[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Base Exchange Reactions of Bentonite and Salts of Organic Bases

BY C. R. SMITH

John Uri Lloyd[1] in 1910 found that certain samples of fuller's earths removed alkaloids from aqueous solutions of their salts. He reservedly accepted the phenomena as "adsorption" of the salts even though he noted the presence of calcium combined with the acids of the alkaloidal salts. Gordin and Kaplan[2] concluded that fuller's earth did not adsorb sodium chloride because no diminution of chlorine ions was found. Seidell[3] considers that fuller's earth reacts by adsorption although he also noted the formation of calcium salts.

Bentonite is a clay of volcanic origin, noted for its highly colloidal character and its ability to enter into base exchange with inorganic salts. Its reactions are probably typical of fuller's earth although it will remove a greater percentage of organic bases than the latter judging from results obtained by the author with a number of samples of bentonite and fuller's earth, including Lloyd's reagent, but not given in this paper.

All of those who have studied these alkaloidal reactions have determined the amount of earth necessary to precipitate a given amount of alkaloid, usually making use of alkaloidal precipitants to show the point of complete precipitation. The author has approached the problem from the standpoint of equilibrium. Right at the outset it was apparent that adsorption of the whole alkaloidal salt was not occurring. There is no detectible absorption of anions. We are dealing with a reaction which may be thus expressed

$$\text{Bentonite}\left\{\begin{array}{l}\text{ONa}_2\\ \text{OCa}\\ \text{OMg,}\\ \quad\text{etc.}\end{array}\right. + \text{B}^+ + \text{Cl}^- \leftrightarrows \text{Bentonite}\left\{\begin{array}{ll}\text{OB} & \\ \text{OB} + \text{M}^+ + & \\ \text{OB} & \text{Cl}^-\end{array}\right.$$

where M may be calcium, sodium, magnesium or other replaceable bases of the silicate. The reaction is not specific for alkaloids but is applicable to all organic bases which form ionized salts. The action is promoted by high ionization of the organic salt and by the insolubility of the organic silicate. The presence of inorganic electrolytes produced in the reaction or of added electrolytes tends to reverse the reaction. A number of the alkaloids first studied by previous workers produced very insoluble alumino silicates, and the presence of an equilibrium escaped notice. The author treats bentonite with the organic salts and determines the unabsorbed base in the filtrate. The weight of alkaloid absorbed approaches a definite limit, and these limits represent equivalent quantities of the various alkaloids. The saturation limit of the organic bases is not reached by this procedure in the case of weak bases and ammonia. However, it has been found that continuous washing with the organic salt or ammonium salt will often serve to remove interfering cations and attain the maximum theoretical figure.

When Gordon and Kaplan treated fuller's earth with sodium chloride they should have determined the sodium and not the chlorine. They assumed that since chlorine ions were not removed no sodium chloride molecules were "adsorbed."

Bentonite is probably maintained in a state of extreme dispersion because of inorganic cations which are attracted in some way by the solvent. We have reason to expect that univalent cations would be most effective in this respect. The addition of salts of univalent and bivalent cations causes a repression of this dissociation, producing flocculation. When organic bases combined with bentonite the product may give but few cations to assist dispersion, and an excess even of organic base cations may cause flocculation. It has been noted that of the organic bases studied those which produce flocculation are those which react well. In general all titrable bases react with bentonite. Flocculation appears usually around the saturation point. If no flocculation occurs there is little or no reaction.

Experimental

Preliminary Studies with Nicotine.—Five grams of finely powdered bentonite was brought into contact with 200 cc. of a solution of free nicotine (0.25 g.) in water. After shaking repeatedly during a period of thirty minutes, the bentonite was removed by filtration and the base determined in an aliquot of the filtrate. It was found that 49% of the base had been removed by the bentonite. When the nicotine was half neutralized by sulfuric acid

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(1) Lloyd, *J. Amer. Pharm. Assoc.*, **5**, 381–490 (1916).

(2) Gordin and Kaplan, *ibid.*, **3**, 627 (1914).

