

No 2,4-dinitrophenylhydrazone was obtained after warming the xanthone for eight hours at 60° with an ethanolic solution of 2,4-dinitrophenylhydrazine and sulfuric acid.

2,2'-Diacetoxy-5,5'-dichlorobenzophenone (XVIII).³⁶—The dihydroxy compound XVII (5.0 g.) was acetylated by refluxing with 11.0 ml. of acetic anhydride for 80 minutes. Then the solution was stirred with water, filtered, and the white precipitate recrystallized from ethanol; yield 6.1 g. (94%), m.p. 99–100°.

Anal. Calcd. for C₁₇H₁₂Cl₂O₃: C, 55.60; H, 3.30. Found: C, 55.10; H, 3.29.

2,2'-Dihydroxy-5,5'-dichlorobenzhydrol (XIX).³⁶—Pulverized lithium aluminum hydride (3.57 g., 0.094 mole) was refluxed one hour in 60 ml. of anhydrous ether. 2,2'-Diacetoxy-5,5'-dichlorobenzophenone (XVIII) (15.0 g.,

0.041 mole) was dissolved for the most part in 200 ml. of anhydrous ether and added fast enough to the stirred suspension to maintain gentle refluxing (50 min.). After an additional two hours of refluxing, 8.0 ml. of water was added slowly. When hydrogen had ceased evolving, the mixture was shaken with dilute sulfuric acid, the ether layer separated, washed with water, and dried with magnesium sulfate. After removal of the ether, the residual oil was dissolved in dilute sodium hydroxide solution and treated with activated carbon. Precipitation with acid gave a white solid which was recrystallized from benzene. When heated 3° per minute from 140° it melted at 149°; yield 8.3 g. (70%). A test with 2,4-dinitrophenylhydrazine was negative for a keto group.

Anal. Calcd. for C₁₃H₁₀Cl₂O₃: C, 54.76; H, 3.54. Found: C, 55.07; H, 3.57.

INDIANAPOLIS, INDIANA

(36) Prepared in the Pitman-Moore Research Department by Robert R. Smith.

[CONTRIBUTION FROM THE CORNING GLASS WORKS AND DOW-CORNING CORPORATION MULTIPLE FELLOWSHIP AT MELLON INSTITUTE, AND THE UNIVERSITY OF PITTSBURGH]

Methyl-Silicon Cleavage of Certain Substituted Carboxylic Acids in Sulfuric Acid. Kinetics and Mechanism

BY LEONARD M. SHORR,¹ HENRY FREISER AND JOHN L. SPEIER

RECEIVED MAY 20, 1954

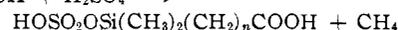
The kinetics of the reactions of β -trimethylsilylpropionic and γ -trimethylsilylbutyric acids with sulfuric acid to cleave one methyl group from silicon as methane has been studied. A mechanism involving both nucleophilic attack on silicon and electrophilic attack on carbon is proposed.

Certain organosilicon compounds containing a trimethylsilyl group, (CH₃)₃Si, linked to a carbon atom undergo displacement of one methyl group by the bisulfate group in the presence of sulfuric acid.²⁻⁶ Swain contends that simple polar displacement reactions in solution involve a concerted attack of a nucleophilic reagent upon a central atom and of an electrophilic agent upon the group to be displaced.⁷ Depending upon the reagent, the reaction with a given compound may be initiated by an electrophilic or nucleophilic attack. The nature of the attack is influenced also by the requirements of the central atom. Displacement of groups from a silicon atom may be favored by an initial attack of a nucleophilic reagent on silicon because silicon can accept the electrons of such a reagent by expanding its valence shell to form penta-valent intermediates.^{8,9} Thus a given nucleophilic reagent can be expected to attack a silicon atom more readily than a carbon atom in a comparable compound because carbon cannot expand its valence shell. By the careful selection of reagent, reacting species and/or reaction conditions a two-fold attack by the reagent may be clearly revealed.

