dl-**Tris-2,2′-dipyridyl Osmium(III) Chloride Monohydrate.**—The corresponding osmium(II) complex chloride (0.5 g.) in water (10 ml.) at 4° was treated with chlorine gas until the color changed to red. After filtering through a sintered glass filter, the solution was evaporated to dryness over phosphorus pentoxide in the presence of a little chlorine. The dark red needles of the compound had a green reflex, and were very hygroscopic. On analysis the substance was found to contain adsorbed chlorine, and was purified by solution in methanol and precipitation with acetone. After removal of traces of these solvents in vacuum over phosphorus pentoxide the substance was obtained as green micro needles.

Anal. Calcd. for $Os(C_{10}H_8N_2)_3Cl_3 \cdot H_2O$: Os, 24.29; Cl, 13.58. Found: Os, 24.13; Cl, 13.6.

dl-**Tris-2,2′-dipyridyl Osmium(III) Nitrate Hexahydrate.**—A saturated solution of tris-2,2′-dipyridyl osmium(II) nitrate in water, was oxidized anodically, using a stout platinum spiral as anode, at 6 volts with 0.2 amp. A sintered glass crucible served as the anode compartment and was suspended in a beaker of dilute acid as the cathode chamber and electrolyte. When the oxidation was complete, the red solution was allowed to evaporate in vacuum over solid sodium hydroxide. The red microcrystalline powder was extremely deliquescent and very soluble in methyl alcohol. Solutions in the methanol rapidly became brown and finally green.

Anal. Calcd. for $Os(C_{10}H_8N_2)_3(NO_3)_3 \cdot 6H_2O$: Os, 19.96; N, 13.23. Found: Os, 19.92; N, 13.3.

d-**Tris-2,2′-dipyridyl Osmium(III) Perchlorate Monohydrate.**—Dextro-tris-2,2′-dipyridyl osmium(II) iodide (0.5 g. in 35 ml. of hot water) was transformed to the chloride with silver chloride, oxidized with chlorine at 4° and treated as the *d,l*-perchlorate above, with sodium perchlorate. The mulberry-red prismatic needles of the active perchlorate were more soluble in water than the *d,l*-perchlorate. A 0.02% solution in water gave $\alpha = +0.05°$ (mean value) whence $[\alpha]^{20}_{5461} = +250°$ and $[M]^{20}_{5461} = +2500°$. The substance had no detectable rotation in the NaD line.

Anal. Calcd. for $Os(C_{10}H_8N_2)_3(ClO_4)_3 \cdot H_2O$: Os, 19.51; N, 8.62. Found: Os, 19.6; N, 8.67.

l-**Tris-2,2′-dipyridyl Osmium(III) Perchlorate Monohydrate.**—This was prepared by the same methods as the dextro compound using instead levo tris-2,2′-dipyridyl osmium(II) iodide. The substance crystallized in mulberry-red prismatic needles. A 0.02% solution in water gave $\alpha = -0.05°$ whence $[\alpha]^{20}_{5461} = -250°$ and $[M]^{20}_{5461} = -2500°$.

Anal. Calcd. for $Os(C_{10}H_8N_2)_3(ClO_4)_3 \cdot H_2O$: Os, 19.51; N, 8.62. Found: Os, 19.4; N, 8.62.

SYDNEY, N. S. W., AUSTRALIA RECEIVED OCTOBER 14, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Ionization Constants of Fluorinated Acids

BY ALBERT L. HENNE AND CHARLES J. FOX

Perfluorinated acetic and butyric acids are strong electrolytes. $CF_3CH_2CO_2H$ and $CF_3(CH_2)_2CO_2H$ are weak electrolytes with ionization coefficients of 1×10^{-3} and 7×10^{-5}, respectively; their unfluorinated analogs have coefficients of only 1.3×10^{-5} and 1.5×10^{-5}, respectively. The shielding effect of one methylene group between the fluorinated cluster and the acid function is considerable, but even two methylene groups do not achieve complete shielding; this emphasizes the magnitude of the electronegative induction exerted by CF_3 groups.

The ionization constants of substituted acetic acids have been used to evaluate the electronegative induction of various elements; for instance, CH_3CO_2H, CH_2FCO_2H, CHF_2CO_2H and CF_3CO_2H have values of 1.8×10^{-5}, 2.2×10^{-3}, 5.7×10^{-2} and 0.5, respectively, and the last of these acids acts as a strong electrolyte.[1] Measurements are now presented on compounds in which a CF_3 group is located at increasing distances from the acid function in order to evaluate as quantitatively as possible the loss of inductive effect in relation to distance. Two experimental procedures have been used, namely: (1) determination of the limiting equivalent conductance and (2) determination of the *p*H curve during neutralization. From these experimental measurements, values have been computed for the ionization constants which were found consistent and are listed in Table I.

