Table I gives a summary of results in pK'. Concentrations were expressed in moles per liter and the range was 0.0018 to 0.0035 molar. K' for phenol and for *p*-methoxyphenol was determined by the same procedure in pure water in order to provide a comparison of degree of dissociation in the two solvents. These results are given in Part B of Table I. The concentration range used in pure water was 0.002 to 0.005 molar.

THE CHEMICAL RESEARCH LABORATORIES
THE LUBRIZOL CORP.
CLEVELAND, OHIO
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The Determination of Silicon in Relatively Nonvolatile Organosilicon Compounds

BY H. GILMAN, R. N. CLARK, R. E. WILEY AND H. DIEHL

In connection with a study of organosilicon compounds a need arose for a rapid and precise method of analysis for silicon. The general procedures for the analysis of silicon in organosilicon compounds have involved the oxidative decomposition of such types to silicon dioxide. The reagents used have been fuming nitric acid,[1] a combination of pyrolysis and atmospheric oxidation,[2] sulfuric acid and potassium permanganate,[3] concentrated sulfuric acid,[4] and sodium peroxide in the Parr bomb fusion procedure of Schumb and co-workers,[5] which is broadly useful for all types of organosilicon compounds.

We have found that heating with 60% perchloric acid is a rapid and accurate procedure for the quantitative conversion of silicon in relatively non-volatile organosilicon compounds to silicon dioxide. A modification of this method which may be useful for some compounds which oxidize very easily is to use a nitric acid–perchloric acid mixture. Mixtures containing nitric acid have been used for the quantitative analysis of tin in organotin[6a] compounds, and for lead in organolead[6b] compounds. The general use of perchloric acid for the destruction of organic matter, alone and mixed with nitric acid or sulfuric acid, has been reviewed recently by Smith.[7] Attention is called specifically to the fact that 60% perchloric acid is used in the procedure now described rather than the 72% acid. The oxidation potential of the acid is thus kept relatively low at the start and increased gradually as the temperature is raised and the acid concentrated. The oxidation of organic matter then proceeds smoothly and with a minimum of carbonization.

Experimental

Procedure (A).—About 0.2 g. of the organosilicon compound is weighed out in a platinum crucible, and then 5 cc. of 60% perchloric acid is added. The crucible and contents are placed in a clay triangle supported on a porcelain casserole; this air-bath is then heated with the full flame of a Meker burner until all of the acid has evaporated and all fumes of perchloric acid have disappeared. The crucible is then ignited to constant weight. The total time required, including initial weighing of sample and final weighing of silicon dioxide, is about three hours. It was shown, in several control analyses, that the precipitate formed by ignition is silicon dioxide by treatment in a customary manner with sulfuric and hydrofluoric acids and weighing the empty crucible. In some fifty analyses there was no violent action using the perchloric acid method of oxidation. When many determinations are to be made attention should be paid to the hazard resulting from the condensation of perchloric acid on combustible flues. Wood saturated with perchlorates burns vigorously and has even produced explosions when heated. A simple device to circumvent this difficulty is a so-called miniature laboratory fume eradicator.[8]

Procedure (B).—The only essential difference between this method and Procedure (A) is the admixture of 2 cc. of concentrated nitric acid with the 5 cc. of 60% perchloric acid. During the initial application of heat there may be foaming with this mixture but this can be corrected by reducing the heat or removing the burner until the foaming subsides. The foaming sometimes leaves a ring of froth near the top of the crucible. When this happens, the froth can be washed down with about 3 cc. of 60% perchloric acid after the initial evaporation. Then the mixture is again evaporated to dryness.

The results of a few representative analyses are given.

TABLE I

RESULTS OF ANALYSES

Compound	Procedure	% Si Calcd.	% Si Found	
Tetraphenylsilane	A	8.35	8.31	8.37
	B		8.30	8.36
Triphenylsilanol	A	10.23	10.24	10.29
	B		10.21	10.16
Methyltriphenylsilane	B	10.22	10.20	10.27
p-Carboxyphenyltrimethylsilane	A	14.43	14.29	
Triphenyl-2-thienylsilane	A	8.19	8.19	

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

(2) See, Polis, *Ber.*, **19**, 1024 (1886) for an account of the procedure by Ladenburg.

(3) Polis, *ibid.*, **18**, 1540 (1885).

(4) Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

(5) Marvin and Schumb, THIS JOURNAL, **52**, 574 (1930); Schumb, Ackermann, and Saffer, *ibid.*, **60**, 2486 (1938). See, also Tseng and Chao, *Science Repts. Natl. Univ. Peking*, **1**, (No. 4) 21 (1936) [*C. A.*, **31**, 655 (1937)]; Gilliam, Liebhafsky and Winslow, THIS JOURNAL, **63**, 801 (1938); and Whitmore and co-workers, *ibid.*, **68**, 480 (1946).

(6) (a) Gilman and King, THIS JOURNAL, **51**, 1213 (1929); (b) Gilman and Robinson, *ibid.*, **50**, 1714 (1928).

(7) Smith, *Ind. Eng. Chem., Anal. Ed.*, **18**, 257 (1946).

(8) Smith, *Monthly Rev. Am. Electroplater's Soc.*, **32**, 1028 (1945).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA
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Acid-Catalyzed Alkylation of Isoparaffins with Alcohols

BY J. D. GIBSON, R. C. COLE AND M. P. MATUSZAK

Tables I and II summarize data obtained several years ago in experiments on the acid-catalyzed alkylation of isoparaffins with alcohols. *t*-Butyl alcohol reacted readily at room temperature; *i*-propyl alcohol, at 30°; *n*-butyl alcohol, not even at 50°.