This appears to be the case in the cleavage of a methyl group from β -trimethylsilylpropionic and γ -trimethylsilylbutyric acids in aqueous sulfuric acid solutions.

Determination of Reactants and Products

The kinetics were studied for the reaction discovered by Sommer, *et al.*,^{5,6} as described nearly quantitatively by the equation (where $n = 2$ and 3)



The formation of methane has been proved by infrared absorption analysis.^{5,6} The other reaction products, 4,4,6,6-tetramethyl-4,6-disila-5-oxa-nonanedioic and 5,5,7,7-tetramethyl-5,7-disila-6-oxa-undecanedioic acids, were isolated in yields of 95 and 82%, respectively.⁶ *n*-Butyric acid also was identified as a product in the latter reaction.

Although Sommer and co-workers¹⁰ extracted di-(trimethylsilyl) sulfate from the solution that resulted when allyltrimethylsilane was treated with concentrated sulfuric acid, later cryoscopic work^{11,12} would indicate that the primary product in this acid medium was the acid sulfate. It is likely that in all such cleavage reactions the product is the acid sulfate, though this has not been proven conclusively. Sommer⁴ also believed this to be true.

Kinetic Results

The observed kinetics for the cleavage of a methyl group from β -trimethylsilylpropionic acid in aqueous sulfuric acid solutions was found to be first or-

(1) Abstracted from the Ph.D. dissertation of Leonard M. Shorr, January, 1954.

(2) J. E. Noll, B. F. Daubert and J. L. Speier, *THIS JOURNAL*, **73**, 3871 (1951).

(3) L. H. Sommer, U. S. Patent 2,607,793.

(4) L. H. Sommer, W. P. Barie and J. R. Gould, *THIS JOURNAL*, **75**, 3765 (1953).

(5) L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett and R. P. Pioch, *ibid.*, **73**, 882 (1951).

(6) L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, *ibid.*, **75**, 2932 (1953).

(7) C. G. Swain, *Record of Chemical Progress*, **12**, 21 (1951).

(8) N. V. Sidgwick, "Electronic Theory of Valence," Oxford University Press, New York, N. Y., 1927, pp. 155-157.

(9) C. G. Swain, *THIS JOURNAL*, **71**, 965 (1949).

(10) L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948).

(11) M. S. Newman, R. A. Craig and A. B. Garrett, *ibid.*, **71**, 869 (1949).

(12) F. P. Price, *ibid.*, **70**, 871 (1948).

der with respect to both the carboxylic acid and un-ionized sulfuric acid. The removal of the methyl group was quantitative and the addition of sodium bisulfate had no effect on the reaction rate. However, the cleavage reaction of γ -trimethylsilylbutyric acid was termolecular—being second order toward un-ionized sulfuric acid and first order with respect to the butyric acid. Cleavage of a methyl group was not quantitative in this case and the addition of sodium bisulfate reduced the reaction rate to a slight degree. The role of un-ionized sulfuric acid is further substantiated by the failure of β -trimethylsilylpropionic acid to cleave in solutions of sulfuric acid in glacial acetic acid in which acetic acid was present in molar excess. Gillespie, *et al.*,¹³ have shown that in this solution the acetic acid is protonated completely. In aqueous sulfuric acid solutions the rate fell off with dilution and the reaction did not take place at all below 76% sulfuric acid.

On the basis of the slight difference in acid dissociation constants for the butyric and propionic acids 1.30×10^{-5} ¹⁴ and 1.24×10^{-5} ,¹⁵ respectively, one could not expect any difference in mechanism because of inductive effects. Secondly, the thermodynamic properties of activation, derived from the assumption of an equilibrium between reactants and an activated complex, do not differ greatly (Table I). Reactions which are effected by differing numbers of reactant molecules or those which occur by greatly differing mechanisms might be expected to yield larger differences in thermodynamic properties.