A direct comparison between strong and weak electrolytes would not be valid, but the weak electrolytes can be contrasted with their unfluorinated analogs. At 25°, propionic and butyric acids have $K_{25} = 1.343 \times 10^{-5}$ and 1.506×10^{-5}, respectively,[2] coefficients which are about $^1/_{70}$th and $^1/_5$th as small as those of $CF_3CH_2CO_2H$ and $CF_3CH_2CO_2H$. The degrees of dissociation α of 0.1 *N* aqueous solutions are: $C_3F_7CO_2H$, 0.878; CF_3CO_2H, 0.877; $CF_3CH_2CO_2H$, 0.0926; $CF_3CH_2CH_2CO_2H$, 0.0263; $C_2H_5CO_2H$, 0.0116 and $C_3H_7CO_2H$, 0.0123; these figures are not absolute constants, but they do give a clear picture of relative acidities.

The above results show how great the electronegative induction of a CF_3 group is, and it is quite consistent to find that it takes two methylene groups to cause an amount of shielding equal to that which a single methylene group causes on less effective groups, as shown by the ionization constants of the monochlorinated butyric acids[3]: $CH_3CH_2CHClCO_2H$, 1.4×10^{-3}; $CH_3CHClCH_2CO_2H$, 8.8×10^{-5} and $C_3H_7CO_2H$, 1.5×10^{-5}.

Experimental

Samples.—Redistilled CF_3CO_2H, b.p. 70.8° (739 mm.), f.p. −15.22° and $C_3F_7CO_2H$, f.p. −19.95° were used. $CF_3CH_2CO_2H$ was taken from a cut b.p. 144.8° (746 mm.), f.p. about 7°; after redistillation with immediate freezing of the distillate, a good sample had: f.p. 9.7°; b.p. 144.8° (746 mm.); $d^{27}{}_4$ 1.441; $n^{27}{}_D$ 1.3316; *MR* (obsd.) 18.20 from which AR_F was computed as 1.31, a value agreeing with 1.33 for CF_3CO_2H. $CF_3CH_2CH_2CO_2H$ was similarly purified: f.p. 32.3°; b.p. 78.0° (18 mm.). Previously reported values[4] are: CF_3CO_2H, f.p. −15.55° (a), −15.5° (b); $C_3F_7CO_2H$, f.p. −17° (b); $CF_3CH_2CO_2H$ f.p. + 12°, b.p. 146° (c); $CF_3CH_2CH_2CO_2H$, f.p. 33.2°, b.p. 166.6° (d).

Electrical Equipment.—The Wheatstone bridge consisted of a Leeds and Northrup Student Potentiometer No. 7651,

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(1) F. Swarts, *Bull. Acad. Roy. Belg.*, 681 (1896), 624 (1903), and 353 (1922).

(2) D. Belcher, THIS JOURNAL, **60**, 2744 (1938).

(3) A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 15.

(4) (a) F. Swarts, ref. 1 (1922); (b) Minnesota Mining and Manufacturing Co.; (c) undescribed sample in documents from I. G. Farben Industrie; (d) E. T. McBee and A. Truchan, THIS JOURNAL, **70**, 2910 (1948).

TABLE I

IONIZATION CONSTANTS

	From limiting conductance		From *p*H	d log·*K*	Δ*H*, kcal.
$C_3F_7CO_2H$	K_{25} 0.678	K_{26} 0.625	Strong	−0.0355	−1.49
CF_3CO_2H	0.588	0.533	electrolytes	− .0439	−1.81
$CF_3CH_2CO_2H$	9.52×10^{-4}	8.65×10^{-4}	1.2×10^{-3}	− .0410	−1.72
$CF_3(CH_2)_2CO_2H$	6.98×10^{-5}	6.80×10^{-5}	1.0×10^{-4}	− .0114	−0.48

a standard 1000 ohm or a 10,000 ohm variable resistance box, earphones, a conductivity cell, and a Hewlett–Packard model 200B audio oscillator wired in the conventional manner.[5] A Frees type conductivity cell was used. The "dipping electrodes" were spaced by glass rods and were "platinized" by the standarized procedure.

Conductivity Water.—The resistance averaged *ca.* 200,000 ohms, and no correction was used for its contribution to the conductance of the solution.

