deviation is ±0.7 kcal. The estimated maximum error is ±1.3 kcal.

We wish to thank Professor G. B. Kistiakowsky for the loan of his equipment and for helpful advice, Mr. Irving Osvar for preparation of the ferrocene used in this experiment and Professor R. B. Woodward and Dr. R. M. Diamond for stimulating discussions.

MALLINCKRODT LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

Identification of Phenols by Paper Partition Chromatography[1]

BY WEN-HUA CHANG, RALPH L. HOSSFELD AND WM. M. SANDSTROM

RECEIVED MAY 19, 1952

A possible method of overcoming many of the difficulties often encountered in the paper partition chromatography of simple phenols was suggested in a recent paper[2] in which it was shown that if a mixture of phenols was allowed to couple with diazotized sulfanilic acid, the resulting mixture of phenylazobenzenesulfonic acid dyes could be satisfactorily chromatographed. The present paper describes a further study of the application of the above method to several series of isomeric and homologous phenols as well as other individual phenols. The compounds studied are listed in Table I in the order of their increasing migration coefficients.

Two-dimensional development as reproduced in Fig. 1 illustrates a satisfactory separation of *o*-cresol from *m*-cresol, and of *p*-methylguaiacol, 2,5-dimethylphenol and 2,4-dichlorophenol, although the migration coefficients of Table I would not indicate such to be possible.

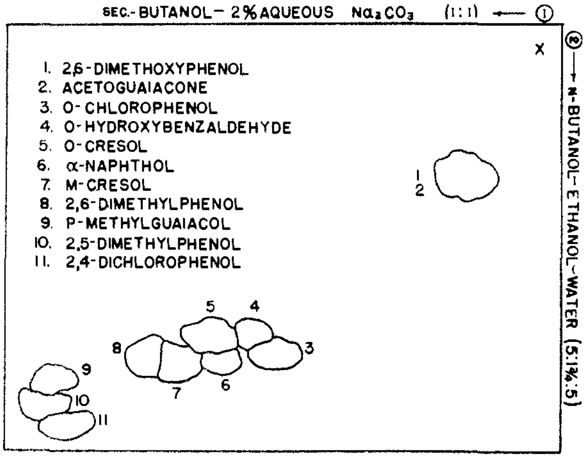

Fig. 1.—Two-dimensional chromatogram developed 40 hr. in each direction.

TABLE I

PHENOLS ARRANGED IN ORDER OF INCREASING MOBILITY OF THE PHENYLAZOBENZENESULFONIC ACID DYE[a]

	Color	Migration coefficient
Acetoguaiacone	Orange	0.11
2,6-Dimethoxyphenol	Pink	.12
Guaiacol	Orange	.19
Phenol	Yellow	.30
o-Chlorophenol	Yellow	.37
o-Hydroxybenzaldehyde	Yellow	.39
α-Naphthol	Pink	.43
o-Cresol	Yellow	.43
m-Cresol	Yellow	.43
2,6-Dimethylphenol[b]	Orange	.48
2,4-Dichlorophenol	Pink	.63
p-Methylguaiacol	Pink	.64
2,5-Dimethylphenol	Yellow	.66
o-Ethylphenol[b]	Yellow	.75
m-Ethylphenol[c]	Yellow	.76
p-Ethylguaiacol	Pink	.80
Eugenol	Pink	.81
3,5-Dimethylphenol	Yellow	.83
o-Phenylphenol	Yellow	.84
m-Phenylphenol	Yellow	.85
p-Phenylphenol	Pink	.86
p-Cresol	Pink	.89
2,3,5-Trimethylphenol[d]	Orange	.90
Dihydroeugenol	Pink	.93
3,4-Dimethylphenol	Pink	.94
β-Naphthol	Orange	.95
p-Ethylphenol[b]	Pink	.95
Thymol	Orange	.96
4-(α-Methylbenzyl)-2-phenylphenol[e]	Pink	.98
2,4-Dimethylphenol	Pink	.99
p-(α-Cumyl)-phenol[e]	Orange	1.00

[a] Prepared from two contiguous chromatograms irrigated 40 hr. with *s*-butanol-2% aqueous Na_2CO_3 (1:1 – v./v.). [b] Courtesy of Dr. J. J. McGovern, Mellon Institute. [c] Courtesy of Reilly Tar and Chemical Corp. [d] Courtesy of Shell Chemical Co. [e] Courtesy of Dow Chemical Co.

