pentachloride, a reaction occurred yielding 16 g. of low boiling material collected in a Dry Ice trap. This distillate gave a positive test for chlorine and formed a gel with water. This indicated a disproportionation of triethyl chlorosilicate to yield silicon tetrachloride, but from a similar mixture, containing no sodium fluoride, the chlorosilicate was recovered unchanged after eight hours of heating.

No reaction was observed on heating mixtures of ethyl orthosilicate and benzoyl fluoride.

Tri-*n*-butyl Fluorosilicate.—A mixture of 36.4 g. (0.2 mole) of triethyl fluorosilicate and 53.3 g. (0.72 mole) of *n*-butyl alcohol was heated in a flask attached to a fractionating column. During a period of one hour, 27.2 g. of ethanol was removed, and the residue was then fractionally distilled at 32 mm. pressure. The yield of tri-*n*-butyl fluorosilicate, b. p. 134.0–134.5° (32 mm.), was 31.4 g. (59%). *Anal.* Calcd. for $Si(OC_4H_9)_3F$: F, 7.13. Found: F, 7.23, 7.18.

Triallyl Fluorosilicate.—An experiment similar to the preceding, taking 36.4 g. of triethyl fluorosilicate and 52.3 g. of allyl alcohol, yielded 25.7 g. ethanol over a period of two and a half hours, and from the residue was isolated 21.3 g. (49%) of triallyl fluorosilicate, b. p. 99.0–99.5° (32 mm.). *Anal.* Calcd. for $Si(OC_3H_5)_3F$: F, 8.70. Found: F, 8.76, 8.64. As in the previous case mechanical losses due to column holdup were proportionately large.

An attempted preparation of diallyl difluorosilicate from diethyl difluorosilicate and allyl alcohol did not yield the desired compound but instead the products were triallyl fluorosilicate and low boiling materials.

Allyl orthosilicate did not react with antimony trifluoride alone or in the presence of any of the following: antimony pentachloride, aluminum chloride, zinc chloride and triallylchlorosilicate. Nor was any reaction observed when allyl orthosilicate was heated with benzoyl fluoride, with or without antimony pentachloride.

Hydrolysis Reactions.—All of the above-mentioned alkyl fluorosilicates were observed to react instantly with cold water to form gels. With dry pyridine, solid (non-gelatinous) products were obtained which were immediately hydrolyzed by water to form gels.

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Summary

1. Triethyl fluorosilicate and diethyl difluorosilicate have been prepared by the action of antimony trifluoride on ethyl orthosilicate in the presence of antimony pentachloride. Allyl orthosilicate failed to react similarly with antimony trichloride.

2. Triallyl fluorosilicate and tri-*n*-butyl fluorosilicate have been prepared from the ethyl compound by alcoholysis reactions.

3. These alkyl fluorosilicates are instantly hydrolyzed by cold water with the formation of gels.

4. Contrasts with the behavior of analogous alkyl chlorosilicates are pointed out.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Transesterification Reactions of Alkyl Silicates

BY DONALD F. PEPPARD,[1] WELDON G. BROWN AND WARREN C. JOHNSON

The interchange of alkoxy groups between one alkyl orthosilicate and another, with the formation of mixed esters, has been effected by Friedel and Crafts,[2] and by Post and Hofrichter.[3] The latter authors refluxed a mixture of *n*-butyl orthosilicate and ethyl orthosilicate under atmospheric pressure for fifteen hours and then isolated the mixed esters by fractional distillation at reduced pressure. Transesterification reactions involving an orthosilicate and esters of other types have not been reported. The work described herein was undertaken to evaluate this method for the introduction of radicals, *e. g.*, vinyloxy, which cannot be introduced by conventional methods.

The present study, covering various combinations of alkyl silicates, borates and carboxylic esters, indicates that the redistribution of alkoxy groups takes place slowly in the absence of catalysts. However, the reactions are catalyzed by the more reactive metal alkoxides, *e. g.*, by alkoxides of aluminum, magnesium and antimony, and also by aluminum chloride. The catalyzed reactions may be utilized to prepare mixed esters, and it is shown that the yield of mixed esters approaches that corresponding to a statistical redistribution of alkoxy groups. Alternatively, the displacement of alkoxy groups may be driven to completion in cases where one of the products is the most volatile component of the system. This constitutes one of the most satisfactory methods available for the preparation of higher alkyl silicates.