Temperature Control.—A mercury expansion regulator activating a Thyratron "on and off" device[6] was used to regulate the thermostat at 25.0 ± 0.05° and 35.0 ± 0.05°.

Cell Constant.—A standard 0.100 molal solution of potassium chloride (Mallinckrodt, reagent grade) with a specific conductance (k) of 0.0128560 ohm at 25° was prepared.[7] The resistance (R) of this solution was measured and the cell constant was calculated from the formula[7]: k = cell constant/R. The cell constant was determined whenever the electrodes were replatinized and frequently checked. It was desired to make measurements on the acid solutions at 35° as well as at 25°; however, the specific conductance of 0.100 molal potassium chloride at 35° was not known. The specific conductance of the KCl solution at 35° was determined using the cell constant calculated for 25° and an increase in specific conductance of 2.05% per degree was observed. Since the temperature coefficient of conductance is about 2% per degree for most ions,[8] an average cell value of 0,403 ± 0.004 was adopted for this temperature range.

Conductance of CF_3CO_2H **and** $C_3F_7CO_2H$.—The dilutions (V), the square root of the concentration ($C^{1/2}$), the resistances (R), the equivalent conductances (Λ), and the degrees of dissociation (α) for the solutions at 25 and 35° are included in Table II. Since both are strong electrolytes, the limiting conductances Λ_0 were extrapolated from a graph of Λ *versus* $C^{1/2}$, as 390 for CF_3CO_2H and 384 for $C_3F_7CO_2H$ at 25°, 448 and 438 at 35°; and the degrees of dissociation: $\alpha = \Lambda/\Lambda_0$ in Table II were computed from these values. The slope for CF_3CO_2H at 25° was read as 154, which agrees with a value of 149 computed from the Onsager equation $\Lambda_0 = \Lambda + (A + B\Lambda_0)\sqrt{C}$, for strong electrolytes in aqueous solutions, where A is 60.2 and B is 0.229. The ionization constant (Table I) was computed as $K = C\alpha^2/(1 - \alpha)$ and is by modern concepts, only an approximation. For $C_3F_7CO_2H$ at 25°, the observed slope, 143, agrees with the Onsager value, 145.7.

TABLE II

STRONG ELECTROLYTES

V	$C^{1/2}$	$R_{25°}$	$\Lambda_{25°}$	$\alpha_{25°}$	$R_{35°}$	$\Lambda_{35°}$	$\alpha_{35°}$
			CF_3CO_2H				
10.3	0.312	12.2	342	0.877	10.8	387	0.864
20.5	.221	23.5	356	.914	20.5	406	.906
41.0	.156	45.5	366	.938	39.8	418	.933
100	.0784	110	378	.969	96.5	432	.964
206	.0698	220	380	.974	192	434	.969
1000	.0312	1083	385	.987	984	439	.980
			$C_3F_7CO_2H$				
9.32	0.328	11.3	337	0.878	9.88	381	0.870
18.6	.232	21.6	351	.914	19.1	397	.906
37.3	.164	42.1	361	.940	36.9	411	.938
93.2	.104	103	370	.964	90.8	418	.954
186	.0732	205	369	...	179	423	.966
373	.0518	404	375	.977	361	421	...
932	.0328	1004	378	.985	875	433	.989

TABLE III

WEAK ELECTROLYTES AND NA SALTS

V	$C^{1/2}$	$R_{25°}$	$\Lambda_{25°}$	$R_{35°}$	$\Lambda_{35°}$
		$CF_3CH_2CO_2H$			
9.91	0.317	111	35.9	102	39.4
19.8	.225	160	50.1	146	55.0
39.6	.159	233	68.6	213	74.7
49.5	.142	264	75.7	240	83.6
99.1	.100	394	102	356	113
198	.0710	609	132	550	146
496	.0449	1070	182	982	204
991	.0317	1784	224	1603	250
1980	.0225	3072	261	2836	282
		$CF_3CH_2CO_2Na$			
19.9	0.224	118	68.3	96.0	84.0
39.8	.158	215	75.0	176	91.7
79.6	.112	410	78.5	339	94.9
199	.0708	985	81.6	808	99.6
398	.0501	1930	83.4	1580	102
796	.0354	3780	85.1	3130	103
1990	.0224	9150	88.0	7300	110
		$CF_3CH_2CH_2CO_2H$			
10.0	0.316	407	10.0	360	11.3
20.0	.223	587	13.9	586	15.7
40.1	.158	833	19.6	725	22.5
80.2	.112	1180	27.7	1047	31.2
100	.0998	1320	30.9	1149	35.5
201	.0706	1936	42.2	1699	48.0
401	.0499	2803	58.2	2475	65.9
802	.0553	4266	76.5	3733	87.7
1604	.0252	6416	101.7	5659	115.5
		$CF_3CH_2CH_2CO_2Na$			
17.8	0.237	106	67.7	86.7	83.0
35.6	.168	209	68.8	171	84.3
71.2	.119	394	73.2	323	88.9
178	.0749	952	75.5	769	93.5
356	.0530	1865	77.2	1515	95.0
712	.0375	3670	78.4	2960	97.1
1780	.0237	8830	81.5	7170	100.3

