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

$$\log p = A - B/T \tag{1}$$

$$\log WT = A' - B/T \tag{2}$$

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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[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).

fluorophosphate 7.2% and fluoroethyl nitrite 10–12%. These two compounds are, however, included for the sake of completeness. The remaining three are bis-(dimethylamido)-fluorophosphate, ethyl fluoroacetate and tris-(2-fluoroethyl)-orthoformate. The points calculated from the constants, A and B, evaluated by the least squares method, for diisopropyl fluorophosphate have a

TABLE I

CONSTANTS FOR SUBSTANCES STUDIED AND PRECISION OF DATA

Substance	Boiling point, °C.	Mm.	Refractive index, n_D	Density g./ml.	°C.	Vapor pressure Constants of equation A	A'	B	Deviation,[v] % Max.	Min.
Fluorophosphates										
Dimethyl[a]	43.5	14	1.3540[c,o]	1.280	25	8.425	11.738	2319.5	1.1	0.59
Ethyl methyl[e]	53–54	11	1.3643[p]	1.2033	20	9.4617	12.8194	2705.7	0.21	0.18
Diethyl[b]	170–171	760	1.3729[c,q]	1.15[d,b]		8.832	12.231	2595	2.7	2.5
2-Chloroethyl ethyl[a]	75	2	1.4048[r]	1.3383	21	9.396	12.882	3119	3.6	2.3
Diisopropyl[a]	66	9		1.0550	27	8.872	12.343	2671	8.2	5.3
Di-*s*-butyl[e]	77	6.5	1.3972[s]	1.0352	20	9.6509	13.1828	3127.1	0.62	0.36
Dicyclohexyl[e,f]	120	0.4	1.4552[p]	1.1315	20	10.7469	14.3737	4182	0.81	0.62
bis-(Dimethylamido)[g]	65	3	1.4141[t]	1.1127	25	8.4200	11.8130	2642.3	0.56	0.33
Fluoroacetates										
Methyl[h]	103–103.5[i]	752		1.0593[j]	23	8.7860	12.0249	2229.4	0.42	0.28
Ethyl[h]	114–118[k]	750	1.3759[p]	1.0826	25	8.4203	11.6510	2188.9	0.35	0.26
2-Chloroethyl[h]	86	23		1.3160	25	9.550	12.903	2945	2.5	1.5
2-Fluoroethyl[h]	85	48				9.713	13.012	2876	1.1	1.0
Allyl[h]	64.5–65	50	1.4063[p]	1.0961	20	9.2237	12.5012	2554.3	0.72	0.58
Isopropyl[h]	121–123	752	1.3804[p]	1.033	20	8.750	12.035	2316	2.5	1.8
γ-Fluorobutyrates										
Methyl[h]	78.5	100	1.3887[p]	1.0662	20	9.0765	12.3611	2471.7	0.76	0.65
2-Chloroethyl[h]	79–80	5.5	1.4283[p]	1.2007	20	9.6882	13.1201	3152.8	0.24	0.19
2-Fluoroethyl[h]			1.3948[p]	1.148	20	9.286	12.673	2861	2.8	2.2
Methyl β-chloro[h]	90–94	40	1.4227[p]	1.2365	20	9.4633	12.8575	2845.4	1.1	0.77
Methyl β-hydroxy[h]	98	19	1.4165[t]	1.2079	25	10.1036	13.4426	3252.1	1.3	0.63
Fluorophosphonates										
Methyl, isopropyl ester[e]	56.5–57	15	1.3790[t]	1.0941	25	9.8990	13.2505	2850.9	0.22	0.21
Ethyl, isopropyl ester[h]	67–68	18	1.3817[t]	1.0552	25	9.4144	12.8073	2763.8	0.33	0.26
Miscellaneous										
2-Fluoroacetonitrile[h]	78	752	1.3224[p]			8.5962	11.5726	1992.8	0.50	0.32
γ-Fluorobutyronitrile[h]	98	100		1.0034	20	8.3504	11.3956	2362.0	0.38	0.26
2-Fluoroethanol[h]	99–100	745	1.3618[u]	1.0913	33	9.060	12.072	2304	2.6	2.0
Epifluorohydrin[h]	83.5–84	753	1.3693[p]	1.0967	20	8.7938	11.8800	2084.6	0.20	0.14
Chloroacetyl fluoride[h]	73–75	743	1.3795[p]	1.3788	20	8.6030	11.7925	1982.5	0.72	0.57
Fluoroacetyl chloride[h]	69–71	750	1.3831[p]	1.3530	20	8.4954	11.6850	1916.6	0.63	0.47
Fluoroacetyl isothiocyanate[h]	76	50	1.5327[p]	1.3527	20	9.0253	12.3064	2576.8	0.29	0.17
2-Fluoroethyl nitrite[h]	58–60[m]	760	1.3589[p]	1.1427	20	8.83	12.00	2000 ± 20	10–12% (estimated)	
1-Chloro-3-fluoropropanol-2[h]	75–76	50	1.4290[p]	1.3014	20	9.7289	12.9853	2801.8	0.54	0.22
2-Fluoroethyl chlorocarbonate[h]	128	750		1.3995	20	9.001	12.309	2435	6.0	3.7
bis-(2-Fluoroethyl) carbonate[h]	71–72	4		1.2939	20	9.912	13.305	3214	1.2	0.69
tris-(2-Fluoroethyl) orthoformate[h]	128	21	1.3946[p]	1.2316	20	8.933	12.444	3118	3.2	2.2
bis-(2-Fluoroethoxy)-methane[h]	75–76	30	1.3809[p]			9.2884	12.6398	2730.6	0.21	0.18
Methyl difluoroacetate[h,l]						9.1298	12.3686	2187.9	0.46	0.33
Methyl fluoroselenolacetate[n]	130–132	742	1.4879[p]	1.573	20	9.0370	12.4326	2420.0	0.37	0.30
2-Fluoroethyl thiolacetate[h]	58–59	30	1.4538[p]	1.1451	20	8.4724	11.7647	2336.2	0.43	0.30