As a result of this study certain limitations of the method become apparent. Those phenols which have a carbonyl function such as an aldehyde group para to the phenolic hydroxyl *may* react through replacement of the group by the entering azo group, thus destroying the identity of the original compound. Catechols because of their sensitivity to oxidation under alkaline conditions were not successfully chromatographed under the conditions thus far studied, in spite of attempts to prevent oxidation by replacement of the air in the chamber with an inert medium such as nitrogen. The presence of catechol interfered with the normal development of chromatograms of phenolic mixtures.

Experimental

The preparation of the dyes and the development of the chromatograms was carried out as previously described[1] with the exception that *s*-butyl alcohol which had been equilibrated with an excess of 2% aqueous sodium carbonate was used throughout on the one dimensional chromatograms. This solvent, although requiring up to 40 hours for full development, greatly decreased trailing and diffusion of spots. The presence of sodium carbonate in the equilibrated solvent helped prevent the formation of a second front which previously had often appeared as a result of temperature fluctuations in the developing chamber.[3]

Acknowledgment.—One of us (R.L.H.) wishes to express appreciation of a Grant-in-aid of Research

---

(1) University of Minnesota Agricultural Experiment Station Scientific Journal Series Paper No. 2824. Abstracted in part from a thesis by Wen-Hua Chang presented to the Graduate Faculty of the University of Minnesota as partial fulfillment of requirements for the M.S. degree, June, 1951.

(2) R. L. Hossfeld, THIS JOURNAL, **73**, 852 (1951).

(3) E. L. Smith, *Nature*, **169**, 60 (1952).

by the Graduate School of the University of Minnesota which made possible part of the work reported herein.

SCHOOL OF FORESTRY
DIVISION OF AGRICULTURAL BIOCHEMISTRY
UNIVERSITY OF MINNESOTA
ST. PAUL, MINNESOTA

Arrhenius Parameters for Acid Hydrolysis of γ-Butyrolactone; Search for a Reaction with Water

BY FRANCES DUNKLE COFFIN[1] AND F. A. LONG

RECEIVED JUNE 24, 1952

Detailed kinetic and equilibrium studies of the acid-catalyzed hydrolysis of γ-butyrolactone have been reported at only one temperature, 25°.[2] In connection with a broader study of this reaction[3] we have investigated rates and equilibria in dilute acid solutions at three temperatures, and from these data have calculated the heat of reaction and energies of activation. A search for an uncatalyzed hydrolysis of this lactone was also made. Evidence for such a reaction of the γ-lactones is inconclusive[2–4] although it occurs readily with β-lactones.[5]

The rates and equilibrium were determined by titration of the hydroxy acid formed. Hydrochloric acid was the only catalyst used since earlier studies[2] showed the rate to be independent of the particular strong acid employed. Temperatures were constant to ±0.005°.

Since the hydrolysis reaction is reversible, the first-order rate constant for the forward reaction is given by

$$k_{\mathrm{h}}' = \frac{1}{(1+K)t}\ln\frac{1}{1-(1+K)C_{\mathrm{HA}}/C_{\mathrm{L_0}}}$$

where $C_{\mathrm{L_0}}$ is initial lactone concentration, C_{HA} is concentration of hydroxy acid formed and K is the concentration equilibrium constant, *i.e.*, $K = k_{\mathrm{l}}'/k_{\mathrm{h}}' = C_{\mathrm{L(eq)}}/C_{\mathrm{HA(eq)}}$. From the values of K and k_{h}', the rate constant, k_{l}', for the reverse reaction may be determined; the second-order rate constants k_{h} and k_{l} for the forward and reverse reactions with hydrogen ion may be calculated from the relations $k_{\mathrm{h}}' = k_{\mathrm{h}}/C_{\mathrm{H^+}}$ and $k_{\mathrm{l}} = k_{\mathrm{l}}'/C_{\mathrm{H^+}}$.

Table I gives detailed data on k_{h}', k_{h} and K at 39°, and the average values of K and k_{h} at 25 and 50°. The agreement between the present results at 25° and those of earlier workers[2] is excellent. From the equilibrium constants of Table I, ΔH for the hydrolysis reaction is calculated to be −710 calories.

The observed constancy of k_{h} at each temperature indicates that the reaction is accurately first-order in the concentration of hydrogen ion. On the basis of studies with added electrolytes,[3] a salt effect might be expected for both rates and equilibria, but the electrolyte concentrations are so low in the present experiments that the effect is negligibly small.