Experimental

Reactions Between Two Orthosilicates.—On refluxing a mixture of ethyl orthosilicate and *n*-butyl orthosilicate for a long period of time, as Post and Hofrichter[3] had done, the mixed esters were obtained in relatively small yields, indicating that the reaction had not reached equilibrium. When the period of reflux was reduced to four and a half hours, no evidence for any reaction was noted. Mixtures of ethyl orthosilicate and allyl orthosilicate behaved similarly. In the presence of a relatively small proportion of magnesium aluminum ethoxide,[4] an essentially statistical redistribution of alkoxy groups occurred within a refluxing period of four and a half hours as is indicated by the relative yields shown in Tables I and II. In these experiments the catalyst was destroyed prior to separation of the components to avoid further reaction during the distillation.

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(2) Friedel and Crafts, *Ann.*, **136**, 203 (1865).

(3) Post and Hofrichter, *J. Org. Chem.*, **5**, 572 (1940).

(4) Prepared according to Meerwein and Bersin, *Ann.*, **476**, 113 (1929).

TABLE I

YIELDS OF MIXED ESTERS FROM THE TRANSESTERIFICATION OF ETHYL ORTHOSILICATE AND *n*-BUTYL ORTHOSILICATE[a]

Compound	B. p., °C. (32 mm.)	n^{20}_D	Yield, moles	Mole ratio (exptl.)	Mole ratio (calcd.)
$Si(OC_2H_5)_4$	77.0– 77.5	1.3837	0.027[c]	0.84	1
$Si(OC_2H_5)_3(OC_4H_9)$	102.0–102.5	1.3934	.125	3.93	4
$Si(OC_2H_5)_2(OC_4H_9)_2$	128.0–128.5	1.4010	.197	6.18	6
$Si(OC_2H_5)(OC_4H_9)_3$	150.0–150.5	1.4075	.126	3.96	4
$Si(OC_4H_9)_4$	141.0–142.0[b]	1.4131	.025[c]	0.77	1

[a] Catalyst $Mg[Al(OC_2H_5)_4]_2$, 0.03 mole. [b] At 3 mm. pressure. [c] Initial quantity, 0.3 mole.

TABLE II

YIELDS OF MIXED ESTERS FROM THE TRANSESTERIFICATION OF ETHYL ORTHOSILICATE AND ALLYL ORTHOSILICATE[a]

Compound	B. p., °C. (32 mm.)	n^{20}_D	Yield, moles	Mole ratio (exptl.)	Mole ratio (calcd.)
$Si(OC_2H_5)_4$	76.5– 77.0	1.3834	0.047[b]	0.84	1
$Si(OC_2H_5)_3(OC_3H_5)$	92.5– 93.0	1.3976	.231	4.12	4
$Si(OC_2H_5)_2(OC_3H_5)_2$	107.0–107.5	1.4097	.342	6.10	6
$Si(OC_2H_5)(OC_3H_5)_3$	120.5–121.0	1.4233	.214	3.63	4
$Si(OC_3H_5)_4$	132.0–132.5	1.4336	.037[b]	0.67	1

[a] Catalyst $Mg[Al(OC_2H_5)_4]_2$, 0.03 mole. [b] Initial quantity, 0.5 mole.

This was done by washing the cold mixture successively with dilute hydrochloric acid, water and sodium carbonate solution, then drying over calcium chloride.

The attempted preparation of mixed methyl–allyl silicates in this manner failed because the cold mixtures reacted rapidly with dilute hydrochloric acid forming a gel.

Reactions of Orthosilicates with Carboxylic Esters.— In experiments with mixtures of ethyl orthosilicate and amyl acetate, heated under reflux at atmospheric pressure, variable results were obtained. Usually a small quantity of ethyl acetate could be distilled off after the first hour, but upon continued heating practically no further reaction occurred. On one occasion, however, a sustained reaction set in and ethyl acetate was removed periodically until the theoretical amount had been collected within six and a half hours. An attempt to duplicate this result, made immediately thereafter with the same apparatus and materials, yielded only 1 g. of ethyl acetate (theoretical, 44 g.) in seven hours of heating.

An investigation of possible catalytic effects revealed that aluminum chloride, aluminum ethoxide, magnesium aluminum ethoxide and antimony triethoxide were effective catalysts. Aluminum ethoxide which had been thoroughly dried by heating *in vacuo* was relatively inactive; best results were obtained with preparations still slightly moist with ethyl alcohol.

The results of some typical experiments, in which these catalysts were used, are given in Table III. In each case the yield given is the yield of the most volatile product which was isolated from the mixture by periodic stripping.