TABLE I

ACID-CATALYZED ALKYLATION OF ISOPARAFFINS WITH ALCOHOLS

Expt.	1	2	3	4	5
Catalyst	HF	HF	HF	HF	H_2SO_4
Isoparaffin	i-BuH	i-BuH	i-BuH	i-BuH	i-AmH
Alcohol	t-BuOH	i-PrOH	i-PrOH	n-BuQH	t-BuOH
Weights used, grams					
Catalyst	160	150	150	154	930
Isoparaffin	145	145	145	142	216
Alcohol	93	75	75	93	111
Isoparaffin/alcohol (mol.)	1.98	2.00	2.00	1.96	2.00
Temp., °C.	19–26	20–22	49–51	48–50	20
Pressure (max.), atm.	4.5	4.5	9.5	8.6	1.0
Stirring time, min.					
Alcohol addition	56	60	45	49	155
Subsequent	64	65	80	87	30
Alkylation product					
Yield, ml.	184	14	142	0	256
% of theory	89	7.9	78	0	95
Specific gravity (20°/4°)	0.6913	0.7073	0.6868	....	0.7153
Refractive index (20°)	1.3947	1.3945	1.3895	....	1.4028
Olefin content, wt. %	0.0	1.8	0.14	....	0.6

TABLE II

PROPERTIES OF ALKYLATE FRACTIONS

Expt.	Fraction	B. p., °C.	Vol. %	d^{20}_4	n^{20}_D	Olefin, wt. %
1	C_{5-6}	23–75	10.2	0.6332	1.3630	0.0
	C_7	75–95	7.3	.6805	1.3880	.0
	C_8	95–125	64.4	.6971	1.3958	.0
	C_9	125–150	4.3	.7186	1.4069	.6
	C_{10}	150–177	5.4	.7383	1.4168	1.1
	C_{11-12}	177–212	6.9	.7538	1.4247	2.0
	Residue	.....	1.5	.6941	1.4454	...
3	C_6	23–75	10.4	.6481	1.3712	0.12
	C_7 (low)	75–85	22.4	.6740	1.3842	.0
	C_7 (high)	85–95	41.7	.6885	1.3920	.14
	C_8	95–125	11.7	.7012	1.3977	.3
	C_9	125–150	3.3	.7218	1.4064	.17
	C_{10}	150–175	7.9	.7358	1.4152	.54
	Residue	.....	2.6	.7614	1.4260	...
5	C_6	40–77	12.8	.6566	1.3725	.0
	C_7	77–95	7.1	.6817	1.3870	.0
	C_8	95–120	15.7	.7070	1.3989	.0
	C_9 (low)	120–125	17.9			
	C_9 (high)	125–152	11.0	.7231	1.4069	.0
	C_{10}	152–180	25.8	.7363	1.4132	.0
	C_{11-12}	180-210	5.3	.7561	1.4239	1.3
	Residue	.....	4.4	.7866	1.4405	19

In experiments 1–4, the alcohol was pumped at a uniform rate into a vigorously stirred mixture of isobutane and anhydrous hydrofluoric acid in a water-cooled 625-ml. steel reactor. The reaction mixture was treated successively with ice, water, and 50% sodium hydroxide, was dried, and was debutanized and fractionated in a 5-foot glass column, 0.5 inch in diameter, packed with 6-mm. glass helices.

In experiment 5, the alcohol, diluted with an equal volume of isopentane, was added from a graduated separatory funnel to a vigorously stirred mixture of isopentane and concentrated sulfuric acid in a 3-liter flask provided with an ice-water-cooled reflux condenser. The reaction mixture was separated into two layers; the hydrocarbon layer was washed, dried, debutanized and fractionated.

The main product in each experiment was of the expected number of carbon atoms per molecule; however, the alkylate from experiment 5, made with isopentane and tertiary butyl alcohol, had a noteworthily large decane fraction. During the fractionation in experiment 3, made with isobutane and isopropyl alcohol, a few crystals of apparently triptane were collected at Dry-Ice temperature, at a pressure corresponding to a boiling point of 79°; the amount was so small that it indicated that this heptane was not a major product.

Whereas t-butyl alcohol resembled a butylene in reactivity, the non-t-alcohols were less reactive than the corresponding olefins—due allowance being made for dilution of acid by by-product water.

RESEARCH DEPARTMENT
PHILLIPS PETROLEUM CO.
BARTLESVILLE, OKLA.

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The Preparation of ε-Aminocaproic Acid

BY ALEXANDER GALAT AND SHIRLEY MALLIN

The preparation of ε-aminocaproic acid according to the procedures described in the literature is rather long and tedious. Thus, ε-caprolactam is hydrolyzed with hydrochloric acid, the excess of acid is removed in vacuum and the ε-aminocaproic acid hydrochloride which remains as residue, is repeatedly treated in a very dilute, aqueous solution with several portions of litharge freshly precipitated lead hydroxide, silver oxide and finally with hydrogen sulfide.[1]

This procedure proved to be very inconvenient and time consuming for the preparation of reasonably large amounts of ε-aminocaproic acid. A much simpler method has been found in the ammonolysis of ε-caprolactam under pressure, which

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[1] "Organic Syntheses," Coll. Vol. 11, John Wiley and Sons, New York, N. Y., p. 28.