl chlorides were considerably more reactive than the corresponding benzyl fluorides.[16] The results obtained were consistent with the low polarizability of the C–F bond.

Experimental Part

Reaction of Benzyl Fluorides with Sodium Ethoxide in Ethyl Alcohol.—A stock solution of sodium ethoxide was prepared by dissolving 10.5 g. of sodium in two liters of 95% ethyl alcohol purified by the method described by Leighton.[17]

A sample of the fluoride, approximately 0.225 mole, was weighed into a 100-cc. volumetric flask and sufficient stock sodium ethoxide solution was added to bring the volume up to 100 cc. A 10-cc. aliquot was pipetted into 25 cc. of 0.1 *N* hydrochloric acid, and the excess acid back-titrated with standard alkali using phenolphthalein indicator to determine the original concentration of sodium ethoxide.

Six 10-cc. aliquots of the reaction mixture were pipetted into clean, dry, Pyrex test-tubes and the tubes closed with cleaned rubber stoppers (thoroughly washed after boiling in sodium hydroxide solution). The tubes were then inserted into a well-stirred paraffin oil-bath, maintained at 76.0 ± 0.1° by refluxing carbon tetrachloride. After forty-five minutes, one of the tubes was removed from the bath, the contents transferred quantitatively to a flask containing 25.0 cc. of 0.1 *N* hydrochloric acid, and the excess acid back-titrated with sodium hydroxide solution. The concentration of sodium ethoxide and the benzyl fluoride were calculated and these values were used as the "zero time" concentrations. At suitable time intervals, usually five points taken over a twenty-four hour period, the other sample tubes were removed and the contents titrated. Rate constants for a second order reaction were then calculated.[18] In the reaction of benzyl fluoride with sodium ethoxide, the extent of reaction was also determined by titration of the fluoride ion present.[19] After the acid–base titration had been carried out, the solution was extracted with petroleum ether, b. p. 30–60°, to remove any unreacted benzyl fluoride. The aqueous solution was then evaporated to 20 cc. and the fluoride ion determined by titration with standard cerous nitrate solution.

Reaction of Benzyl Fluorides with Aqueous Alcohol, Aqueous Alcoholic Hydrochloric Acid and Aqueous Alcoholic Sodium Hydroxide.—A sample of the fluoride, approximately 0.025 mole, was weighed into a 250-cc. volumetric flask and 95% ethanol added to make up the required volume. Fifty cc. aliquots were transferred to 100-cc. round-bottom flasks fitted with ground glass joints; the first contained 25 cc. of distilled water; the second contained 25 cc. of 0.1013 *N* hydrochloric acid; the third contained 25 cc. of 0.927 *N* hydrochloric acid; and the fourth contained 25 cc. of 0.989 *N* sodium hydroxide solution. The flasks were then fitted with reflux condensers and placed in an oil-bath at 130 ± 5°. The solutions began to reflux within ten minutes; the reflux temperature was 81.5 ± 0.2°.

The solution of the benzyl fluoride in aqueous alcohol was refluxed for one hundred and twenty hours, cooled and the hydrofluoric acid formed titrated with 0.1 *N* sodium hydroxide solution to determine the per cent. of reaction.

The solution of the benzyl fluoride, alcohol, and 0.1 *N* hydrochloric acid was refluxed for one hundred and twenty hours, cooled and the acid present titrated with 0.1 *N* sodium hydroxide solution. The amount of hydrofluoric acid formed was calculated and the percentage of reaction determined. For complete reaction about 85% of the theoretical quantity of hydrofluoric acid was found after one hundred and twenty hours of reflux.

The solution of the benzyl fluoride, alcohol and 0.927 *N* hydrochloric acid and the solution of the benzyl fluoride, alcohol and 0.989 *N* sodium hydroxide solution were refluxed for ten hours. The solutions were cooled and the organic fluoride extracted with petroleum ether, b. p. 30–60°. The aqueous solution was analyzed for fluorine ion by titration with cerous nitrate solution to determine the extent of reaction. For complete reaction with acid catalysis about 95% of the theoretical quantity of fluoride ion was found after ten hours of reflux. The results are summarized in Table II.

Reaction of *p*-Nitrobenzyl Fluoride with Sodium Iodide.—A sample of *p*-nitrobenzyl fluoride, 3.1077 g., 0.020 mole, was weighed into a 100-cc. volumetric flask and a solution of 0.5996 g., 0.004 mole, of reagent grade sodium iodide per 100 cc. of reagent grade acetone was added to the required volume. A 50-cc. aliquot of this solution was refluxed for one hundred and forty-four hours and then titrated for fluoride ion, after extraction of the organic fluoride with petroleum ether. The aqueous solution required 6.0 cc. of 0.02442 *N* cerous nitrate solution, indicating 7.3% reaction of the iodide.

Summary

The relative rates of reaction of a series of substituted benzyl fluorides with alcoholic sodium ethoxide, aqueous alcoholic sodium hydroxide and aqueous hydrochloric acid have been determined. In alkaline solution the reaction mechanism and relative effects of substituent groupings were indicated as closely paralleling those found for the other benzyl halides, although the benzyl fluorides exhibited a considerably lower order of reactivity. In acid solution acid-catalyzed replacement of fluorine was found to occur in contrast to the behavior found for the other benzyl halides.