(3) Seidell, THIS JOURNAL, **40**, 312 (1918).

and diluted to the same volume of solution, the absorption was raised to 80%. When the nicotine was completely neutralized with either sulfuric, hydrochloric, arsenic or oxalic acid the absorption was found to be about 92%. Bentonite is an alkaline silicate, and the sample used required about 16 cc. of 0.1 *N* acid to neutralize five grams. When this quantity of acid was added to the neutralized nicotine a still further increased absorption resulted in the removal of about 95%.

The following results were obtained with nicotine hydrochloride to which the 16 cc. of additional 0.1 *N* hydrochloric acid had been added so that the absorption mixture reacted slightly acid to alizarine sulfonate indicator.

TABLE I

ABSORPTION OF NICOTINE FROM THE HYDROCHLORIDE BY BENTONITE DUST

Nicotine used G.	Nicotine used 0.1 *N*, cc.	Free nicotine G.	Free nicotine 0.1 *N*, cc.	Combined nicotine G.	Combined nicotine 0.1 *N*, cc.	Combined, %
0.235	14.5	0.011	0.7	0.224	13.8	95.2
.282	17.4	.013	.8	.269	16.6	95.4
.329	20.3	.018	1.1	.311	19.2	94.6
.376	23.2	.026	1.6	.350	21.6	93.1
.423	26.1	.039	2.4	.384	23.7	90.8
.482	30.0	.066	4.1	.416	25.9	86.3
.530	32.7	.089	5.5	.441	27.2	83.2
.578	35.7	.120	7.4	.458	28.3	79.3
.611	37.7	.149	9.2	.462	28.5	75.6
.663	40.9	.180	11.1	.483	29.8	72.9
.758	46.8	.262	16.1	.496	30.7	65.4
.852	52.6	.350	21.6	.502	31.0	58.9
.947	58.4	.444	27.4	.503	31.0	53.0

These results show that 5 g. of this sample of bentonite dust combines with a maximum of 0.5 g. of nicotine under the conditions of the experiment, equivalent to 31 cc. of 0.1 *N* nicotine.

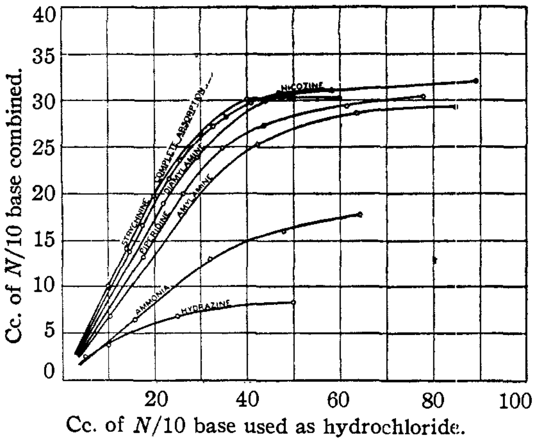

Fig. 1.—Reaction of organic bases with bentonite. Five grams of bentonite to 200 cc. of solution containing the base as hydrochloride.

Other Bases.—Table II shows the absorption of a number of other organic bases under the same conditions.

The results given in Table II with piperidine, strychnine, amylamine, and diamylamine show that saturation of the bentonite is reached at very near the same figure found for nicotine. Ammonia and hydrazine are less reactive; very high concentrations of ammonia would probably approach the saturation point but hydrazine might fall short of saturation. The results of Table II are shown diagrammatically in Fig. 1.