TABLE I

ACID HYDROLYSIS OF γ-BUTYROLACTONE

t, °C.	$C_{\mathrm{L_0}}$, mole/l.	$C_{\mathrm{H^+}}$, mole/l.	K	$10^4 k_{\mathrm{h}}'$, min.$^{-1}$	$10^2 k_{\mathrm{h}}$, l. mole^{-1} min.$^{-1}$
39.00					
	0.1023	0.01008	2.74	4.90	4.86
	.1025	.01008	2.78	4.88	4.84
	.0934	.0427	2.72	19.29	4.79
	.0835	.04025	2.87	18.15	4.51
	.3148	.06037	2.77	29.52	4.89
	.3618	.06040	2.79	28.87	4.78
	.0982	.08083	2.87	36.86	4.56
	.0999	.09090	2.88	40.81	4.49
		Av.	2.80	Av.	4.72 × 10^{-2}
25.00		Av.	2.67	Av.	1.32 × 10^{-2}
50.00		Av.	2.93	Av.	11.9 × 10^{-2}

Plots of log k_{h} and log k_{l} against $1/T$ give excellent straight lines showing that the Arrhenius equation is obeyed. Table II gives the resulting values of energies of activation and frequency factors as well as comparison values for other esters and lactones. The several values of energy of activation are nearly identical but the frequency factors vary considerably.

TABLE II

ARRHENIUS CONSTANTS FOR REACTIONS WITH HYDROGEN ION FOR k IN L. MOLE^{-1} SEC.$^{-1}$

Compound	E, cal.	$\log_{10} A$
γ-Butyrolactone		
Hydrolysis	16810	8.67
Lactone formation	17540	9.63
γ-Valerolactone		
Hydrolysis[6]	16690	7.85
Lactone formation[7]	16630	9.66
Methyl acetate[7]	16920	8.59
Ethyl acetate[7]	16830	8.22

The Water Reaction.—If one makes the assumption that a spontaneous water reaction contributes to the lactone hydrolysis, then the total rate of hydrolysis in dilute aqueous solution would be given by

$$\mathrm{d}C_{\mathrm{HA}}/\mathrm{d}t = [k_{\mathrm{w}} + k_{\mathrm{h}}C_{\mathrm{H^+}} + k_{\mathrm{b}}C_{\mathrm{OH^-}}]C_{\mathrm{L}} - k_{\mathrm{l}}C_{\mathrm{HA}}C_{\mathrm{H^+}} - k_{\mathrm{w}}'C_{\mathrm{HA}}$$

From the previous rate data at 50° for the acid hydrolysis and from rate data on the hydroxide ion reaction obtained by extrapolating the results of Hegan and Wolfenden[8] to this same temperature (which gives $k_{\mathrm{b}} = 296$ at 50°), the optimum pH for detection of the water reaction may be calculated by minimizing the above equation with respect to $C_{\mathrm{H^+}}$. The pH value so determined (for 1% hydrolysis) is 4.9 at 50°.

Several experiments were made on the initial rate of hydrolysis of the lactone at 50° and at pH values close to 5 using acetic acid–sodium acetate buffers. To calculate k_{w}, a differential form of the above equation was used

---

(1) Holder of a Wilson College Fellowship, Sept., 1945, to June, 1948.

(2) (a) P. Henry, *Z. physik. Chem.*, **10**, 96 (1892); (b) H. Johansson and H. Sebelius, *Ber.*, **51**, 480 (1918); (c) A. Kailan, *Z. physik. Chem.*, **94**, 111 (1920); **101**, 63 (1922).

(3) (a) F. A. Long, W. F. McDevit and Frances B. Dunkle, *J. Phys. Colloid Chem.*, **55**, 813 (1951); (b) F. A. Long, Frances B. Dunkle and W. F. McDevit, *ibid.*, **55**, 829 (1951).

(4) E. J. Boorman and R. P. Linstead, *J. Chem. Soc.*, 577 (1933).

(5) (a) A. R. Olson and R. J. Miller, THIS JOURNAL, **60**, 2687 (1938); (b) F. A. Long and Mary Purchase, *ibid.*, **72**, 3267 (1950).

(6) H. S. Taylor and H. W. Close, *J. Phys. Chem.*, **29**, 1085 (1925).

(7) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solutions," 2nd ed., Clarendon Press, Oxford, 1947, p. 321.

(8) D. S. Hegan and J. H. Wolfenden, *J. Chem. Soc.*, 508 (1939).