COMMUNICATIONS TO THE EDITOR

THE GELATION OF MAGNESIUM SILICATE SUSPENSIONS BY CARBON DIOXIDE AND OTHER AGENTS

Sir:

Several months ago, in the course of some experiments with precipitated and washed silicates of magnesium, we observed that the passage of carbon dioxide through fluid suspensions of these silicates in water soon caused the suspensions to "set up" or gel. The resulting gels were found to be thixotropic,[1] that is, capable of an isothermal, reversible sol-gel transformation, being liquefied on shaking and setting spontaneously.[2]

Thus, within one and one-half minutes following the treatment of 10 cc. of an 8.1% suspension of MgO, $1.6SiO_2$ (*p*H 9.3) with a rapid stream of carbon dioxide for one-half minute, the originally fluid suspension had "set up," so that the test-tube (16 by 150 mm.) containing it could be inverted without flow taking place. Vigorous shaking of the solidified material (*p*H 7.2) produced liquefaction; upon standing undisturbed, spontaneous reversion to the gel state occurred in less than a minute. The process could be repeated indefinitely.

Similar observations were made with suspensions of MgO, $1.1SiO_2$ (6.1%) and MgO, $3.6SiO_2$ (8.4%).

The magnesium silicates were prepared by slowly adding water solutions of various silicates of sodium to water solutions of magnesium sulfate,[3] with vigorous stirring. The resulting precipitates were collected and washed in a filter press,[4] and portions of the wet products[5] were ground with water for a few minutes in a mortar to yield the rather coarse suspensions which, after vigorous shaking, were employed in the above experiments.

More recently, we found that hydrochloric acid, sulfuric acid, or acetic acid, in small amounts, could be substituted for carbon dioxide in the above experiments, to give similar results. Thus, following the addition of 0.4 cc. of *N* hydrochloric acid (0.0004 mole) to 10 cc. of an 8.1% suspension of MgO, $1.6SiO_2$ (0.006 mole; *p*H 9.3), contained in a 16 by 150-mm. test-tube, gelation occurred in about half a minute. The setting time of the thixotropic product (*p*H 7.7) was less than fifteen seconds. Further work along these lines is in progress.

Aside from its scientific interest, the present phenomenon may find some application in the arts.[6]

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[1] *Cf.* Freundlich and Gillings, *J. Chem. Soc.*, 546 (1938); MacArthur, U. S. Patent 2,168,228 (1939).

[2] For an excellent summary of our knowledge of the phenomenon of thixotropy, see Freundlich, "Thixotropy," No. 267 of "Actualités scientifiques et industrielles," Hermann et Cie, Paris, 1935.

[3] The proportions, concentrations, and composition of the reactants were:

$MgSO_4 \cdot 7H_2O$	Sodium silicate	Magnesium silicate[5]
3.22 moles (0.13 *M* soln.)	3.25 moles Na_2O, 1.00 SiO_2 (1.6 *M* soln.)	MgO, $1.1SiO_2$
3.44 moles (0.13 *M* soln.)	3.49 moles Na_2O, 1.48 SiO_2 (1.1 *M* soln.)	MgO, $1.6SiO_2$
2.71 moles (0.13 *M* soln.)	2.77 moles Na_2O, 3.27 SiO_2[a] (0.5 *M* soln.)	MgO, $3.6SiO_2$

[a] "E" Brand sodium silicate, of the Philadelphia Quartz Company from which the other sodium silicates were prepared by the addition of the requisite amounts of sodium hydroxide.

[4] Washing was continued at least until portions of the filtrates showed no tests (or only faint tests) for sodium (with uranyl zinc acetate) and sulfate (with $BaCl_2$, HCl).

[5] Complete analyses of the products, first dried (55°) and pulverized, were made, with the following results:

SiO_2, %	44.35	52.58	67.05
MgO, %	27.90	22.20	12.49
H_2O, %	27.14	24.05	18.67
R_2O_3, %	0.46	0.42	0.34
CaO, %	.26	.18	.12
Na_2O, %	.24	.35	1.21
SO_3, %	< .01	None	< 0.01
	100.35	99.78	99.88
Molecular ratio, MgO: SiO_2,	1:1.07	1:1.59	1:3.60

[6] *Cf.* Mutch, *Brit. Med. J.*, **1**, 143, 205, 254 (1936); Levin and co-workers, *Rev. Gastroenterol.*, **6**, 299 (1939); Hauser and Le Beau, *J. Phys. Chem.*, **42**, 961 (1938); **43**, 1037 (1939).

