[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Dissociation Constants of Acids in Salt Solutions. VI. Carbocyclic Carboxylic Acids

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The dissociation constants of carbocyclic carboxylic acids of the homologous series $(CH_2)_{n-1}CHCOOH$ have been determined in various hydroxylic solvents. The relative order of acid strength in water is not the same as in the non-aqueous hydroxylic solvents.

Predictions of the relative order of physical properties of a series of compounds are often attempted on the basis of the influence of structural changes within the series of these physical properties. Predictions such as the order of acid strengths in small ring monocarboxylic acids are often difficult if they are based on structure alone. The effect of adding a methylene group to straight chain acids or increasing the ring size in cyclic acids has been shown to decrease the strength of the acid.[2] The order of decreasing acid strength is $HCOOH > CH_3COOH > CH_3CH_2COOH$.

TABLE I

PURITY OF THE CARBOCYCLIC CARBOXYLIC ACIDS

Acid	Boiling point Obsd. °C.	Mm.	Lit. °C.	Mm.	Ref.	Freezing point, °C. Obsd.	Lit.	Ref.	n_D^{20} Obsd.	Lit.	Ref.	Analysis by titration, %
Acrylic[a]	77.5– 77.8	75	140	760	[e]	13.0	13.0	[e]	1.4221	1.4224	[e]	99.8
$(CH_2)_2CHCOOH$[b]	72.0	9	94–95	26	[f]	18.1	18.1	[g]	1.4372	1.4370	[h]	100.0
$(CH_2)_3CHCOOH$[c]	84.0– 84.5	10	96	15	[i]	−5.4	−6.0	[h]	1.4433	1.4434	[j]	100.0
$(CH_2)_4CHCOOH$[d]	106.5–107.0	10	104	7	[k]	4.6	4.5	[l]	1.4530	1.4532	[m]	100.1

[a] Product of Monomer–Polymer Company. [b] Prepared by C. G. Bergstrom from trimethylenechlorobromide. See Ph.D. Dissertation, Illinois Institute of Technology, June, 1951, p. 12. [c] Prepared by D. L. Kantro from trimethylene dibromide and diethyl malonate. See J. Cason and C. F. Allen, *J. Org. Chem.*, **14**, 31 (1949). [d] Prepared by J. S. Scott from cyclopentyl bromide. See N. Zelinsky, *Ber.*, **41**, 2627 (1908); also, R. H. Talbot and R. Adams, THIS JOURNAL, **49**, 2041 (1927). [e] C. N. Ruber and R. Schetelig, *Z. physik. Chem.*, **48**, 348 (1904). [f] C. M. McClosky and G. H. Coleman, *Org. Syntheses*, **24**, 36 (1944). [g] P. Bruylants and A. Stassens, *Bull. acad. roy. Belg.*, 702 (1921). [h] G. J. Östling, *J. Chem. Soc.*, **101**, 472 (1912). [i] W. H. Perkin, *ibid.*, **75**, 921 (1889). [j] J. H. Gladstone, *ibid.*, **51**, 11 (1887). [k] W. H. Perkin, *ibid.*, **47**, 815 (1885). [l] N. Faworski and R. Boshowski, *Chem. Zentr.*, I, 984 (1915). [m] S. S. Nametkin and A. K. Rushenzowa, *J. Russ. Phys. Chem. Soc.*, **46**, 1540 (1914).

Extension of the above observations to *n*-butyric acid, the next higher member in the homologous series does not follow the qualitative rule. The deviation has been attributed to ring formation through hydrogen bonding.

Likewise, for the cyclic acids the predicted order of acid strengths is $CH_2{=}CHCOOH > (CH_2)_2CHCOOH > (CH_2)_3CHCOOH > (CH_2)_4CHCOOH > (CH_2)_5CHCOOH$. This subject has been treated recently by Roberts and Chambers,[3] who determined the apparent dissociation constants in 50% water–50% alcohol and apparently think the order of acid strength is independent of the solvent.

The measurements reported in the present paper were carried out by the techniques described in the earlier papers of this series, the ratio of the dissociation constants of the various acids to cyclohexanecarboxylic acid in the solvents water, methyl and ethyl alcohol, and ethylene glycol, were determined.

