powder, fused vanadium pentoxide, iron filings, manganese dioxide, potassium nitrite or sodium fluoride in the carbon tetrachloride medium, the yields of potassium acid saccharate varied from 12 to 44%.

Oxidation of Glucose in Nitrogen Tetroxide Medium.—In a similar manner except for a 100-ml. round-bottom flask and 60 ml. of nitrogen tetroxide as solvent, a 25 to 44% yield of potassium acid saccharate was obtained by the oxidation of glucose (0.1 mole). A solution of urea was used to remove the last traces of the oxides of nitrogen. When 5 g. of potassium carbonate was added to the reaction mixture the yield of potassium acid saccharate, neut. equiv. 247.6, increased to 45%. When 5 g. of potassium carbonate was added to the reaction mixture at 35 ± 0.2°, the yield of potassium acid saccharate, neut. equiv. 247.4, was 50%.

Treatment of Gluconic Acid and Its Lactone with Nitrogen Tetroxide.—D-Gluconolactone (0.05 mole) was dried over phosphorus pentoxide under a vacuum and then treated with nitrogen tetroxide (0.17 mole) in 150 ml. of carbon tetrachloride for 24 hours at 25 ± 1°. The product was treated as was the glucose oxidation run to obtain 4.6 g. (37%) of potassium acid saccharate, neut. equiv. 246.5. Gluconic acid (0.1 mole) was dried in a vacuum over phosphorus pentoxide and treated with nitrogen tetroxide (0.35 mole) in 150 ml. of carbon tetrachloride for 9 hours at 25 ± 1°. The product was treated as was the glucose oxidation run to obtain 8.39 g. (34%) of potassium acid saccharate, neut. equiv. 252.5. Gluconic acid (0.1 mole) was also treated with nitrogen tetroxide in a nitrogen tetroxide medium for 3 hours at 25 ± 1°. The product was treated as was the glucose oxidation run to obtain 10.4 g. (42%) of potassium acid saccharate, neut. equiv. 248.2.

Treatment of Oxalic Acid with Nitrogen Tetroxide.—Anhydrous oxalic acid (0.05 mole) was treated with nitrogen tetroxide (0.17 mole) in carbon tetrachloride at a temperature of 25 ± 1° for 24 hours. After the period of oxidation, the excess nitrogen tetroxide was blown out and the water soluble component was extracted and transferred to a 250-ml. volumetric flask. To aliquots was added ammonium hydroxide to a *p*H of approximately 4. The calcium salt was precipitated out using calcium acetate. Following isolation and the dissolution of the calcium oxalate in sulfuric acid, the solution was titrated with standard potassium permanganate. The amount of oxalic acid found agreed within experimental error with that initially treated with nitrogen tetroxide.

Treatment of Potassium Acid Saccharate with Nitrogen Tetroxide.—Potassium acid saccharate (0.1 mole) and 6 ml. of glacial acetic acid were treated with nitrogen tetroxide (0.35 mole) in 150 ml. of carbon tetrachloride at 25 ± 1° for 8 hours. The product was treated to obtain 22.3 g. (90%) unreacted potassium acid saccharate, neut. equiv. 251.4. Potassium acid saccharate (0.1 mole) was also treated with nitrogen tetroxide in a nitrogen tetroxide medium for 3 hours at 25 ± 1°. The product was treated to obtain 20.9 g. (84%) of potassium acid saccharate, neut. equiv. 249.3.

CHICAGO, ILLINOIS RECEIVED AUGUST 14, 1950

L-Rhamno-2,4-dinitrophenylhydrazone

BY JORGE ALEJANDRO DOMÍNGUEZ

In 1927 Glaser and Zuckermann[1] reported the preparation of glucose and galactose 2,4-dinitrophenylhydrazones. Subsequently, Allen[2] and Brady,[3] unaware of this work, claimed that 2,4-dinitrophenylhydrazine did not give precipitates with the sugars.

L-Rhamno-2,4-dinitrophenylhydrazone.—Five ml. of glacial acetic acid and 0.8 g. of 2,4-dinitrophenylhydrazine were added to a solution of 1 g. of rhamnose in 5 ml. of water. This mixture was heated at 50° during 20 minutes, and allowed to stand at room temperature for 12 hours. The precipitated orange mass was collected, washed with water and a little cold alcohol, and recrystallized from hot alcohol. The yield of the dry yellow crystals was 1.0 g. (71%) m. p. 164–165° (uncor.). The melting point did not change after three recrystallizations.

Anal. Calcd. for $C_{12}H_{16}O_8N_4$: N, 16.27. Found: N, 16.18.