TABLE II

ABSORPTION OF ORGANIC BASES AND AMMONIA FROM THEIR HYDROCHLORIDES

	Used, 0.1 *N* cc.	Combined 0.1 *N* cc.		Used, 0.1 *N* cc.	Combined, 0.1 *N* cc.
Piperidine	17.5	13.2	Amylamine	10.5	6.7
	26.2	20.0		21.1	14.3
	35.0	24.6		42.1	25.4
	43.7	27.3		63.2	28.7
	61.2	29.3		84.3	29.4
	78.7	30.5			
Ammonia	16.0	6.4	Diamylamine	22.0	19.0
	32.0	13.0		29.8	23.6
	48.0	16.0		44.0	30.2
	64.0	17.0		66.0	31.0
				88.0	32.0
Strychnine	10.0	All	Hydrazine	5.0	2.5
	14.0	All		10.0	3.7
	20.0	19.8		25.0	6.8
	30.0	26.3		50.0	8.3
	40.0	30.1			
	50.0	30.2			
	60.0	30.2			

Experiments have also been made with hydroxylamine, triamylamine and anabasine. Hydroxylamine is probably weakly reactive, producing no coagulation. Also, since no ready method for its estimation was available, the experiments were abandoned. The triamylamine as well as the amylamine and diamylamine were known to be mixtures of isomers, but having the same molecular weight they would be expected to show the same reactivity. With triamylamine, however, difficulty was encountered because of instability of the hydrochloride, difficulties in distillation, etc., and the experiments were abandoned, although apparently it was reacting in approximately the same way as the other two. Anabasine reacting in two different concentrations showed an absorption close to that of nicotine. Because analytical methods were not readily available, a complete set of concentrations have not as yet been studied.

The results obtained with ammonium chloride show that saturation of the bentonite was not obtained in the concentrations used. With 50 cc. of 0.1 *N* ammonium chloride in 200 cc. we can expect only about 17 cc. absorption, but when bentonite was washed with successive portions of this concentration, thereby removing the inorganic salts and the excess of ammonium chloride was washed away, the bentonite contained more than 95% of the theoretical amount. A similar effect was found with dilute solutions of nicotine.

Washing with Water and Salt Solution.—When bentonite saturated with nicotine is washed with successive portions of water, the washings are alkaline and contain a small amount of nicotine. When washing with water was alternated with washing with an equal volume of

1% sodium chloride solution it was noted that the salt removed about five times more nicotine. The successive portions of water and salt solution removed decreasing amounts of nicotine. Five grams of fully saturated bentonite lost about 20% of its nicotine when in contact with 200 cc. of salt solution. The experiments further substantiate the reverse effect of inorganic salt cations. It is quite probable that an equilibrium may not have been reached in these experiments, and a further study will be made of the reverse effect of salt solutions.

Summary

1. The reaction between bentonite and salts of organic bases is principally one of base exchange.
2. Bentonite enters into base exchange with a definite chemical equivalent of organic bases where saturation can be reached. In the one sample of bentonite used one gram combined with 6.2 to 6.4 cc. of 0.1 *N* organic base.
3. When saturation is approached with most bases flocculation is produced. Flocculation indicates that a reaction has taken place with partial or complete saturation of the silicate.
4. Saturation is promoted by the insolubility of the silicate complex and by removal of the inorganic salts by washing.

WASHINGTON, D. C. RECEIVED MARCH 9, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Synthesis of Unsaturated Fatty Acids. Synthesis of Oleic and Elaidic Acids

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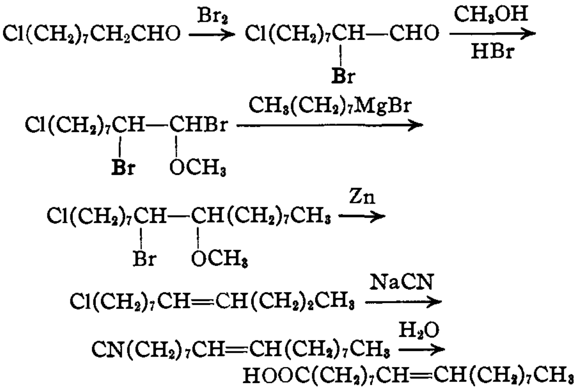
In view of the difficulty of isolating pure unsaturated fatty acids from natural sources and the fact that the methods of synthesis commonly used lead to mixtures of structural isomers, a general method of synthesis yielding products free of structural isomers should be of value. It appears from an examination of the literature that even oleic acid has not been synthesized in such a way as to definitely place the position of the double bond. Thus it has merely been obtained as one of the products of the dehydration of 10-hydroxystearic acid or of the action of alcoholic potassium hydroxide on 10-iodostearic acid.[1] Both 10-hydroxystearic and 10-iodostearic acids have been obtained from 10-ketostearic acid, which has been synthesized.[2] The preparation of oleic and elaidic acids from stearolic acid[2,3] can hardly be termed a synthesis since stearolic acid has not been synthesized and was presumably obtained from natural oleic acid.