Experimental

The tests for purity of the acids and methods of preparation are given in Table I. The liquid acids were purified by a preliminary dilution with an equal volume of benzene, followed by the distillation of the azeotrope and finally the benzene. The residue was fractionated under reduced pressure and the material distilling at constant temperature was collected. This fraction was redistilled under reduced pressure and the middle fraction collected for use.

Table II gives the ratios of the dissociation constants to that of cyclohexanecarboxylic acid in aqueous sodium chloride solution. The ratio is essentially independent of the equivalent salt concentration and can therefore be taken as the ratio at infinite dilution.

TABLE II

RATIO OF DISSOCIATION CONSTANTS OF CARBOCYCLIC CARBOXYLIC ACIDS TO CYCLOHEXANECARBOXYLIC ACID IN WATER

μ[a]	Acrylic	$(CH_2)_2$-CHCOOH	$(CH_2)_3$-CHCOOH	$(CH_2)_4$-CHCOOH
0.108	4.53	1.19	1.31	0.826
.206	4.58	1.17	1.28	.851
.304	4.50	1.17	1.27	.850
.402	4.62	1.16	1.27	.854
.500	4.64	1.17	1.28	.848
Av.	4.57	1.17	1.28	.846

[a] Mainly NaCl.

Table III illustrates the independence of the ratio of dissociation constants with lithium chloride concentration for the solvent ethyl alcohol.

Tables IV and V summarize the ratios for the four solvents and give the dissociation constants at $\mu = 0.10$ and the dissociation constant at infinite

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[1] This paper was abstracted from the dissertation presented by Jerome Gilbert Morse to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1952.

[2] J. F. S. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1008 (1937).

[3] J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5030 (1951).

TABLE III

$K_{A_xB_0}$ FOR CYCLOPROPANECARBOXYLIC ACID IN ETHANOL

μ^a	$K_{A_xB_0}$
0.059	1.99
.109	1.99
.209	1.97
.309	2.01
.409	1.99
.508	1.99
Av.	1.99

[a] Mainly LiCl.

dilution except in the case of the solvent ethylene glycol.

TABLE IV

DISSOCIATION IN WATER AT 25°

Acid	$K_{A_xB_0}{}^a$	$K_c \times 10^{5a}$	$K_a \times 10^5$
Cyclohexanecarboxylic	1.00	1.96^b	1.25
Acrylic	4.53	8.87	5.66
$(CH_2)_2CHCOOH$	1.19	2.33	1.49
$(CH_2)_3CHCOOH$	1.31	2.57	1.64
$(CH_2)_4CHCOOH$	0.826	1.62	1.03

[a] Total ionic strength is 0.10 *M*, mainly NaCl. [b] Measured against HCl.

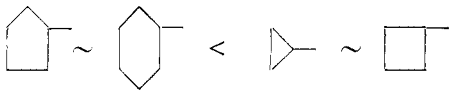
TABLE V

DISSOCIATION IN METHANOL AT 25°

Acid	$K_{A_xB_0}{}^a$	$K_c \times 10^{10a}$	$K_a \times 10^{10}$
Cyclohexanecarboxylic	1.00	8.32^b	0.923
Acrylic	5.81	48.3	5.36
$(CH_2)_2CHCOOH$	1.60	13.3	1.48
$(CH_2)_3CHCOOH$	1.40	11.7	1.29
$(CH_2)_4CHCOOH$	0.775	6.45	0.715
DISSOCIATION IN ETHANOL			
Cyclohexanecarboxylic	1.00	7.61^b	0.170
Acrylic	7.30	55.5	1.24
$(CH_2)_2CHCOOH$	2.03	15.5	0.345
$(CH_2)_3CHCOOH$	1.39	10.6	.236
$(CH_2)_4CHCOOH$	1.03	7.84	.173
DISSOCIATION IN ETHYLENE GLYCOL			
Cyclohexanecarboxylic	1.00	95.0^b	
Acrylic	5.58	530.0	
$(CH_2)_2CHCOOH$	1.46	138.0	
$(CH_2)_3CHCOOH$	1.39	131.0	
$(CH_2)_4CHCOOH$	0.944	89.7	

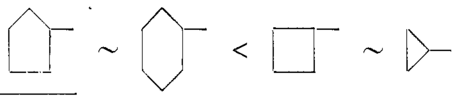
[a] Total ionic strength is 0.10 *M*, mainly LiCl. [b] Measured against HCl.