TABLE I

Compound	E^* , kcal.	S^* , cal./degree	F^* , kcal.	A , sec. ⁻¹
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{-COOH}$	20.5	-6.41	22.4	2.41×10^{11}
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{-COOH}$	19.3	-14.06	23.4	5.23×10^9

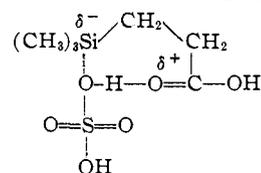
It would, therefore, appear unreasonable to consider a mechanism for the cleavage of the propionic acid in sulfuric acid which is greatly different from that for the cleavage of the butyric acid. Yet the differences between the two must be resolved. The mechanism proposed here satisfies the facts.

Discussion of Mechanism

In the case of γ -trimethylsilylbutyric acid, two molecules of sulfuric acid are involved in an attack on the silicon atom. One sulfuric acid molecule acting as a nucleophilic reagent attacks the silicon atom and the second, functioning as an electrophilic reagent attacks a methyl carbon to cleave the silicon-carbon bond. If the groups attached to silicon cleaved with equal facility, then 75% methyl cleavage would be expected. However, methyl group cleavage occurred to a greater extent because of the somewhat greater electronegativity of a methyl carbon than the γ -carbon of the butyric acid group, especially after protonation of the car-

boxyl group in the acid medium. This protonation also serves to decrease the electron density around the silicon atom facilitating attack by the "nucleophilic" molecule of sulfuric acid. Addition of sodium bisulfate would compete with the carboxylic acid for the proton resulting in an increase of electron density on the silicon. This would have the effect of facilitating the cleavage of a silicon-carbon bond as well as decreasing the possibility of an attack by the "nucleophilic" sulfuric acid molecule. The over-all effect is a slight one, but since the reaction is retarded, it suggests that attack on silicon is necessary.

An initial attack by the "nucleophilic" molecule of sulfuric acid on the silicon atom of β -trimethylsilylpropionic acid may result in the very rapid, non-rate-determining formation of a hydrogen bonded chelate structure of the type postulated



The stabilization of the carboxylic acid side chain by such a chelate structure could explain the quantitative removal of only a methyl group when the second molecule of sulfuric acid attacks a methyl carbon. Likewise, the higher degree of order accompanying chelate formation would explain the smaller negative entropy of activation found for this cleavage as compared with that of the γ -trimethylsilylbutyric acid reaction. However, the similar over-all reaction mechanisms in the two cases yielded like values for the energies of activation. The more nucleophilic bisulfate ion could probably coordinate with silicon more readily than sulfuric acid, but the resulting complex would decompose reversibly and rapidly. Therefore, the addition of sodium bisulfate to the reaction medium does not alter the reaction rate.

Swain found that a simultaneous termolecular reaction was kinetically indistinguishable from one involving a very rapid, reversible formation of a low equilibrium concentration of a complex between two of the molecules accompanied by a slow reaction of the complex with the third molecule.¹⁶ The reactions studied in this work differ from polar displacements of organic compounds in that the silicon atom forms an intermediate of exceptional stability and long life. The stability of the transition state may be ascribed to the known ability of silicon to enter covalent states above four. This ability provides stability to the complex not available during replacement reactions of carbon structures.

Sommer, Barrie and Gould⁴ have reported recently the kinetic study of the cleavage of a methyl group from β -trimethylsilylpropionic acid by the action of aqueous sulfuric acid at 20°. The observations and procedure employed for their investigation was essentially the same as that to be reported here. The rate observed was pseudo-first-order, being monomolecular in both un-ionized sulfuric acid and the silylpropionic acid. Applying a correc-

(13) R. J. Gillespie, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

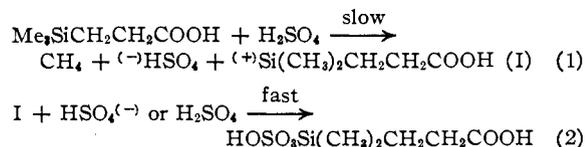
(14) L. H. Sommer, G. M. Goldberg, G. H. Barnes and L. S. Stone, Jr., *This Journal*, **76**, 1609 (1954).