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DE MONTERREY
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[1] E. Glaser and N. Zuckermann, *Z. physiol. Chem.*, **167**, 37 (1927).

[2] C. F. H. Allen, THIS JOURNAL, **52**, 2955 (1930).

[3] O. L. Brady, *J. Chem. Soc.*, **133**, 756 (1931).

The "Exponential" Adsorption Isotherms of Fatty Acids on Activated Charcoal

BY E. GLUECKAUF

F. H. M. Nestler and H. G. Cassidy[1] have investigated the simultaneous adsorption of acetic, propionic and butyric acids on active charcoal from aqueous solution. They have tried to interpret these data by utilizing the binary exponential isotherm by Glueckauf[2] which should apply when the exponential form is caused by a statistical distribution of adsorbing centers of different affinity.[2,3] However, they were able to obtain agreement with the observations only, by introducing an extra constant not provided by the theory. This note is intended to show that the exponential single-solute isotherms in this case need not be due to non-uniformity of the adsorbent, but can be caused by the strong affinity of activated charcoal for hydrogen ions, and that Nestler and Cassidy's binary adsorption data can be explained as an anion exchange process.

It has been shown by Steenberg[4] that charcoal in a mixture of strong acids displays all the characteristics of an anion-exchanger, the primarily adsorbed group being the H_3O^+ ion. The chromatographically obtained data of Nestler and Cassidy fully support this view also for the weaker fatty acids, as the values obtained for the exchange factor k_3 are independent of the concentrations both for the pairs of acetic + propionic and propionic + butyric acids (see Table I). This feature is characteristic of exchange and of Langmuir isotherms, but is quite improbable for exponential ones.

TABLE I

ACETIC (1) AND PROPIONIC (2) ACID

$$k_3 = \frac{q_1 c_2}{c_1 q_2} = 1 - \frac{c_{1,1}(w_2 - w_1^0)}{c_1^0 w_2} \qquad (1)$$

$c_{1,1}$ and w_1^0 = concentration and breakthrough volume of solute 1 (concentrations in wt. %). c_1^0 = concentration of solute 1 at breakthrough of solute 2. w_2 = breakthrough volume of solute 2 (see ref. 1)

c_1^0	$c_{1,1}$	w_2	w_1^0	k_3
0.982	1.521	18.35	9.47	0.25
.759	1.145	22.35	11.05	(.24)
.752	1.153	22.75	11.79	.26
.503	0.751	27.70	14.24	.28
.379	.566	32.96	16.83	.27
.251	.376	41.35	20.75	.26
.152	.210	55.60	27.0	.29

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[1] F. H. M. Nestler and H. G. Cassidy, THIS JOURNAL, **72**, 680 (1950).

[2] E. Glueckauf, *J. Chem. Soc.*, 1322 (1947).

[3] G. D. Halsey and H. S. Taylor, *J. Phys. Chem.*, **15**, 624 (1947).

[4] B. Steenberg, Thesis, Uppsala University, Sweden, 1944.

The following mechanism is suggested:

(1) H_3O^+ is adsorbed according to a Langmuir adsorption. The H_3O^+ concentration of the dilute solutions of the weak acids is proportional to $\sqrt{c}$ (c = total acid concentration), the coefficient of adsorption being somewhat dependent on the nature of the anion which, for reason of electroneutrality, must remain close to the adsorbed H_3O^+, presumably forming an ion-pair. As long as only one species of acid is present, this mechanism is indistinguishable from molecular adsorption following an "exponential" isotherm.

(2) When two or more acids are present, the adsorbed H_3O^+ acts as an anion-exchanger with respect to the acids in solution according to the mechanism

$$[H_3O^+_{ads} + A_1^-] + HA_2 \overset{k_3}{\rightleftharpoons} [H_3O^+_{ads} + A_2^-] + HA_1$$

(3) In mixtures of two acids, the coefficient $k_{1,2}$ of adsorption of H_3O^+ is taken as the appropriate mean of the single solute coefficients k_1 and k_2, *i.e.*

$$k_{1,2} = (c_1k_1 + c_2k_2)/(c_1 + c_2) \qquad (2)$$

which covers at the same time differences in the dissociation constants of the two acids. Equation 2 is an approximation only, but exact treatment would be unjustifiably laborious; it implies that total adsorption of acids (q) can be calculated from the single-solute data without the introduction of the new constant k_3 (see Fig. 1 line C.).