From Table IV and V it is evident that there is no regular incremental increase in the dissociation constants on going from cyclohexanecarboxylic acid to cyclopropanecarboxylic acid. The order of increasing acid strengths in water is



which is in agreement with the results of Zelinsky and Izgaruishev.[4]

In the non-aqueous solvents the order is



if we discount the small difference between cyclopentane and cyclohexane carboxylic acid in ethyl alcohol. This result is in agreement with the rate data of Roberts and Chambers for the reaction of cycloalkanecarboxylic acids with diphenylazomethane in the same solvent. The order of the dissociation constants in 50% alcohol-water mixtures reported by these authors is

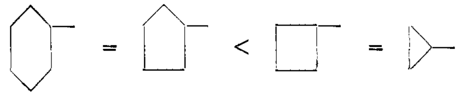


Figure 1 presents graphically the effect of ring size on relative acid strengths for the various solvents together with the change in intrinsic acid strength with number of methylene groups. The intrinsic acid strength is obtained by a plot of the logarithm of the ratio of the dissociation constant

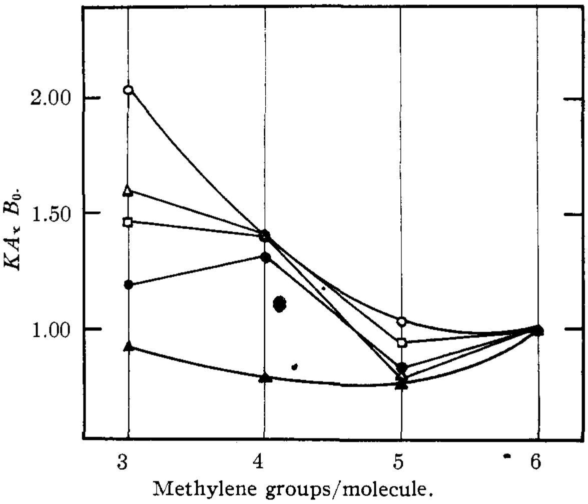


Fig. 1.—Effect of ring size on acid strength: ○, ethanol; △, methanol; □, ethylene glycol; ●, water; ▲, intrinsic strength ($1/D = 0$).

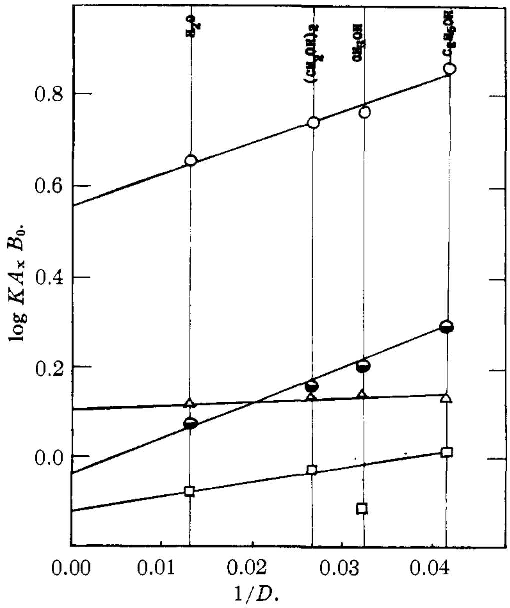


Fig. 2.—Wynne-Jones relationship: ○, acrylic; ◒, cyclopropanecarboxylic; △, cyclobutanecarboxylic; □, cyclopentanecarboxylic.

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[4] N. Zelinsky and N. Izgaruishev, *J. Russ. Phys. Chem. Soc.*, **40**, 1379 (1908).

of the given acid to the dissociation constant of cyclohexanecarboxylic acid against the reciprocal of the dielectric constant[5] of the solvent as shown in Fig. 2.

The fact that the dissociation constant of acrylic acid was found to be larger than those of the other carbocyclic carboxylic acids in each solvent may be attributed to stabilization of the anion of acrylic acid by resonance.

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(5) W. F. K. Wynne-Jones, *Proc. Roy. Soc. (London)*, **A140**, 440 (1933).