In comparison with the acetate esters, and with ethyl formate, the transesterification reactions of ethyl *n*-butyrate and of ethyl carbonate with methyl orthosilicate were extremely slow, as is shown by the yields given in Table III.

Vinyl acetate could not be made to react with methyl orthosilicate when mixtures of the two were refluxed under atmospheric pressure, either alone, or with the addition of any of the above-mentioned catalysts, or with numerous other substances tested for catalytic effect, including sodium ethoxide, mercuric acetate, potassium acid sulfate and zinc chloride. Likewise vinyl acetate could not be made to react with methyl borate under any of the conditions tried. Vinyl formate and methyl orthosilicate in the presence of magnesium aluminum ethylate did not react. The choice of higher boiling components, *viz.*, *n*-butyl orthosilicate and vinyl benzoate, was fruitless; no reaction occurred in four hours of refluxing of a mixture containing these substances together with aluminum ethoxide.

However, vinyl acetate and methyl orthosilicate were made to react, with aluminum ethoxide as the catalyst, by the use of a high boiling solvent (nitrobenzene or tetralin) to raise the refluxing temperature of the mixture. Yields of 85–95% of methyl acetate were obtained in four to six hours. The following experiment is typical. A mixture of 76.1 g. (0.5 mole) of methyl orthosilicate, 43.0 g. (0.5 mole) of freshly distilled vinyl acetate, and 195 g. of nitro-

TABLE III

YIELDS OBTAINED IN TRANSESTERIFICATION REACTIONS

Ester A (1 mole)	Ester B	Moles B	Catalyst (0.03 mole)	Time, hrs.	% Reaction
Ethyl orthosilicate	*n*-Butyl acetate	1	$Al(OC_2H_5)_3$	5.5	99
		1	$AlCl_3$	2.5	98
		1	$Sb(OC_2H_5)_3$	8	75
Methyl orthosilicate	Ethyl acetate	1	$Al(OC_2H_5)_3$	5	90
		2	$Al(OC_2H_5)_3$	6	95
		5	$Al(OC_2H_5)_3$	3	50
		5	$AlCl_3$	10	55
				2	42
				15	58
Methyl orthosilicate	*n*-Butyl acetate	4	$Al(OC_2H_5)_3$	6	95
		6	$AlCl_3$	5.5	98
Methyl orthosilicate	Allyl acetate	2	$Al(OC_2H_5)_3$	6.5	98
Methyl orthosilicate	Ethyl formate	2	$Al(OC_2H_5)_3$	4	70
		2	$AlCl_3$	5	73
				7	87
		4.4	$AlCl_3$	10	98
Methyl orthosilicate	Ethyl *n*-butyrate	2	$Al(OC_2H_5)_3$	3	0
		2	$AlCl_3$	2	0
		4	$Al(OC_2H_5)_3$	15	47
Methyl orthosilicate	Ethyl carbonate	1	$Al(OC_2H_5)_3$	5	0
		1	$AlCl_3$	3	0
		1	$Mg[Al(OC_2H_5)_4]_2$	4	27[a]
Allyl orthosilicate	*n*-Butyl acetate	5	$Al(OC_2H_5)_3$	6	95
n-Butyl silicate	Ethyl antimonite	1.3	None	2.5	84
n-Butyl borate	Methyl orthosilicate	1.5	$Mg[Al(OC_2H_5)_4]_2$	5.5	96
Methyl borate	*n*-Butyl acetate	3	$Mg[Al(OC_2H_5)_4]_2$	2	87
n-Butyl borate	Methyl *n*-butyrate	3	$Mg[Al(OC_2H_5)_4]_2$	6.5	32
n-Butyl borate	Antimony triethoxide	1	None	1	90

[a] Product isolated, methyl ethyl carbonate.

benzene was refluxed for one hour. There was no evidence of reaction. One gram of aluminum ethoxide was added and reflux resumed. The theoretical quantity of methyl acetate was removed over a five-hour period. The residual liquid was distilled at reduced pressure, and upon refractionation of the distillate some methyl orthosilicate was recovered but none of the fractions decolorized bromine solution. The residue from the original distillation was a black, tarry mass with a pungent odor. Since a monomeric vinyl silicate was not isolated, the question as to whether transesterification occurred prior to or subsequent to polymerization of the vinyl groups is not answered by this experiment.