Conductance of $CF_3CH_2CO_2H$ and $CF_3CH_2CH_2CO_2H$.—Since both are weak electrolytes, the graph Λ *versus* $C^{1/2}$ is curved and does not permit extrapolation to the limiting conductance Λ_0; the latter is however obtainable from measurements on the sodium salts, related by the equation: Λ_0 (acid) = Λ_0 (salt) + $\lambda_0(H^+)$ − $\lambda_0(Na^+)$. $CF_3CH_2CO_2Na$ was prepared by exact neutralization with methyl red as indicator, and $CF_3CH_2CH_2CO_2Na$ was obtained in the presence of brom thymol blue. Experimental results are in Table III. For CF_3CO_2Na, extrapolation of the Λ *versus* $C^{1/2}$ lines gives limiting conductances, Λ_0, of 88.5 at 25° and 107 at 35°. Since the limiting conductance of the sodium ion is 50.11 at 25° and 60.56 at 35° and that of the hydrogen ion is 349.82 at 25° and 399.5 at 35°,[9] Λ_0 for $CF_3CH_2CO_2H$ is computed as 388 at 25° and 446 at 35°. A similar procedure gives Λ_0 for $CF_3CH_2CH_2CO_2Na$ as 81.5 at

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(5) Direction Book, Std. 10962, Leeds and Northrup Co., Philadelphia, p. 9.

(6) D. F. Swinehart, *Anal. Chem.*, **21**, 1577 (1949).

(7) T. Shedlovsky, in Weissberger's "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1946, Vol. II, pp. 1024–1025.

(8) *Ibid.*, p. 1032.

(9) Ref. 8, page 1047.

25° and 100 at 35°, from which the values for $CF_3CH_2CH_2CO_2H$ are computed as 381 at 25° and 439 at 35°. From these figures, the values in Table IV were computed.

TABLE IV

WEAK ACIDS

V	$\alpha_{25°}$	$K_{25°}$	$\alpha_{35°}$	$K_{35°}$
		$CF_3CH_2CO_2H$		
9.91	0.0926	9.54×10^{-4}	0.0884	8.64×10^{-4}
19.8	.129	9.64×10^{-4}	.123	8.75×10^{-4}
39.6	.177	9.56×10^{-4}	.168	8.50×10^{-4}
49.6	.195	9.53×10^{-4}	.187	8.72×10^{-4}
99.1	.262	9.35×10^{-4}	.253	8.66×10^{-4}
Average selected: $K_{25} = 9.52 \times 10^{-4}$ and $K_{35} = 8.65 \times 10^{-4}$				
		$CF_3CH_2CH_2CO_2H$		
10.0	0.0263	6.93×10^{-5}	0.0257	6.78×10^{-5}
20.0	.0366	6.91×10^{-5}	.3058	6.61×10^{-5}
40.1	.0515	6.95×10^{-5}	.0513	6.89×10^{-5}
80.2	.0727	7.10×10^{-5}	.0711	6.78×10^{-5}
100	.0811	7.14×10^{-5}	.0808	7.08×10^{-5}
201	.1108	6.88×10^{-5}	.8907	6.69×10^{-5}
Average selected: $K_{25} = 6.98 \times 10^{-5}$ and $K_{35} = 6.80 \times 10^{-5}$				

Equivalent Points.—Using a MacBeth *p*H meter, curves were obtained for *p*H *versus* ml. of 0.1 N sodium hydroxide added, and they were used for the selection of the indicators in the preparation of the salts needed for conductance measurements. At the half-neutralization point the *p*H of $CF_3CH_2CO_2H$ and $CF_3CH_2CH_2CO_2H$ solutions were read as 2.90 and 3.95, which correspond to K values of 1.2×10^{-3} and 1.0×10^{-4}, respectively, on the basis of $pH = pK$; this equality should however be restricted to the range of *p*H between 4 and 10,[10] yet when k values were computed from other points of the *p*H curves, practically the same values were obtained for K.