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XXVI. Effect of Solvent and of Temperature on the *cis–trans* Isomerization of Azo Dyes

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The photochemical *trans* → *cis* isomerization of ten typical azo dyes was studied spectrophotometrically in five solvents of different polarities. In general, hydrocarbon solvents favored isomerization, whereas ethanol appeared to suppress it most extensively. Upon heating benzene solutions of more than 20 azo dyes to 65° the isomerization equilibrium was shifted toward the stable (*trans*) form, whenever possible. The main absorption band of the dye at 65° appeared at a slightly shorter wave length than at room temperature. Spectral absorption data are presented for 12 typical azo dyes at 65°, together with suggested explanation for this hypsochromic shift.

Introduction

The rapid photochemical isomerization of a number of azo dyes in benzene solutions was described in an earlier paper in this series.[1] This work has been extended to include a study of the effect of solvent on the photochemical isomerization of dyes of this type, by determining the spectra in four additional common solvents of widely different polarities. In addition, the effect of heat on the isomerization equilibria of some azo dyes in benzene solutions was evaluated.

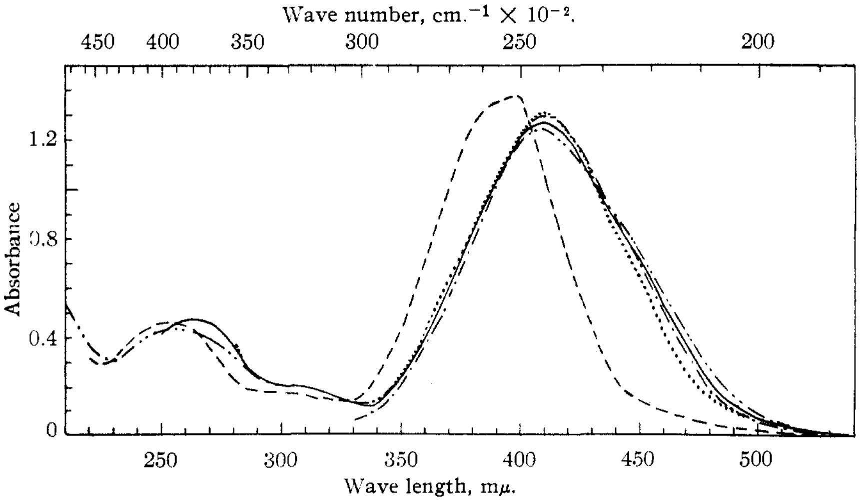

Fig. 1.—Absorption spectra of 4-dimethylaminoazobenzene in five solvents: - - -, in isoöctane; -·-·-·-·, in alcohol; ——, in chloroform; ......, in benzene; -·-·-, in methyl ethyl ketone after storage in darkness. Concentration, 0.0052 g./l.; cell length, 2.00 cm.

I. Solvent Effect

Experimental. Preparation of Solutions.—The technique employed in the preparation of solutions and the physical properties of the dyes used have been described in the previous paper.[1]

Apparatus.—Irradiation of the solutions during the measurement was effected by means of the rotating shutter described in an earlier paper.[2]

Measurement of Spectra.—The absorption spectra were determined by means of a Cary recording quartz spectrophotometer with the appropriate solvent as reference standard.

Discussion of Results

Results.—The absorption spectra of the stable form of a typical strongly phototropic azo dye, 4-dimethylaminoazobenzene, in five solvents are shown in Fig. 1.

These absorption curves are very similar in shape and differ but slightly with respect to the position and the intensity of the main absorption band, as is usually the case when no new molecular species are formed in the different solvents.[3,4] The curve obtained in isoöctane (2,2,4-trimethylpentane) differs most from the spectra obtained in the other solvents, in that the main absorption band appears at a shorter wave length (by about 10 mμ). This effect is in accordance with earlier observations on the spectra of benzeneazophenol in various solvents[3] and the results of Sheppard and Newsome on the effect of solvents on the spectrum of 4-dimethylamino-4′-nitroazobenzene.[5] Although the reasons for this relation between the position of an absorption band

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(1) W. R. Brode, J. H. Gould and G. M. Wyman, THIS JOURNAL, **74**, 4641 (1952).

(2) J. H. Gould and W. R. Brode, *J. Opt. Soc. Am.*, **42**, 380 (1952).

(3) W. R. Brode, *J. Phys. Chem.*, **30**, 56 (1926).

(4) C. D. Mason and F. F. Nord, *J. Org. Chem.*, **17**, 778 (1952).

(5) S. E. Sheppard and P. T. Newsome, THIS JOURNAL, **64**, 2937 (1942).