By making use of the Boord olefin synthesis[4] it has been possible to synthesize a mixture of oleic and elaidic acids in satisfactory yields. The reactions used were as follows



$$\mathrm{Cl(CH_2)_7CH_2CHO} \xrightarrow{\mathrm{Br_2}} \mathrm{Cl(CH_2)_7}\underset{\mathrm{Br}}{\mathrm{CH}}\mathrm{-CHO} \xrightarrow[\mathrm{HBr}]{\mathrm{CH_3OH}}$$

$$\mathrm{Cl(CH_2)_7}\underset{\mathrm{Br}}{\mathrm{CH}}\mathrm{-}\underset{\mathrm{OCH_3}}{\mathrm{CHBr}} \xrightarrow{\mathrm{CH_3(CH_2)_7MgBr}}$$

$$\mathrm{Cl(CH_2)_7}\underset{\mathrm{Br}}{\mathrm{CH}}\mathrm{-}\underset{\mathrm{OCH_3}}{\mathrm{CH}}\mathrm{(CH_2)_7CH_3} \xrightarrow{\mathrm{Zn}}$$

$$\mathrm{Cl(CH_2)_7CH{=}CH(CH_2)_2CH_3} \xrightarrow{\mathrm{NaCN}}$$

$$\mathrm{CN(CH_2)_7CH{=}CH(CH_2)_7CH_3} \xrightarrow{\mathrm{H_2O}}$$

$$\mathrm{HOOC(CH_2)_7CH{=}CH(CH_2)_7CH_3}$$

Strictly speaking this is not a complete synthesis since the starting material was obtained by the series of reactions

$$\text{Butyl oleate} \xrightarrow[\text{alcohol}]{\text{Na}} \text{oleyl alcohol} \xrightarrow{\mathrm{SOCl_2}}$$

$$\text{9,10-octadecenyl chloride} \xrightarrow{\mathrm{O_3}} \omega\text{-chlorononylaldehyde}$$

However, since azelaic acid has been obtained by the ozonation of oleic acid[5] and has been synthesized by several methods,[6] there seemed no urgent need for the synthesis of ω-chlorononylaldehyde.

It is interesting to note that the synthetic mixture of acids contained approximately 63% of elaidic acid which is in fair agreement with the

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[1] M., C., and A. Saizew, *J. prakt. Chem.*, [2] **35**, 385 (1887); Saizew and Lebedew, *ibid.*, **50**, 61 (1894); Arnaud and Posternak, *Compt. rend.*, **150**, 1525 (1910); Veseley and Majtl, *Bull. soc. chim.*, [4] **39**, 230 (1926).

[2] Robinson and Robinson, *J. Chem. Soc.*, **127**, 175 (1925).

[3] González, *Anales soc. españ. fís. quím.*, **24**, 156 (1926); *Chem. Centr.* II, 183 (1926); Paal and Schiedewitz, *Ber.*, **63**, 770 (1930).

[4] Shoemaker and Boord, THIS JOURNAL, **53**, 1505 (1931).

[5] Harries and Thieme, *Ann.*, **343**, 355 (1905).

[6] Haworth and Perkin, *Ber.*, **26**, 2249 (1893); v. Pechmann and Sidgwick, *ibid.*, **37**, 3821 (1904); Reformatsky, Grischkewitsch and Semenzow, *ibid.*, **44**, 1886 (1911); Dionneau, *Ann. chim.*, [9] **3**, 249 (1915).