(15) L. H. Sommer, J. R. Gold, G. M. Goldberg and N. S. Marans, *ibid.*, **71**, 1509 (1949).

(16) C. G. Swain, *ibid.*, **70**, 1119 (1948).

tion for the incomplete dissociation of sulfuric acid in water¹⁷ (discussed below) one obtains a mean of 1.28×10^{-4} l. mole⁻¹ sec.⁻¹ with a standard deviation 0.04×10^{-4} l. mole⁻¹ sec.⁻¹ for the second-order reaction rate constant over the range of 87–97% aqueous sulfuric acid.

The following mechanism for the sulfuric acid cleavage of β -trimethylsilylpropionic acid was suggested by Sommer, *et al.*

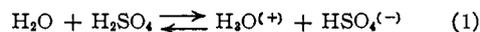


On the basis of this mechanism it would be difficult to explain the second order dependency of γ -trimethylsilylbutyric acid on the concentration of molecular sulfuric acid.

Sommer and co-workers⁴ cited as evidence against a nucleophilic attack on silicon the experimental observation that methane and not methyl chloride is cleaved from chloromethyltrimethylsilane upon treatment with concentrated sulfuric acid. They called attention to the work of Krieble and Elliott¹⁸ who stated that in a nucleophilic attack by bases on chloromethyltrimethylsilane the more electronegative chloromethyl group was selectively cleaved from the silicon. However, consideration of only the relative electronegativities of the groups attached to silicon in the parent compound is insufficient to predict the course of cleavage in the reaction medium. Thus, the benzyl group was more easily cleaved from silicon by alkalis than was phenyl,^{19,20} though the benzyl group is less electronegative than a phenyl.^{21,22} In an alkaline medium, the chloromethyl group of chloromethyltrimethylsilane may indeed be the more electronegative. But this need not be so in concentrated sulfuric acid. Association of the acid with the chlorine electrons in the manner of its apparent action in alkylation reactions,²³ may deplete the electron density around the carbon atom to such a degree that the electrophilic attack (in the twofold attack) occurs preferentially on the methyl group. This supposition certainly demands further investigation, but a nucleophilic attack by sulfuric acid cannot be discounted.

Concentration of Un-ionized Sulfuric Acid

The concentrations of un-ionized sulfuric acid were calculated assuming a mole fraction equilibrium constant of fifty¹⁷ for reaction 1 below and complete protonation in reaction 2



This procedure yielded far more consistent results

(17) N. C. Deno and R. W. Taft, Jr., *THIS JOURNAL*, **76**, 244 (1954).

(18) R. H. Krieble and J. R. Elliott, *ibid.*, **67**, 1810 (1945).

(19) A. R. Steel and F. S. Kipping, *J. Chem. Soc.*, 1431 (1928).

(20) L. S. Miller, Doctoral Dissertation, Iowa State College, 1950.

(21) F. C. Whitmore and H. Bernstein, *THIS JOURNAL*, **60**, 2626 (1938).

(22) F. C. Whitmore and L. H. Sommer, *ibid.*, **68**, 481 (1946).

(23) C. C. Price, "Organic Reactions," Vol. III, Chap. I, John Wiley and Sons, Inc., New York, N. Y., 1946.

than the assumption of complete dissociation of sulfuric acid in water.

Experimental

The apparatus used for the kinetic study consisted of a jacketed erlenmeyer flask fitted with a glass stopper containing a dropping tip and a gas outlet tube which was connected to a gas buret. Water from a thermostatically controlled bath was pumped through the jacket of the erlenmeyer flask. A sample of approximately 0.1 to 0.2 g. was drawn into the dropping tip. An accurate determination of the quantity of sample used was made by weighing the entire glass stopper assembly before and after each reaction. Sulfuric acid solutions immersed in the thermostatically controlled bath were measured into the reaction flask with a 10-ml. pipet. While the solution was being stirred with a magnetic stirrer, the silicon compound was pulled down into the solution by applying a slight vacuum to the system. The rate at which methane was liberated at a given temperature was then measured.