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(16) Benzyl fluoride polymerizes much more rapidly than benzyl chloride in the presence of a suitable condensing agent. Similarly alkyl fluorides with hydrogen on adjacent carbons may eliminate hydrogen halide to form olefins more readily than chlorides. A mechanism involving hydrogen bonding for hydrogen fluoride catalysis of alkyl fluoride reactions is indicated and is supported, for example, by the observation that alkyl fluorides are more soluble in liquid hydrogen fluoride than in hydrocarbons ("Hydrofluoric Acid Alkylation," Phillips Petroleum Company, Bartlesville, Oklahoma, 1946).

(17) Leighton, Crary and Schipp, THIS JOURNAL, **53**, 3017 (1931).

(18) Getman and Daniels, "Outlines of Theoretical Chemistry," 5th ed., John Wiley and Sons, Inc., New York, N. Y., 1931, p. 326.

(19) Batchelder and Meloche, THIS JOURNAL, **53**, 2131 (1931); Hubbard and Henne, *ibid.*, **56**, 1078 (1934); this titration has since been carefully investigated by Nichols and Olson in this laboratory and an improved procedure described: *Ind. Eng. Chem., Anal. Ed.*, **15**, 342 (1943).

A mechanism involving hydrogen bonding with fluorine attached to carbon was proposed to explain acid catalyzed reactions of alkyl fluorides.

The reaction of the benzyl fluorides with sodium iodide in acetone was found to be extremely slow.

ITHACA, N. Y. RECEIVED MAY 10, 1948

[CONTRIBUTION FROM THE UNIVERSITY OF CHICAGO TOXICITY LABORATORY]

The Vapor Pressures of Forty-one Fluorine-containing Organic Compounds[1]

BY C. ERNST REDEMANN,[2] SAUL W. CHAIKIN, RALPH B. FEARING,[3] GEORGE J. ROTARIU, JOSEPH SAVIT AND DRUSILLA VAN HOESEN[4]

A systematic investigation of the toxicity[5] of certain fluorine-containing organic compounds required a knowledge of their volatility in order to assess their maximum potential toxic action. Most of the compounds investigated were not recorded in the literature, and since, for the few that were recorded, no vapor pressure or other data from which the volatility could be computed were found, it was necessary to measure their volatility over the temperature range 0 to 60°. The method employed for these measurements has been described.[6] From our experimentally determined volatilities the vapor pressure has been computed and two-constant logarithmic equations have been used to express both the volatility and vapor pressure of these compounds over the temperature range studied.

Experimental

The apparatus used and details of the measurements have been given in earlier reports.[6] As in previous work, pure dry nitrogen was used as the entrainment gas since its inertness avoided possible side reactions with certain sensitive compounds.

The compounds studied were all prepared in laboratories other than that of the authors. The source of each compound has been indicated in a footnote to Table I. The authors did not verify the identity of the compounds but assumed that the identity had been adequately established by the submitter before sending the sample for study. These compounds had all been purified in the laboratory in which they were prepared, nevertheless, whenever possible, the sample was carefully redistilled just prior to filling the vaporizer unit from all-glass apparatus, rejecting appropriate fractions at the beginning and end of the distillation. In several cases, noted in Table I, the sample submitted was too small to allow any further purification before use. In all cases except that of fluoroethyl nitrite, dry nitrogen was passed through the sample until a constant volatility was attained before actual measurements were recorded. Because of the apparent slow decomposition of fluoroethyl nitrite during vaporization this compound was not able to meet the above criterion.

The boiling points reported in the table are not intended as precision boiling points, for they were not determined by use of special equipment, but rather are the boiling ranges observed during the final distillation through a 10-cm. Vigreux column just prior to filling the saturator. A range of one degree was thought to arise from variations in the rate of distillation and fluctuation in the pressure. Larger ranges in boiling point were considered to indicate lack of complete purity or slight decomposition during distillation. A small amount of silicon tetrafluoride may have been an impurity in certain samples due to the procedure followed in synthesis.

The curve for each substance represents the composite of four to seven experimental points.

Results

In Table I are recorded, in addition to the physical constants of the compound studied, the three constants A, A' and B for the two equations

$$\log p = A - B/T \qquad (1)$$

$$\log WT = A' - B/T \qquad (2)$$

The constants were computed by the method of least squares from the mean experimental points at each temperature studied. These constants apply when pressure is expressed in millimeters of mercury, the temperature, T, is the absolute temperature and the volatility, W, is expressed in milligrams of agent per liter of nitrogen (or air). From these equations vapor pressure, volatility, mean molar heat of vaporization, etc., may be calculated.

Discussion

The mean values from which the constants A, A' and B were calculated have not been corrected for the increase in vapor pressure which results from the liquid phase evaporating into an inert gas rather than into its own vapor.[7] Since the desired quantity at the time the measurements were made was the volatility in air or nitrogen no additional measurements were made by which the thermodynamic vapor pressure could be computed. However, since the systemic errors of the transpiration method tend to give values which are too small and the use of an inert gas tends to give values too large, the two sources of error should partially compensate, making the over-all error of reasonable size.

In Table I are summarized data concerning the precision of the measurements. The mean deviation of the *experimental* points (not included in the table) from the smoothed curve is less than 2% for all but five compounds. Two of these five compounds have large mean deviations, dicyclohexyl

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(1) This work was carried out under contract with the National Defense Research Committee of the Office of Scientific Research and Development.

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(5) Most of the compounds mentioned in this report are sufficiently toxic that one should observe care in working with them in the laboratory.

(6) (a) Bent and Francel, THIS JOURNAL, **70**, 634 (1948); (b) Redemann, Chaikin and Fearing, *ibid.*, **70**, 631 (1948).

(7) Gerry and Gillespie, *Phys. Rev.*, **40**, 269 (1932).