TABLE I (*Concluded*)

Substance	Boiling point, °C.	Mm.	Refractive index, n_D	Density g./ml.	°C.	Vapor pressure Constants of equation A	A'	B	Deviation,[v] % Max.	Min.
bis-(2-Fluoroethyl) sulfate[h]	80–81	2	1.4177[p]	1.3678	25	9.8117	13.2961	3335.6	0.38	0.22
Ethyl fluorosulfonate[b]	112	755				8.0880	11.4004	2010.7	0.32	0.27
ω-Fluoroacetophenone[h]	79–80	3	1.5309[p]	1.1747	25	9.7533	13.0988	3236.4	0.67	0.45
Methyl γ-fluorothiolbutyrate[h]	54	6	1.4587[p]	1.1135	20	9.233	12.572	2735	2.1	1.6

[a] Submitted by Dr. J. C. Bailar. [b] Submitted by Dr. L. F. Audrieth. [c] These values are from Lange and Krueger (*Ber.*, **65**, 1598 (1932)). [d] Lange and Krueger give d^{25}_4 1.136. [e] Submitted by Dr. R. C. Fuson. [f] The accuracy of this determination may not be better than ±20% due to instability of the compound and its very low volatility. [g] Supplied by Dr. Anton B. Burg. The accuracy for this determination is low, probably −10% due to the fact that the compound would occasionally give a smoke which would fail to condense in the weighing trap. [h] Submitted by Dr. M. S. Kharasch. [i] Price and Jackson (THIS JOURNAL, **69**, 1065 (1947)) give the boiling point as 102°, while Ray and Ray (*J. Indian Chem. Soc.*, **13**, 427 (1936)) give 104°. [j] Swarts (*Bull. soc. chim.*, [3] **15**, 1134 (1896)) gives the density as 1.16126 (15°). [k] It seems doubtful that this material was pure for it was made by alcohol exchange from methyl fluoroacetate. Equipment was not available for doing a precision fractionation on the small sample submitted. Desreux (*Bull. soc. chim. Belg.*, **44**, 258 (1935)) gives the density as 1.0912 (20°). [l] This sample was too small to purify further before use. [m] This material could not be purified beyond this point due to a constant slow decomposition. [n] Submitted by Dr. C. D. Hurd. [o] 23.8°. [p] 20°. [q] 24.2°. [r] 27°. [s] 22°. [t] 25°. [u] 32°. [v] Per cent. deviation of observed points from points calculated from least squares equation.