The temperatures maintained by the thermostatically controlled bath were measured with a thermometer calibrated by the National Bureau of Standards.

Cleavage of β -Trimethylsilylpropionic Acid

When stirring was rapid enough, the data obtained for the cleavage of β -trimethylsilylpropionic acid in aqueous sulfuric acid solutions conformed with first-order kinetics. This can be seen from Figs. 1 and 2 and Tables II and III which contain the graphic and numerical representation of the first-order kinetics for the data obtained at 25 and 15°. The percentage methane evolved was calculated from the total volume expected from quantitative cleavage of a methyl group. The experimental data for two of these runs appear in Table VI.

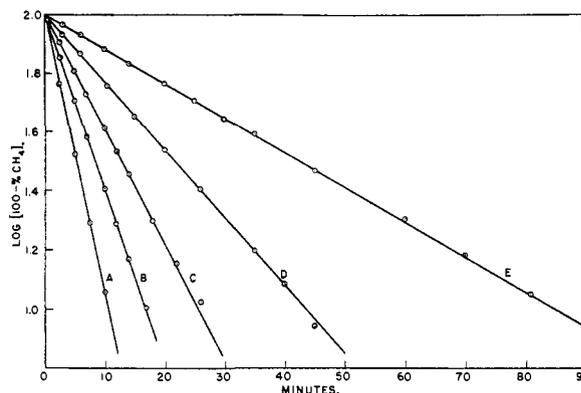


Fig. 1.—First-order reaction curves for cleavage of $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{COOH}$ in aqueous sulfuric acid at 25°.

Curve	A	B	C	D	E
% aq. H_2SO_4	97.2	92.7	89.7	87.7	85.0

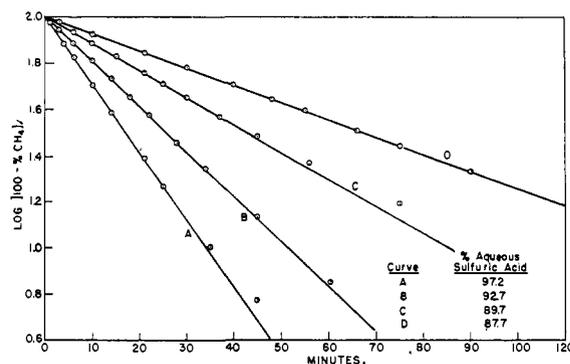


Fig. 2.—First-order reaction curves for cleavage of $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{COOH}$ in aqueous sulfuric acid at 15°.

TABLE II
CLEAVAGE OF $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{COOH}$ AT 25°

Aqueous H_2SO_4 , %	Concn. un-ionized H_2SO_4 , molar	S , slope of first-order plot, sec. ⁻¹	$k = \frac{S}{[\text{H}_2\text{SO}_4]}$, l.-mole ⁻¹ sec. ⁻¹
97.2	15.21	36.08×10^{-4}	2.37×10^{-4}
95.2	12.82	32.85	2.56
95.2	12.82	32.28	2.52
95.2	12.78	32.28	2.53
92.7	9.83	22.90	2.33
89.7	6.41	14.74	2.30
89.7	6.39	14.47	2.26
89.7 ^a	6.43	14.74	2.29
89.7 ^b	6.41	14.47	2.26
89.7 ^c	6.43	14.91	2.32
87.7	4.33	8.76	2.02
85.0	2.09	4.47	2.14

^a 2.00 g. of ground Pyrex glass added. ^b Stirrer coated with Dow-Corning Antifoam A. ^c 0.853 M NaHSO_4 added.