Reaction of Alkyl Borates.—The results obtained with simple alkyl borates in combination with a silicate ester (methyl orthosilicate) and with carboxylic esters (*n*-butyl acetate and methyl butyrate) are included in Table III. The reaction of butyl borate with methyl orthosilicate is noteworthy in that it provides a convenient means of preparing pure methyl borate, the direct preparation of which is troublesome because of a difficultly separable azeotropic mixture. In no case was a reaction achieved without the aid of a catalyst. Methyl borate could not be made to react with vinyl acetate under any of the conditions tried.

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Summary

Transesterification reactions of alkyl silicates with each other and in combination with carboxylic esters can be effected by the use of catalysts such as aluminum chloride, aluminum ethoxide, antimony triethoxide, etc. Under equilibrium conditions mixed esters are obtained in very nearly theoretical proportions, but by continuous or intermittent removal of volatile products the reactions in most cases can be driven to completion. The carboxylic esters show large differences in reactivity, the rate of reaction with methyl orthosilicate decreasing markedly in the order ethyl formate, ethyl acetate, ethyl butyrate and ethyl carbonate. Attempts to introduce vinyloxy groups on silicon by this process are described.

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[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

The Action of Ultraviolet Light upon Cellulose and Cellulose Triacetate[1]

BY E. HEUSER AND GEORGE N. CHAMBERLIN[1c]

The results of previous investigations in this Laboratory on the action of ultraviolet light upon cellulose in a system in which the oxygen had been reduced to an infinitesimal quantity were interpreted as being those of an immediate photochemical reaction.[2] In the discussion which followed the presentation of the first part of this investigation,[3] it was suggested that the ultraviolet light effect might be the result of a photochemical combination of nitrogen with traces of oxygen to form nitrogen di- and tetroxides, followed by hydrolysis of cellulose by the nitrogen oxides in the presence of traces of water left in the exposed sample. A direct combination of nitrogen with oxygen within the wave length range used in these studies (the lower limit being 2300 Å.) is not very probable.[4] Moreover, the results of the second part of the investigation were obtained with nitrogen in which the oxygen had been still further reduced (to 3.4×10^{-4} as compared with $2 \times 10^{-3}\%$).

It also has been suggested that the traces of water (less than 0.02%) would alone suffice to bring about hydrolysis of the cellulose, possibly catalyzed by the ultraviolet light energy.[5] Although such an effect would seem to be possible, it would not explain the fact that irradiated cellulose undergoes the post-irradiation effect,[2] *i. e.*, continues to suffer degradation when stored in air or oxygen. The effect of a simple hydrolysis, even if catalyzed by ultraviolet light, consists of an increase in free aldehyde and hydroxyl groups. If the aldehyde groups were considered as weak spots at which the oxygen would attack in the post-irradiation step, the question arises why unirradiated cellulose, which also contains a considerable number of free aldehyde groups, remains entirely unaffected when exposed to oxygen.[2] Hence, it would appear that, even if accelerated hydrolysis took place in the presence of the traces of moisture left in the sample, it cannot be the only reaction which occurs under the action of ultraviolet light in the absence of air oxygen.

Whereas an attempt to eliminate hydrolysis entirely would have to overcome difficult obstacles, it was thought that the use of purified helium instead of nitrogen would offer a direct means of deciding whether or not the nitrogen oxide argument may be discarded.

Methods

The cotton linters, the ultraviolet lamp, the apparatus, and the techniques used for the exposure and for the puri-

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[1] (a) Prepared for the 1945 Meeting-in-Print, Division of Cellulose Chemistry, A. C. S. (b) Installments III and IV of the series "The Action of Ultraviolet Light upon Cellulose." Installments I and II appeared in THIS JOURNAL, **66**, 753 (1944). (c) The material presented in this paper constitutes a portion of a dissertation submitted by George N. Chamberlin to Lawrence College (The Institute of Paper Chemistry) in partial fulfillment of the requirements of the M.S. degree, June, 1943. Present address, U. S. Navy.

[2] Stillings and Van Nostrand, THIS JOURNAL, **66**, 753 (1944).

[3] Presented by E. Heuser before the Division of Cellulose Chemistry at the 106th Meeting of the American Chemical Society, Pittsburgh, Pa., Sept., 1943.

[4] Ellis, Wells and Heyroth, "The Chemical Action of Ultraviolet Rays," Reinhold Publishing Company, New York, 1941, pp. 324, 431–436.

[5] Montonna and Winding, *Ind. Eng. Chem.*, **35**, 782 (1943).