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REDUCTION OVER A RANEY CATALYST OF THE ESTERS OF α-AMINO ACIDS TO CORRESPONDING ALKAMINES

Sir:

P. L. de Benneville and Ralph Connor report [THIS JOURNAL, **62**, 283 (1940)] on the reduction of an ester to an alcoholic group by the aid of a nickel catalyst. This is regarded by the authors as the first instance of such a reaction.

We wish to report that within the last two years we have carried out the reduction over nickel catalyst (Raney) of the esters of α-aminoacids to the corresponding alkamines. The reaction was successfully carried out on the esters of leucine ethyl ester, of aminophenylacetic acid ethyl ester and of phenylalanine ethyl ester. In the case of the ester of *l*-leucine and of *levo*-phenylaminoacetic ethyl ester, the alkamines were obtained in active form. Depending on conditions of the reaction, it was possible to obtain from the ester of phenylaminoacetic acid either 2-phenyl-2-aminoethanol, or 2-cyclohexyl-2-aminoethanol. Under still other conditions it was possible to obtain from the esters corresponding secondary amines. Also, condensation to piperazine takes place over nickel (Raney) catalyst. The primary and the secondary amino groups may remain unsubstituted or alkylated, depending upon conditions of the reaction.

In the present note we report the analytical data of the alkamines only. The smallest yield of the active leucinol is 40% of the theoretical and the smallest yield of the phenylaminoethanol is 60%. The yields undoubtedly could be improved on working with larger quantities.

PROPERTIES AND ANALYSES

Ethyl ester		*d,l*-Leucine	*l*-Leucine	*levo*-Phenylaminoacetic acid	*d,l*-Phenylaminoacetic acid
$\alpha^{25}\mathrm{D}$ (hom. 1 dm.)		..	+9.75°	−70.5°	..
t, °C.		135	70	40	40
p (initial), atm.		150	150	150	150
Duration, hours		24	9	9	18
Product		$C_6H_{15}ON \cdot HCl$	$C_6H_{15}ON$	$C_8H_{11}ON$	$C_8H_{17}ON$
$(\alpha)^{25}\mathrm{D}$ (in CH_3OH)		..	+1.9°	− 5.61°	..
Carbon, %	Calcd.	46.87	61.47	70.02	67.07
	Found	47.19	61.59	69.86	67.30
Hydrogen, %	Calcd.	10.5	12.90	8.09	11.96
	Found	10.3	12.84	8.27	11.77

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NEW BOOKS

Ausführliches Lehrbuch der organischen Chemie. (Comprehensive Textbook of Organic Chemistry.) Vol. II. By WILH. SCHLENK. Verlag von Franz Deuticke, Helferstorferstrasse 4, Wien I, Germany, 1939. xvii + 896 pp. 11 figs. 17.5 × 26 cm. Price, RM. 30; bound, RM. 33. (Vol. I, now RM. 30; bound, RM. 33.)

This second volume of a contemplated three, the last of which according to the author will appear soon, covers the chemistry of the carbocyclic aromatic compounds. The first volume, published in 1932, was devoted to aliphatic chemistry and the third presumably will describe the heterocyclic compounds.

This publication when complete will be the most extensive modern textbook in organic chemistry available in any language. About 1600 pages have been consigned to aliphatic and aromatic chemistry. Since this work approaches more closely than any other the "Lehrbuch der organischen Chemie" by V. Meyer and P. Jacobson, a comparison is pertinent. Both works are presented in essentially the same style. Meyer and Jacobson, however, include a multitude of original references and devote much space to a description of the physical and chemical properties not only of the basic compounds but of their more important derivatives. Schlenk omits these and consequently is able to include in considerably less space the same amount of textual material. This publication, thus, becomes more literally a textbook from which a reader may acquire many of the important facts about any class of organic compounds, organic theories or mechanisms of reaction. It is not intended as a reference work for the investigator. In view of the ever-broadening scope of organic chemistry, Schlenk's plan appears to the reviewer to be the more feasible since the research man must of necessity search the original literature; such a text as this will supply him with general information about any class of compounds with which he happens to be less familiar.

Each class of aromatic compounds is systematically discussed. The theoretical considerations are correlated with the description of those substances which have been studied most in developing a theory or mechanism. Thus, the theories on the orientation of substituents introduced into the benzene nucleus are given in the chapter on benzene and its simple derivatives; the Fries rearrangement under the discussion of phenol esters and ethers; restricted rotation under biphenyls and the use of oxidation–reduction potentials under quinones, etc. The theoretical discussions are concise and give the reader sufficient information to understand the subjects.

These three volumes should serve admirably as an advanced text of organic chemistry for the student who is beyond the first year of study in this subject as well as for the research man who always requires general reading