large mean deviation of 5.3%, which would indicate that the two-constant equation used does not describe the curve satisfactorily. About one-fourth of the compounds show mean deviations of 1 to 5% between the calculated points and the smoothed curves. This may be attributed to difficulty in measurement, for these compounds appeared to undergo slight decomposition in glass apparatus at the higher temperatures, but not at the lower ones, thus giving a distinct curvature to the smoothed curve. 2-Fluoroethyl nitrite underwent a continuous slow decomposition and hence the precision of the measurements is estimated at 10–12%.

Summary

1. The volatility of forty-one fluorine-containing organic compounds has been measured by the transpiration method.

2. The corresponding vapor pressures have been computed from the volatilities and constants for logarithmic equations for both the volatility and vapor pressure have been calculated.

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[CONTRIBUTION FROM ORGANIC RESEARCH LABORATORY, THE DOW CHEMICAL COMPANY]

Synthesis and Identification of Propylene Glycol Phenyl Ethers

BY A. R. SEXTON AND E. C. BRITTON

The observation of Chitwood[1] and others[2,3,4] that reaction of aliphatic alcohols with propylene oxide in the presence of an alkaline catalyst yields a secondary alcohol almost exclusively, and in the presence of an acid catalyst a mixture of the primary and secondary alcohols, has been confirmed by us. In this Laboratory the structures of the primary and secondary alcohols were determined by dehydrogenation to an aldehyde and ketone, respectively, and further confirmed by infrared absorption spectra which show an absorption band for primary alcohols at 9.3–9.6 μ and an absorption for secondary alcohols at 8.9–9.1 μ (Figs. 1 and 3).

In extending the work to cover reaction of phenols with propylene oxide, the infrared absorption spectra indicated that the reaction product using alkaline catalyst was a primary alcohol, which, compared with the similar reaction using aliphatic alcohols, was extremely unusual. To clarify this anomaly, the two possible isomers from the reaction of phenol and propylene oxide have been prepared by other methods and their properties determined.

1-Phenoxy-2-propanol was prepared by (A) the reaction of potassium phenoxide with chloroacetone according to Hurd[5] and (B) by the reaction of phenol with propylene oxide using sodium hydroxide as a catalyst. The ether prepared by method (B) was oxidized catalytically in 80% yields to phenoxyacetone with no aldehyde being detected. The products by both methods had absorption curves corresponding to primary alcohols (Fig. 4), and both had identical properties, namely: b. p. 116–117° (10 mm.) 233° (760 mm.); d^{25}_{25} 1.0610; n^{25}_D 1.5200; α-naphthylcarbamate m. p. 83–84°; N-phenylcarbamate m. p. 85–87°.

2-Phenoxy-1-propanol was prepared (C) from α-phenoxypropionaldehyde according to Stoer-

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(1) Chitwood and Freure, THIS JOURNAL, **68**, 680 (1946).

(2) Petrov, *J. Gen. Chem.*, *U. S. S. R.*, **14**, 1038 (1944).

(3) Kadesch, THIS JOURNAL, **68**, 41 (1946).

(4) Bartlett, *ibid.*, **70**, 926 (1948).

(5) Hurd and Perletz, *ibid.*, **68**, 38 (1946).