TABLE III
CLEAVAGE OF $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{COOH}$ AT 15°

Aqueous H_2SO_4 , %	Concn. un-ionized H_2SO_4 , molar	S , slope of first-order plot, sec. ⁻¹	$k = \frac{S}{[\text{H}_2\text{SO}_4]}$, l.-mole ⁻¹ sec. ⁻¹
97.2	15.30	11.19×10^{-4}	0.731×10^{-4}
92.7	9.91	7.36	.743
89.7	6.45	4.43	.687
87.7	4.34	2.81	.648

Cleavage of γ -Trimethylsilylbutyric Acid

The data obtained for the sulfuric acid cleavage of γ -trimethylsilylbutyric acid required adjustment to yield good

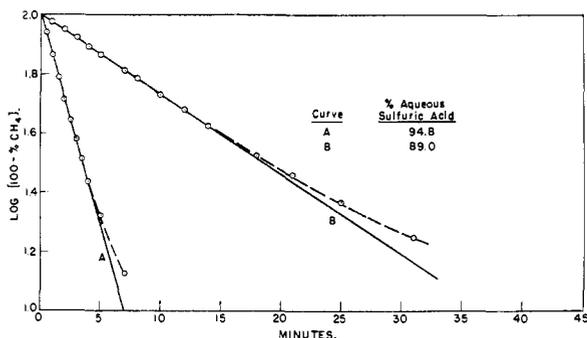


Fig. 3.—First-order reaction curves for cleavage of $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ in aqueous sulfuric acid at 25° .

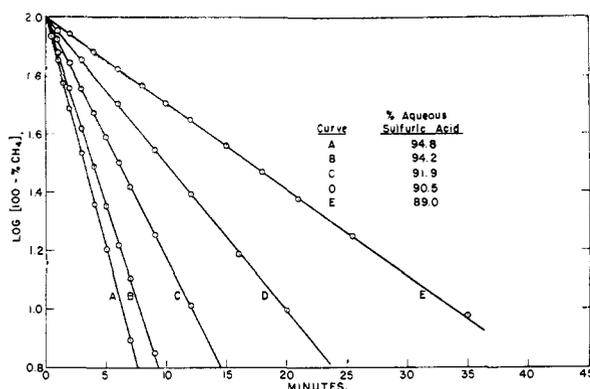


Fig. 4.—Adjusted first-order reaction curves for cleavage of $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ in aqueous sulfuric acid at 25° .

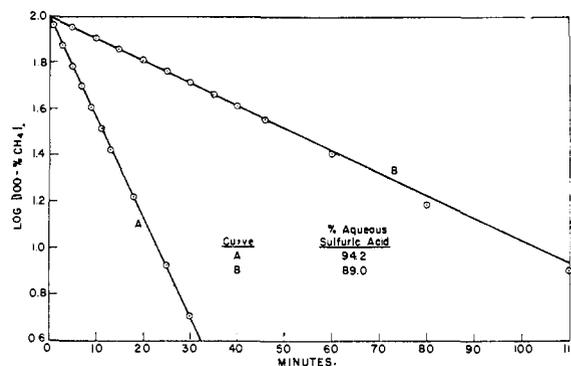


Fig. 5.—Adjusted first-order reaction curves for cleavage of $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ in aqueous sulfuric acid at 15° .

TABLE IV
CLEAVAGE OF $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ AT 25°

Aqueous H_2SO_4 , %	Concn. un-ionized H_2SO_4 , molar	S , slope of first-order plot, sec. ⁻¹	$S/[\text{H}_2\text{SO}_4]$, l.-mole ⁻¹ sec. ⁻¹	$k = \frac{S}{[\text{H}_2\text{SO}_4]^2}$, l. ² -mole ⁻² sec. ⁻¹
94.8	12.31	59.33×10^{-4}	4.84×10^{-4}	0.390×10^{-4}
94.2	11.62	49.53	4.28	.367
94.2	11.59	48.70	4.22	.363
94.2 ^a	11.63	48.18	4.17	.356
91.9	8.90	31.67	3.62	.400
91.9	8.92	31.47	3.59	.396
91.9 ^b	8.91	27.60	3.15	.348
90.5	7.30	19.38	2.75	.364
89.0	5.63	11.34	2.16	.358
89.0	5.64	11.57	2.20	.364

^a 0.597 M NaHSO_4 added. ^b 0.669 M NaHSO_4 added.