Heat of Dissociation.—The conductances of the acids were measured at 35° as well as 25° in order to obtain values for the heats of dissociation or heats of activation of the acids in solution. By means of a form of the Arrhenius equation,[11] $d \ln K/dT = \Delta H/RT^2$ the values for $-\Delta H$ listed in Table I were calculated from the ionization constants of the acids. The values of K for CF_3CO_2H and $CF_3CF_2CF_2CO_2H$ were calculated from the conductance ratio for a 0.1 N solution, and since they are not representative of true ionization constants, a direct comparison with the weak acids is impossible. Although the ΔH value for CF_3CO_2H is more negative than for $CF_3CF_2CF_2CO_2H$, indicating a greater tendency for CF_3CO_2H to dissociate in solution, the magnitudes are approximately the same. This serves to substantiate the claim, based on the conductance ratio, that the acidity of CF_3CO_2H is approximately the same as that of $CF_3CF_2CF_2CO_2H$. A direct comparison of the ΔH values calculated for $CF_3CH_2CO_2H$ and $CF_3CH_2CH_2CO_2H$ should be valid. The more negative value for the stronger acid, $CF_3CH_2CO_2H$, indicates a greater tendency for the acid to dissociate and this is in accord with what is expected.

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[10] Bennet, Brooks and Glasstone, *J. Chem. Soc.*, **57**, 1821 (1935).

[11] F. Daniels, "Outlines of Physical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 375.

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[CONTRIBUTION FROM THE UNIVERSITY OF WASHINGTON]

Ultraviolet Absorption Spectra of Chromatographic Fractions of Lignins

BY A. BAILEY

Chromatographic fractions of two softwood lignins have been examined with the aid of ultraviolet absorption spectroscopy.

The recent separation of lignin preparations into chromatographically heterogeneous fractions[1] posed the problem of ascertaining the validity of fluorescence phenomena as evidence of chemical difference and of establishing whether chemical differences actually existed in the fractions.

Curves of the ultraviolet absorption of lignin preparations and related compounds have been presented and their significance discussed by Aulin-Erdtman,[2] Glading,[3] Jones[4] and Patterson and Hibbert.[5] Patterson and Hibbert[6] employed ultraviolet absorption to determine the effects of the solvent precipitation of lignin.

Butanol lignins from different genera, fir and spruce, selected because of close similarity in fluorescence behavior,[1] were separated into four zones by adsorption on cellulose sheets. The zones were cut apart, each extracted separately by the capillary action of dioxane, and the ultraviolet absorption of the dioxane solutions of the lignin components was measured.

The ultraviolet absorptions of these materials are shown in Figs. 1 and 2. The primary purpose of this study was to investigate identity or non-identity. The non-identity was so distinctive that any of the ten materials examined could be easily identified by its absorption curve alone. In view of the fact that the complete curve is an unique property of a particular compound, the conclusion that the lignins studied contained components of different chemical species appears to rest on a solid foundation.

The curves of the fractions of fir lignin had absorption maxima at 280 mμ and in the 220–240 mμ region, although the curves varied somewhat in shape and the corresponding values of specific extinction varied several-fold. The curves suggest that similar chromophoric groupings are responsible for these maxima and that perhaps the fractions stand in near chemical relationship. These curves, of course, reflect principally the effect of those structures capable of resonance between several configurations and are not an accurate index of the minor and other architecture of the molecule which do not give rise to strong chromophoric effects.

The curves of the fractions of spruce lignin showed inflection points but no true absorption maxima at 280 mμ with the exception of Zone I. Curiously, the parent lignin material showed two definite maxima at 281 and 277 mμ. The difference in the absorption curves of the individual zones of spruce was generally comparable to that existing in the absorption curves of fir lignin. The

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[1] A. Bailey, *Paper Ind. and Paper World*, **32**, 395 (1950).

[2] G. Aulin-Erdtman, *Tappi*, **32**, 160 (1949).

[3] R. E. Glading, *Pap. Trade J.*, **111**, TS 288 (1940).

[4] E. J. Jones, Jr., *Tappi*, **32**, 311 (1949).

[5] R. F. Patterson and H. Hibbert, THIS JOURNAL, **65**, 1862 (1943).

[6] R. F. Patterson and H. Hibbert, *ibid.*, **65**, 1869 (1943).