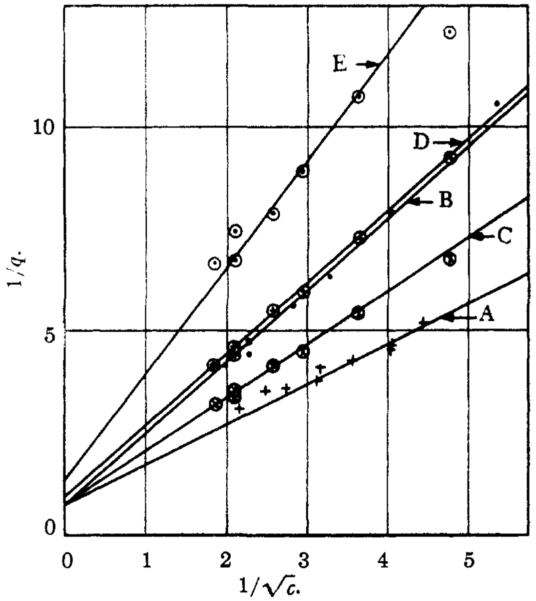

Fig. 1.—Adsorption from mixture of acetic and propionic acids calculated from adsorption data of the pure acids (c = total acid concentration in moles/liter, q in millimoles/g.): A, + + +, propionic acid (single solute) (eqn. 3); B, . . ., acetic acid (single solute) (eqn. 3); C, ⊗⊗⊗, total adsorption from mixture (eqn. 3); D, ⊕⊕⊕, propionic acid (from mixture) (eqn. 5a); E, ⊙⊙⊙, acetic acid (from mixture) (eqn. 4a); (curve E shows $1/q$-values halved).

The assumption of a Langmuir adsorption for H_3O^+ means then that the total adsorption of acids is in all cases represented by the equation

$$q = \frac{Qk\sqrt{c}}{1 + k\sqrt{c}} \qquad (3)$$

where k is k_1, k_2 or $k_{1,2}$ according to whether one deals with single or multiple solutes. In the example of the acetic and propionic acids, the constants $Q = 1.43$, $k_1 = 0.399$ and $k_2 = 0.690$ are obtained from Nestler and Cassidy's single solute experiments, *i.e.*, from the slopes and intercepts of line A and B of the figure. For the 5:4 molar mixture of acids used, the value $k_{1,2} = 0.528$ follows from eqn. 2 as the mean of k_1 and k_2. The only new constant to be obtained from the binary adsorption data is thus the ion-exchange constant $k_3 = 0.27$ (from Table I). These constants are to be applied to concentrations in mole/liter and to specific adsorptions (q) in millimole/g.

The final equations for q_1 and for q_2 in mixed adsorption taking account of the anion-exchange, then follow from eqn. (1) and (3) combined with the fact that $q_1 + q_2 = q$

$$q_1 = \frac{Qk_{1,2}\sqrt{c}}{(1 + k_{1,2}\sqrt{c})}\,\frac{k_3c_1}{(c_2 + k_3c_1)} \qquad (4)$$

$$q_2 = \frac{Qk_{1,2}\sqrt{c}}{(1 + k_{1,2}\sqrt{c})}\,\frac{c_2}{(c_2 + k_3c_1)} \qquad (5)$$

and for the fixed molar ratio of 5:4 we obtain for acetic (subscript 1) and propionic (subscript 2) acids the equations

$$q_1 = 0.191\,\sqrt{c}/(1 + 0.528\sqrt{c}) \qquad (4a)$$

$$q_2 = 0.565\,\sqrt{c}/(1 + 0.528\sqrt{c}) \qquad (5a)$$

For a check of the experimental data it is convenient to plot $1/q$ against $1/\sqrt{c}$, whence the equations 3, 4a and 5a result in straight lines. The experimental data of Nestler and Cassidy are shown as points in the figure and they agree well, within the limits of their accuracy, with the calculated lines.

This calculation does not exclude the possibility that some acid is adsorbed in undissociated form as well, but such an assumption alone does not explain the data satisfactorily, while the ion-exchange model alone does. This discussion is intended to emphasize the need to differentiate between exponential isotherms due to dissociation phenomena and those due to a statistical distribution of adsorbing sites of different affinity. This difference, though not apparent in single solute isotherms, becomes important for the adsorption of mixtures.

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Dicyclic Hydrocarbons. II. 2-Alkylbicyclohexyls

BY I. A. GOODMAN AND P. H. WISE

The syntheses and physical properties of a series of 2-substituted alkylbiphenyls have recently been reported from this Laboratory.[1] The alkyl substituents included methyl, ethyl, propyl, isopropyl and butyl. In this communication we wish to present the results of the catalytic hydrogenation of these hydrocarbons, including data on the separation of the geometrical isomers, and the analyses and physical properties of the five pairs of isomers which were obtained. The

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[1] I. A. Goodman and P. H. Wise, THIS JOURNAL, 72, 3076 (1950).