TABLE V
CLEAVAGE OF $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ AT 15°

Aqueous H_2SO_4 , %	Concn. un-ionized H_2SO_4 , molar	S , slope of first-order plot, sec. ⁻¹	$S/[\text{H}_2\text{SO}_4]$, l.-mole ⁻¹ sec. ⁻¹	$k = \frac{S}{[\text{H}_2\text{SO}_4]^2}$, l. ² -mole ⁻² sec. ⁻¹
94.2	11.70	17.18×10^{-4}	1.48×10^{-4}	0.126×10^{-4}
89.0	5.69	3.79	0.716	.117
89.0	5.67	3.83	.727	.119

TABLE VI

Min.	CH_4 , ml. ^e	CH_4 , %	Min.	CH_4 , ml. ^e	CH_4 , %
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{COOH}$					
Run 24 ^a			Run 33 ^b		
0.5	1.25	4.60	1.0	1.00	4.02
1.0	3.30	12.13	3.0	2.90	11.66
1.5	4.75	17.46	4.0	3.80	15.27
2.0	6.30	23.16	6.0	5.70	22.91
2.5	7.70	28.31	8.0	7.25	29.14
3.0	8.90	32.72	10.0	8.75	35.17
3.5	10.20	37.50	12.5	10.45	42.00
4.0	11.30	41.54	14.0	11.40	45.82
5.0	13.40	49.26	18.0	13.65	54.86
6.0	15.20	55.88	22.0	15.50	62.29
7.0	16.70	61.39	28.0	17.70	71.14
9.0	19.25	70.76	34.0	19.35	77.77
11.0	21.10	77.56	45.0	21.50	86.41
14.0	23.20	85.28	60.5	23.10	92.84
20.0	25.30	93.00	135.0	24.70	99.27
40.0	26.80	98.52	---	---	---

TABLE VI (Continued)

Min.	CH ₄ , ml. ^c	CH ₄ , %	Min.	CH ₄ , ml. ^e	CH ₄ , %
	(CH ₃) ₃ SiCH ₂ CH ₂ CH ₂ COOH				
	Run 45 ^e			Run 47 ^d	
1.0	1.30	5.48	5.0	2.60	9.52
2.0	2.75	11.60	10.0	5.20	19.05
3.0	4.15	17.51	15.0	7.40	27.11
4.0	5.60	23.63	20.0	9.50	34.80
5.0	6.72	28.35	25.0	11.40	41.76
7.0	8.94	37.72	30.0	13.10	47.99
8.0	9.90	41.77	35.0	14.70	53.85
10.0	11.75	49.57	40.0	16.10	58.97
12.0	13.30	56.11	46.0	17.50	64.10
14.0	14.75	62.23	60.0	20.30	74.36
18.0	16.93	71.43	80.0	23.10	84.62
21.0	18.20	76.79	95.0	24.45	89.56
25.0	19.57	82.57	110.0	25.40	93.04
31.0	21.00	88.60	192.0	27.30	100.00
45.0	22.54	95.10			
100.0	23.70	100.00			

^a 730.1 mm., 25.0°, 1.060 × 10⁻³ mole sample, gas collected at 27°, % CH₄ calcd. ^b 738.4 mm., 15.0°, 0.995 × 10⁻³ mole sample, gas collected at 23°, % CH₄ calcd. ^c 743.3 mm., 25.0°, 1.017 × 10⁻³ mole sample, gas collected at 26.5°, % CH₄ based on final volume. ^d 735.0 mm., 15.0°, 1.180 × 10⁻³ mole sample, gas collected at 28°, % CH₄ based on final volume. ^e Uncorrected.

first-order kinetics and constant reaction rate constants. This was caused by a small amount of cleavage to form butyric acid. When the percentage of methane evolved was calculated from that expected from quantitative cleavage of a methyl group the poor first-order kinetics shown by the dashed line in Fig. 3 was obtained. If, however, the percentage methane was calculated as the percentage of the final volume obtained in each of the reactions, excellent first-order kinetics resulted. This is shown in Figs. 4 and 5 and in Tables IV and V for the cleavages conducted at 25 and 15°. The experimental data for two of these runs appear in Table VI. It is noteworthy that constant values were obtained for a reaction rate constant which was doubly dependent upon the concentration of un-ionized sulfuric acid.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Organic Peroxides. IV. Higher Dialkyl Peroxides

BY FRANK WELCH, HOMER R. WILLIAMS AND HARRY S. MOSHER

RECEIVED AUGUST 30, 1954

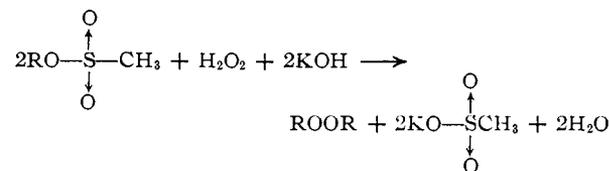
Several new primary and secondary saturated dialkyl peroxides have been prepared by the direct alkylation of hydrogen peroxide with two equivalents of alkyl methanesulfonate in homogeneous methanol-water-potassium hydroxide solution. These peroxides have been found to be relatively stable to mineral acids but labile to alkali and to resemble di-*t*-butyl peroxide in their thermal stability and other observed properties.

Dialkyl peroxides have been prepared in the past by three main methods¹: first, the alkylation of hydrogen peroxide with alkyl sulfates in the presence of base; second, the alkylation of hydrogen peroxide by tertiary carbonium ions or their equivalent; and third, the alkylation of alkyl hydroperoxides with either alkyl sulfates, alkyl hydrogen sulfates or alkyl halides.¹ The first of these methods appears to be limited to the preparation of the lower dialkyl peroxides because of the relative inaccessibility of the alkyl sulfates above butyl. The second method has been reported only for the preparation of ditertiary alkyl peroxides. The third method is the most general and the only usable method for the preparation of unsymmetrical dialkyl peroxides. Since the higher primary and secondary alkyl hydroperoxides have only recently become available,² this third method has been limited in the past to those dialkyl peroxides containing a tertiary radical or to the few lower members of the series where the normal or secondary hydroperoxide was available. Thus the di-*n*-alkyl peroxides above propyl have not been reported previously.

(1) For reviews on the preparations of peroxides see: (a) A. Rieche, "Alkyl Peroxyde und Ozonide," Theodor Steinkoff, Dresden, 1931, pp. 27-34; (b) W. Eggersglüss, "Peroxyde," Verlag Chemie, Weinheim, 1950; (c) R. Criegee, "Methoden der Organische Chemie," Vierte Auflage, Vol. VIII, Georg Thieme Verlag, Stuttgart, 1952, pp. 9-61; (d) A. V. Tolbolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publ. Inc., New York, N. Y., 1954; (e) N. A. Milas, Encyclopedia of Chemical Technology, Interscience Publ. Inc., New York, N. Y., Vol. 10, 1953, p. 38.

(2) H. R. Williams and H. S. Mosher, THIS JOURNAL, **76**, 2984, 2987, 3495 (1954).

It has now been demonstrated that alkyl methanesulfonates can be employed successfully in the alkylation of hydrogen peroxide to give primary and secondary dialkyl peroxides in satisfactory yields. The conditions for the dialkylation of hydrogen peroxide differ only in the ratio of the reactants from those previously reported² for the monoalkylation. When a large excess of hydrogen peroxide was used, the formation of the hydroperoxide was favored,² but when two moles of alkyl methanesulfonate were used for each mole of hydrogen peroxide according to the following equation, the dialkyl peroxide was the predominant reaction product.



When one considers the competing side reactions, basic hydrolysis of the alkyl methanesulfonate, decomposition of the hydrogen peroxide and the intermediate alkyl hydroperoxide, and basic decomposition of the dialkyl peroxide itself, it is quite remarkable that yields as high as 45 to 65% as reported in Table I have been obtained.

Some idea of the relative rate of the desired reaction as compared to the rate of the competing reaction of hydrolysis of the alkyl methanesulfonate is obtained from the data represented in Fig. 1